ABSTRACT

GOETZ, STEPHEN BURGOYNE. Measurement, Analysis, and Modeling of Fine Particulate Matter in Eastern North Carolina. (Under the direction of Dr. Viney Aneja)

An analysis of fine particulate mass concentrations in eastern North Carolina was conducted in order to investigate the impact of the hog industry and its emissions of ammonia into the atmosphere. This analysis included collecting acidic gas and inorganic fine particulate concentrations at a hog facility and at a site ~10 miles away, while the regional impact of hog industry was studied with data, which was obtained from the North Carolina Division of Air Quality, for multiple regional sites (Fayetteville, Goldsboro, Jacksonville, Kenansville, Kinston, Raleigh, Wilmington). This regional fine particulate data was then simulated using ISORROPIA, a thermodynamic model that simulates the gas and aerosol equilibrium of inorganic atmospheric species. The local analysis showed the dominance of the ammonium sulfate aerosol, and the seasonal observations showed the impact of both urban areas and marine areas on this region. While no meteorological trends were seen in the local data, the time series plots showed an environment where regional sulfate plays a large part. While nitrate is present in this environment, it is present 1 order of magnitude less than the sulfate aerosol. The ammonium and sulfate values are highly correlated, and the molar ratio is consistent with the relative values of ammonium, sulfate, and nitrate present. The regional observational data analyses show that the major constituents of fine particulate matter are organic carbon, sulfate, nitrate, ammonium and elemental carbon. The observed $PM_{2.5}$ concentration is positively correlated with temperature but negatively-correlated with wind speed. The correlation between $PM_{2.5}$ mass and wind direction at some locations indicates the impact of the emissions from hog facilities on $PM_{2.5}$ formation. The

modeled results overpredict the observed results in each case, where the nitrate concentrations had the largest percentage overprediction. The predicted total inorganic PM concentrations are overpredicted by 40-45% of the observed values under conditions with median initial total PM species concentrations, median RH and median temperature. The ambient conditions with high PM precursor concentrations, low temperature and high relative humidity favor the formation of the secondary PM. The model runs of the individual days at the three speciated sites showed overprediction for all species, where some predicted values of ammonium were within a factor of 2 of the observed concentrations.

MEASUREMENT, ANALYSIS, AND MODELING OF FINE PARTICULATE MATTER IN EASTERN NORTH CAROLINA

by
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Biography

Stephen Burgoyne Goetz was born on November 9, 1980, in Abington, Pennsylvania to Michael and Jane Goetz. As he progressed through school, it was clear that he possessed a clear aptitude and passion for the natural sciences, while he also remained extremely active with other activities in athletics and in the arts.

Upon graduation from Upper Dublin High School in Fort Washington, Pennsylvania, Stephen entered the University of Michigan in Ann Arbor, Michigan to pursue a double major of Chemistry and Music. After one year, he abandoned the goal of becoming a professional musician, and become completely focused on earning his Chemistry degree. After completing a research project, which involved producing and analyzing an emulsion of silver halide and 4-[4-(dimethylamino)-á-styrl]-1-methylpyridinium, he became interested in Atmospheric Chemistry, and then performed a senior research project involving atmospheric ozone concentrations in Northern Michigan. In 2003, Stephen graduated with a Bachelor's of Science with a Concentration in Chemistry.

In the fall of 2003, Stephen entered the North Carolina State Air Quality Research Group in order to further his study of air quality. While a graduate student, he assisted the group as a research assistant, and as a teaching assistant for two different meteorology classes. Before beginning his own graduate research work, he assisted on making the measurements associated with Project OPEN. (Odor, Pathogens, and Emissions of Nitrogen)

Presently, Stephen has accepted an offer to work with URS, an internationally-known engineering company with over 27,000 employees, to work in their

Environmental Transportation Group assisting on preparing Environmental Impact Statements for their various engineering projects.

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Chapter 1. Introduction

1.1 Background

In the past 20 years, the hog industry of North Carolina has experienced rapid growth. Between 1986 and 2005, the hog population expanded from 2.4 million up to 9.7 million, which makes it rank the second in terms of pig production by state nationwide (Figure 1.1, North Carolina Department of Agriculture & Consumer Services, 2005). This rapid growth can be linked to the adoption of contract production, which provided the capital necessary for the hog operations to consolidate and achieve major growth. (McBride and Key, 2003) "Consequently, more hogs are confined to smaller areas, thereby releasing increasing amounts of odorous and potentially harmful compounds due to a higher amount of excretion. 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) This rapid growth has been concentrated in the coastal plain region of North Carolina, which is located in the southeast corner of the state covering Bladen, Duplin, Greene, Lenoir, Sampson, and Wayne counties (Walker, 1998).

In response to increasing complaints over air and water quality, the Clean Water Responsibility Act was adopted in 1997, which created a moratorium on any new or expanded hog farms so that this environmental problem could be better understood. This moratorium, which stood until 2003 originally, was extended by House Bill 1113 until September 2007.

1.2 Particulate Matter

Particulate matter has become a major concern for air quality of certain regions, including the southeast United States. In order to tackle this problem, the U.S. Environmental Protection Agency originally created ambient air quality standards for "Total Suspended Particulate" (TSP) in the 1970 Clean Air Act. After many years of study, it was discovered that the behavior and impact of a particle is extremely dependent on the particle's size. In 1997, the Environmental Protection Agency modified the National Ambient Air Quality Standards for particulate matter by dividing the total suspended particulate standard into two separate modes of particulates, fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) particles, with the standards for fine particulates being 65 $\mu g\ m^{-3}$ daily and 15 $\mu g\ m^{-3}$ annually. The fine mode of PM is known to contribute to human respiratory problems, dry and wet acidic deposition, reduced visibility, and radiative forcing (US EPA, Office of Air & Radiation, 2005). $PM_{2.5}$ is composed of primary and secondary pollutants; primary $PM_{2.5}$ species may include organic carbon, elemental carbon, soil dust, ash, and sulfate. Secondary $PM_{2.5}$ may include sulfate, nitrate, ammonium, and organic carbon, which are formed through the oxidation of their gas-phase precursors such as sulfur dioxide, nitrogen dioxide, ammonia, and volatile organic compounds. This gas/particle interface is a unique process for each major precursor of secondary fine particulate matter, and will be discussed individually for each gas/particle pair.

1.2.1 Sulfur Dioxide/Sulfate

Sulfur Dioxide (SO_2) is the most common anthropogenic sulfur air pollutant. The primary atmospheric sources of sulfur dioxide are fossil fuel burning, biomass burning, and the eruption of volcanoes as seen in Table 1.1. (Berresheim et. al, 1995) Sulfur also exists in

many other forms such as H_2S, $(CH_3)_2S_2$, CS_2, and OCS, but SO_2 is the most prevalent. Sulfur dioxide concentrations vary over a large scale from 20 ppt (parts per trillion) in the marine surface layer to 1500 ppt in polluted continental air. (Berresheim et. al, 1995) The transformation from sulfur dioxide to sulfuric acid (which will be either in the liquid or solid phase) can occur through gas-phase or aqueous-phase reactions. In the gas phase reactions (detailed below), sulfur dioxide joins together with the hydroxyl free radical to form one large extremely reactive free radical. (HSO_3) This molecule will quickly react with oxygen gas to form the HO_2 radical along with sulfur trioxide. (SO_3) In the presence of water vapor, the sulfur trioxide will quickly be transformed into sulfuric acid. (Seinfeld & Pandis, 1998)

$SO_2 + OH + M \rightarrow HSO_3 + M$

$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$

$SO_3 + H_2O + M \rightarrow H_2SO_4 + M$

Sulfur dioxide can also become dissolved in atmospheric water, and become sulfuric acid through an aqueous phase reaction. When sulfur dioxide initially comes in contact with water, it will quickly take the form of either sulfite (HSO_3^-) or bisulfite (SO_3^{2-}) depending on the pH of that particular water droplet. After this process, the sulfite/bisulfite will be transformed into aqueous sulfate (SO_4^{2-}) by oxidation by either dissolved ozone or dissolved hydrogen peroxide. The oxidation via ozone or hydrogen peroxide are the two primary pathways, but the sulfite/bisulfite can also be oxidized by organic peroxides, oxygen, iron, manganese, hydroxyl radical, or oxides of nitrogen. The two primary pathways are shown in the following reactions. (Seinfeld & Pandis, p. 1998)

$SO_2 (g) + H_2O \rightarrow SO_2 (l) + H_2O$

$SO_2 (l) + H_2O \rightarrow H^+ + HSO_3^-$

$HSO_3^- \rightarrow H^+ + SO_3^{2-}$

$SO_3^{2-} + O_3 \longrightarrow SO_4^{2-} + O_2$

$HSO_3^- + H_2O_2 \longrightarrow SO_2OOH^- + H_2O$

$HSO_3^- + H^+ \longrightarrow H_2SO_4$

1.2.2. Nitrogen Oxide/Nitrogen Dioxide/Nitrate

Nitric oxide (NO) and nitrogen dioxide (NO_2) (together they are known as NO_x) are the two primary precursors to the main acidic gas nitric acid (HNO_3) and its corresponding particulate form nitrate (NO_3^-). The main global sources of NO_x into the atmosphere include fossil fuel combustion, biogenic soil release, biomass burning, lightning, and oxidation from ammonia. (Table 1.2) (IPCC, 1995) The atmospheric chemistry of NO_x is extremely complicated with respect to the formation of tropospheric ozone, but a few coupled reactions will be mentioned, as they are important for this study. During the circular reactions involving nitric oxide, nitrogen dioxide, and ozone, the cycle can be terminated by the formation of nitric acid. This reaction is also a chain-terminating step in the oxidation of methane into various oxidized hydrocarbons, which adds an additional set of conditions under which nitric acid can form. When the gaseous nitric acid forms, it is not very stable in the gaseous form, and there is liquid water or other aerosols in the area, it will transfer over into the liquid or solid phase as detailed in the following reactions. If possible, it will form a solid or liquid aerosol with gaseous ammonia, which will be highlighted. (Seinfeld & Pandis, p. 1998)

$OH + NO_2 + M \longrightarrow HNO_3 + M$

$NH_3 + HNO_3 \longleftrightarrow NH_4^+ + NO_3^-$

$NH_3 + HNO_3 \rightarrow NH_4NO_3$ (s)

1.2.3 Ammonia/Ammonium

Ammonia is the main basic gas in the atmosphere, and one of the most abundant nitrogen-containing compounds in the atmosphere. The main atmospheric sources of ammonia are natural sources from the ocean & vegetation and anthropogenic sources from various livestock, fertilizer, and biomass burning. Globally, it is estimated that a total of 49.3 Tg of NH_3 is emitted into the atmosphere with 56% of this total being "anthropogenic." The largest contributor to these ammonia emissions is domestic animal waste decomposition, which accounts for 22 Tg NH_3 (Table 1.3) (Warneck, 1988; Schlessinger and Hartley, 1992; Crutzen and Andrae, 1990; Duce et al., 1991). In the state of North Carolina alone, the largest source of ammonia emission is domestic animal waste (Aneja et al., 2001). The swine in North Carolina are estimated to emit 68,540 tons of ammonia per year, which makes swine the largest contributor among all domesticated animals in North Carolina (Aneja et al., 1998). Ammonia and ammonium have become a significant contributor to total $PM_{2.5}$ concentration. Ammonia can react with acidic compounds to form various aerosols such as ammonium nitrate (NH_4NO_3), ammonium chloride (NH_4Cl), ammonium sulfate ($(NH_4)_2SO_4$), and ammonium bisulfate (NH_4HSO_4) as detailed in the reactions below. In addition to the reactions shown, there are even more complicated salts made up of sulfate and ammonium, which complicate the impact of ammonia even more. (Seinfeld & Pandis, p. 1998)

$$NH_3\,(g) + HNO_3 \longleftrightarrow NH_4^+ + NO_3^-$$

$$NH_4HSO_4 + NH_3 \longrightarrow (NH_4)_2SO_4$$

$NH_3 + HCl \longleftrightarrow NH_4^+ + Cl^-$

$NH_4HSO_4 \longleftrightarrow NH_4^+ + HSO_4^-$

$NH_3 + HSO_4^- \longleftrightarrow NH_4^+ + H_2SO_4^{2-}$

1.2.4 Hydrochloric Acid/Chlorine

Chlorine does not enter the atmosphere just as chlorine, but as some sort of compound containing carbon, hydrogen, and other halogens, such as bromine, and fluorine. The sources of atmospheric chlorine are mostly anthropogenic, with some fluxes coming naturally from the oceans and from biomass burning. (Summarized in Table 1.4) (IPCC, 1995, Singh, 1995) When chlorine enters the atmosphere in this form, it quickly turns into atomic chlorine through the reactions shown below. Once in this form, the chlorine atom is extremely reactive with hydrocarbons, and will quickly react to form hydrochloric acid. Just as with the other atmospheric acids, hydrochloric acid is much more stable in a water droplet then in a gaseous state. If it is present in the form of water, it will move into the aqueous state and disassociate into the hydrogen ion and the chloride ion. (Seinfeld & Pandis, p. 1998)

$CH_3Cl + OH \longrightarrow CH_2Cl + H_2O$

$CH_2Cl + O_2 + M \longrightarrow CH_2ClO_2 + M$

$CH_2ClO_2 + NO \longrightarrow NO_2 + HCHO + Cl$

$Cl + RH \longrightarrow R + HCl$

$HCl\,(aq) \longleftrightarrow H^+\,(aq) + Cl^-\,(aq)$

1.3 Aerosol Model

A number of aerosol modules have been developed to simulate fine particulate matter. A particular area of focus has been studying the inorganic aerosols of fine particulate matter, which make up 25-50% of total fine particulate matter (Grey et al., 1986). Some

examples of these aerosol modules are MARS-A, SEQULIB, SCAPE2, EQUISOLV II, and AIM2, which have been thoroughly reviewed for their similarities and differences (Zhang et al., 2000). ISORROPIA is a thermodynamic equilibrium model used for predicting the partitioning of major inorganic species between the gas phase and aerosol phase. This model was selected due to its efficiency in computation and its overall satisfactory performance against more comprehensive aerosol thermodynamic models. With an input of temperature, relative humidity, and the total (gas + aerosol) concentrations of sodium, ammonium, nitrate, chloride, and sulfate, ISORROPIA predicts how much the total amount will be in the gas and aerosol phases (Nenes et al., 1998; 1999).

1.4 Objectives of Research

Due to the need for more information on the hog operations, a proposal titled "Characterization and Fate of Ammonia and Hydrogen Sulfide from Animal Feeding Operations: Their Emissions, Transport, Transformation, Deposition, and Impact on Fine Particulate Matter (PM_{fine})" was submitted for funding to the United States Department of Agriculture through the National Research Initiative Integrated Program and was accepted.

As a part of this USDA sponsored research project, this study focuses on the effect of the gaseous ammonia emissions from the hog industry on fine particulate matter in eastern North Carolina on a local and regional scale. While studies have been done to measure the concentrations of fine particulates at the hog farm site, this analysis of both the local and regional concentrations stemming from the hog facilities has not been attempted. Due to the impact that the primary emissions of ammonia from the hog industry has the area, this study will involve measuring and collecting only inorganic fine particulate matter, which does not include particulate matter made up of elemental and/or inorganic carbon.

The primary objective of this study is to investigate the effect of increased ammonia emissions on the $PM_{2.5}$ concentrations throughout eastern North Carolina. The source of these increased ammonia emissions is the presence of the hog industry. The work conducted here includes analysis of the constituents of $PM_{2.5}$, their correlations with meteorological variables, and the impact of the hog facilities on $PM_{2.5}$ concentrations. Another objective is to test how well ISORROPIA can predict the $PM_{2.5}$ concentrations and under what ambient conditions the model has its best performance in reproducing $PM_{2.5}$ concentrations.

The primary objective and subsequent goals of this study are:

1) To measure gases/fine particulate concentrations at a farm using a annular denuder/filter pack system

2) To obtain regional gas/particulate data to try to understand regional impacts

3) The data collected from the farm site and regional monitoring sites will be used to

a) Calculate the sum of Inorganic $PM_{2.5}$ concentrations (Sulfate, Nitrate, Ammonium, & Chloride)
b) Observe any meteorological trends that might be present
c) Investigate any seasonal variations
d) Investigate impact of increased ammonia concentrations on $PM_{2.5}$ concentrations
e) Use an atmospheric aerosol model to simulate PM2.5 concentrations and study the impact of changing initial conditions

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Source	H_2S	DMS	CS_2	OCS[d]	SO_2	SO_4	Total[a]
Fossil-fuel combustion + industry		Total reduced S: 2.2			70	2.2	71–77 (mid-1980s) (68/6)
Biomass burning	<0.01?	—	<0.01?	0.075	2.8	0.1	2.2–3.0 (1.4/1.1)
Oceans	<0.3	15–25	0.08	0.08	—	40–320	15–25 (8.4/11.6)[b]
Wetlands	0.006–1.1	0.003–0.68	0.0003–0.06	—	—	—	0.01–2 (0.8/0.2)
Plants + soils	0.17–0.53	0.05–0.16	0.02–0.05	—	—	2–4	0.25–0.78 (0.3/0.2)[c]
Volcanoes	0.5–1.5	—	—	0.01	7–8	2–4	9.3–11.8 (7.6/3.0)
Anthropogenic (total)							73–80
Natural (total, without sea salt and soil dust)							25–40
Total							98–120

[a]Numbers in parentheses are fluxes from Northern Hemisphere/Southern Hemisphere.
[b]Excluding sea-salt contributions.
[c]Excluding soil dust contributions.
[d]Andreae and Crutzen (1997)
Source: Berresheim et al. (1995).

Table 1.1, Global Sulfur Emissions Estimates (Tg(S) yr^{-1})(from Seinfeld and Pandis, 1998, p. 59)

Sources	Magnitude ($Tg(N)\ yr^{-1}$)	Comments
Fossil-fuel combustion	24	Surface source; >95% NH
Soil release (natural and anthropogenic)	12	Continental surface source
Biomass burning	8	Tropical surface source
Lightning	5	Free tropospheric source
NH_3 oxidation	3	Tropospheric source
Aircraft	0.5	6–12 km source; 95% NH
Transport from stratosphere	0.1 (0.6 total NO_y)	Free tropospheric source

Source: IPCC (1995).

Table 1.2, Estimated Global Emissions of NO_x Typical of the Last Decade (from Seinfeld & Pandis, 1998, p. 70)

Process	Flux (Tg NH_4–N/yr)	Percent of Total	Anthropogenic as Percent of Total
Input sources:			
Domestic animal waste decomposition	22	45	45
Soil loss from organic matter (excluding fertilizer)	10	20	
Fertilizer release	4	8	8
Coal combustion	0.03	<<1	<<1
Biomass burning	1.3	3	3
Sea surface release	12	24	
Total input	49.3	100	56
Removal:			
Reaction in atmosphere with OH	1		
Land—rainfall	23		
Land—dry part. NH_4 deposition (1/3 wet)	8		
Ocean—rainfall (Duce et al. 1991)	14		
Ocean—dry deposition—particulate NH_4	2		
Total removal	48		

Sources: Warneck 1988; Schlesinger and Hartley 1992; Crutzen and Andrae 1990; Duce et al. 1991.

Table 1.3, Fluxes of Ammonia: The Atmospheric Ammonia Cycle (from Berner & Berner, 1996, p. 117)

Compound	Generic Name	1992 Mixing Ratio (ppb)	Atmospheric Burden (Tg)	Lifetime (yr)	Sources[a]	Sinks[b]
$CFCl_3$	CFC-11	0.268	6.2	50 ± 5	A	Strat. $h\nu$
CF_2Cl_2	CFC-12	0.503	10.3	102	A	Strat. $h\nu$
$CF_2ClCFCl_2$	CFC-113	0.082	2.6	85	A	Strat. $h\nu$
CF_2ClCF_2Cl	CFC-114	0.020	—	300	A	Strat. hν
CCl_4	Carbon tetrachloride	0.132	3.4	42	A	Strat. $h\nu$
CH_3CCl_3	Methyl chloroform	0.160	3.5	5.4 ± 0.6	A	Trop. OH
CH_3Cl	Methyl chloride	0.6	5.0	1.5	N(O),BB	Trop. OH
CF_2HCl	HCFC-22	0.105	1.5	13.3	A	Trop. OH
CH_3Br	Methyl bromide	0.012	0.15	1.3	N(O),A,BB	Trop. OH
CF_3Br	H-1301	0.002	0.05	65	A	Strat. $h\nu$
CF_4	Perfluoromethane	0.070	0.9	50,000	A	Meso. $h\nu$
SF_6	Sulfur hexafluoride	0.0025	—	3200	A	Meso. electrons
CF_3CHCl_2	HCFC-123			1.4	A	Trop. OH
CF_3CHFCl	HCFC-124			5.9	A	Trop. OH
CH_3CFCl_2	HCFC-141b			9.4	A	Trop. OH
CH_3CF_2Cl	HCFC-142b	0.0035		19.5	A	Trop. OH
$CF_3CF_2CHCl_2$	HCFC-225ca			2.5	A	Trop. OH
$CClF_2CF_2CHClF$	HCFC-225cb			6.6	A	Trop. OH
$CHCl_3$	Chloroform			0.55	A,N(O)	Trop. OH
CH_2Cl_2	Methylene chloride			0.41	A	Trop. OH
CF_3CF_2Cl	CFC-115	<0.01		1700	A	Strat. $O(^1D)$
C_2Cl_4	Tetrachloroethene	0.002		0.4	A	Trop. OH

[a]A = anthropogenic; N(O) = natural (oceanic); BB = biomass burning.
[b]Strat $h\nu$ = photolysis in stratosphere; Trop OH = hydroxyl radical reaction in troposphere; Meso. electrons = mesosphere electron impact; Strat $O(^1D)$ = reactions in stratosphere with excited atomic oxygen.
Source: IPCC (1995) and Singh (1995).

Table 1.4, Atmospheric Halogens (from Seinfeld & Pandis, 1998, p. 88)

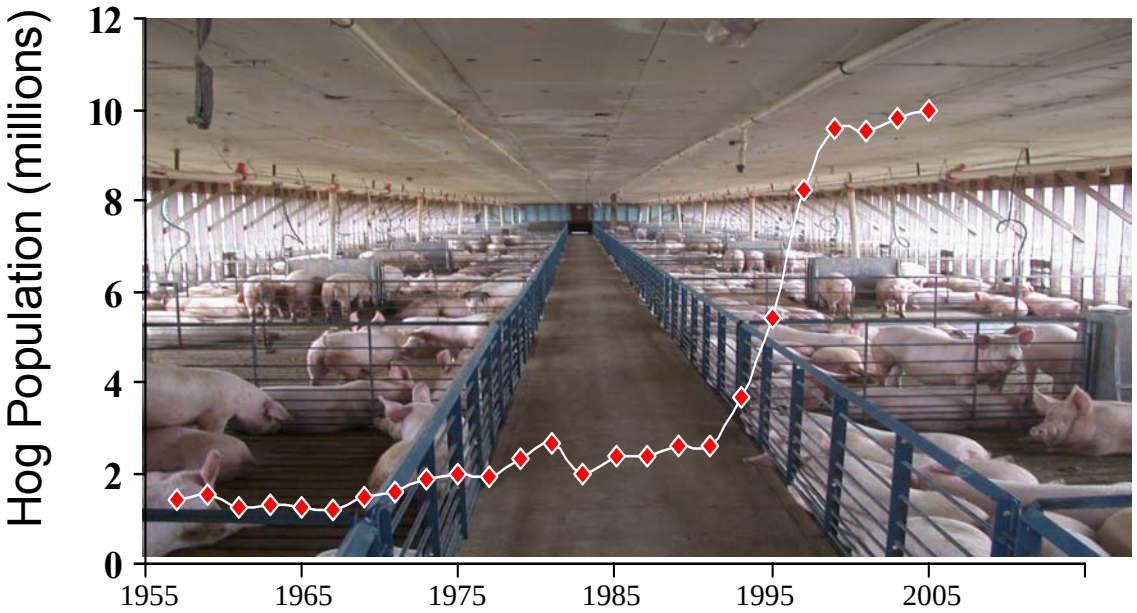

Figure 1.1, Hog Population Trends in North Carolina over the past 50 years (NCDA, 2000)

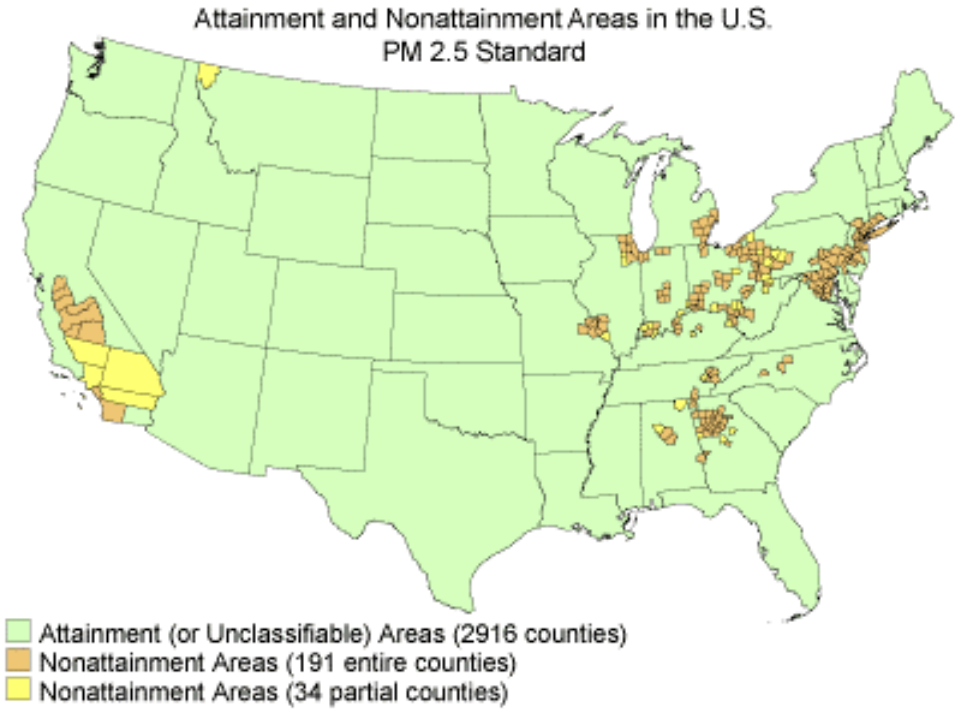

Figure 1.2 (EPA, http://www.epa.gov/pmdesignations/nonattaingreen.htm)

Chapter 2. Measurement and Analysis of Acidic Gases and Inorganic Fine Particulate Matter in Rural Ammonia-rich Areas

2.1 Data Measurement Schedule and Site Description

Samples were collected at two near-by sites in eastern North Carolina. (Figure 2.1) Each site was sampled for approximately two weeks four different times over one calendar year, one sampling period during each season. (The exact dates of collection are documented in Table 2.1) The samples collected were daily samples, which were converted into daily average values in the analyzation process.

The first sampling site was Moore Brothers Farm, which was located in Jones County near Kinston, NC (35.14°N, 77.47°W) (An aerial view of the farm and data collection instrument can be seen in Figure 2.2) This farm can be characterized as a lagoon and spray technology farm, which is the common type of hog farm in North Carolina. The farm pigs are being kept in a number of closely-spaced houses. Each house has a fan ventilation system, which keeps the air within the houses constantly flushed out into the surrounding environment. The effluents from the houses are flushed directly into a nearby storage lagoon. Periodically, the effluent is pumped out of the lagoon and sprayed as a fertilizer over agricultural crops. The ammonia flux originates from each step as the waste is transported from the production houses to the agricultural crops. (See Figure 2.4) The second sampling site was at Lenoir County Community College, which is located in Lenoir County in the outskirts of Kinston, NC (35.23°N, 77.56°W) (A map of the community college with the exact positioning of the instrument can be seen in Figure 2.3)

2.2 Data Collection and Analysis

2.2.1 Meteorological Data Collection

To monitor all of the important meteorological conditions, a 10 meter meteorological tower (See Figure 2.5) was put up to record the following meteorological parameters: air temperature, relative humidity, solar radiation, wind speed, and wind direction. The air temperature and relative humidity values were measured at a height of two meters with a Campbell Scientific (Model CS500-L Vaisala 50Y) temperature and relative humidity probe housed in a Campbell Scientific Model 41303 RM Young 6-plate gill solar radiation shield. This instrument is accurate to ±3% over 10-90% relative humidity and ±6% over 90-100% while the air temperature accuracy is 0.2-0.5°C. The solar measurements, which were also made at a height of two meters using a Campbell Scientific (Model LI200X) Silicon Pyranometer fixed calibration probe, have an absolute error in natural daylight of 3-5%, and a sensitivity of 0.2 kW m^{-2} mV^{-1}. The wind speed and wind direction were measured using a Campbell Scientific Met One Instruments Windset (Model 034-B) with an integrated cup anemometer and wind vane mounted on a common shaft. This instrument will accurately measure wind speed ± 0.12 m s^{-1} for wind speeds below 10.1 m s^{-1} and ± 1.1% of reading for wind speeds above 10.1 m s^{-1}. The wind direction component has an accuracy of ± 4° and a threshold of 0.4 m s^{-1}. To record the meteorological values, all of the instruments are hooked up to Campbell Scientific (Model CR10X) Data logger with an attached Campbell Scientific (Model AM) 16/32 Channel Relay Multiplexer, which acts as an automated data acquisition system. The Data logger will record 15-minute averaged measurements from all of the meteorological instruments, which will then be converted into daily values to use with the daily acidic gas/fine particulate concentrations. Using a Dell Inspiron 600m laptop

computer, the meteorological data is converted into a useable computer format. The recorded values were checked periodically in order to ensure that the detection instruments are operating properly. The Data logger is housed in a temperature-controlled mobile laboratory, which is owned and operated by the North Carolina State University Air Quality Research Lab. (The Ford Aerostar mobile lab is seen in Figure 2.6)

2.2.2. Acidic Gas and Fine Particulate Matter Collection

The acidic gas samples and fine particulate matter samples were collected using a URG Dual Sequential Fine Particle Sampler (URG-2000-01K) on loan from the North Carolina Division of Air Quality. (A picture of the instrument is seen in Figure 2.7) As a sample is collected, air is pulled through the instrument by the two external attached pumps. The air is pulled in through the inlet, and immediately passes through a cyclone, which removes all particles with a diameter larger than 2.5 micrometers. (μm) After traveling through a channel splitter, the air traveled through a 30 mm-diameter, 150 mm-length sodium carbonate coated annular denuder to collect the acidic gases, and then through a filter pack containing one Teflon filter and one nylon filter in series to collect the inorganic particulates. The air is then pulled all the way into the pumps, and is released out of the back of the pumps. A small computer, which is part of the instrument, is used to turn the pumps on and off, and to dictate which channel and thus what denuder/filter pack the air flows through. The flow rate of the instrument was set to 10 meters per second, which is the recommended flow rate for the instrument and the 24-hour sample was collected from 12:01 a.m. to midnight each day.

To capture a particular atmospheric species, an annular denuder (Figure 2.8) is coated on the inside with a chosen compound that will retain that particular atmospheric species.

The interior of an annular denuder is made to maximize the amount of surface area, which allows for an extremely high retention rate of the pertinent atmospheric species. In this case, a coating of sodium carbonate was chosen, because it is able to collect sulfur dioxide (SO_2), nitrous acid (HNO_2), nitric acid (HNO_3), and hydrochloric acid. (HCl) This coating was prepared by mixing glycerol and solid sodium carbonate with a solvent of 50/50 water and ethanol. In order to coat the denuder, ten milliliters of the coating solution was placed into the denuder, and the denuder was rotated in order to ensure even coating. The excess coating solution was decanted out, and the denuder was dried in order to remove any excess solvent while leaving a coating of sodium carbonate inside the denuder. At this point, the annular denuder is ready to be placed in the instrument out in the field. After the sample has been collected, the annular denuder was brought back to the laboratory, and the sample was extracted. For sample extraction, five milliliters of water was placed into each denuder, and it was rotated in order to ensure complete removal of the extracted gases. This five milliliter sample was poured into an extraction vial, and then this entire procedure was repeated. To complete the extraction process, one milliliter of hydrogen peroxide was added to the sample in order to convert all of the sulfite (SO_3^-) into sulfate (SO_4^{2-})

For capturing the fine particulates, a URG 47-millimeter, 2 stage filter pack is used with a Teflon filter and a nylon filter in series. (See Figure 2.8) The Teflon filter will collect sulfate, nitrate, and ammonium in the particulate phase, while the nylon filter will collect any particulate nitrate that evaporates off of the Teflon filter. To prepare the filter packs for use, the filter pack is disassembled and the Teflon and nylon filter are placed into the filter pack with some filter forceps. Once the filter pack is reassembled, the pack is ready for data collection. Once the filter pack is used, the process of sample extraction can be done. In an

ammonia-free environment, the Teflon filter should be placed filter-side down in an extraction vial, and saturated in six milliliters of 0.0001N perchloric acid. The extraction vial should then be placed in the dark at 4°C until the filters can be analyzed. Once the filters are ready to be analyzed, they are wet down in the extraction vial with 200 microliters of ethanol, and then placed in an ultrasonic bath for 15 minutes. For the nylon filter, saturate the filter in ten milliliters of water, and place in an ultrasonic bath for 30 minutes. For both the annular denuders and the filter packs, it should be noted that each case, it is assumed that each denuder/filter pack collects 100% of the acidic gases/particulates. In addition, particle losses are assumed to be less than 1% when passing through the annular denuder. (This preparation and extraction information can all be found in the EPA document at http://www.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-4-2.pdf)

The analysis of the samples was performed with a Dionex DX500 ion chromatograph at the Analytical Service Laboratory at North Carolina State University. It should be mentioned that during this analysis, many of the Teflon filter samples were determined to have a large amount of contaminants, which limited the amount of particulate data that was able to be collected. From a number of trial and error experiments, it is believed that the original plastic extraction vials were reacting with some or all of the chemicals used in extracting the Teflon filters, and these vials were replaced with 25 milliliter Wheaton glass sample vials. Once these vials were replaced, the contaminant problem in the Teflon filter samples ceased. Therefore, while acidic gas data was collected for each season, fine particulate matter data was only collected for the last summer season. The atmospheric concentrations are obtained from the ion chromatograph in micrograms per milliliter, and need to be converted into a suitable atmospheric concentration. In order to begin, the total

sample volume of air that flows through the machine in one day must be calculated, as follows:

$V_s = F\ t$ (2.1)

Where: F = flow rate from the instrument output

t= net elapsed time

V_s = total sample volume

Finally, to calculate the volume of the sample at EPA-reference conditions, the following equation must be used:

$$V_{std} = V_s \left(\frac{P_{bar}}{P_{std}}\right)\left(\frac{T_{std}}{T_m}\right) F_c \quad (2.2)$$

Where,

V_{std}= Total sample volume at Standard Temperature and Pressure (STP) of 298K and 1.0133×10^5 Pa, m^3

V_s= Total sample volume at actual conditions, m^3

T_{std} = Standard temperature = 298 K

P_{std} = Standard pressure = 1 atm = 1.0133×10^5 Pa

T_m = Dry Gas Meter temperature , K

P_{bar} = Actual barometric pressure, Pa

F_c=Dry Gas Meter calibration factor (if applicable), dimensionless

For this equation, given the extremely small pressure variations at the earth's surface, the actual barometric pressure was assumed to be 1 atmosphere at all times, and the T_m value was taken to be the daily measured average temperature. Finally, using the V_{std} for each day, each aqueous concentration can be converted over to the proper gaseous concentration using the following equation.

$$C_g[\mu g/m^3] = \frac{\left(\frac{MW_g}{MW_{ion}}\right)\left(C'_{ion}\left[\frac{\mu g}{ml}\right] \times v[ml]\right)}{V_{std}} \quad (2.3)$$

where,

$C_g\ [\mu g/m^3]$ = Concentration of pollutant gas, $\mu g/m^3$

MW_g = Molecular weight of pollutant gas, g/mole

MW_{ion} = Molecular weight of equivalent ion in sample extraction, g/ mole
C'_{ion} = Concentration of equivalent ion in sample extraction, µg/ml
v = Extraction volume, ml
V_{std}= Total sample volume at standard temperature and pressure (STP) of 298K and 1.0133 x 10^5 Pa, m^3

The concentrations can then easily be converted into ppb if the analysis calls for a concentration that does not change with respect to temperature and pressure.

2.3 Analysis of Local Acidic Gas and Fine Particulates Concentrations Data:

In Table 2.2, we see the average concentrations, minimum, and maximum for each atmospheric pollutant irrespective of their seasonal changes. This shows that in most cases, the farm site has higher inorganic particulate concentrations than the C.C. (Community College) site, while the observations are mixed for the acidic gases with nitrous acid higher at the C.C. site, sulfur dioxide and hydrochloric acid higher at the farm site, and nitric acid had the same average concentration. The minimum and maximum values were consistent with the average values except for the maximum values of sulfur dioxide and nitric acid. This can be explained by the possibility of regional transport from the urban areas of Raleigh/Durham or Fayetteville. In Figure 2.9, we see the seasonal differences in the four acidic gases for each site. Given the range of the plots, most of the acidic gases do not exhibit seasonal changes. The nitrous acid and nitric acid concentrations are relatively constant around 0.085 ppb and 0.045 ppb, respectively, at both sites. Somewhat puzzling are the sulfur dioxide concentration measurements, which vary uncharacteristically at the farm site, yet are remarkably constant for three of the four seasons at the community college site. It is believed that these values are again the result of regional transport from urban areas. The other curious values are the elevated hydrochloric acid values in winter at the C.C. site and in

winter and spring at the farm site. Even in these seasons, most of the hydrochloric acid concentrations were below the detection limit of the analytical instruments, but in a few cases where it was detected, the wind direction was within or just outside the southeast quadrant of the compass. This suggests that the probable source of the measured hydrochloric acid was atomic chloride from a marine air mass that was quickly converted into hydrochloric acid in the atmosphere.

One of the project goals was to investigate the relationships between meteorological conditions and fine particulate matter, but the limited amount of fine particulate matter data does not allow for these to be investigated.

In Figure 2.10 & 2.11, we see a group of time series plots, which show the various gaseous and particulate concentrations that we have for each site. These time series plots confirm what was seen when looking at the relative concentrations of the various acidic gases and particulates: that particulate sulfate is the dominant anion. The time series plots also show that ammonium, not surprisingly, is the dominant cation. To study these trends more, Figures 2.12-2.14 show these same time series plots, but in gas/particulate pairs. The sulfur dioxide/sulfate plot shows that these two pollutants move concurrently as the concentration changes, but the interesting fact is that there is always more sulfate then sulfur dioxide, with there being 2-3 times more sulfate at the later dates. This indicates the impact of regional sulfur having an impact on the area, because the amount of sulfate measured could not be produced by the measured concentrations of sulfur dioxide. The nitric acid/nitrate and nitrous acid/nitrate plots show some concurrent variations from day to day, but no overall trend is seen. While the nitrate concentrations are greater at some times than the nitrous acid and nitric acid concentrations combined, this does not necessarily indicate another nitrogen

source, because of the relatively small scale differences. This difference could be explained by oxidation from other minor atmospheric nitrogen sources, such as nitrogen dioxide. One more interesting relationship can be seen in a time series plot of nitrous acid and nitric acid in Figure 2.15. It seems from the eight days of the time series, that in this environment, there are conditions when nitric acid is the dominant nitrogen-containing acidic gas, and there are other conditions when nitrous acid is the dominant gas. This small dataset is unable to fully explain the relationship between these two acidic gases.

In Figures 2.16, 2.17, & 2.18, we see scatter plots of each $PM_{2.5}$ substituent versus the other substituents. The strongest correlations are seen between sulfate and ammonium, which is to be expected from the reactivity of sulfur dioxide in the atmosphere. The regression relations for this relationship are shown here with y representing the ammonium $PM_{2.5}$ and x representing the sulfate $PM_{2.5}$.

Moore Farm Site: $y = 0.6067x + 0.598$ $R^2 = 0.9792$

Community College Site: $y = 0.6231x + 0.3285$ $R^2 = 0.9898$

As one can see, the very high correlation (R^2) values would allow for the estimation of the concentration of atmospheric ammonium present by measuring by measuring the atmospheric sulfate and vice versa. It should be noted that this method should only be an estimation, because the mixture of aerosol compounds ($(NH_4)_2SO_4$, NH_4HSO_4, etc.) would cause some variability given the conditions for each case. The molar ratio between ammonium and sulfate was also calculated for each site, and these ratios are practically identical with a value of 0.875 (0.70-1.04) at the farm site and a value of 0.878 (0.68-1.26) at the C.C. site. These values are within the range of other measured continental aerosol ratios,

and also indicate the lack of nitric acid in the area, or in this case a negligible concentration. (Warneck, 1999) The ammonium/nitrate and sulfate/nitrate plots show the same trend with the farm site showing a higher R^2 value for each pairing when compared to the C.C. site. This would be apparent to the proximity of the farm site to the actual ammonia emissions, while the distance between the C.C. site and rural pig farms makes the relationship less apparent.

2.4 Conclusion

Local acidic gases and fine particulate matter were monitored using an annular denuder/filter pack system, and samples were prepared and chemically analyzed according to EPA documentation. These concentrations showed a domination of the ammonium sulfate aerosol with concentrations for sulfate and ammonium varying between 0.58-5.50 ppb and 0.57-3.94 ppb respectively. While some nitrate was present, it was present in concentrations one order of magnitude less than both ammonium and sulfate. The measurements in different seasons showed constant nitrous acid and nitric acid concentrations with respect to season, but with interesting variations in both sulfur dioxide and hydrochloric acid, which were thought to be due to the impact of urban and marine environments respectively. The time series plots illustrated the connections between the ammonium and sulfate aerosols, while also suggesting that another fine particulate source of sulfur is present. The plots between the various $PM_{2.5}$ constituents show a very strong relationship between ammonium and sulfate, and also showing correlations between ammonium/nitrate and between sulfate/nitrate.

2.5 References:

Aneja, V.P., Roelle, P.A., Murray, G.C., Southerland, J., Erisman, J.W., Fowler, D., Asman, W.A.H., Patni, N., 2001. Atmospheric Nitrogen Compounds: Emissions, transport, deposition and assessment, *Atmospheric Environment 35*, 1903-1911.

Warneck, Peter, 1999. Chemistry of the Natural Atmosphere, 2nd edition, Academic Press, San Diego, CA.

Winberry, William T., Ellestad, Thomas, Stevens, Bob, 1999. Compendium Method IO-4.2: Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles (< 2.5 μm), United States Environmental Protection Agency, http://www.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-4-2.pdf.

	Fall	Winter	Spring	Summer
Start Date	10/26/04	2/16/05	4/8/05	6/15/05
End Date	11/6/04	3/1/05	4/19/05	6/24/05

Table 2.1 Seasonal Sampling Dates for Moore Farm Site and Community College Site

Acidic Gases	SO_2	HNO_2	HNO_3	HCl	
C. C. Site	0.788 (0.08-3.82)	0.159 (0-0.34)	0.034 (0-0.11)	0.282 (0-0.282)	-
Farm Site	0.815 (0.10-2.45)	0.098 (0-0.23)	0.034 (0-0.25)	0.387 (0-0.67)	-
Particulates	SO_4		NO_3		NH_4
C. C. Site	2.017 (0.58-4.17)	-	0.067 (0.03-0.10)	-	1.585 (0.57-3.21)
Farm Site	2.805 (1.20-5.50)	-	0.148 (0.09-0.25)	-	2.299 (1.13-3.94)

Table 2.2 Average, Minimum, and Maximum Concentrations of Acidic Gases and Fine Particulates

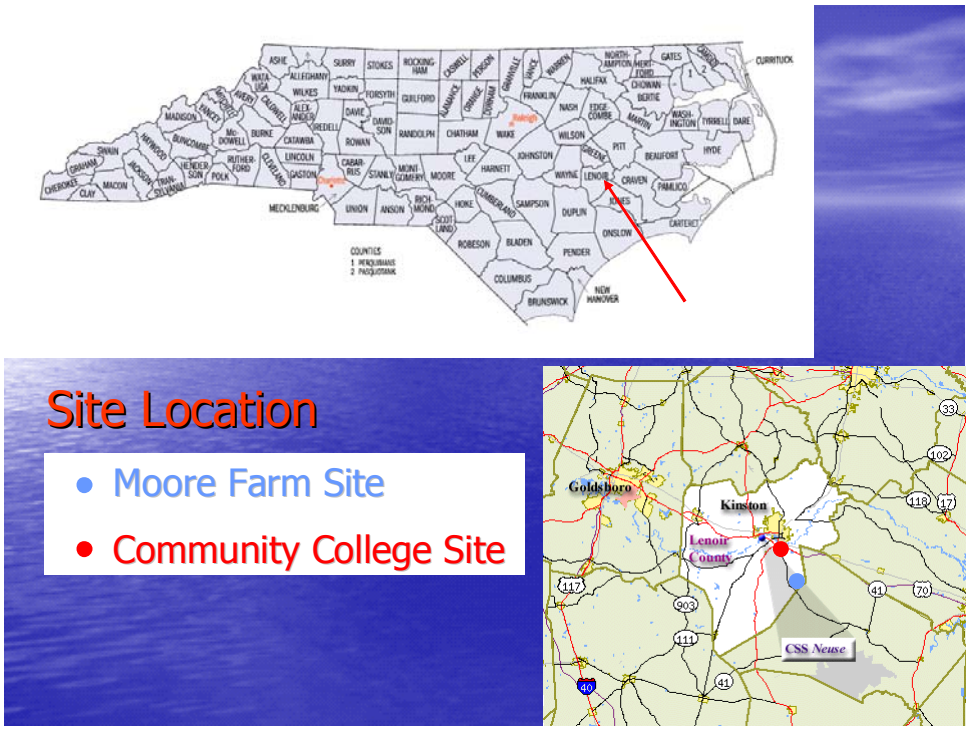

Figure 2.1 Sampling Map of Local Measurement Sites: Moore Farm and Lenior County Community College

Figure 2.2 Ariel Picture of Moore Farm with Sampling Location

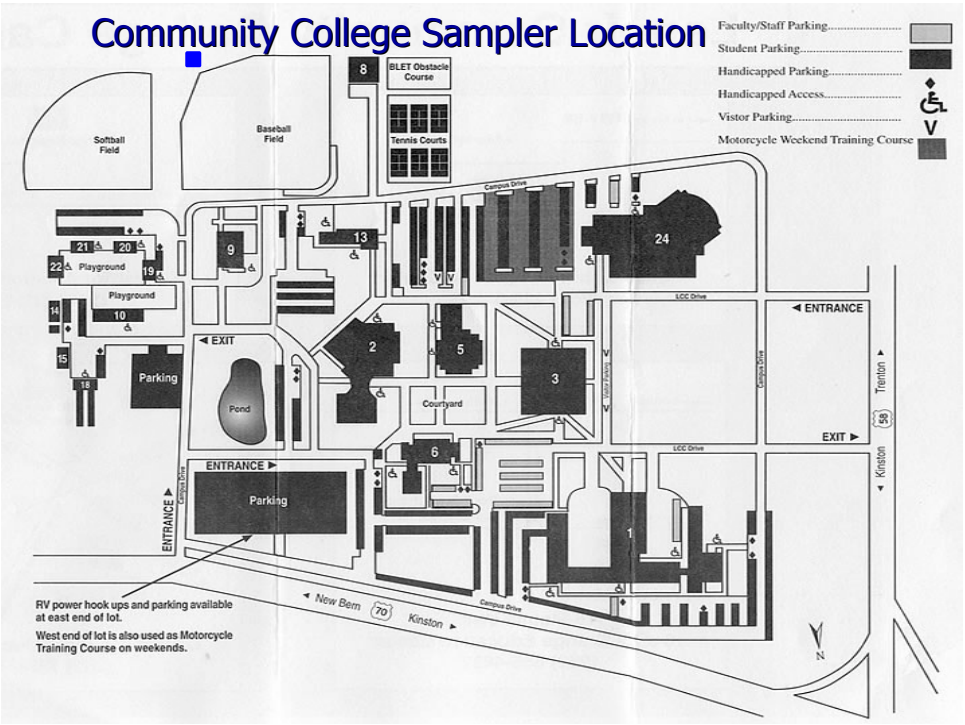

Figure 2.3 Map of Lenoir County Community College with Sampling Location (http://www.lenoircc.edu/nsite/images/campusmaps/lccmain.htm)

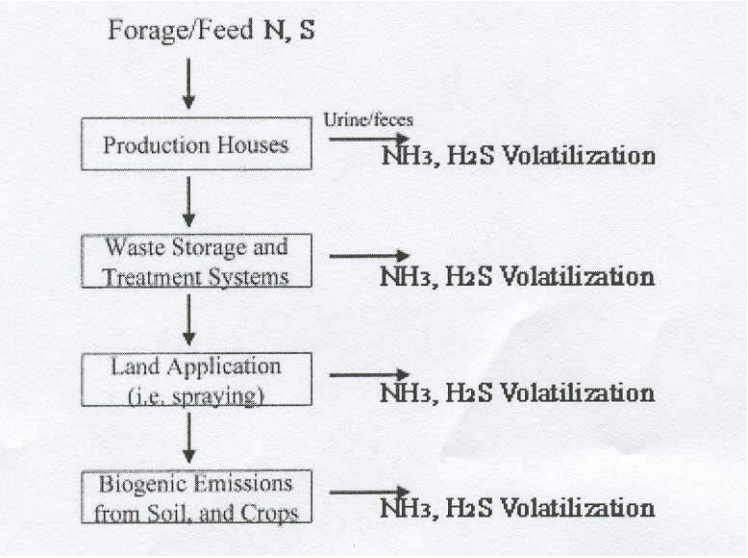

Figure 2.4 Routes for Ammonia emissions from Conventional Confined Animal Feeding Operations in North Carolina (Aneja et. al, 2001)

Figure 2.5, Meteorological Tower used in Meteorological Measurements at the Moore Farm Site

Figure 2.6, Mobile Laboratory used for temperature-controlled storage at the Moore Farm Site

Figure 2.7, URG Sequential Fine Particle Sampler (URG-2000-01K)

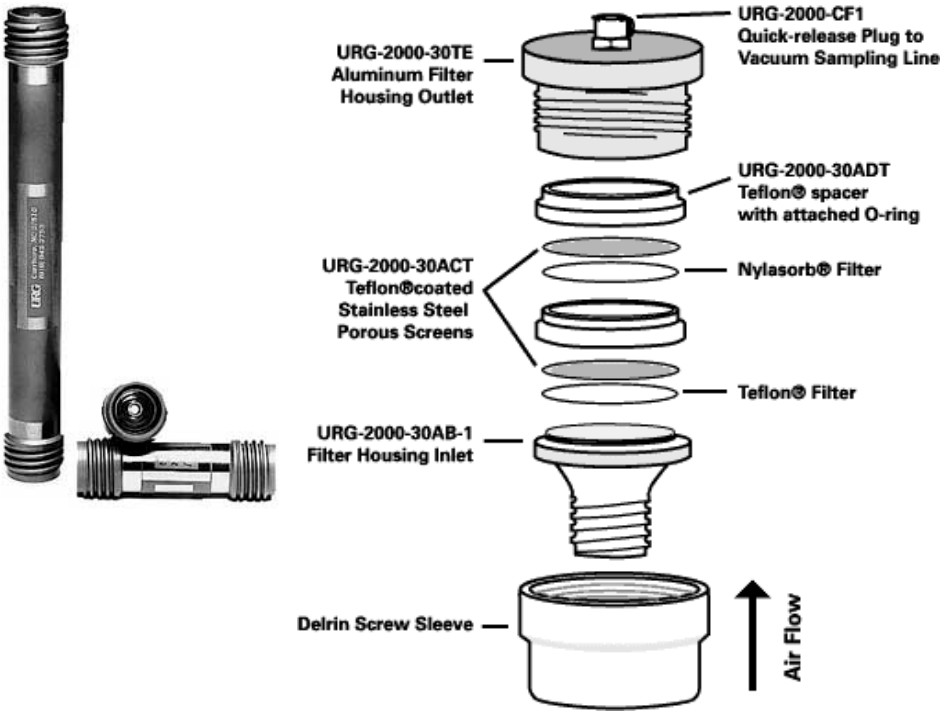

Figure 2.8, Annular Denuder and Filter Pack Sideview

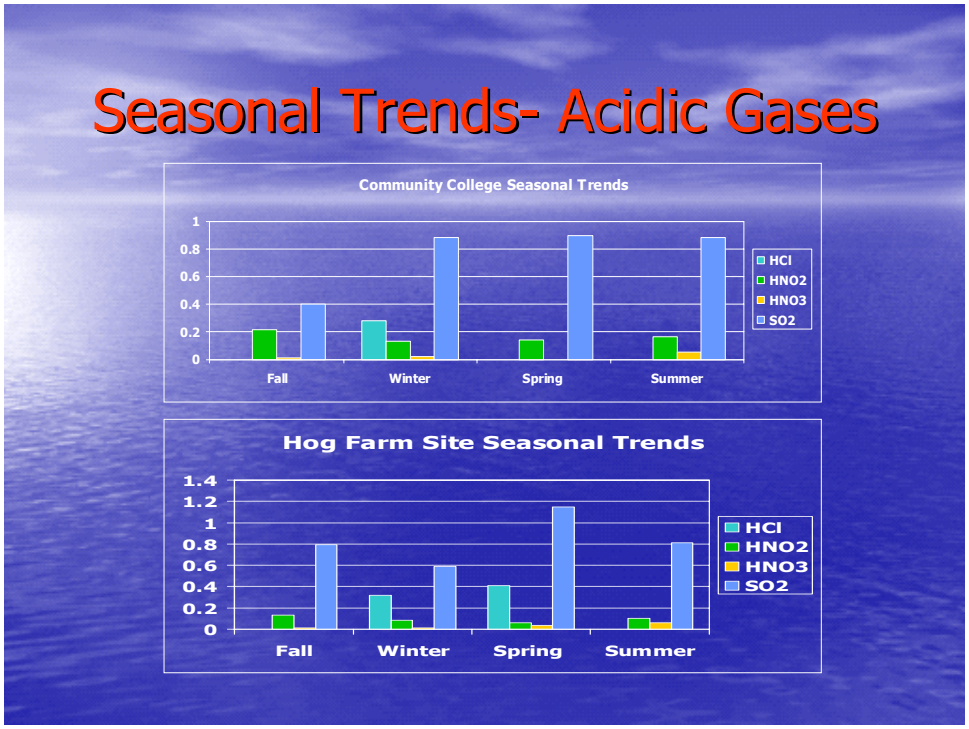

Figure 2.9, Seasonal Variations in Concentration (ppb) of Acidic Gases at Lenoir County CC Site and at Moore Farm Site

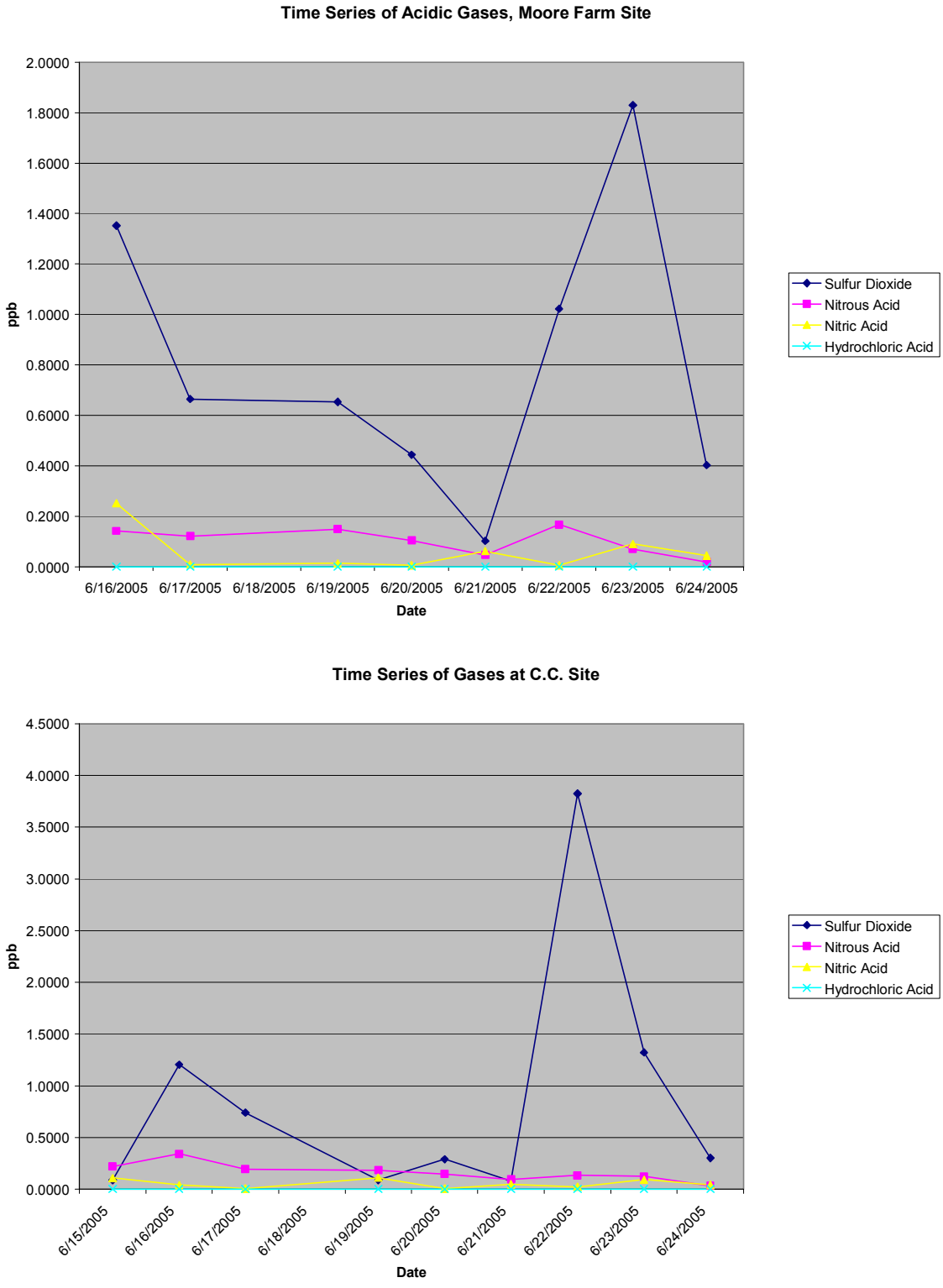

Figure 2.10, Time Series of Acidic Gases during Summer Sampling Period for C.C. Site and Farm Site

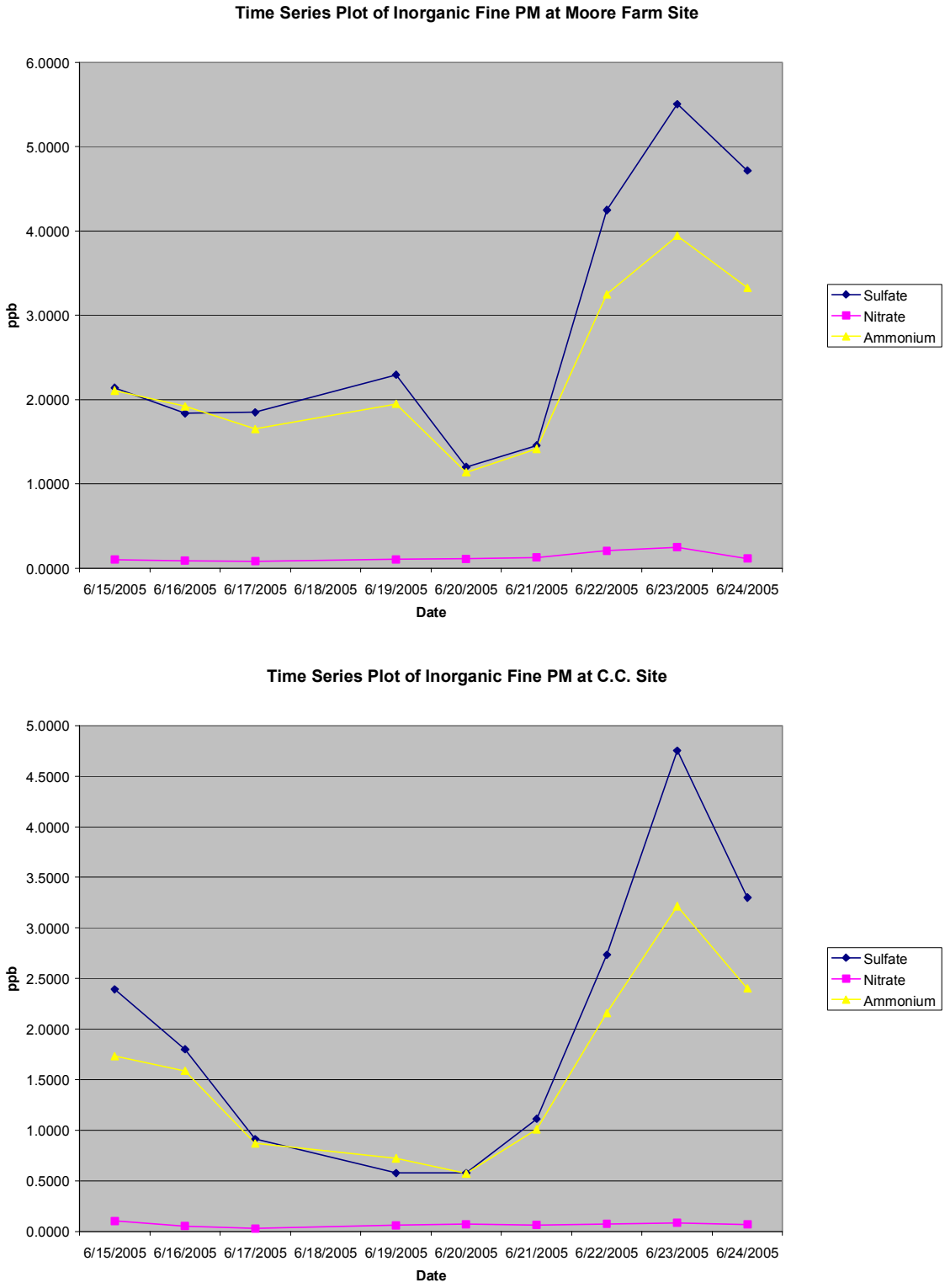

Figure 2.11, Time Series of Sulfate, Nitrate, and Ammonium during Summer Sampling Period for C.C. Site and Farm Site

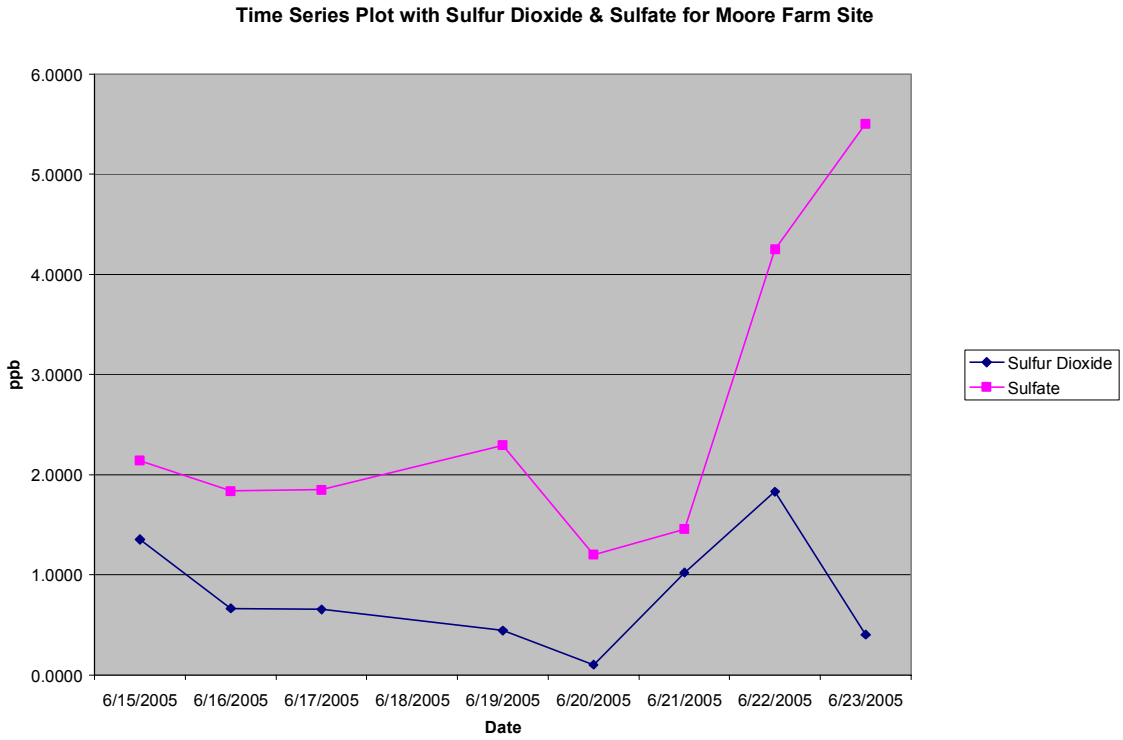

Figure 2.12, Time Series of Sulfur Dioxide and Sulfate during Summer Sampling Period for Farm Site

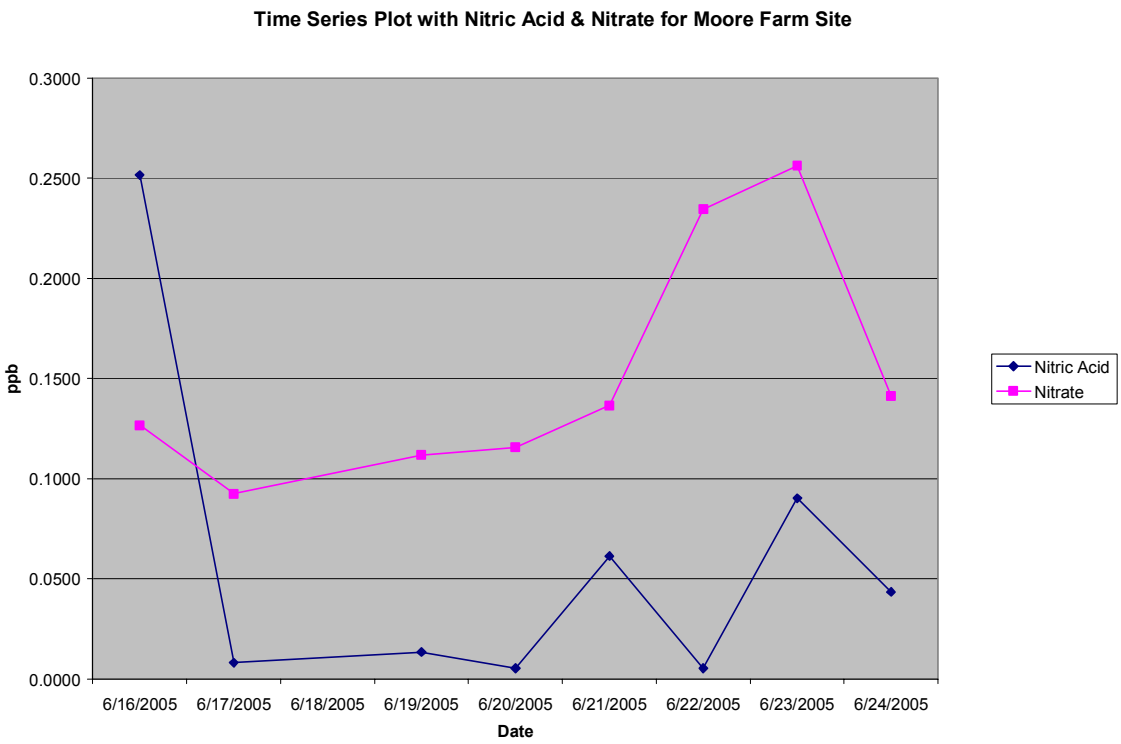

Figure 2.13, Time Series of Nitric Acid and Nitrate during Summer Sampling Period for Farm Site

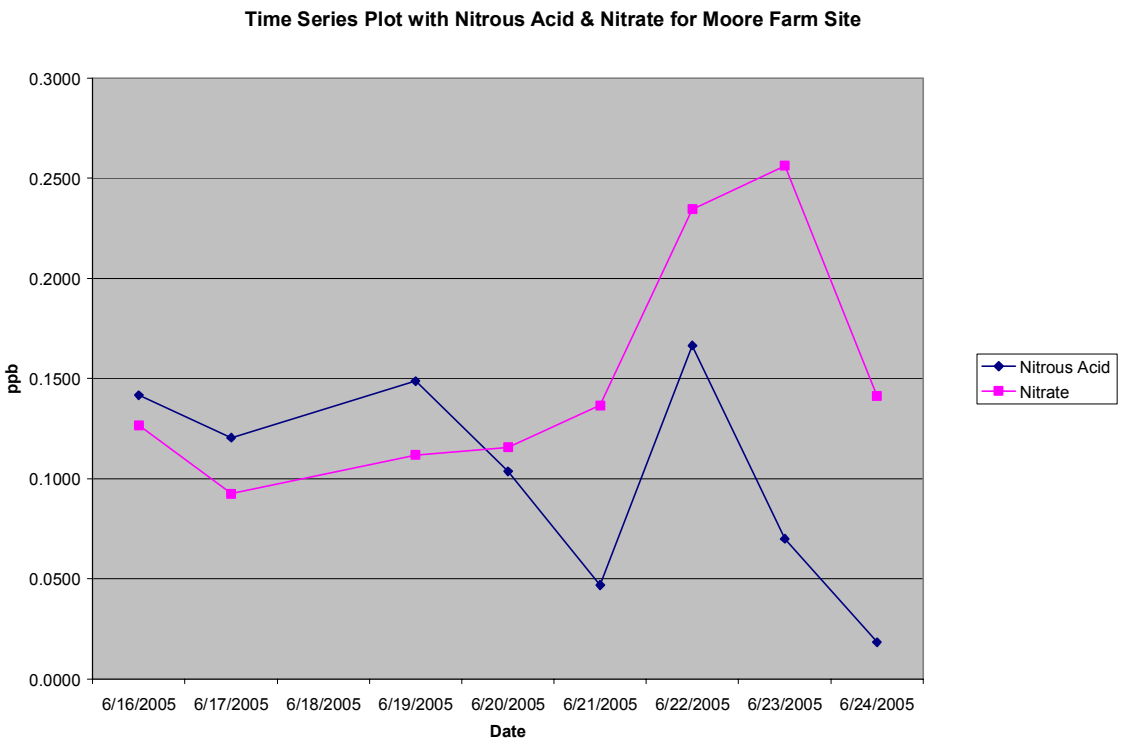

Figure 2.14, Time Series of Nitrous Acid and Nitrate during Summer Sampling Period for Farm Site

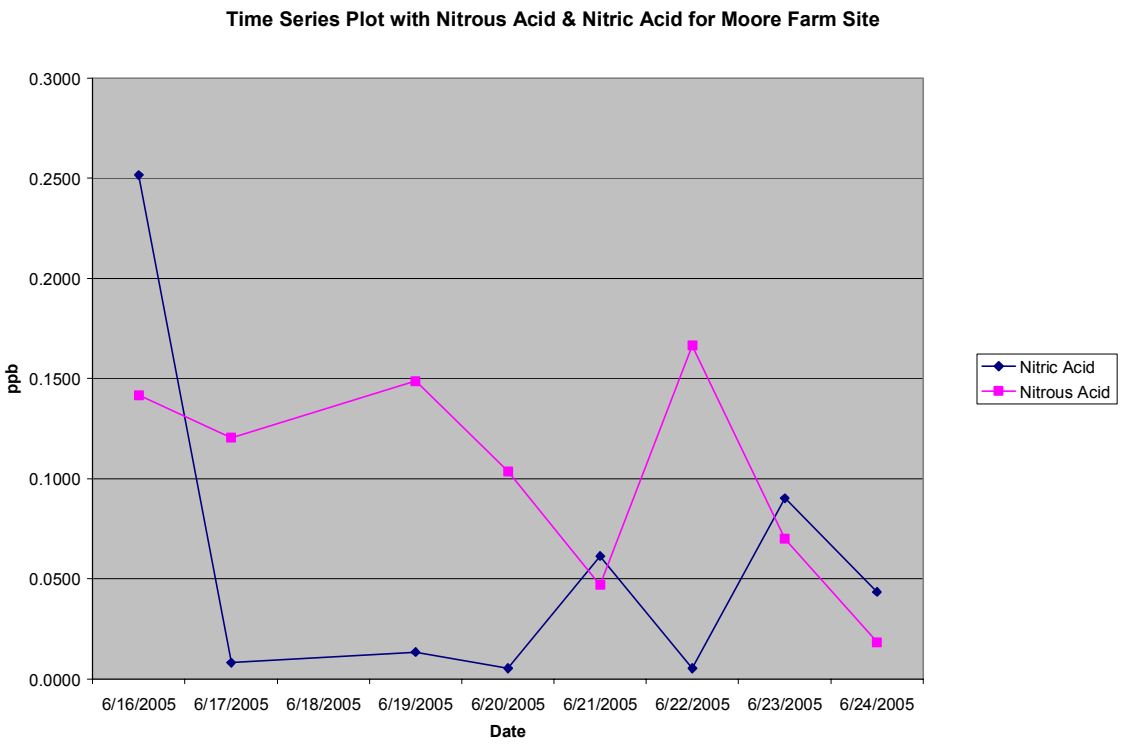

Figure 2.15, Time Series of Nitrous Acid and Nitric Acid during Summer Sampling Period for Farm Site

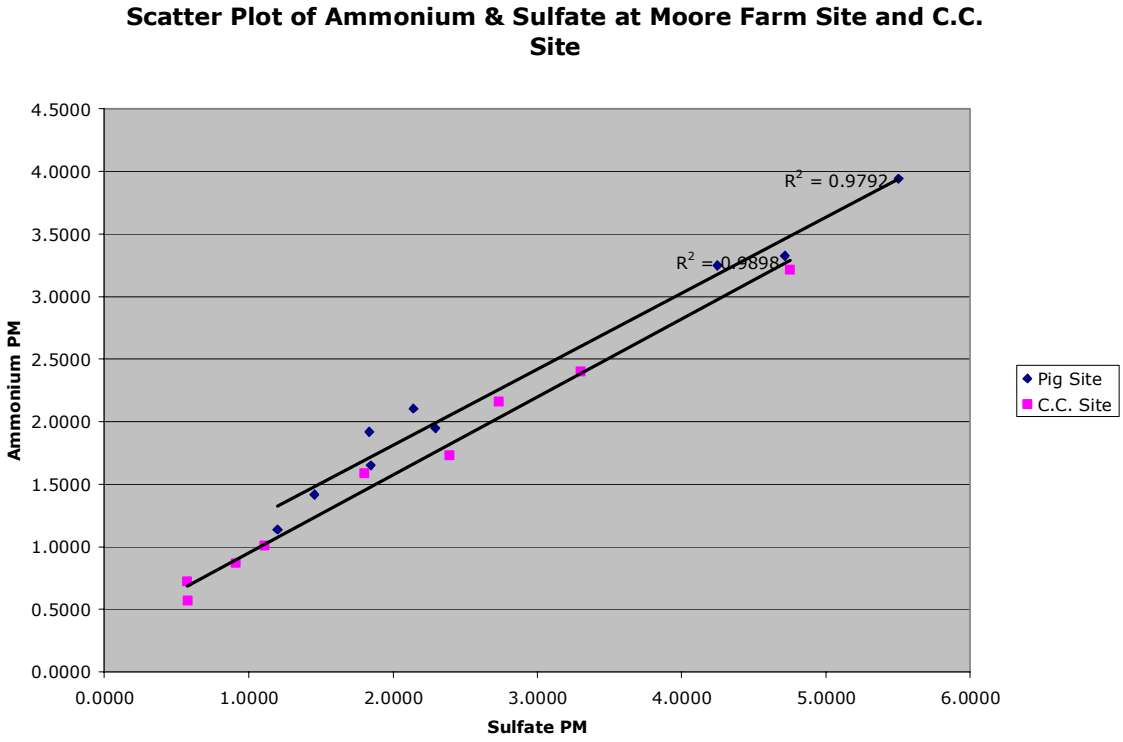

Figure 2.16, Scatter Plot of Sulfate vs. Ammonium during Summer Sampling Center for C.C. Site and Farm Site

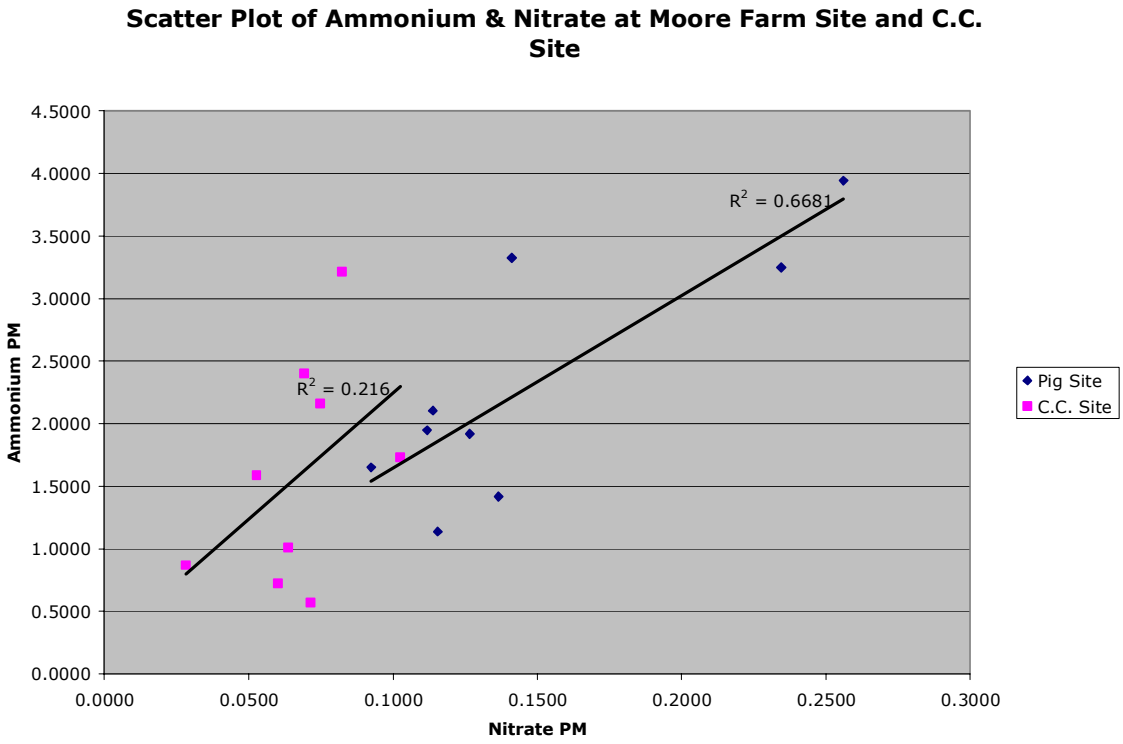

Figure 2.17, Scatter Plot of Ammonium vs. Nitrate during Summer Sampling Center for C.C. Site and Farm Site

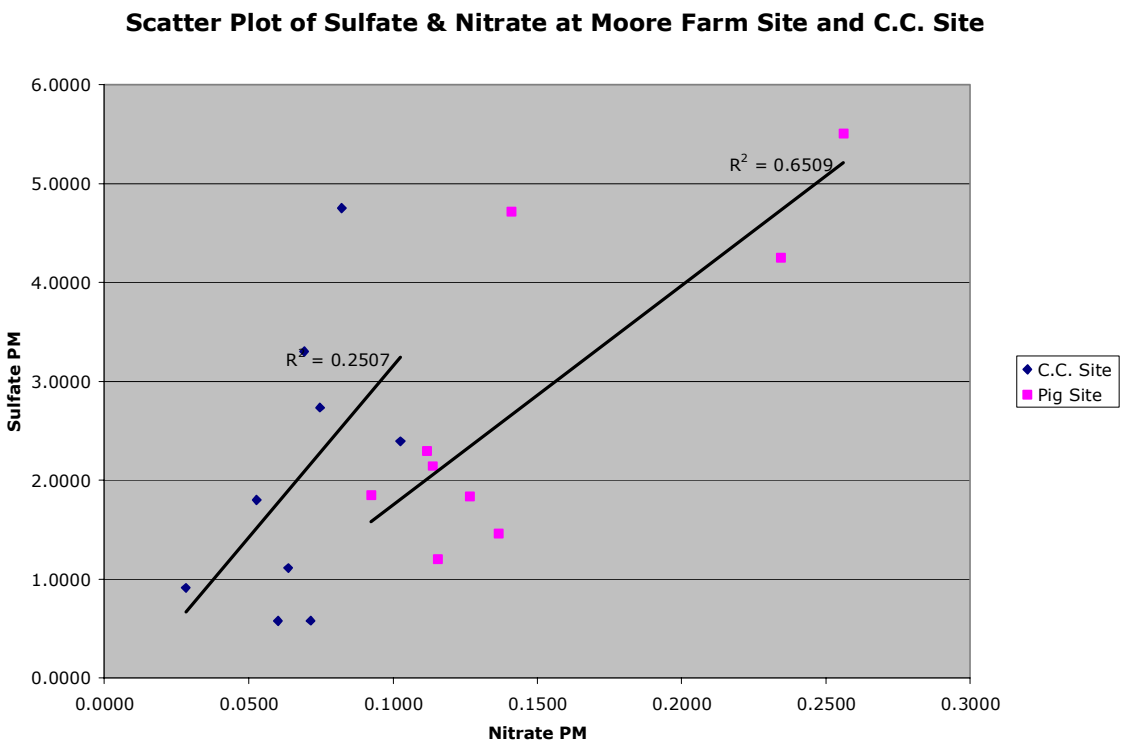

Figure 2.18, Scatter Plot of Sulfate vs. Nitrate during Summer Sampling Center for C.C. Site and Farm Site

Chapter 3. Regional Analysis and Modeling of Fine Particulate Matter in Eastern North Carolina

3.1 Methods

3.1.1 Regional Data Collection and Site Description

$PM_{2.5}$ observational data was obtained from the North Carolina Division of Air Quality. (http://daq.state.nc.us/) This data consists of average daily values for seven sites in Eastern North Carolina between 2001 and early 2004. The specifics of the particulate sampling sites, periods, and number are listed in Table 3.1. Fayetteville and Raleigh are the urban sites, which are situated to the west of the majority of the hog facilities. Goldsboro, Kenansville, and Kinston are the rural sites, with Kenansville being both the smallest city and the most surrounded by the hog facilities. Jacksonville and Wilmington are two coastal sites with the hog facilities to the north and west of their positions. Figure 3.1 shows the locations of the seven sites in North Carolina and their relative positions to hog facilities (Blunden, 2003). For all these sites, when the average daily value consists of less than 90% of the individual hours reporting, the average daily data point is considered inaccurate and is discarded. Meteorological data was obtained for each site from the North Carolina State Climate Office (http://www.nc-climate.ncsu.edu/). While $PM_{2.5}$ data is available for all seven sites, speciated $PM_{2.5}$ data is only available for two urban sites, Fayetteville and Raleigh, and one rural site, Kinston.

3.1.2 Model Settings and Initial Conditions

The model ISORROPIA is set for a forward problem, in which the total (both gas and aerosol) concentrations of ammonium, sulfate, sodium, chloride, and nitrate concentrations in addition to relative humidity (RH) and temperature (T) are used to calculate the total aerosol mass. It should be noted that the model does not need the gas and aerosol concentration for

sulfate; it just requires the total sulfate concentration in the air. Also, the model is set to run in the thermodynamically stable state (i.e., solids can be formed when RH decreases below its deliquescence relative humidity (DRH)) instead of the metastable state (i.e., aerosols are in liquid even when RH < DRH). The initial conditions for the median ISORROPIA model simulations are listed in Table 3.2. These conditions were selected based on available observational data in North Carolina and literature values from North Carolina when observational data was not available. The aerosol section of the input conditions (sulfate, nitrate, ammonium, and chloride) were obtained from the available observational data obtained from the North Carolina Division of Air Quality. (Discussed in 3.1.1) The gas section of the input conditions (nitric acid, ammonia, and hydrochloric acid) were obtained from Baek et al., 2004a (Fayetteville and Raleigh site) and Walker et al., 2004 (Kinston site), where ranges of concentrations for each gas are given. To obtain the values in Table 3.2, the gaseous median, minimum, and maximum concentrations from the NCDAQ are summed respectively with the aerosol median, minimum, and maximum concentrations from the cited papers at each respective site. For each modeled site (i.e., Kinston, Fayetteville, and Raleigh), three levels of initial total PM species were used: median, minimum and maximum, representing the median, lower and upper limits of the observations respectively. For each concentration level, the model was run under three meteorological conditions: median RH/median T, minimum RH/ maximum T, and maximum RH/minimum T. In addition to the median runs, ISORROPIA was run for each individual daily average at each site using the daily relative humidity values, the daily average temperature values, and the daily average fine particulate matter values as input. As in the earlier case, literature values from North Carolina were used for the gaseous concentrations at each site due to the lack of

observational data. These nitric acid and ammonia concentrations were modified for each month, because monthly averages were given in Baek et al, 2004a, but the hydrochloric acid concentrations were assumed to be constant year round, because no seasonal variations could be located. The output variables include concentrations of gaseous species (i.e., ammonia, hydrochloric acid, and nitric acid) and aerosol species (i.e., sulfate, ammonium, nitrate, sodium, chloride, and water), as well as the pH value. The difference between the input and output variables is that the gas/aerosol pairs are entered as one input variable ($\mu g\ m^{-3}$) representing the sum of both species, while the output gives the gas and aerosol concentrations separately. Even though the input variable is constructed from gas and particle sums, the output is used to see how accurately the model predicts the distribution of the gas/particulates pairs. (Nitric acid/nitrate, ammonia/ammonium, and hydrochloric acid/chloride)

3.2 Results and Discussion

3.2.1 Regional Observed $PM_{2.5}$ and its Correlations with Meteorological Variables:

The particulate data was first analyzed for its main constituents by percentage at the three sites with detailed speciated $PM_{2.5}$ data over the entirety of the sampling period, as shown in Figure 3.2. The plot shows the major constituents of $PM_{2.5}$ to be organic carbon (OC), sulfate, and ammonium consistent with the results by Harrison et al. (2004), and Tanner et al. (2004). The additional components of $PM_{2.5}$ include nitrate, elemental carbon (EC), and over fifty trace elemental species. The $PM_{2.5}$ OC concentrations were higher in the urban areas, due to large local emissions of primary OC and volatile organic compounds

(VOCs). The sulfate and ammonium emissions were found to be larger at the rural Kinston site, due to the influence of the hog farming facilities in the rural area.

Figure 3.3 shows the scatter plots of $PM_{2.5}$ concentration vs. RH at Raleigh, Kinston, and Wilmington that represent urban, rural, and coastal areas. High $PM_{2.5}$ concentrations (> 20 $\mu g/m^3$) occur with the range of RH between 60 and 90%, and this effect is more prominent in the urban areas. This trend fits, because as the overall RH increases, the film of water formed on the surface of the particles favors the formation of $PM_{2.5}$. The trend drops off at extremely high relative humidities because of the differences in daytime and nighttime $PM_{2.5}$ formation, but since the data only reflects daily averages, the diurnal variation cannot be analyzed for this study. Figure 3.4 shows the correlation between $PM_{2.5}$ concentrations and the inverse of wind speeds at three sites. The observed positive correlation between PM concentration and the inverse of wind speed is consistent with that of Chu et al. (2004) and de Hartog et al. (2005). This relationship also makes sense empirically, because concentration is proportional to the inverse of wind speed in most dispersion and dispersion-deposition models. The $PM_{2.5}$ versus temperature plots for Raleigh, Kenansville, and Wilmington are shown in Figure 3.5 to represent urban, rural, and coastal areas respectively. Most of the high $PM_{2.5}$ concentrations occurred at high temperatures, but some occurred at low temperatures typical of nighttime inversion conditions, especially in winter. The slopes range from 0.08 to 0.18 at the urban and the rural sites and 0.01 to 0.02 (indicating no significant trend) at the coastal site. To investigate the correlation between wind direction and PM distributions, a box whisker plot is made for all seven sites with respect to the eight cardinal directions, as shown in Figure 3.6. The minimum, 25th percentile, average, 75th percentile, and the maximum of each distribution are plotted. The

impact of the hog facilities on $PM_{2.5}$ concentrations can be seen at some sites. For example, higher $PM_{2.5}$ average concentrations were found from a southeast flow at Raleigh (urban), which corresponds to Raleigh's orientation to the hog facilities. High $PM_{2.5}$ concentrations at Kinston (rural) were from the southwest and west directions, which correspond to Kinston's orientation to the majority of hog facilities. The highest average concentrations at Fayetteville were found from the southeast direction, rather than the east from which the emissions of hog facilities come. The weak correlation between the $PM_{2.5}$ concentrations and the east wind direction at Fayetteville is likely due to the fact that fewer measurements were available at this site and the easterlies were not the prevailing winds during those days with observations. At the other two rural sites (i.e., Goldsboro and Kenansville), relatively homogeneous correlation between $PM_{2.5}$ concentrations and cardinal directions were found. High $PM_{2.5}$ average concentrations at Goldsboro were from the southeast, southwest, west, and north directions with the peak concentrations coming from the southeast. The $PM_{2.5}$ concentrations range from 2.7 to 31.4 with an average of 10.8 at Kenansville ($\mu g\ m^{-3}$), which are very high for a small rural town. This indicates the impact of the hog facilities. The two coastal sites (i.e. Jacksonville and Wilmington) have higher concentrations from the southwest and west directions, indicating the impact of emissions from the state of South Carolina. High correlation was also found for the east direction at Jacksonville and the northwest direction at Wilmington.

3.2.2 Regional Fine Particulate Modeling Analysis

Figure 3.7 shows the observed and predicted average total inorganic $PM_{2.5}$ concentrations and its composition at three sites: Fayetteville, Kinston, and Raleigh ("total inorganic $PM_{2.5}$ or total inorganic PM" is defined as the sum of the four major inorganic

constituents: ammonium, chloride, nitrate, and sulfate). The predicted values were obtained under the conditions with median initial total PM species concentration, median RH and median T, as shown in Table 3.2. The observations at all three sites show that sulfate has the largest contribution (approximately 2/3 of the total observed inorganic aerosol), followed respectively by ammonium, nitrate, and chloride. The simulation results from ISORROPIA generally agree well with observed $PM_{2.5}$ in terms of relative magnitude, but it overestimates every modeled component. Compared with observed total inorganic $PM_{2.5}$ concentration, ISORROPIA overestimates by 2.29 $\mu g\ m^{-3}$ (40.0%) at Fayetteville, 2.37 $\mu g\ m^{-3}$ (41.8%) at Kinston, and by 2.36 $\mu g\ m^{-3}$ (44.3%) at Raleigh. At all three sites, sulfate has the largest contribution followed respectively by ammonium, nitrate, and chloride. The ammonium concentrations at all the sites are overpredicted by 0.59-0.61 $\mu g\ m^{-3}$. (43.1-45.5%) The largest differences between observed and predicted values are in the nitrate concentration. It is overpredicted by 1.32 $\mu g\ m^{-3}$ at Fayetteville, 1.35 $\mu g\ m^{-3}$ at Kinston, and 1.37 $\mu g\ m^{-3}$ at Raleigh. (160%, 148% and 204% respectively) The observed chlorine concentrations are nearly zero while the predicted chlorine concentrations at the three sites are from 0.38-0.41 $\mu g\ m^{-3}$. At each site, the predicted pH and aerosol water concentrations are in the range of 7.60-7.65, and 7.68-9.09 $\mu g\ m^{-3}$ respectively. The model does not predict the concentrations better at any one particular site when compared with the other sites.

Figure 3.8 shows the predicted total inorganic $PM_{2.5}$ concentration at the maximum initial pollutant concentrations at each site under the three different meteorological settings. The maximum observed values are also plotted for comparison. For the median RH/median T and the maximum RH/minimum T conditions, the predicted total $PM_{2.5}$ inorganic aerosol concentrations are relatively constant ranging between 26.46 to 28.68 $\mu g\ m^{-3}$ at the three sites

with the largest difference between any pair being 0.21 μg m^{-3}. These pair of conditions consistently overpredicts the observed maximum concentrations (5-12 μg m^{-3}) at all sites, but the overprediction does decrease as the urban development of the modeled city increases. (Kinston (rural), Fayetteville (small city), Raleigh (large city)) These observed maximum concentrations have a T range on par with the maximum values (300-303 °K) and a RH range just below the median value range (68-74%), which explains the concentration similarities to the minimum RH/maximum T condition concentrations. Under the maximum RH/minimum temperature setting, the predicted particulate ammonium and nitrate are within 0.5 and 1.5 μg m^{-3} respectively, while the chloride concentrations are constant at 1.21 μg m^{-3}. With the slightly higher sulfate concentrations at Kinston and Raleigh, the aerosol pH is slightly more acidic at these sites (with pH values of 5.61-5.80), whereas that at Fayetteville is more neutral (7.47). The predicted total inorganic aerosol concentrations range from 17.23 to 20.24 μg m^{-3} at the three sites under the minimum RH/maximum T condition. Such a condition favors evaporation of nitrate and water, resulting in zero or very low nitrate and water concentrations in the aerosol phase. The aerosol in this case will consist of primarily ammonium sulfate salt. The differences in predicted total inorganic aerosol concentrations among these sites are thus much smaller.

A similar plot is shown at the minimum pollutant concentrations at each site in Figure 3.9. The model overestimates the observed minimum concentrations with the maximum RH/minimum T and Median RH/Median T settings by 1.52-2.42 μg m^{-3} (350-490%) at the Kinston site, and by only 0.76-1.67 μg m^{-3} (147-206%) at the Fayetteville and Raleigh sites. The minimum RH/maximum T concentrations range from 0.61-0.86 μg m^{-3} where these values accurately predict the observed values at Kinston and underpredict the values at

Fayetteville and Raleigh by 53% and 54% respectively. In all of these conditions, particulate sulfate is constant for each site at a value < 1 μg m^{-3}. The other three constituents increase as the relative humidity increases in the three settings. Under the minimum RH/maximum T conditions, the particulate nitrate, ammonium, and chloride all measure ~0 μg m^{-3} with the constant particulate sulfate concentration being the only major contributor. Under the median RH/median T, the nitrate is the largest contributor, followed by sulfate, ammonium, and chloride. Under the maximum RH/minimum T condition, the relative contributions are the same except for the ammonium concentration having overtaken the sulfate concentrations.

In Figure 3.10-3.12, we have the predicted vs. observed plots of nitrate, ammonium, and chloride for each of the three modeled sites respectively. In each case, the observed nitrate concentrations are overpredicted by more then a factor of two. The observed values range from 0-5 μg m^{-3} while the majority of the predicted values range between 5-15 μg m^{-3}. The predicted ammonium values are also overpredicted on average, but there are a number of values within a factor of two of the observed concentrations. The values tend to between within the seasonal ranges of August-October and February-May with the month of August having the most points (9 points over the three sites) within a factor of two. This indicates that this model has a higher rate of accuracy during these seasonal periods of late summer/early fall and late winter/spring. The chloride observed concentrations are also overpredicted by the model as most of the observed values are < 0.1 μg m^{-3} and most of the predicted values lay in the 0.1-0.5 μg m^{-3} range.

3.3 Conclusions

The regional concentrations and trends of $PM_{2.5}$ in all of eastern North Carolina are studied with data analysis and an aerosol thermodynamic box model that predicts the gas/particle partitioning of PM. The unique emission fluxes of pollutants (e.g. ammonia) from the hog industry and their impacts on PM concentrations make this region a unique environment to understand the role of these emissions in PM formation. The major constituents of fine $PM_{2.5}$ from the greatest to the least are organic carbon (OC), sulfate, ammonium, nitrate, and elemental carbon (EC). Higher $PM_{2.5}$ concentrations tend to occur between 60 and 90% RH with this effect being more pronounced in urban areas. There is a positive relationship between temperature and $PM_{2.5}$ concentrations, and a negative relationship between wind speed and $PM_{2.5}$ concentrations. The box-whisker plots of wind direction demonstrate that there is a connection between hog facility density and fine particulate concentration, but with the limited data, these concentrations could not be attributed to any specific pollutant.

ISORROPIA is used to simulate the gas/particle partitioning and the total inorganic aerosol concentration at three sites in eastern North Carolina. The model predictions show that the major predicted constituents of inorganic aerosols are sulfate, ammonium, and nitrate, which agrees with the overall measurements. The predicted average total inorganic concentrations are higher by the same degree at all three sites. (2.29-2.37 $\mu g\ m^{-3}$, 40.0-44.3%) While the ammonium concentrations are overpredicted by 43-45% and the chloride concentrations are overpredicted by 0.38-0.41 $\mu g\ m^{-3}$, the most significant overprediction occurred with the nitrate concentrations. (148-204%) The simulation results are sensitive to initial total PM concentrations and meteorological conditions, with the highest secondary PM formation occurring under the condition with maximum initial total PM concentrations,

maximum RH, and minimum temperature, but the condition with maximum initial total PM concentration, median RH, and median RH was similar in concentration. The individual runs should the same result as the median runs with the model overestimating the observed concentrations in almost all cases. The ammonium concentrations are predicted within a factor of two for some days with most of these days occurring in August-October and February-May.

3.4 References

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Site Names	Time Period of Sampling	# of Points	Site Type	Kind of Sample
Fayetteville	Jan 2002- Jan 2004	124	Urban	Speciated Fine PM Conc.
Goldsboro	Jan 2001- Dec 2003	362	Rural	Fine PM Concentrations
Jacksonville	Jan 2001- Dec 2003	354	Coastal	Fine PM Concentrations
Kenansville	Jan 2001- Dec 2003	361	Rural	Fine PM Concentrations
Kinston	Jan 2002- Jan 2004	123	Rural	Speciated Fine PM Conc.
Kinston	Jan 2001- Dec 2003	360	Rural	Fine PM Concentrations
Raleigh	Jan 2002- Jan 2004	146	Urban	Speciated Fine PM Conc.
Raleigh	Jan 2001- Dec 2003	1084	Urban	Fine PM Concentrations
Wilmington	Jan 2001- Dec 2003	348	Coastal	Fine PM Concentrations

Table 3.1, Description of the Regional North Carolina $PM_{2.5}$ Sampling Sites

Input Variables [a]		Kinston	Fayetteville	Raleigh
Sodium		0.22	0.19	0.17
Sulfate	Median Minimum Maximum	3.43 0.58 14.3	3.53 0.75 12.9	3.36 0.72 13.8
Ammonium	Median Minimum Maximum	37.56 [b] 17.89 60.0	37.59 [c] 17.95 58.4	37.52 [c] 18.04 59.2
Nitrate	Median Minimum Maximum	2.42 [b] 1.65 6.12	2.33 [c] 1.63 6.0	2.18 [c] 1.61 5.0
Chloride	Median Minimum Maximum	0.50 [b] 0.23 1.24	0.50 [c] 0.23 0.99	0.50 [c] 0.23 0.98
Relative Humidity	Median Minimum Maximum	77 46 97	74 38 100	74 36 98
Temperature	Median Minimum Maximum	291.00 269.61 302.44	291.39 271.22 304.39	289.86 268.72 301.94

Table 3.2, Initial Species Concentrations and Meteorological Conditions for the ISORROPIA simulations

[a] All concentrations are given in $\mu g\ m^{-3}$
[b] (Walker et al., 2004, Table 1)
[c] (Baek et al., 2004a, Table 3)

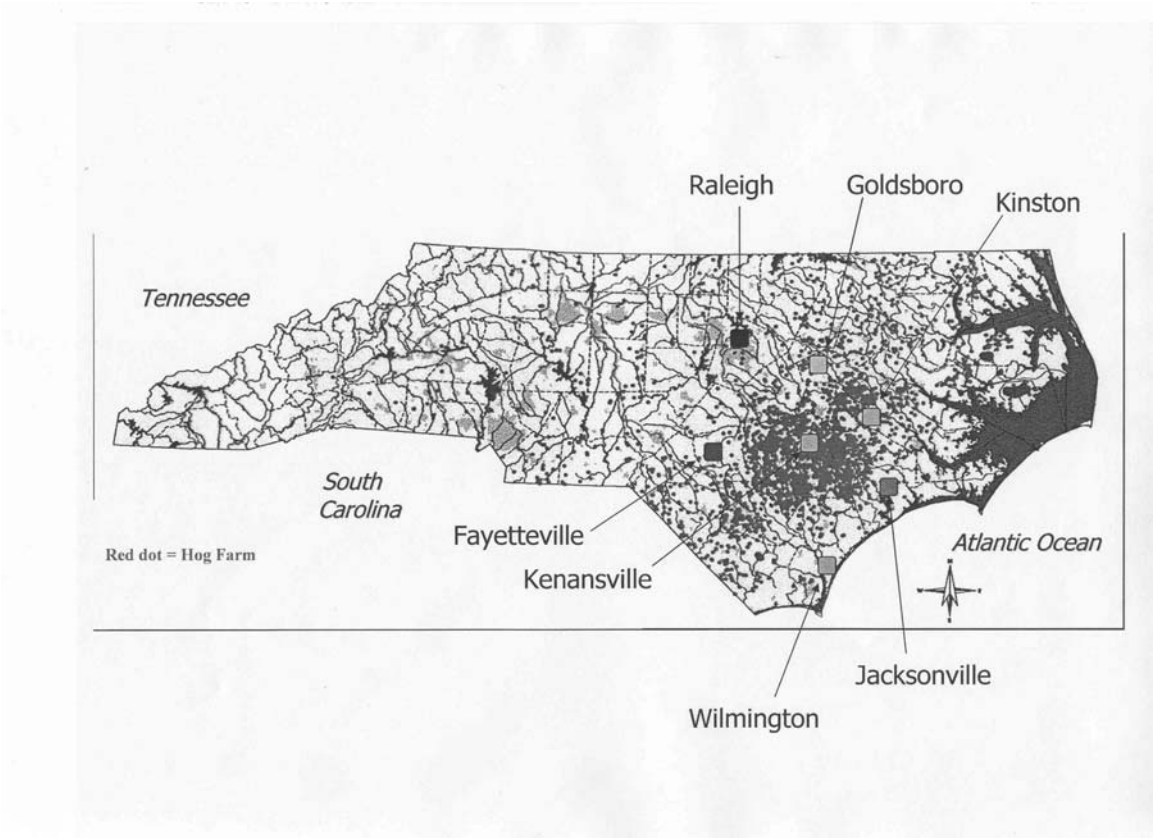

Figure 3.1, Map of Regional Fine Particulate Sampling Sites

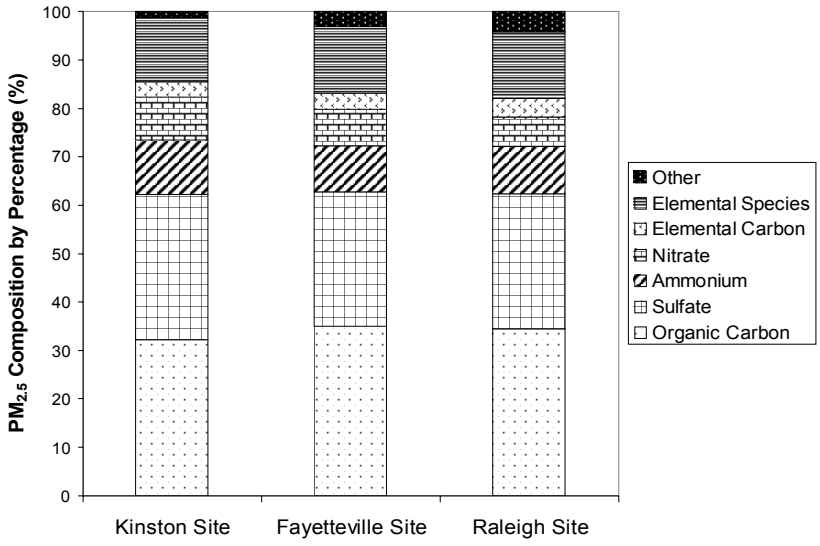

Figure 3.2, $PM_{2.5}$ Composition (%) at Three Speciated Sites (Kinston, Fayetteville, Raleigh) over entire sampling period

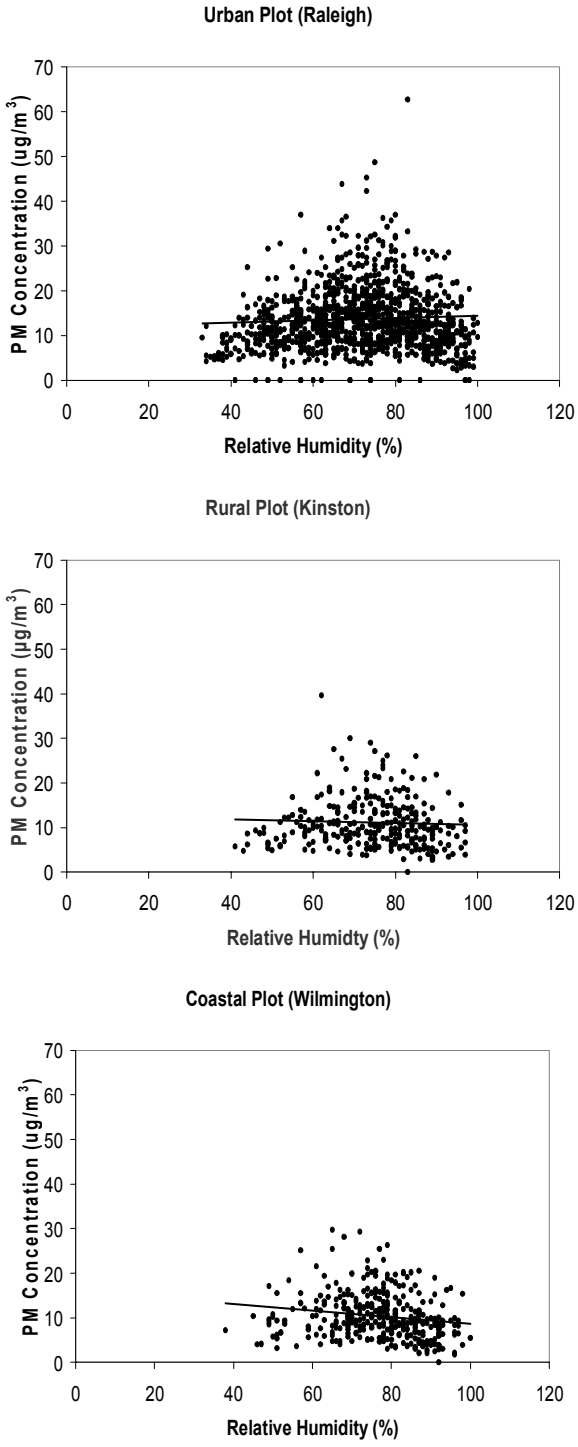

Figure 3.3, (a) Urban (Raleigh) Relative Humidity vs. $PM_{2.5}$ Concentration
(b) Rural (Kinston) Relative Humidity vs. $PM_{2.5}$ Concentration
(c) Coastal (Wilmington) Relative Humidity vs. $PM_{2.5}$ Concentration

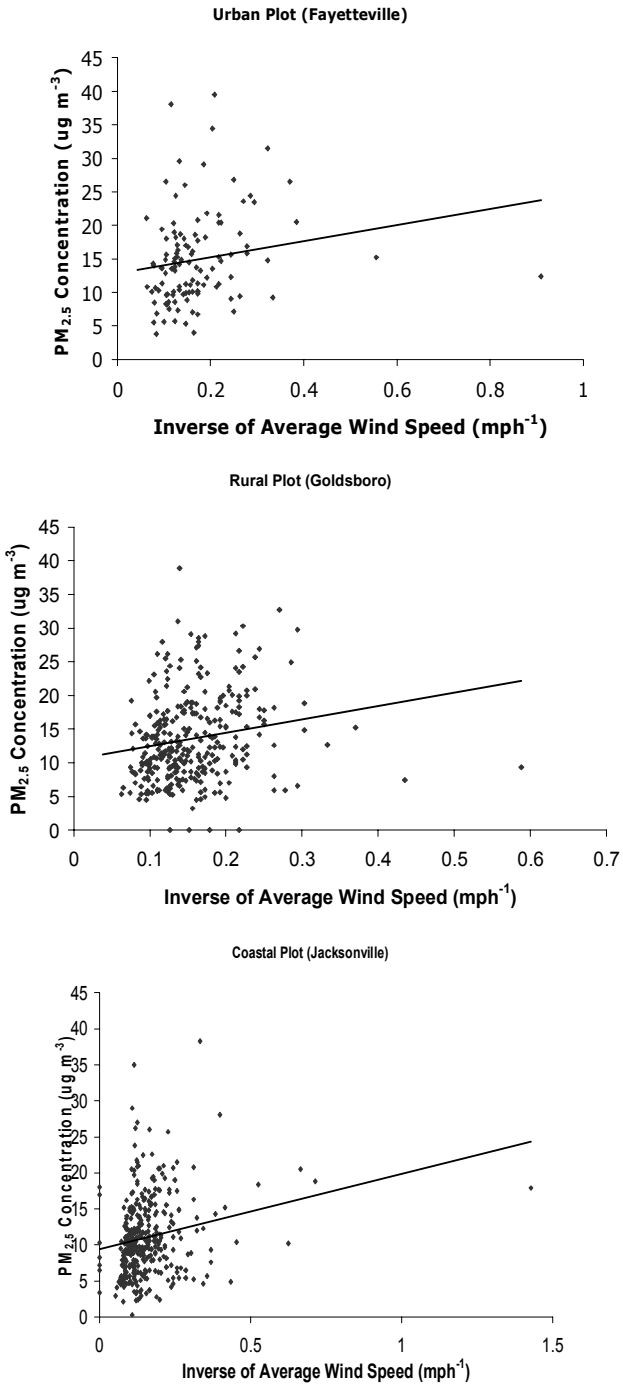

Figure 3.4,
(a) Urban (Fayetteville) Inverse of Wind Speed vs. $PM_{2.5}$ Concentration
(b) Rural (Goldsboro) Inverse of Wind Speed vs. $PM_{2.5}$ Concentration
(c) Coastal (Jacksonville) Inverse of Wind Speed vs. $PM_{2.5}$ Concentration

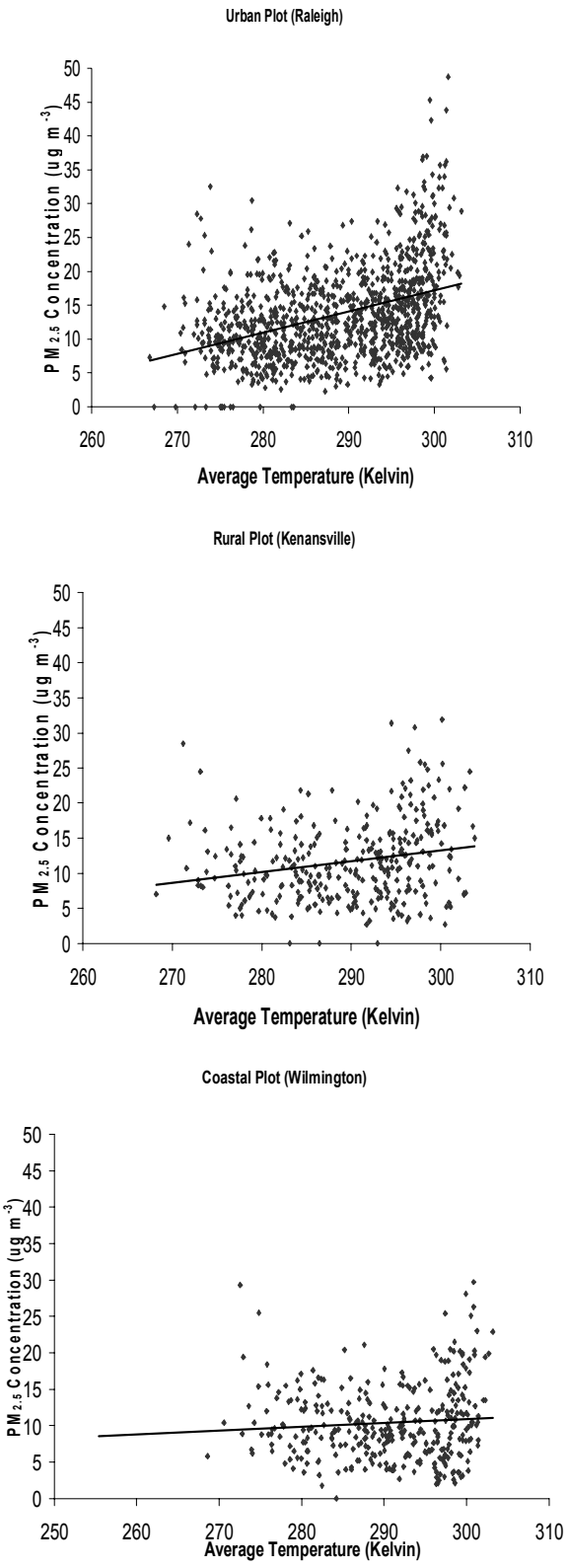

Figure 3.5, (a) Urban (Raleigh) Temperature vs. $PM_{2.5}$ Concentration
(b) Rural (Kenansville) Temperature vs. $PM_{2.5}$ Concentration
(c) Coastal (Wilmington) Temperature vs. $PM_{2.5}$ Concentration

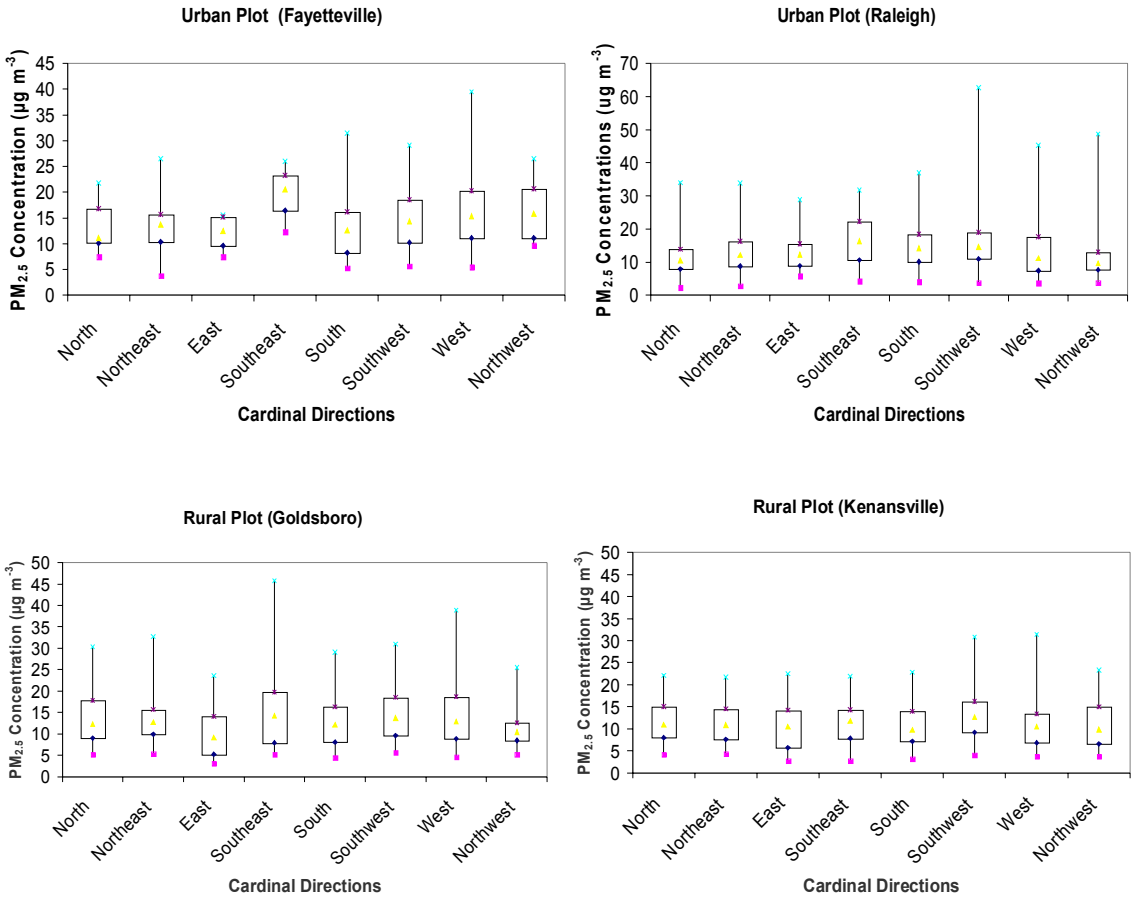

Figure 3.6, (a) Urban (Fayetteville) Wind Direction Box-Whisker Plot
(b) Urban (Raleigh) Wind Direction Box-Whisker Plot
(c) Rural (Goldsboro) Wind Direction Box-Whisker Plot
(d) Rural (Kenansville) Wind Direction Box-Whisker Plot

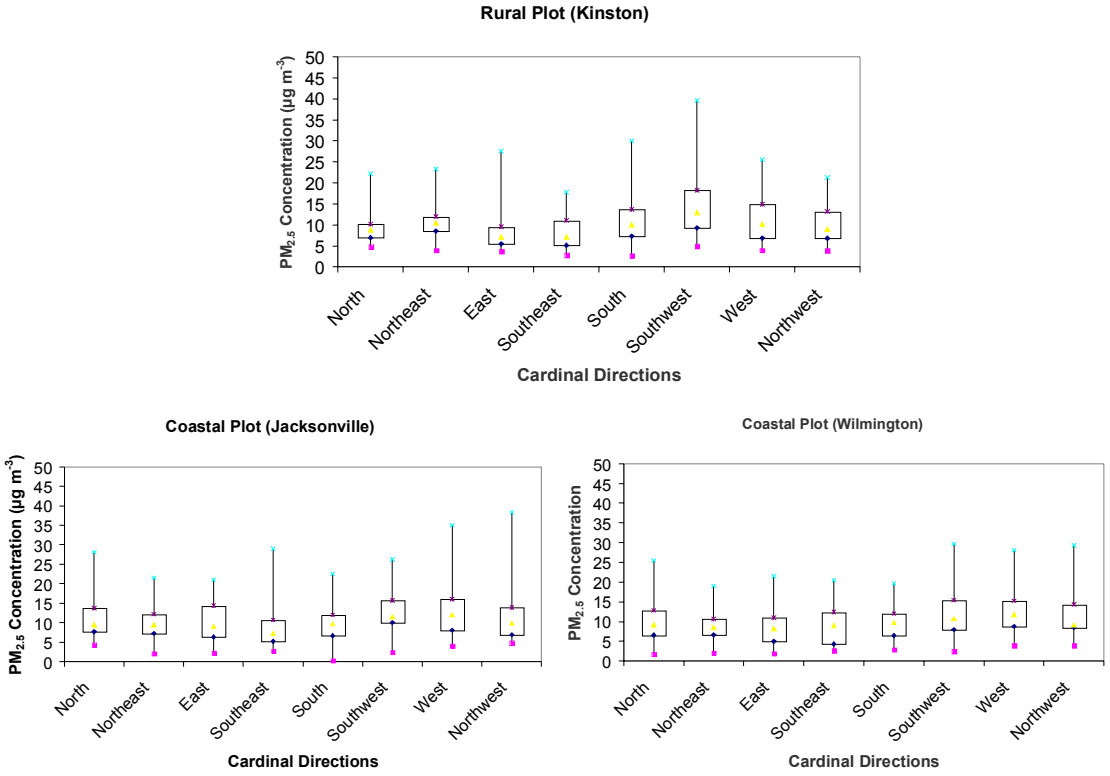

Figure 3.6, (e) Rural (Kinston) Wind Direction Box-Whisker Plot
(f) Coastal (Jacksonville) Wind Direction Box-Whisker Plot
(g) Coastal (Wilmington) Wind Direction Box-Whisker Plot

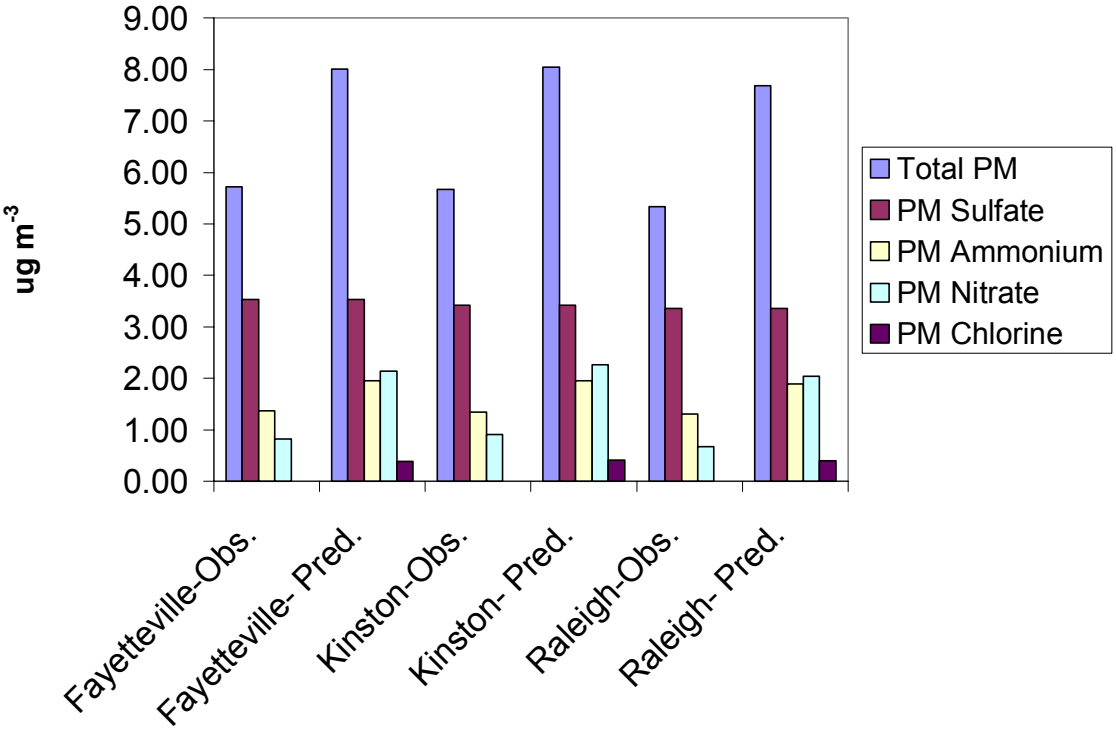

Figure 3.7, Observed and Predicted Total Inorganic $PM_{2.5}$ Concentrations at Kinston, Fayetteville, and Raleigh, NC under median RH and temperature conditions

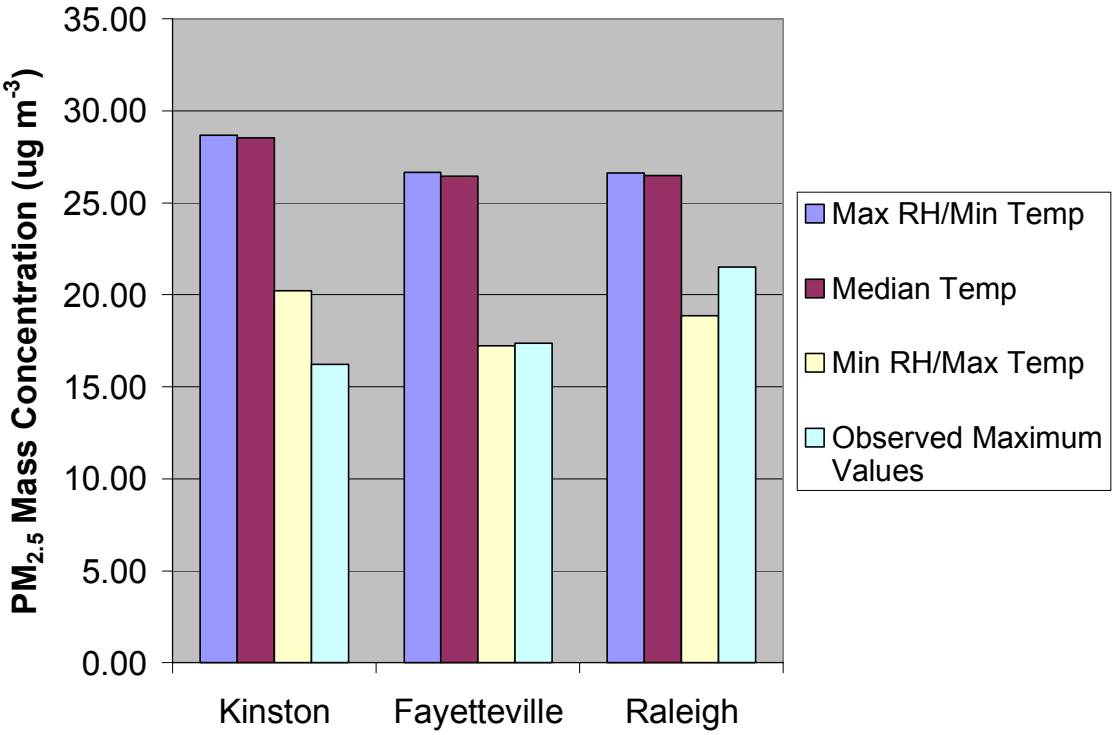

Figure 3.8, Predicted Total Inorganic $PM_{2.5}$ Concentrations under three meteorological conditions and maximum observed Total Inorganic $PM_{2.5}$ Concentrations at Kinston, Fayetteville, and Raleigh, NC

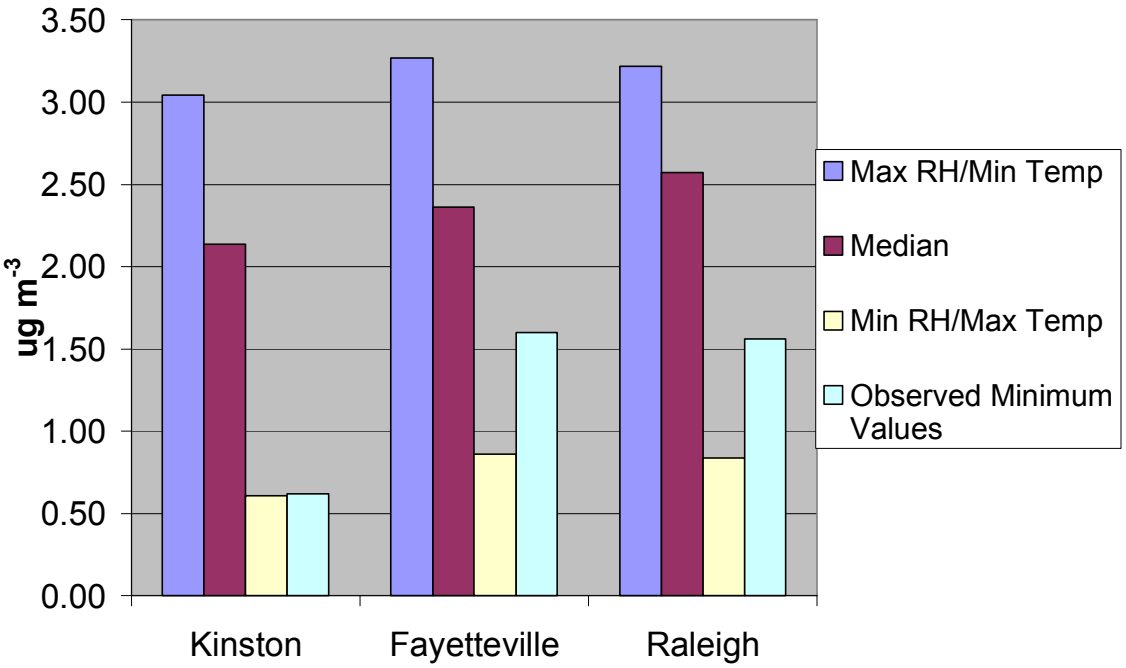

Figure 3.9, Predicted Total Inorganic $PM_{2.5}$ Concentrations under three meteorological conditions and minimum observed Total Inorganic $PM_{2.5}$ Concentrations at Kinston, Fayetteville, and Raleigh, NC

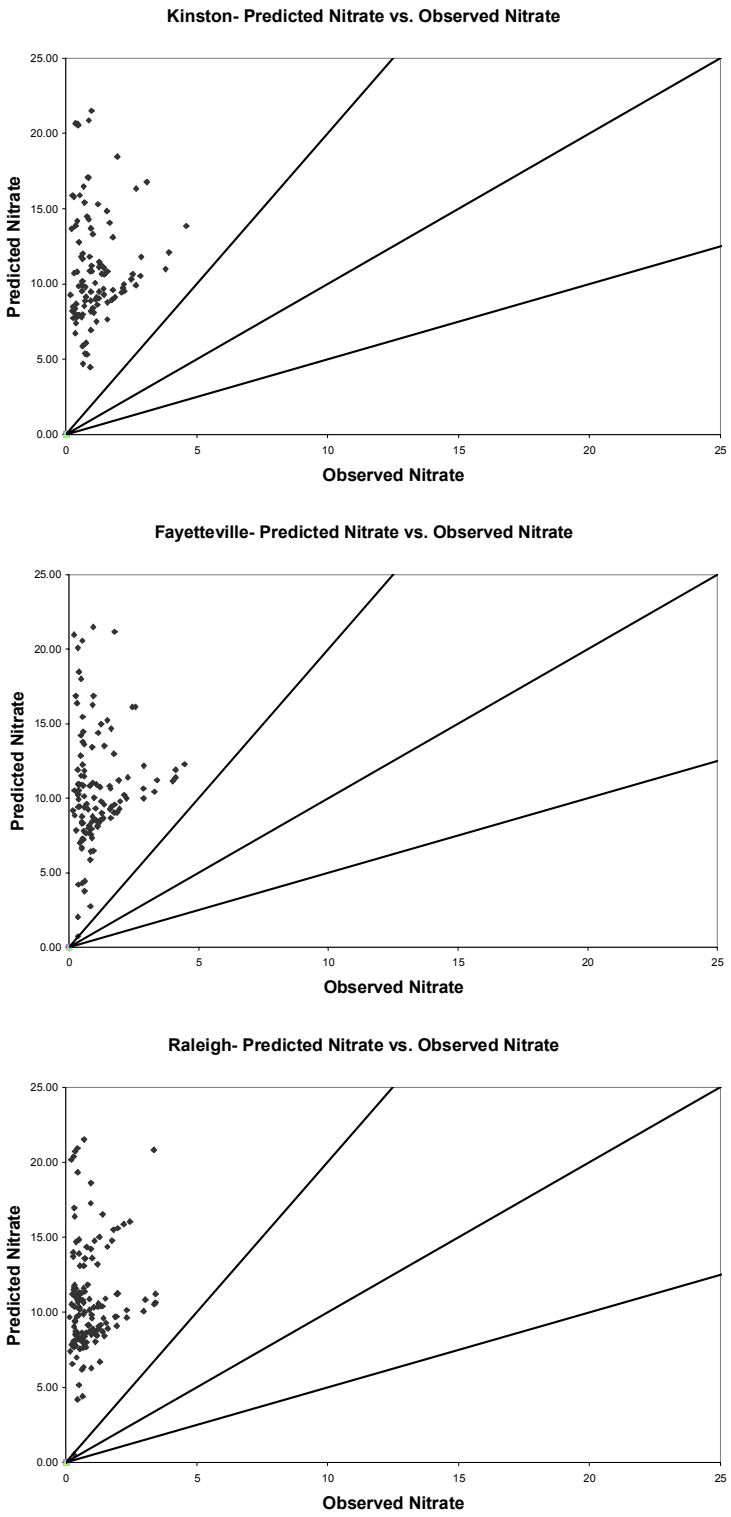

Figure 3.10, Predicted Individual $PM_{2.5}$ Nitrate Concentrations vs. Observed Individual $PM_{2.5}$ Nitrate Concentrations at Kinston, Fayetteville, and Raleigh

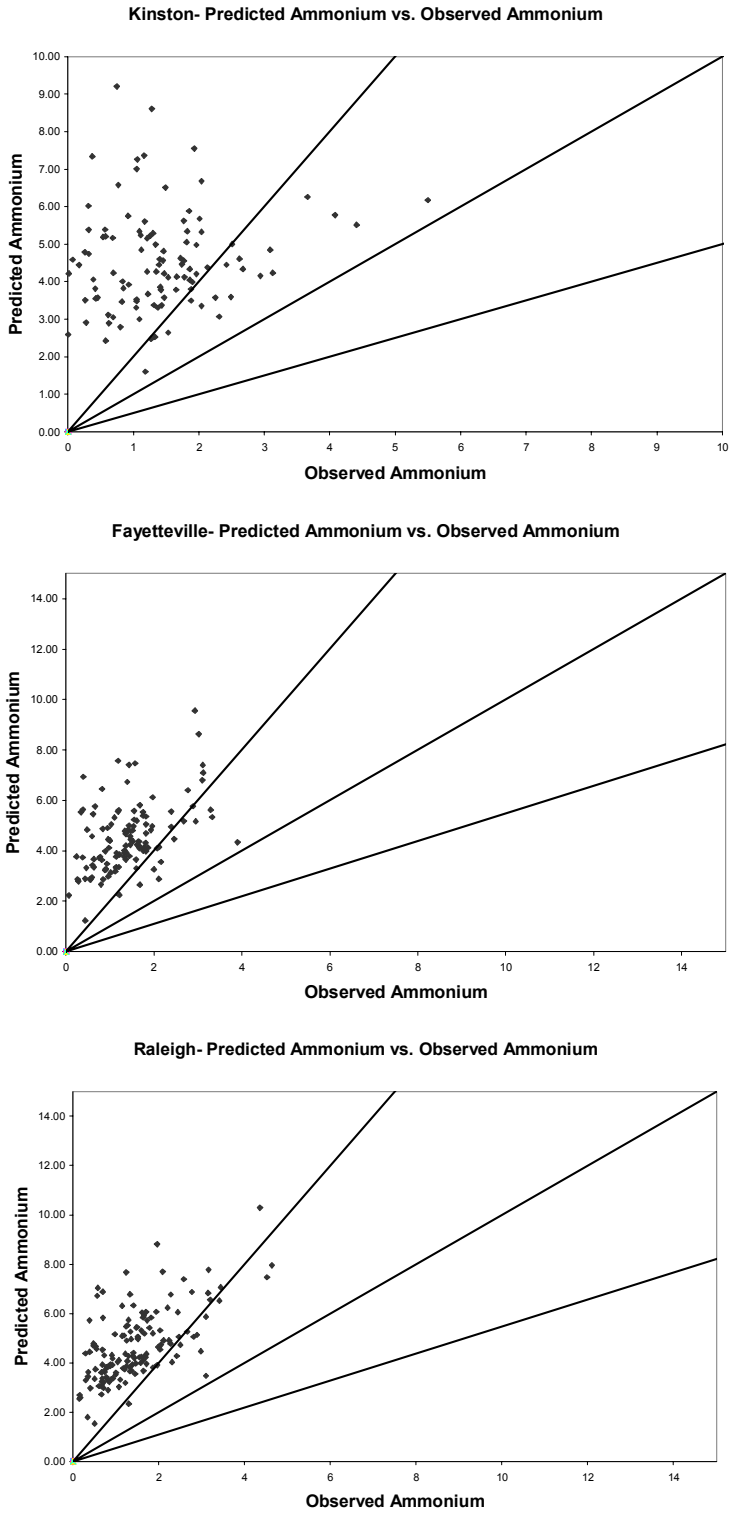

Figure 3.11, Predicted Individual $PM_{2.5}$ Ammonium Concentrations vs. Observed Individual $PM_{2.5}$ Ammonium Concentrations at Kinston, Fayetteville, and Raleigh

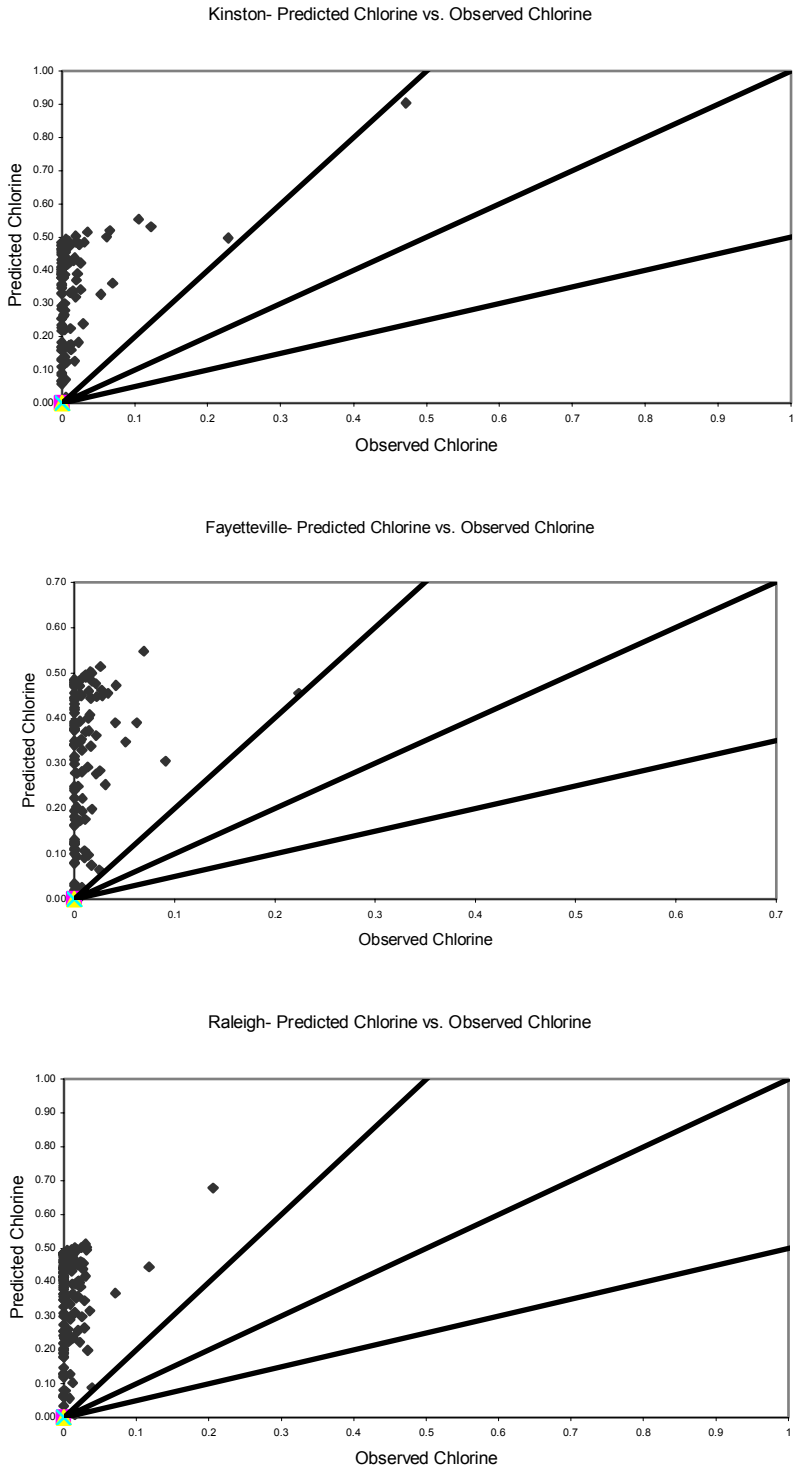

Figure 3.12, Predicted Individual $PM_{2.5}$ Chlorine Concentrations vs. Observed Individual $PM_{2.5}$ Chlorine Concentrations at Kinston, Fayetteville, and Raleigh

Appendix

4.1Local Denuder Data

			µg /L	µg N/L	µg N/L	µg SO4/L
Lab ID	**Site**	**Date**	**HCl**	**HNO2**	**HNO3**	**SO2**
SG-004	CC	10/26/2004	**50**	690	60	3430
SG-008	CC	10/27/2004	<50	740	50	2010
SG-005	CC	10/28/2004	<50	750	**20**	1460
SG-014	CC	11/03/2004	<50	420	<20	1480
SG-006	CC	11/04/2004	<50	480	<20	1810
SG-015	CC	11/06/2004	<50	660	<20	4300
SG-032	PIG	10/26/2004	<50	670	60	1970
SG-047	PIG	10/27/2004	<50	50	60	3820
SG-025	PIG	10/28/2004	<50	510	50	14710
SG-043	PIG	11/03/2004	<50	270	<20	3270
SG-042	PIG	11/04/2004	<50	340	<20	1300
SG-030	PIG	11/06/2004	<50	410	<20	3660
			µg /L	µg N/L	µg N/L	µg SO4/L
Lab ID	**Site**	**Date**	**HCl**	**HNO2**	**HNO3**	**SO2**
SG-010	CC	02/16/2005	<50	550	100	2650
SG-012	CC	02/17/2005	<50	570	140	7610
SG-007	CC	02/18/2005	<50	590	140	6100
SG-013	CC	02/19/2005	<50	360	<20	4870
SG-009	CC	02/20/2005	<50	330	110	4290
SG-017	CC	02/21/2005	<50	300	80	1590
SG-018	CC	02/22/2005	<50	310	40	2190
SG-001	CC	02/24/2005	<50	150	60	5360
SG-003	CC	02/25/2005	690	**20**	40	18590
SG-002	CC	02/26/2005	<50	470	50	830
SG-019	CC	02/27/2005	<50	330	180	8120
SG-016	CC	02/28/2005	<50	410	<20	5430
SG-011	CC	03/01/2005	<50	480	<20	7210
SG-024	PIG	02/16/2005	<50	390	190	2840
SG-049	PIG	02/17/2005	<50	<20	110	2510

SG-045	PIG	02/18/2005	<50	390	60	6150
SG-026	PIG	02/19/2005	<50	50	40	5810
SG-035	PIG	02/20/2005	<50	380	50	3840
SG-027	PIG	02/21/2005	<50	<20	50	2420
SG-023	PIG	02/22/2005	<50	<20	30	1720
SG-021	PIG	02/24/2005	<50	<20	70	1740
SG-022	PIG	02/25/2005	260	<20	<20	1980
SG-020	PIG	02/26/2005	1290	100	40	3740
SG-044	PIG	02/27/2005	<50	<20	50	8870
SG-028	PIG	02/28/2005	<50	370	<20	4740
SG-036	PIG	03/01/2005	<50	460	30	3610
			µg /L	**µg N/L**	**µg N/L**	**µg SO4/L**
Lab ID	**Site**	**Date**	**HCl**	**HNO2**	**HNO3**	**SO2**
SG-039	CC	04/08/2005	<50	520	<20	5110
SG-031	CC	04/17/2005	<50	320	<20	5770
SG-041	PIG	04/08/2005	<50	200	50	3050
SG-040	PIG	04/13/2005	<50	<20	<20	5480
SG-037	PIG	04/14/2005	1550	<20	110	7740
SG-033	PIG	04/15/2005	620	30	230	5680
SG-034	PIG	04/16/2005	<50	390	<20	4670
SG-046	PIG	04/17/2005	440	<20	130	7520
SG-029	PIG	04/18/2005	860	<20	180	10220
SG-038	PIG	04/19/2005	1210	100	210	11920
			µg /L	**µg N/L**	**µg N/L**	**µg SO4/L**
Lab ID	**Site**	**Date**	**HCl**	**HNO2**	**HNO3**	**SO2**
SG-102	CC	06/15/2005	<50	570	380	470
SG-103	CC	06/16/2005	<50	910	140	6710
SG-104	CC	06/17/2005	<50	530	<20	4220
SG-105	CC	06/19/2005	<50	500	410	490
SG-106	CC	06/20/2005	<50	410	20	1680
SG-107	CC	06/21/2005	<50	260	170	450
SG-108	CC	06/22/2005	<50	360	80	21560
SG-109	CC	06/23/2005	<50	330	330	7470
SG-110	CC	06/24/2005	<50	80	150	1710
SG-111	PIG	06/16/2005	<50	380	910	7570
SG-112	PIG	06/17/2005	<50	330	30	3800

SG-113	PIG	06/19/2005	<50	410	50	3760
SG-114	PIG	06/20/2005	<50	290	20	2590
SG-115	PIG	06/21/2005	<50	130	230	590
SG-116	PIG	06/22/2005	<50	450	<20	5770
SG-117	PIG	06/23/2005	<50	190	330	10370
SG-118	PIG	06/24/2005	<50	50	160	2290
SG-048	PIG	UNKNOWN	<50	<20	<20	2920

4.2 Local Filter Pack Data

Lab ID	Sample ID	Date	NO3	SO4	NH4
			µg N/L	µg SO4/L	µg N/L
SG-119	CC Teflon	06/15/2005	120	21830	2970
SG-120	CC Teflon	06/16/2005	**20**	16420	2720
SG-121	CC Teflon	06/17/2005	<20	8310	1490
SG-122	CC Teflon	06/19/2005	80	5250	1240
SG-123	CC Teflon	06/20/2005	400	5260	980
SG-124	CC Teflon	06/21/2005	230	10140	1730
SG-125	CC Teflon	06/22/2005	<20	24940	3700
SG-126	CC Teflon	06/23/2005	210	43360	5510
SG-127	CC Teflon	06/24/2005	<20	30110	4120
SG-137	CC Nylon	06/15/2005	300		
SG-138	CC Nylon	06/16/2005	180		
SG-139	CC Nylon	06/17/2005	90		
SG-140	CC Nylon	06/19/2005	170		
SG-141	CC Nylon	06/20/2005	<20		

SG-142	CC Nylon	06/21/2005	90		
SG-143	CC Nylon	06/22/2005	260		
SG-144	CC Nylon	06/23/2005	170		
SG-145	CC Nylon	06/24/2005	240		
Lab ID	**Sample ID**	**Date**	**NO3**	**SO4**	**NH4**
			µg N/L	**µg SO4/L**	**µg N/L**
SG-128	Pig Teflon	06/15/2005	590	19540	3610
SG-129	Pig Teflon	06/16/2005	520	16740	3290
SG-130	Pig Teflon	06/17/2005	480	16850	2830
SG-131	Pig Teflon	06/19/2005	610	20930	3340
SG-132	Pig Teflon	06/20/2005	660	10950	1950
SG-133	Pig Teflon	06/21/2005	740	13280	2430
SG-134	Pig Teflon	06/22/2005	1220	38760	5570
SG-135	Pig Teflon	06/23/2005	1460	50220	6760
SG-136	Pig Teflon	06/24/2005	670	43030	5700
SG-146	Pig Nylon	06/15/2005	50		
SG-147	Pig Nylon	06/16/2005	140		
SG-148	Pig Nylon	06/17/2005	40		
SG-149	Pig Nylon	06/19/2005	30		
SG-150	Pig Nylon	06/20/2005	<20		
SG-151	Pig Nylon	06/21/2005	40		
SG-152	Pig Nylon	06/22/2005	100		
SG-153	Pig Nylon	06/23/2005	30		
SG-154	Pig Nylon	06/24/2005	100		