

ABSTRACT

BINYU WANG. Analysis and Modeling of Fine Particulate Matter (PM_{fine}) in the Southeast United States. (Under direction of Viney p. Aneja)

Particulate matter in the atmosphere with aerodynamic diameter 2.5 micrometer or less ($PM_{2.5}$) has been studied extensively due to its impact on human health, climate, and other environmental effects. $PM_{2.5}$ in the southeast US as a whole and particularly in North Carolina (NC) are the focus of this research. The main body of this study includes two parts. The first part focuses on regional i.e. Southeast U.S. $PM_{2.5}$ analysis consisting of two urban inland sites including locations N.Birmingham, AL (BHM) and Jefferson, GA (JST); two urban coastal sites viz., Gulfport, MS (GFP), Pensacola and FL (PNS); and three rural sites including Yorkville, GA (YRK), Centreville, AL (CTR), and Oak Grove, MS (OAK) (Chapter 2). The second part focuses on North Carolina counties consisting of three urban sites and two rural/agriculture sites in NC. The three urban N.C. sites are located in Forsyth County, Mecklenburg County, and Wake County, respectively; and the two rural/agriculture sites are located in Lenoir County and Caswell County, respectively (Chapter 3).

The analysis of data and results indicate that the annual National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ (annual standard: $15\mu\text{g}/\text{m}^3$) is exceeded in all of urban inland areas and one agriculture site which is surrounded by several power plants, but the annual average of $PM_{2.5}$ is less than the annual standard at all of the other agricultural sites and urban coastal sites. High annual average concentrations are dominated by elevated values during summer. The 24-hour standard ($65\mu\text{g}/\text{m}^3$) for $PM_{2.5}$ is not exceeded at any of the urban and/or agriculture sites.

In the first part, analysis of chemical species revealed that yearly average fractions of organic matter (OM) with yearly average $4.26 \mu\text{g}/\text{m}^3$, sulfate (SO_4^{2-}) with yearly average $4.23 \mu\text{g}/\text{m}^3$, ammonium (NH_4^+) with yearly average $1.89 \mu\text{g}/\text{m}^3$ and nitrate (NO_3^-) with yearly average $0.67 \mu\text{g}/\text{m}^3$, elemental carbon (EC) with yearly average $1.04 \mu\text{g}/\text{m}^3$ to total $\text{PM}_{2.5}$ range between 28~33%, 27~37%, 11~19%, and 3-7%, 5-12% respectively. In the second part, OM (47-50%) with yearly average $7.22 \mu\text{g}/\text{m}^3$, SO_4^{2-} (27-32%) with yearly average $4.63 \mu\text{g}/\text{m}^3$ and NH_4^+ (9-11%) with yearly average $1.54 \mu\text{g}/\text{m}^3$, NO_3^- (5-7%) with yearly average $1.04 \mu\text{g}/\text{m}^3$ and EC (1-4%) with yearly average $0.51 \mu\text{g}/\text{m}^3$ dominate the identifiable components at all sites. Difference in measured fractions of organic carbon matter between the two parts may be partly accounted by different carbon measurement technologies used. Total $\text{PM}_{2.5}$ mass concentrations are found higher during summer, suggesting that warm conditions favor the formation of secondary aerosol components such as sulfate and organic matter. The equivalent ratio of NH_4^+ to SO_4^{2-} equals or is less than 1, suggesting that in most areas in southeast US, NH_4^+ combines with SO_4^{2-} and exists as $(\text{NH}_4)_2\text{SO}_4$ not NH_4NO_3 . Which suggests that the particle nitrate is limited by the availability of NH_3 at most locations in the southeast.

Analysis of major chemical components also shows that ratios of organic carbon/elemental carbon (OC/EC) at all sites are higher than 2, especially at rural sites, mirroring the significant presence of secondary organic aerosols (up to 90%) formed perhaps through VOCs gas-to-particle conversion processes. Minimum OC/EC ratio method has been used to estimate the secondary organic carbon (OC_{sec}) formation using the equation

$$\text{OC}_{\text{sec}} = \text{OC}_{\text{tot}} - \text{EC} \times (\text{OC}/\text{EC})_{\text{min}}$$

where $(OC/EC)_{\min}$ is the minimum ratio observed.

The secondary OC is found to consist of 41- 50% of the total OC at the seven sites analyzed in the first part; but the OCsec/OC ratios are higher (47-68%) for the North Carolina sites, due to different measurement technique, and different environmental conditions.

The correlation analysis and regression analysis show $PM_{2.5}$ is well correlated with O_3 . Also, $PM_{2.5}$ mass concentration exhibits a negative correlation with wind speed, and precipitation and a positive association with temperature, and solar radiation. Finally, origins of pollutant sources were addressed using the combinations of back trajectory analysis (HYSPLIT4 model) and hierarchical cluster analysis. This reveals that transport from northeast (North Carolina) direction exerts strong influence on $PM_{2.5}$ mass concentrations in the study areas. Back trajectory analysis also reveals air trajectories coming from marine sector (east and south direction) or from the upper troposphere and then transferring down to the surface carry low $PM_{2.5}$. Comparably, air trajectories from continental direction of lower atmosphere bring air mass with high $PM_{2.5}$ to NC.

**Analysis and Modeling of Fine Particulate Matter (PM_{fine})
in the Southeast United States**

by

Binyu Wang

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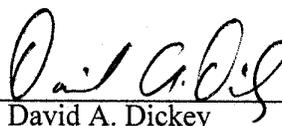
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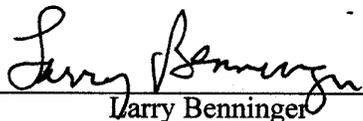
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DEDICATION

This thesis is dedicated to my family. First my parents, who brought me to the world and always are providing their deep love and courage. I am also dedicated to my bright older brother, my warm-hearted sister-in-law and my pretty nephew; they always treat me as a member of their home. Finally, this work dedicates to both my brilliant husband and my lovely son, who build another home and offer the ever-harbor to me. I love all of you.

BIOGRAPHY

Binyu Wang was born in May, 1974 in Jimo city, Shandong province of China where she spent most of her childhood. She had a very happy life there with her parents and old brother in her hometown. After finished her primary school, middle school (when she used to dream to be a writer in the future) and high school, she went to Ocean University of Qingdao (Ocean University of China at present) in 1992 majoring in chemistry. She studied hard in the four years and got awarded each year. With her academic score rating in No. 1 in her four-year studies in her class, she was admitted for graduate study in the same department waive of test in 1996.

Binyu was rewarded “Excellent Graduate Student” when she finished her master study in 1999. She had joined several open-sea cruise researches during her three-year studies and began to build her strong belief to work for protecting our environment. Upon graduating from Ocean University of Qingdao, she went to University of South Florida in USA for further studying. Binyu transferred to NC State University in 2000 to join her boyfriend Quansong Tong (husband now). They got married in 2001 and had a very lovely son name “Bill W Tong” in 2002, who brings them a lot, a lot of happiness. Binyu feels happy whenever she thinks of her son.

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I am also grateful to Dr. Hunt in statistical department who had helped me with statistical analysis about $PM_{2.5}$ and Nealson Watkins in U.S. Environmental Protection Agency (USEPA) who provided some documents and data inquiry. I am also thankful for the help from members of Air Quality group. They all helped me, in some way, to determine my goals and focus on what was needed in order to complete this work.

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I. Introduction

1.1 Statement of the Problem

Particulate matter (PM) is a general term used for a mixture of solid particles or liquid droplets found in the air. PM_{10} refers to all particles less than or equal to 10 μm in mean aerodynamic diameter. “Coarse fraction” refers to the particles with aerodynamic diameter greater than 2.5 μm , but less than or equal to 10 μm . $PM_{2.5}$ describes the “fine” particles that are less than or equal to 2.5 μm in aerodynamic diameter. They are represented by two subdistributions or modes named the Aitken and accumulations modes [Whitby, 1978]. Aitken modes refer to the particles with aerodynamic diameter less than or equal to 0.1 μm while accumulations modes cover particles with aerodynamic diameter ranging from 0.1 μm to 2.5 μm .

Since the earliest recognition of its existence as suspended particle in the air [Schmasuss and Wigand, 1929], the physical and chemical properties of particular matter have been extensively studied over the past decades [Malm et al., 1994; Harrison et al., 1997; Meng et al., 1997; Lin, 2002]. Expanding observational and modeling results have demonstrated a strong connection between PM and adverse health effects, because the smaller size particles can penetrate into the lungs, causing the asthma increases in respiratory symptoms like coughing and difficult or painful breathing, decreased lung function, chronic bronchitis, even increased premature death [Seaton et al., 1995; Schwarzd et al., 1996; US EPA report, 1999]. US EPA has indicated that the smaller the particle, the more serious a health risk it poses, i.e., the very smallest particles having the worst effects on health

The climate effects of aerosols had already been recognized in the early to mid-1970s. After that, the role of aerosols in climate and atmospheric chemistry has received intense interest: they scatter sunlight, provide condensation nuclei for cloud droplets, and participate in heterogeneous chemical reactions [Andreae and Crutzen, 1997]. On one side, the infrared absorbing aerosol can absorb infrared which will lead to the increase of both daytime maximum and nighttime minimum temperature, on the other hand, the increase of visible reflectors like sulfate aerosols will result in the decrease of the daytime maximum temperature [Karl et al., 1993; Yu et al., 2001]. When the size of the particles is comparable to or larger than the wavelength of any incident radiation, the scattering of light by PM can be explained through the theory of Mie scattering; otherwise, the Rayleigh scattering theory applies [Hidy, 1994]. Both Hansen et al. [1997] and Ackerman et al. [2000] reported that airborne absorbing aerosols have the capability to raise the regional temperature more effectively than CO₂ by transferring the absorbed energy to the surface and reducing the local large-scale cloud cover (cloud-burning effect).

Fine particles (PM_{2.5}) are the major cause of reduced visibility in parts of the United States because they can scatter and absorb light [Conner et al., 1991]. They may also act as condensation nuclei to cause or aggravate fogs; in addition to that, PM_{2.5} may be deposited on plants causing some kind of damage. The most obvious effect of this particulate deposition on vegetation is the physical smothering of the leaf surface, and reducing light transmission to the plants. Particles containing nitrogen and sulfur that are deposited onto land or water bodies may change the nutrient balance and acidity of those environments, as well as interfering with plant metabolism and damage culturally important objects [US EPA, 1999].

The chemical composition and physical properties of fine particles vary widely in different regions and at different times. The origin of PM_{2.5} may be grouped into two categories including primary source and secondary source. Figure 1 shows the “routes of incorporation of chemical species into atmospheric particulate matter”. Primary PM_{2.5} are formed by the chemical species emitted directly from a variety of identifiable sources, such as cars, trucks, buses, factories, construction sites, tilled fields, unpaved roads, stone crushing, and burning of wood. The source categories of the directly emitted PM_{2.5} for nonfugitive dust sources are shown in Figure 2, which indicates that different kinds of combustion are the predominant source of the primarily emitted PM_{2.5}. Among the various combustion sources, the area source combustion is the major contributor, and then the on-road and non-road engines and vehicles. Secondary PM_{2.5} is formed from the primary pollutants by chemical formation [Wayne, 2000]. Scientific evidence indicates that the predominant source for PM_{2.5} is secondary formation processes [Nealson, 2002]; but “1998 Emission report” by EPA [U.S. EPA, 2000] also shows that “secondary” fine particles can comprise as much as half the PM_{2.5} measured in the United States, in contrast to the directly emitted particles from combustion and fugitive dust.

Adverse effects of pollution are often associated more with the secondary than with the primary pollutants [Wayne, 2000]. The major precursors to secondary PM_{2.5} are NO_x, SO_x, NH₃, and VOCs, and the major oxidants are hydroxyl radical (OH), O₃, hydrogen peroxide (H₂O₂), and hydroperoxyl radical (HO₂). It is believed that the gas-phase reactions are photochemically stimulated and dominated by OH interaction as an intermediate product of NO_x - HC or NO_x - VOCs reactions. Another factor is the secondary reaction of SO₂ and intermediate products in the O₃ reaction sequence. The

aqueous – phase chemistry is dominated by an oxidation reaction involving dissolved H_2O_2 [Hidy, 1994]. Figure 3 indicates the gas-to-particle conversion route from the several major precursors to the products of the oxidant process. One of the most important examples among these reactions is the oxidation of SO_2 to SO_3 and ultimately sulfate - containing aerosols. Table 1 lists the estimation of the main precursors from man made and natural sources, indicating that man directly releases very large quantities of materials to the atmosphere. The detailed breakdown of anthropogenic emission sources listed in Table 2 shows that fuel combustion is by far the largest source of the oxidized species (NO_x , SO_x , CO) [Wayne, 2000].

The vertical distributions of the aerosol over the continents have been plotted by Warneck [2000]. The number densities of particles decline rapidly with altitude in the lower troposphere, with a scale height of roughly 1 km. The bulk of the atmospheric aerosol mass is present in the lower troposphere, reflecting the short residence time of aerosols against deposition (~ 1-2 weeks) [Jacob, 1999]. Figure 4 illustrates the different process involved in the production, growth, and eventual removal of atmospheric aerosol particles. Aitken particles (diameter < 0.1 μm) are removed mainly by coagulation with other particles; particles in the 0.1- 10 μm size range are mainly removed by wet deposition; and sedimentation becomes increasingly significant for removing particles exceeding 10 μm in size [Warneck, 2000].

1.2 PM_{2.5} Monitoring and Measurement

This study is based upon the data collected at some research sites, all chemical data used and related meteorology data in the second chapter are downloaded from

“Search” website: <http://www.atmospheric-research.com> [Search, 2002]. Division of Air Quality (DAQ) in N.C. Department of Environment and Natural Resources (DENR) provided all chemical data and meteorology data used in the third chapter.

PM_{2.5} monitoring is traditionally performed by drawing a known volume of air through filter media of a known weight, and then re-weighing that filter after sampling to find the change in mass, allowing the PM_{2.5} concentration to be computed [Nealson, 2002]. Rupprecht & Patashnick Partisol brand model 2025 monitor is used for PM_{2.5} sampling measurements used in the second chapter. Figure 5 shows one type of FRM. PM_{2.5} monitor which uses a sequential filter sampler designed to collect 24-hour integrated samples of particulate matter in the PM_{2.5} size fraction within the guidelines of the Class 1 Federal Reference Method (FRM) given in EPA (1998). The sampler automatically switches up to 3 filters for multiple day operation. A USEPA PM-2.5 WINS impact is installed downstream of the denuders to reduce the particle size to 2.5 μm [Search, 2002]. The speciation data at research sites are collected using a sequential, multi-channel sampler known as the Particle Composition Monitor (PCM) which consists of three parallel sampling channels, each sampling ambient air at 16.7 lpm. The inlet for each channel consists of a 10 μm cyclone, followed by one or more denuders to remove contaminant gases. Channel 1 (PCM1) consists of a Teflon filter preceded by sodium carbonate and citric acid denuders. The Teflon filter is analyzed gravimetrically for mass, then by X-ray fluorescence for trace elements and finally by ion chromatography (IC) for sulfate, nitrate, and ammonium. Values from PCM2 or continuous monitors are substituted for missing values in the order of their availability. The sample collected by the third PCM channel (PCM3) is analyzed for PM_{2.5} carbon. Analysis method is totally

different between carbonaceous species and solvable ion. The DRI thermal/optical carbon analyzer which is based on the preferential oxidation of organic carbon (OC) and elemental carbon (EC) compounds at different temperatures is used. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. Figure 6 shows the thermogram for carbon (both OC and EC) determination. OC is derived from the filter punch in a He atmosphere at 120, 250, 450, and 550°C plus pyrolyzed organic carbon while EC is obtained from the filter punch in a helium/ oxygen (He/O₂) atmosphere at 550, 700, and 800°C minus pyrolyzed organic carbon. Total Carbon refers to all carbon obtained from the filter punch between ambient and 800°C under He and O₂/He atmospheres. The filter used for different species, analysis methods and the corresponding minimum detection limit (MDL) is listed in Table 3.

PM_{2.5} data used in the second part (Chapter 3) are provided by N.C.DENR/DAQ. Tapered Element Oscillating Microbalance (TEOM), provided by Rupprecht and Patashnick Inc., with a sharp cut cyclone is deployed as continuous monitor for PM_{2.5} sampling. TEOM series 1400a monitor uses exchangeable Teflon coated with borosilicate filter. It incorporates an inertial balance that directly measures the mass collected on an exchangeable filter cartridge by monitoring the corresponding frequency changes of a tapered element. The TEOM mass transducer does not require recalibration because it is specially designed and constructed from non-fatiguing materials. In the process of monitoring, moisture is removed by heating the sample to 50°C. The minimum detection level is 0.1µg/m³. More information about TEOM can be found in the “R &P Co” web page [Rupprecht and Patashnick website]. The speciation monitors used are

called SASS Teflon monitors made by Met-One Inc. Figure 7 shows the type of SASS that is used by DAQ. A Sharp Cut Cyclone (SCC) with a flow of 6.7 liters/min is integrated in every sampling canister to remove particles larger than 2.5 μ m aerodynamic diameters. SASS also incorporates convective solar shield in order to maintain cassettes to less than 5°C over ambient temperature. Ion chromatography (Dionex system) is used to analyze the concentrations of anion (like SO₄²⁻, NO₃⁻) and cation species (like NH₄⁺, K, Na). The eluent used for anion analysis is a 2.7 mM Na₂CO₃/ 0.3 mM NaHCO₃ solution while The 22 mN H₂SO₄ solution is use for cation eluent. The measurement method is selective and sensitive, allowing measurement to below 0.05 ppm in the filters extracts. Duplicate injections show a relative percent difference of better than 5% above about 0.05 μ g/mL. Analysis of quality control check samples shows the recovery of better than 95%. Though the thermal-optical carbon analyzer used in the second part has the similar principle applied for the carbon determination in the Search program, the detailed procedure is different. The thermogram of carbon measurement procedure is plotted in Figure 8. Carbon analysis is carried out by performing a fixed-time heating ramp using Thermal-optical Transmittance Analysis, based on the thermal desorption/oxidation of particulate carbon to CO₂, and then reduce to methane, which is subsequently measured using a flame ionization detector (FID). The analysis starts in a nonoxidizing atmosphere (helium) with a 10-second purge followed by four temperature ramps to a maximum of 900°C. A cooling blower then comes on and the temperature drops to 600°C before oxygen is added. Detailed description of the measurement and analysis of carbonaceous species are given by Peterson et al. [2002]. The temperature is held at this point until the transmittance or reflectance returns to the initial point before

the sample was heated at all. This point determines the distinction between OC and EC. All of the carbon measured up to this point is OC. All of the carbon measured after this point is EC. Total Carbon is equal to EC plus OC. The precision is 0.19 at 1 µg C and 0.01 at 10 to 72 µg C.

1.3 Chemical Properties

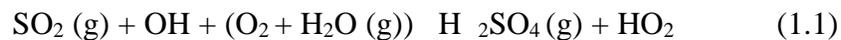
In order to shape more successful strategies to control the aerosol pollution problem, it is necessary to examine the chemical characteristics of the atmospheric aerosol and investigate the seasonal variations of the major components. In all of our calculations and analyses, to be consistent with program of Interagency Monitoring of Protected Visual Environments (IMPROVE) and U.S. Environmental Protection Agency (U.S.EPA), a multiplier of 1.4 is used to convert Organic Carbon (OC) to Organic Matter (OM) to account for the unmeasured oxygen and hydrogen. It is widely recognized that this multiplier is in reality not a constant [Search website].

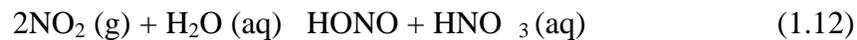
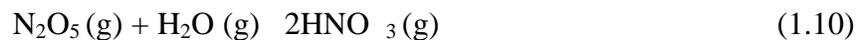
The major components of PM_{2.5} are in general identified as sulfate (SO₄²⁻), nitrate (NO₃⁻), ammonium (NH₄⁺), organic carbon (OC), and elemental carbon (EC) [Turnbull and Harrison, et al., 2000; Lee et al., 2001; Lin, 2002]. Some crustal materials make up the remaining fractions. In 1997, a new national ambient air quality standard has been established by US EPA, which gives the primary standard as 15 µg/m³ and 65 µg/m³ for the annual and 24-hour NAAQS, respectively. Hundreds of counties in the United States, in addition to that already in exceedance of the earlier standards, are estimated to exceed /violate the new PM_{2.5} standard [Parkhurst, 1999; SEARCH website].

Spatial and seasonal trend of PM have been investigated in previous studies [Malm et al., 1994; US EPA, 1999; Danalatos and Glavas, 1999; Lee et al., 2001; Lin, 2002]. Over the continental US, the largest single component of PM_{2.5} in the east is sulfate, while in the Pacific Northwest it is organics, and in Southern California it is nitrate [Malm et al., 1994]. The high PM_{2.5} concentrations in the eastern United States are attributed to regional emissions from power plants and motor vehicles in combination with local emissions from transportation and other sources [US EPA, 1999]. Similar spatial variability of major chemical components has been reported outside the United States. Organics are reported as the dominant constitute of aerosols in many areas of Asia and Europe (e.g., Beijing, China [He et al., 2001]; Sapporo, Japan [Kaneyasu, et al., 1995]; Birmingham, United Kingdom [Harrison et al., 1997]) while sulfate or nitrate in some other areas (e.g., Chongju, South Korea [Lee and Kang, 2001]; Rion, Greece [Danalatos and Glavas, 1999]). The difference of chemical speciation of atmospheric aerosols is attributed to the diversity of primary sources and atmospheric constituents along with those measurement sites.

Generally, urban areas have higher PM_{2.5} concentration than rural sites. This is expected since there are larger primary emissions in urban area compared to the rural area: larger concentrations of oxidant and other species such as OH and O₃, and greater mechanical activity (e.g., automobile traffic) [Finlayson-Pitts and Pitts, 1986]. In most cases, major aerosol types are highest during the summer and lowest during the winter months [Malm et al., 1994]. It suggests that there is increased formation of SO₄²⁻ and secondary OC in summer because of more favorable conditions for gas/particle conversion of SO₂ and VOCs as a result of photochemical activity.

As the most ubiquitous basic gas in the atmosphere, NH₃ provides a route for the formation of ammonium sulfate, ammonium chloride, and ammonium nitrate aerosol. It has been well recognized that ammonia preferentially binds with sulfuric acid; few NH₄NO₃ particles will be formed until all SO₄²⁻ particles are fully neutralized [SAMI, 2002]. NH₄⁺ can combine with SO₄²⁻ and present in the forms of either (NH₄)₂SO₄, NH₄HSO₄, or combination; it can also combine with HNO₃ to form NH₄NO₃. Based on several previous reports, molar NH₄⁺ / SO₄²⁻ ratio monitored for the continental aerosol is less than 2 at most sites [Table 4], which means that particle nitrate is limited by availability of ammonia at most locations in the US. NO₃⁻, SO₄²⁻ and NH₄⁺ are coupled together by the chemical reaction among NH₃, SO₂ and NO_x. Change in one of the gas precursors will lead to changes in all the major soluble ions. Conversion of NH₃ to NH₄⁺ aerosol strongly depends on the concentration of strong acids and water vapor in the atmosphere. The main reactions leading to the production of NH₄⁺ aerosol are listed below. The following gas (g) and aqueous (aq) phase reactions summarize NH₄⁺ aerosol production within the sulfur dioxide (SO₂), NO_x, sulfuric acid (H₂SO₄), HNO₃ and NH₃ system in the atmosphere [Finlayson-Pitts and Pitts, 1986]:





The following reactions involving hydrochloric acid (HCl) will also contribute to the formation of NH_4^+



But Cl^- concentration is low in the atmosphere, so the principle fate of NH_3 in the atmosphere is to combine with NO_3^- or SO_4^{2-} , rather than Cl^- .

Carbonaceous particles consist of a complex mixture of substances containing carbon atoms, usually being classified in two major fractions as, OC and EC [Gray and Cass, 1986; Castro et al., 1999]. EC originates predominately from combustion processes while OC originates either from direct emissions of particles or forms through VOCs gas-to-particle conversion processes. VOCs are emitted from both terrestrial and marine sources of which the most reactive are terpene compounds from trees and brush [Hidy, 1994]. Secondary organic carbon is formed by condensation of low vapor pressure products during photo-oxidation of hydrocarbons [Pandis et al., 1992, 1993; Chow et al., 1996]. Since there is no simple direct analytical technique available, previous carbonaceous analysis has widely employed the ratio of OC/EC exceeding 2.0 as

indicator to the presence of secondary organic aerosols based on their previous indirect methods [Gray, 1986; Hildemann et al., 1991; Chow et al., 1996]. Compared to the ratio of secondary carbon to total carbon between rural sites and urban sites, usually secondary OC formation is more available in rural areas since time allows chemical transformation and gas-to-particle conversion during air mass transport from urban areas [Castro et al., 1999].

Due to the lack of a direct chemical analysis method separating primary and secondary organic aerosol, researchers have tried to find several indirect methods. These methods include the use of mathematical modeling coupling the formation, transport and deposition of secondary organic aerosol (SOA) with air back trajectory [Pandis et al, 1992; Strader et al., 1999] and receptor model to identify primary OC and secondary OC [Schauer and Cass, 2000]. Another approach is called minimum OC/EC ratio method, which is the one most widely used [Turpin et al., 1991; Castro et al., 1999; Lin, 2001]. In this method, EC is used as a good tracer for primary OC. In minimum OC/EC ratio method, the secondary organic carbon (OC_{sec}) formation is estimated with the following equation:

$$OC_{sec} = OC_{tot} - EC \times (OC/EC)_{min} \quad (1.15)$$

where $(OC/EC)_{min}$ is the minimum ratio observed. Application of this method is based on three assumptions [Castro et al., 1999]: (1) weak contribution of non-combustion primary particulate OC; (2) spatial and temporal homogenizing of contributing sources and (3) low contribution of semi-VOCs compared to non-volatile organics.

In addition to the major species, there is a host of major, minor, and trace metals found in $PM_{2.5}$, including ZnO, Fe_2O_3 , CaO, Al_2O_3 , etc. There are natural sources of

metals, such as seas salt, forest fires, volcanic emissions, and emissions from vegetation. Anthropogenic sources include the combustion of coal and oil, wood burning, waste incineration, etc, and a variety of trace elements are present in combustion – derived $PM_{2.5}$, like Cd, Pb, Zn, As etc. Trace elements are often used for air source analysis. Fang et al. [2003] illustrated that principal components PC1 (Fe and Mg), PC2 (Pb), and PC3 (Cr and Cu) in ambient air were interpreted as soil, traffic and industrial metallurgical processes, respectively. Calcium has been used as an indicator element for construction dust in Beijing [He et al., 2001]. Biomass burning has the highest abundance of both total K and soluble K of all source emissions [He et al., 2001]; therefore, the presence of K and Zn in $PM_{2.5}$ could be explained as the symbol of primary biogenic origin [Andreae and Crutzen, 1997].

1.4 Forecasting and Modeling of $PM_{2.5}$

Currently O_3 , as one of six criteria pollutants reported for daily air quality index, is being modeled and forecasted the best, while $PM_{2.5}$ modeling and forecasting is just starting. Few groups have used statistical models to link meteorology and $PM_{2.5}$ [Ryan and Piety, 1999; Domaghy et al., 2003]. After Meng et al. [1997] theoretically explored the relationship between $PM_{2.5}$ and O_3 , some work has been started to link O_3 and $PM_{2.5}$ using measurement data [Parkhurst et al, 1999; Lim and Turpin, 2002]. Studies from Cox et al. [2000 & 2001] show certain parameters, mainly O_3 , specific humidity, wind speed, and mixing height, appear to have a strong association with $PM_{2.5}$ concentration in their study areas. Most studies show that wind speed is inversely related to $PM_{2.5}$, since increased wind speed will decrease the particle concentration [Harrison et al., 1997;

Sorrell et al., 2003]. But different studies may get different results for the influence of other meteorological parameters. Though there is a general agreement that increasing atmospheric moisture can aid in particle formation [Finlayson-Pitts and Pitts, 1986; Cox et al., 2000, Hidy et al., 2000], different publications have represented different results between $PM_{2.5}$ and humidity based on the simple regression analysis, without considering influence of other factors. Seinfeld et al. [2001] reported that that secondary organic aerosol (SOA) formation is highly dependent on relative humidity, that is, high RH will favor SOA condensation. Jung et al. [2002] pointed out there is no significant relationship between $PM_{2.5}$ and RH, while Pérez et al. [2000] show a small negative correlation between $PM_{2.5}$ and RH.

Among numerical models, the U.S. EPA's Model -3/Community Multiscale Air Quality (CMAQ) model, a 3D Eulerian model, is accepted by EPA as the best tool to carry $PM_{2.5}$ modeling research. CMAQ can be employed to carry out a series of studies that can't be realized with simple measurement only, like sensitivity to the gas precursors, meteorology, contribution from emission sources and the removal processes. The modeling system has been described elsewhere [Byun and Ching, 1999], The aerosol component of CMAQ has also been described [Binkowski and Roselle, 2003] and evaluated [Mebust et al., 2003]. To run this model, the configurations must be set properly. There are several options for each submodel, and the fifth-generation Pennsylvania State University / National Center for Atmospheric Research (NCAR) Mesoscale Model (MM5) is adopted at present as the meteorology model. The emission models include GEMAP (EMS-95), EPS, FREDs and SMOKE. The Sparse Matrix Operator Kernel Emission System (SMOKE) is the emission-processing model used in

this study. Chemistry module consists of gas-phase chemistry, aerosol formation and aqueous chemistry, where three chemical mechanisms are included in the gas-phase chemistry: CB4 [Gery et al., 1989], RADM2 [Stockwell et al., 1990], and SAPRC-97 [Carter, et al., 1997]. Finally, to consider the transport and dispersion of pollutants, advection and diffusion are included in the transport model.

The primary objective of this study is to identify the major species and to explore the chemical characterization of PM_{2.5} in the Southeast US. There are four goals:

- To identify and characterize the major chemical species of PM_{2.5} in the Southeast U.S., and North Carolina state as a case study
- To address the sources of PM_{2.5} by means of back trajectory analysis using the 3-D HYSPLIT4 model
- To examine the correlation between PM_{2.5}, O₃, and meteorology variables, such as temperature, wind speed, wind direction, relative humidity, precipitation, solar radiation, and pressure
- To examine the sensitivity of the major PM_{2.5} components including NH₄⁺, SO₄²⁻, and NO₃⁻ to SO₂, NO_x and NH₃ emissions using Model-3/CMAQ.

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Species	Emission estimate (10^9 kg/yr)	
	Anthropogenic	Natural
CO ₂	$2.6 \cdot 10^7$	$5.5 \cdot 10^8$
CH ₄	375	160
CO	1815	430
SO ₂	146	~ 15
H ₂ S	4	1-2
N ₂ O	16	26
NO _x (as NO)	85	24
NH ₃	30	15
PM (all size)	408	1964
PM _{2.5}	280	1135

Table 1: Global anthropogenic and natural emissions of various species
 Natural CO₂ emission estimates are assumed to be the primary production from land ($2.2 \cdot 10^{17}$ kg yr⁻¹) and exchanged from the oceans ($3.3 \cdot 10^{17}$ kg yr⁻¹)

(Source: Wayne, R.P, 2000 and Warneck, 2000)

Source	Emission estimate (10^9 kg/yr)						
	Particles	SO ₂	N ₂ O	NO _x (as NO)	CO	CH ₄	NMHC
Fuel combustion	5	} 140	-	51	890	} 100	115
Industry	40		3.7	-	425		18
Biomass burning	60	6	1.4	17	500	40	-
Cultivated soils	-	-	10	13	-	60	-
Other	200	-	1.1	4	-	175	10

Table 2: Global emissions of anthropogenic species (1985-1995)
Source: Wayne, R.P., 2000

Analyte	Sampler	Filter	Frequency	Analysis	MDL, $\mu\text{g}/\text{m}^3$
Mass	FRM	Teflon	Daily	Gravimetry	0.2
SO_4^{2-}	PCM (CH1)	Teflon	3 rd , 6 th , 12 th d	IC	0.03
NO_3^-	PCM (CH1)	Teflon	3 rd , 6 th , 12 th d	IC	0.01
NH_4^+	PCM (CH1)	Teflon	3 rd , 6 th , 12 th d	AC	0.03
Vol. NO_3^-	PCM (CH1)	Nylon	3 rd , 6 th , 12 th d	IC	0.02
Vol. NH_4^+	PCM (CH1)	Citric acid	3 rd , 6 th , 12 th d	AC	0.04
Organic C	PCM (CH3)	Quartz	3 rd , 6 th , 12 th d	TOR	0.08
Black C	PCM (CH3)	Quartz	3 rd , 6 th , 12 th d	TOR	0.05
Trace Elem.	FRM	Teflon	3 rd day	XRF	0.0005-0.003

Table 3: Daily Average $\text{PM}_{2.5}$ measurement parameters

Source: <http://www.atmospheric-research.com/PDFs/AWMA%204%20yrs%20and%20counting.pdf>

Authors	Location	$\text{NH}_4^+/\text{SO}_4^{2-}$	Comment
Moyers et al. (1977)	Tucson, Arizona	1.5	Average
Pierson et al. (1980)	Allegheny Mountains	0.5-2.3 0.87	Summer Average
Tanner et al. (1979)	New York City	1.9 1.2-1.5	February August
Stelson et al. (1981)	Greater Los Angeles, CA	2.244	Summer
Kellus et al. (1991)	Newton, Connecticut	1.72	Summer average
Aneja et al. (1998)	Continental, Eastern NC	1.70	Summer
Wang et al. (2002)	Urban sties, NC	1.55-2.33	Average
	Lenoir, NC	1.87-2.02	
	Caswell, NC	1.36-1.84	
This result (2000+2001)	Rural, SEARCH	2.11	Average
	Urban Inland, SEARCH	3.22	
	Urban Coast, SEARCH	2.09	

Table 4. Observed Molar $\text{NH}_4^+ / \text{SO}_4^{2-}$ ratios monitored for the continental aerosol in the U.S.

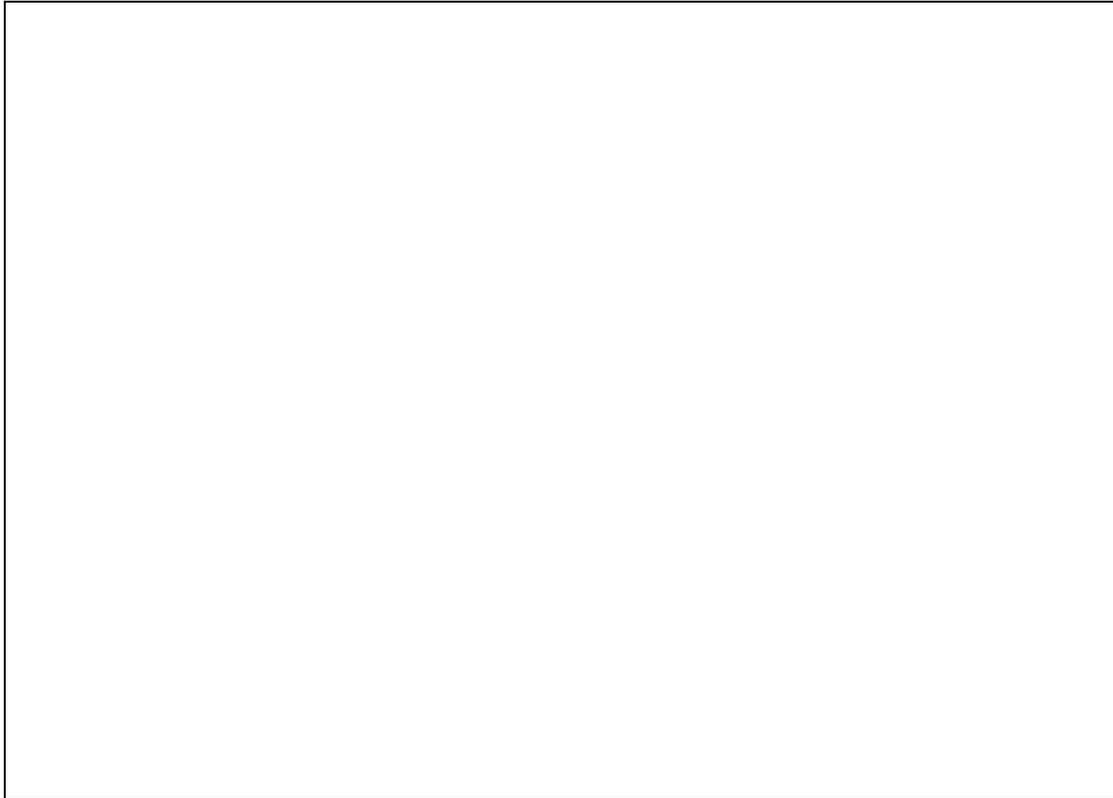


Figure 1. Route of incorporation of chemical species into atmospheric particulate matter (Meng et al., 1997)

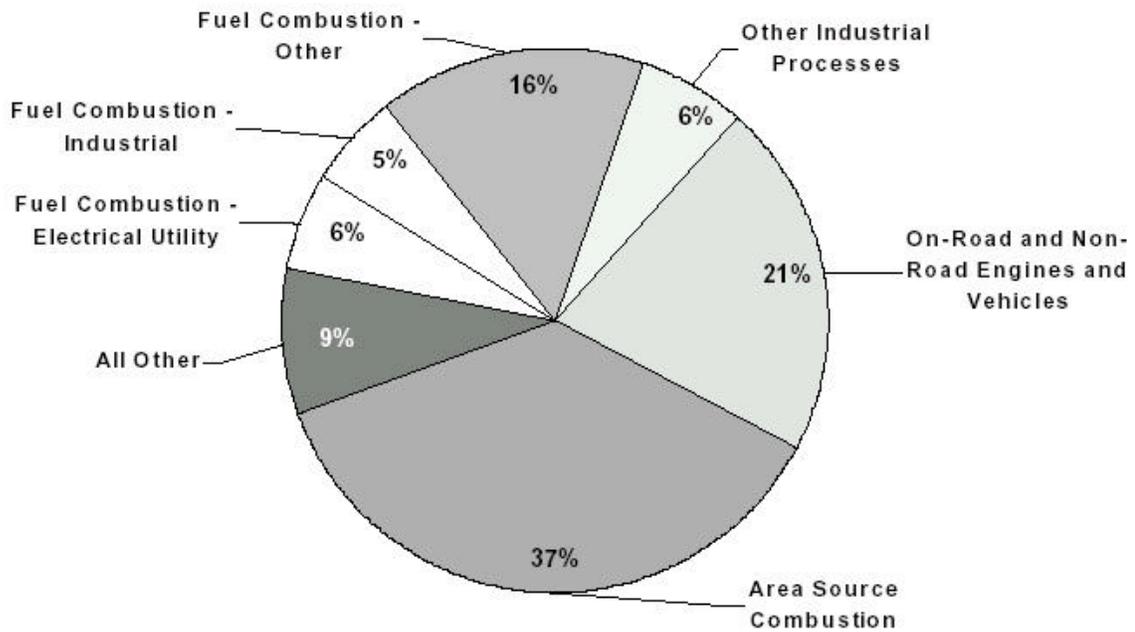


Figure 2: 1998 Directly Emitted National Particulate Matter (PM_{2.5}) emissions by principal source categories for nonfugitive dust sources.

Note: emissions from fugitive dust sources are not included in the figure

(Source: <http://www.epa.gov/ttn/chief/trends/trends98/chapter2.pdf>)

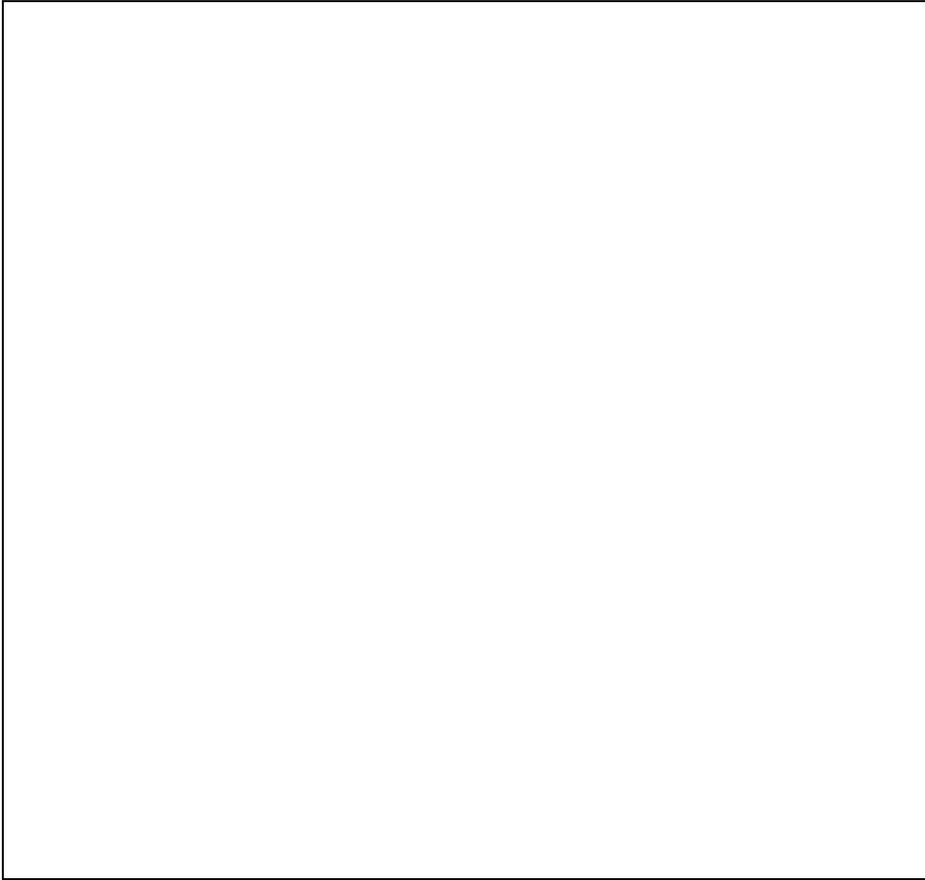


Figure 3: Chemical coupling in the atmospheric gas, particle, and droplet phases
(Source: Meng et al., 1997)

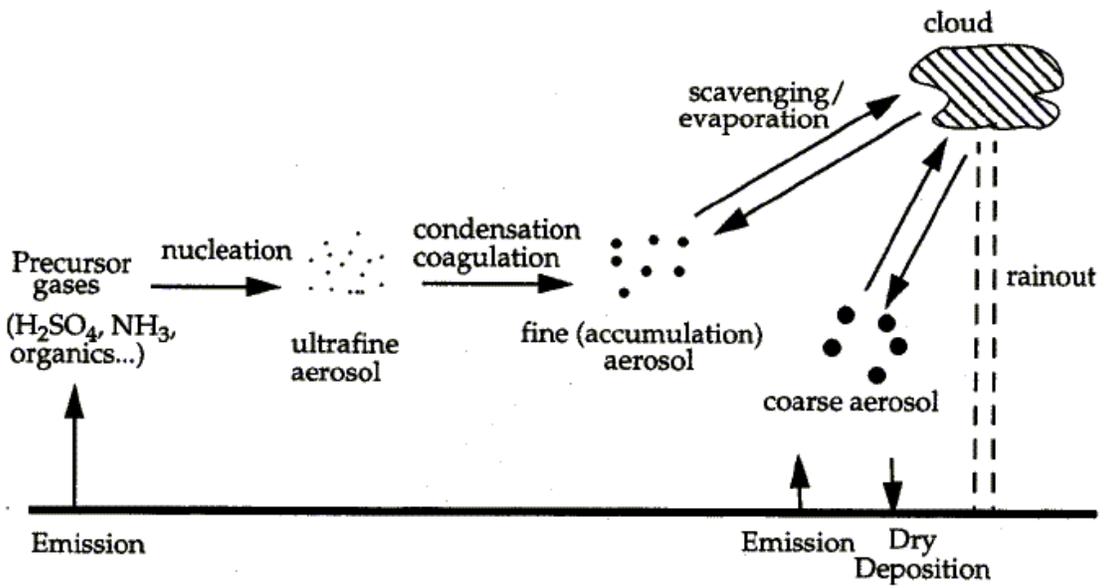


Figure 4: production, growth, and eventual removal of atmospheric aerosol particles.

(Source: Jacob, D. J., 1999)



Figure 5. R&P (Rupprecht and Patashnick) brand FRM (Federal Reference Method) PM_{2.5} monitor

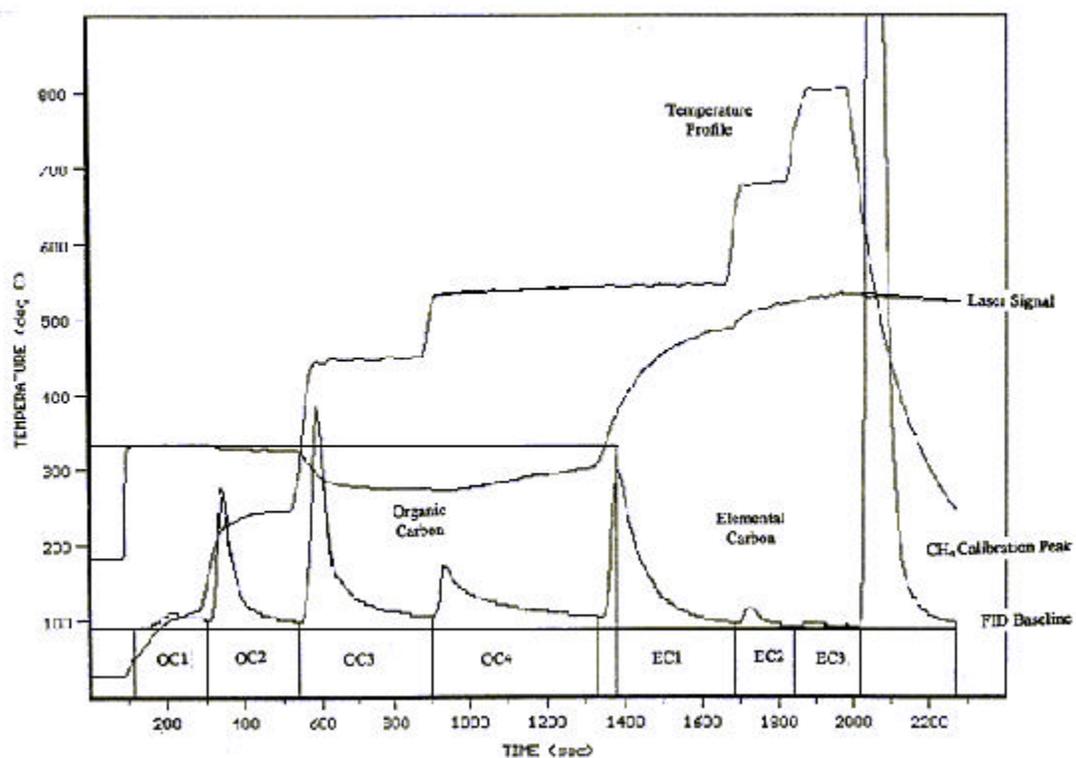


Figure 6. Thermogram for filter sample containing organic carbon (OC) and elemental carbon (EC) employed in SEARCH program

(Source: search website: <http://www.atmospheric-research.com>)



Figure 7: "SASS" Met One's Particulate Matter Speciation Samplers operated by NC Division of Air Quality.

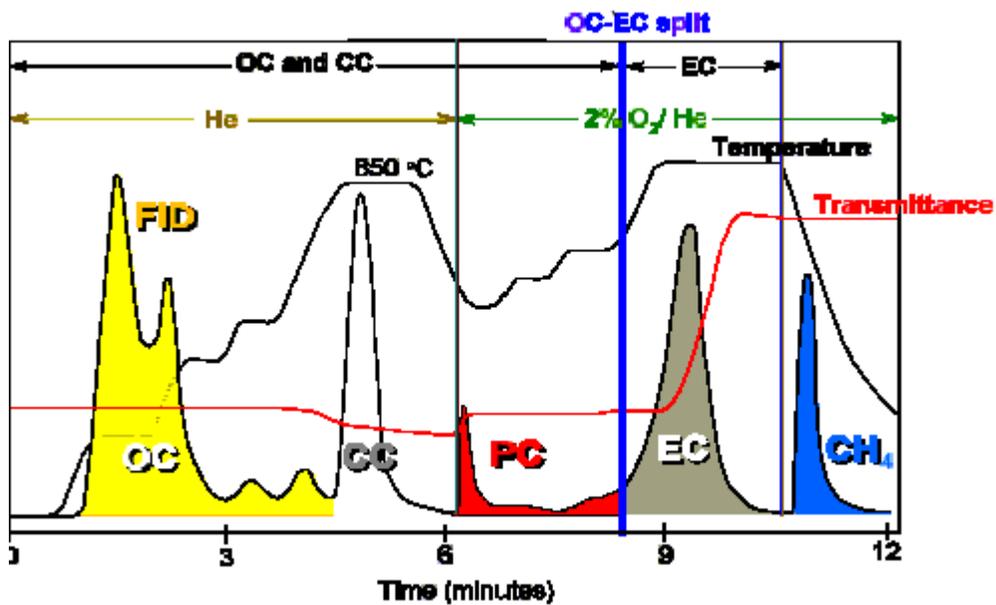


Figure 8: Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak. Carbon sources are pulverized sugar beet pulp, rock dust (carbonate), and diesel particulate.

(Source: <http://www.cdc.gov/niosh/nmam/pdfs/5040.pdf>)

II. Characterization of Fine Particulate Matter (PM_{2.5}) in the Southeast United States

Abstract

Characteristics of the major chemical components in ambient fine particulate matter ($PM_{2.5}$) have been investigated from seven diversely located sites in Southeast United States during 2000 and 2001. Three sites are categorized as rural while two others as inland urban, and two as coastal urban sites. Analysis of chemical species revealed that sulfate (SO_4^{2-}) (27~37%) with annual average $4.23\mu\text{g}/\text{m}^3$, ammonium (NH_4^+) (11~19%) with annual average $1.89\mu\text{g}/\text{m}^3$, and organic matter (OM)(28~33%) with annual average $4.26\mu\text{g}/\text{m}^3$, dominated the identifiable components at all the sites. Total $PM_{2.5}$ mass concentrations are found higher during warm seasons (Summer and Fall) than in cold season (Spring and Winter), suggesting that warm summer conditions favor the formation of secondary aerosol components such as sulfate and organic matter. The equivalent ratio of NH_4^+ to SO_4^{2-} is 0.92 and 0.83 at the CTR (Centrevi, AL) site and OAK (Oak Grove, MS) site, respectively, indicating SO_4^{2-} has not been completely neutralized by NH_4^+ . Equivalent ratio of NH_4^+ to SO_4^{2-} is 1.46 and 1.58 at JST (Jefferson) and BHM (N.Birmingham), respectively, but the ratios are close to 1.0 at GFP (Gulfport) and PNS (Pensacola), which may be attributed to the coastal effects. Analysis of major chemical components also shows that ratios of organic carbon/elemental carbon (OC/EC) at rural sites can be as high as 4.3, mirroring the significant presence of secondary organic aerosols (up to 90%) formed perhaps through VOCs gas-to-particle conversion processes. Interactions between $PM_{2.5}$ mass and meteorology exhibits a negative correlation of $PM_{2.5}$ with wind speed, and a positive association with temperature. No obvious correlation between $PM_{2.5}$ and relative humidity is found. Finally, origins of pollutant sources are addressed using the combinations of back trajectory analysis (HYSPLIT4

model) and hierarchical cluster analysis. This reveals that transport from northeast (North Carolina) direction exert a large effect on $PM_{2.5}$ mass concentration on our analysis sites.

1. Introduction

Since the earliest recognition of its existence as suspended particle in the air [Schmasuss and Wigand, 1929], the importance of particular matter (PM) has been extensively studied [Harrison et al., 1997; Lee, 2001; Lin, 2002]. Expanding observations and modeling evidence have demonstrated a strong connection between PM and adverse health effects, including decreased lung function, increased hospital admissions and emergency room visits, even increased premature death [Seaton et al., 1995; Schwarz et al., 1996]. Particulate matter can also cause adverse impacts to the environment. Small particles with diameters less than or equal to $2.5\mu\text{m}$ ($\text{PM}_{2.5}$) are referred as fine particulate matter and they are a mixture of solid particles and/or liquid droplets in the air. Fine particles are the major cause of reduced visibility in parts of the United States [Conner et al., 1991]. Particles containing nitrogen and sulfur that are deposited onto land or water bodies may change the nutrient balance and acidity of those environments, as well as interfering with plant metabolism and damage culturally important objects [US EPA, 1999].

The major components of $\text{PM}_{2.5}$ are, in general, identified as sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), organic carbon (OC), and elemental carbon (EC) [Turnbull and Harrison, 2000; Lee et al, 2001; Lin, 2002]. The $\text{PM}_{2.5}$ may consist of directly emitted particles from fuel combustion, residential fireplaces and wood stoves, and secondary particles formed when emitted NO_x , SO_2 , VOC, NH_3 , and other gaseous species react in the atmosphere. High $\text{PM}_{2.5}$ concentrations in the eastern United States are attributed to regional emissions from power plants and motor vehicles in combination with local emissions from transportation and other sources [US EPA, 1999]. In 1997, a

new national ambient air quality standard (NAAQS) was established by US EPA, which specifies the primary standards as $15 \mu\text{g}/\text{m}^3$ and $65 \mu\text{g}/\text{m}^3$ for the annual and 24-hour periods, respectively. Hundreds of counties in the United States, in addition to those already in violation of the previous standards, are estimated to exceed the new $\text{PM}_{2.5}$ standard [Parkhurst et al., 1999; SEARCH program].

In order to formulate more successful strategies to control the aerosol pollution problem, it is necessary to examine the chemical characteristics of the atmospheric aerosol and investigate the seasonal variations of the major components. Numerous programs have been initiated on $\text{PM}_{2.5}$ measurements and monitoring (e.g., EPA's Federal Reference Method Monitoring network, IMPROVE network, etc.). A few studies have been carried on the chemical components and meteorological analysis of fine PM in Southeast United States. This paper presents (1) chemical characterization; (2) driving meteorological conditions; and (3) source identification of measurement data collected from seven southeast US sites. These seven sites include three rural sites: Yorkville (YRK) in GA, Centreville (CTR) in AL, and Oak Grove (OAK) in MS; two continental urban sites: Jefferson (JST) in GA, and N.Birmingham (BHM) in AL; and two coastal urban sites: Pensacola (PNS) in FL, and Gulfport (GFP) in MS. The results from different sites are compared and summarized. Since the seven measurement sites are indicative of the typical settings throughout much of the southeast US, it is expected that the measurement and modeling based analysis presented in this paper may shed light on the regional characteristics of fine particulate matter in the southeast U.S.

2. Methodology

2.1 Site information and data acquisition

Sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), organic carbon (OC), and elemental carbon (EC) and other meteorological parameters were measured at three rural sites and four urban sites in the southeast United States. The measurement sites are shown in Figure 1 and the site characteristics are given in Table 1.

Yorkville (latitude 33.93N, longitude 85.05W), GA, is located in Paulding County with a population of 82,000. The area around the site consists of rolling terrain and is covered mainly with hardwood oak forest interspersed with tilled farmland and open pasture. No secondary road is located within 300m and no highway is located within 5 km of the site. Centreville (latitude 32.90N, longitude 87.25W), AL, is located in Bibb County. The surrounding area is heavily forested with mixed deciduous and coniferous forest. To the southwest, at roughly 200 m from the site there is a lightly traveled county road (CR25). Oak Grove (latitude 30.99N, longitude 87.38W), MS, is located in Perry County and has a population of about 12,000. Land use surrounding the site is primarily forested with interspersed areas of cropland and pasture. A lightly traveled dirt road is approximately 125 m north of the site, but no secondary roads or highways are within 5 km of the site. Jefferson (latitude 33.776N, longitude 84.413W), GA, 4.2km NW of downtown Atlanta, is a small city located in Jackson County. It is surrounded by parking lots, city streets and warehousing buildings. The coast site is Pensacola (latitude 30.437N, longitude 87.256W), FL, and Gulfport (latitude 30.437N, longitude 87.256W), MS, are close to the Gulf Coast (no more than 1.2 miles to the Gulf of Mexico). They are primarily residential areas. North Birmingham (latitude 33.533N, longitude 86.816W), a

city with population 243, 000 is located in Jefferson County, AL. There are a few kilometers of heavy transportation and industrial activities around the site, including a main high way (RED65) about 1 km to the west.

Rupprecht & Patashnick Partisol brand model 2025 monitors are used for PM_{2.5} mass sampling at the above sites. The PM_{2.5} sampler is a sequential filter sampler designed to collect 24-hour integrated samples of particulate matter in the PM_{2.5} size fraction within the guidelines of the Class 1 Federal Reference Method (FRM) given in EPA (1998). Particle speciation data are collected using a sequential, multichannel sampler known as the Particle Composition Monitor (PCM). The PCM consists of three parallel sampling channels, each sampling ambient air with independent mass flow control (16.7lpm at 760mm and 298k). The inlet for each channel consists of a 10µm cyclone, followed by one or more denuders to remove contaminant gases, followed by a 2.5 µm WINS impactor. Channel 1 (PCM1) consists of a Teflon filter preceded by sodium carbonate and citric acid denuders. The Teflon filter is analyzed gravimetrically for mass, then by X-ray fluorescence for trace elements, and finally by ion chromatography (IC) for sulfate, nitrate, and ammonium. Values from PCM2 or continuous monitors are substituted for missing values in their order of availability. The sampling collected by the third PCM channel (PCM3) is analyzed for PM_{2.5} carbon. The DRI thermal/optical carbon analyzer based on the preferential oxidation of organic carbon (OC) and elemental carbon (EC) compounds at different temperatures is used for carbonaceous species determination. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. OC evolves from the filter punch in

a He atmosphere at 120, 250, 450, and 550°C plus pyrolyzed organic carbon, while EC is derived from the filter punch in a helium/ oxygen (He/O₂) atmosphere at 550, 700, and 800°C minus pyrolyzed organic carbon. Total Carbon refers to all carbon obtained from the filter punch between ambient and 800°C under He and O₂/He atmospheres. [SEARCH website].

2.2 Air mass categorization and determination

Origins of air masses approaching the measurement site were investigated by the combination of cluster analysis [Dorling et al., 1992] and HY-SPLIT Model [Draxler, 1997] results and emission sources categorization based on EPA emission inventory [Ulman et al., 1997; EPA, 2000]. Cluster analysis, which allocates a data set into several dominant groups according to the directions of air masses, is frequently employed in air pollution studies to identify pollutant source regimes, e.g., Slanina et al. (1983) and Pio et al. (1991) identified continental, maritime, and anthropogenic source regimes for pollutants approaching their sites. This method aims to maximize inter-group variance and minimize within-group variance. Numeric algorithms have been developed for cluster analysis [Anderberg, 1973]. The approach chosen in this study is the one proposed by Dorling et al. (1992a, b). Briefly, end points of each trajectory are taken as input to clustering algorithm. The first step chooses a large number of seed trajectories and all other trajectories are assigned to the seeds that can achieve minimum root mean square deviation (RMSD). The seed or average trajectory of each cluster is then recalculated from its members continuously until all trajectories are correctly assigned. After that, the number of clusters is decreased by merging two closest clusters. Sudden drop in the total RMSD as the number of clusters is reduced are interpreted as the merging of clusters of

trajectories that are significantly different in terms of the wind directions and speeds associated with them.

The hybrid single-particle Lagrangian integrated trajectories (HY-SPLIT) [Draxler et al., 1997] model was chosen to calculate air mass trajectories for cluster analysis. This model is an analytical algorithm that, without the aid of tracers, balloons, and even aircraft, can provide important transport history information for an air mass arriving at a particular point. The actual operation routines are explained and demonstrated by Draxler et al. [1992, 1997] and will not be discussed here. Back trajectories were initialized at 11:00pm local time, and at 500m height above the ground level of the measurements site. The results were obtained using 180-km 2-hourly output from the Eta Data Assimilation System (EDAS) (<http://www.arl.noaa.gov/ready-bin/edas.pl>) for both horizontal and vertical air mass streams. All data were archived and processed by NOAA/ARL covering the continental United States and its immediate coastal waters. The residence time of sulfate aerosol, which is the primary component of fine PM presented at our measurement sites, has been estimated as “several days” [Charlson et al., 1992]. Speed of travel for air parcels carrying sulfates can be important since air moving quickly over a particular source region will have less time available to load up pollutant emissions than a volume of air moving slowly, which might result in enhanced pollutant or other aerosols levels due to the longer residence time [Ulman et al., 1997]. On the basis of these statements and assumptions, we have chosen to calculate 24-hour back trajectories, which can cover a distance 600 km from the site (assuming air parcel speeds averaging 25 kmph) and identifying all important source regions affecting each site.

Figure 2 shows the percentage change in the total root mean square deviation (TRMSD) with decreasing number of clusters, which consist of back trajectories for the YRK (Yorkville, GA) site. The x-axis represents the number of clusters, while y-axis refers to the percentage change in RMSD when the number of cluster increases from x-1 to x. Figure 2 indicates when the number of clusters increases from 1 to 20, large changes in the TRMSD occur at 4, 7, and 18 clusters. As in any other clustering methodology, some decisions have to be made by the user [Romesburg, 1984]. The user can define a percentage change in RMSD which, when exceeded at some stage in the reduction of the number of clusters, signifies an optimum number of clusters to be retained in the analysis. Hence Figure 2 indicates a “break” or significant percentage change in reducing the distinct number of clusters from 8 to 7. 7 clusters were therefore retained as best describing significantly different forms of air flow to YRK site in the period considering both the number of clusters and the change of RMSD. Once these distinct (optimum number of) clusters of trajectories have been identified, the average back-trajectories for the 7 clusters at YRK (Yorkville, GA) site will be plotted. For further reference, clusters are named according to their general direction: N, NE, S, etc. The cluster that stays relatively closer to the reception site is named C (close) because speed of air parcel has influence on the level of pollutant as discussed in proceeding part.

3. Result and discussion

3.1 PM_{2.5} mass concentration and chemical compositions

The data set of total PM_{2.5} mass concentration and its major components were collected continuously from the seven sampling sites between January 2000 and

December 2001. Mass concentration of $\text{PM}_{2.5}$, SO_4^{2-} , NO_3^- , NH_4^+ , OC, and EC are averaged for 24 hours, so the hourly metrological data is also converted into daily averaged data. For rural sites, we also compared the $\text{PM}_{2.5}$ mass concentrations in the southeast region to that measured by the Interagency Monitoring of the Protected Visual Environments (IMPROVE), $\text{PM}_{2.5}$ is typically higher in the East than that in the West due to the higher SO_4^{2-} concentration in the former regions. This regional difference is largely due to differences in the SO_2 emission density in different regions. The eastern United States has a higher concentration of coal-burning power plants that emit significant amounts of SO_2 , while the western United States has relatively low SO_2 emission density [Malm et al., 1994]. The east-west differences in $\text{PM}_{2.5}$ are generally much less in urban based on the measurement of EPA network. This may be explained by higher concentrations of carbon from soot and organic compounds and also NO_3^- in the urban areas of the West.

Annual average concentrations of total $\text{PM}_{2.5}$ vary from 12.1 to 13.8 $\mu\text{g}/\text{m}^3$ at rural sites and from 11.4 to 17.8 $\mu\text{g}/\text{m}^3$ at urban sites (as shown in Figure 3). Among the seven sites, BHM (N.Birmingham, AL) site has the highest yearly average $\text{PM}_{2.5}$ concentration of 17.8 $\mu\text{g}/\text{m}^3$ while GFP (Gulfport, MS) sites has the lowest, with yearly average of 11.4 $\mu\text{g}/\text{m}^3$. The high level of $\text{PM}_{2.5}$ can be attributed to local anthropogenic emission of particulate matter from point sources and mobile sources [US EPA, 1999]. The 2000 and 2001 yearly averages of $\text{PM}_{2.5}$ at JST (Yorkville, GA) and BHM (N.Birmingham, AL) sites were above US National Ambient Air Quality Standards (NAAQS), which is 15 $\mu\text{g}/\text{m}^3$ for yearly average while the averages at others five sites were below NAAQS. No site had daily average concentration above the NAAQS daily standard of 65 $\mu\text{g}/\text{m}^3$. The

ratios of annual average mass concentrations of sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) to total $\text{PM}_{2.5}$ vary between 27~37%, 3-7%, and 11~19%, separately [Figure 1]. Water-soluble inorganic components constitute 44-56% of total $\text{PM}_{2.5}$ mass concentration. Organic Materials (OM) account for 28~33% of total $\text{PM}_{2.5}$. Mass concentration of OM is obtained from that of OC multiplied by a factor of 1.4 [Lin, 2002] to account for the unmeasured hydrogen and oxygen that are present in organic materials. The average fraction of EC is 4.2% and 9.5% of $\text{PM}_{2.5}$, at rural and urban sites, respectively. The “others” portion mainly consists of crustal materials and trace elements, but it may also include bioaerosols. As the dominant components of $\text{PM}_{2.5}$ (See Figure 1), SO_4^{2-} and OM constituted approximately 70% of total $\text{PM}_{2.5}$ mass for all data set.

The average $\text{PM}_{2.5}$ mass concentration at inland urban sites is higher than that at rural sites (Figure 3). This phenomenon is largely explained by differences in carbonaceous material, since urban areas are generally associated with higher concentration of carbonaceous materials [EPA report, 1999]. Figure 3 also illustrates that GFP (Gulfport, MS) and PNS (Pensacola, FL) sites, which are categorized as coastal sites, have much lower $\text{PM}_{2.5}$ mass concentrations as compared to inland urban (JST and BHM) sites, and not much different from rural sites. Concentrations of all the major soluble components (i.e., SO_4^{2-} , NH_4^+ , and NO_3^- in our case) and carbonaceous components (i.e., OC and EC) at JST (Yorkville, GA) and BHM (N. Birmingham, AL) (inland sites) are found significantly higher than those at coastal sites. The reasons for such a difference are given later, when we discuss individual species.

Seasonally, maximum concentration of SO_4^{2-} has been observed in the summer (June, July, August), which suggests the abundant occurrence of photochemical oxidation and existence of higher concentrations of secondary aerosols in the summer atmosphere [Day et al., 1997; Lin, 2002]. To evaluate the degree of atmospheric conversion from SO_2 to SO_4^{2-} , the fraction of sulfate to total sulfur have been used in earlier $\text{PM}_{2.5}$ analyses [Lee and Kang, 2001; Lin, 2002]. Figure 4 displays the seasonal conversion ratio of sulfate to total sulfur at both rural and urban sites. The conversion ratios are higher in summer (0.32-0.50) than in winter (0.14-0.28) for all sites. It also can be found that the yearly average conversion ratios are higher at rural sites than those at urban sites, which reflects air mass aging and the existence of fresh sulfur oxides emitted in the urban areas.

At the rural sites the average equivalent ratio of NH_4^+ to SO_4^{2-} is 0.92 and 0.83 for CTR (Centrevi, AL) site and OAK (Oak Grove, MS) site, respectively. The ratios are less than 1.0 at both sites, indicating the SO_4^{2-} is not completely charge-balanced by NH_4^+ due to the high concentration of SO_4^{2-} present. It has been well recognized that ammonia preferentially binds with sulfuric acid; few NH_4NO_3 particles will be formed until all SO_4^{2-} particles are fully neutralized [SAMI report]. Therefore, the majority of NH_4^+ contained in particles presented at CTR (Centrevi, AL) and OAK (Oak Grove, MS) sites could be in the form of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , or their combination, but not of NH_4NO_3 [Kim et al., 1994; Lee and Kang, 2001]. Due to the high NH_4^+ concentration at YRK site, the equivalent ratio is as high as 1.41, so most SO_4^{2-} should be combining with NH_4^+ to form $(\text{NH}_4)_2\text{SO}_4$. At all urban sites, the average equivalent ratio of NH_4^+ to SO_4^{2-} is greater than 1.0. The ratio of NH_4^+ to SO_4^{2-} are 1.48 and 1.60 at JST (Jefferson, GA) and BHM (N. Birmingham, AL), respectively, but the ratios are close to 1.0 at GFP (Gulfport,

MS) and PNS (Pensacola, FL) which may be attributed to the coastal effects because they have much lower ammonium concentration there. It is reported that if the airborne NH_3 concentration is higher in the inland atmosphere than that above the sea, there is a net flux of NH_3 from the continental atmosphere to marine atmosphere [Asman and Harrison, 1994]. Such transport is expected to be responsible for the low NH_3 concentration at the coastal sites. Accordingly, the average equivalent ratios of NH_4^+ to the sum of SO_4^{2-} and NO_3^- at JST (Jefferson, GA) and BHM (N. Birmingham, AL) sites are higher than 1.0 (1.04 and 1.38, respectively), but they are lower than 1.0 at GFP (Gulfport, MS) and PNS (Pensacola, FL) sites. This suggests that both sulfuric acid and nitric acid have been completely neutralized at JST and BHM sites. But, at coastal sites (i.e., GFP and PNS), there is certain amount of HNO_3 left unneutralized. This result agrees well with that from the Southeast Appalachian Mountains Initiative (SAMI) (<http://www.saminet.org>). For most of the year in the rural southeastern US, sulfate particles are not fully neutralized by NH_4^+ , and NO_3^- particle concentrations are low [SAMI, 2002]. Table 2 lists the molar $\text{NH}_4^+ / \text{SO}_4^{2-}$ ratios monitored for the continental aerosol at several other sites in the USA. For most cases molar $\text{NH}_4^+ / \text{SO}_4^{2-}$ ranges between 1 and 2, but at a few locations where ratio is higher than 2, the excess can be attributed to the presence of nitric acid, which also binds some ammonia [Warneck, 2000].

Given its tendency for neutralization, sulfate concentrations is not as high as that of carbonaceous particles, which consist of elemental carbon (EC) and organic carbon (OC), for all sites in our analysis (Figure 1). EC originates predominately from combustion processes, while OC originates either from direct emissions of particles or it forms through VOCs gas-to-particle conversion processes. Secondary organic carbon is

formed by condensation of low vapor pressure products during photo-oxidation of hydrocarbons [Pandis et al., 1992, 1993; Chow et al., 1996]. Since there is no simple direct analytical technique available, previous carbonaceous analyses have widely employed the ratio of OC/EC exceeding 2.0 as an indicator of the presence of secondary organic aerosols [Gray, 1986; Hildemann et al., 1991; Chow et al., 1996]. Table 3 presents the ratios of OC/EC at different sites in this study. The ratios for all sites are much larger than 2.0, which imply prevalence of secondary organic aerosols [Gray, 1986; Chow et al., 1996]. Table 4 tabulates the results calculated with the minimum OC/EC ratio method. Only urban sites are listed to minimize land cover effect. It can be seen that OC/EC ratios in this study are in good agreement to the measurement results from that obtained by Chow et al. (1994). The OC/EC ratios at rural sites, are higher than those at urban sites (Table 3). This is due to the relatively lower EC concentration at rural sites. Table 3 also reveals a strong correlation ($R^2 = 0.72-0.84$) between EC and OC, which implies they are emitted from the same source [Lee and Kang, 2001].

The minimum OC/EC ratio method has been used to estimate the secondary organic carbon (OC_{sec}) formation with the following equation [Castro et al., 1999; Lin 2002]:

$$OC_{sec} = OC_{tot} - EC \times (OC/EC)_{min} \quad (1)$$

Where $(OC/EC)_{min}$ is the minimum ratio observed. Application of this method is based on three assumptions [Castro et al., 1999]: (1) weak contribution of non-combustion primary particulate OC; (2) spatial and temporal homogeneity of contributing sources, and (3) low contribution of semi-VOCs compared to non-volatile organics. Using the minimum OC/EC ratio, the average secondary OC concentration was

calculated from measurement data and found to consist over 40% of the total OC concentration for all sites (Table 4). This result agrees well with other studies [Castro et al., 1999; Lin, 2002], and it suggests that the formation of secondary OC due to the gas/particle conversion of gaseous hydrocarbon precursors is significant at these sites.

3.2 Effect of Meteorology on PM

Meteorological parameters have long been recognized to play an important role in the creation, maintenance and removal of high levels of fine particles [Harrison, et al., 1997]. Figure 3 displays the seasonal variation of total PM_{2.5} mass at various rural and urban sites. For all sites, total PM_{2.5} mass concentration reaches its maximum in summer and minimum in winter, which suggests that higher temperature and stronger solar radiation favor PM_{2.5} formation. Table 5 summarizes the correlation between total PM_{2.5} mass concentration and ambient air temperature. The correlations are very weak and insignificant at all the urban sites, and all rural continental sites show a lightly better correlation between PM_{2.5} and temperature, with slope from 0.21 to 0.38. The higher level of PM_{2.5} mass during high temperature periods is mainly attributed to the conversion of SO₂ to SO₄²⁻, since sulfate is one of dominant component of PM_{2.5} in southeast of US [Malm et al., 1994]. Moreover, it was reported that ammonia, another key PM_{2.5} precursor, has higher concentrations when temperature increases [Aneja et al., 1997; Walker et al., 2000]. Lower NO₃⁻ concentrations may dampen summer peaks as the highest nitrate concentration occurs in winter due to highest total NO_x levels [Lee and Kang, 2001]. However, impact of seasonal variation of nitrate on total PM_{2.5} mass is

limited in magnitude due to the small portion of nitrate (Figure 1) to total fine particulate matter mass in southeast United States.

Harrison et al. [1997] demonstrated the important influence of wind speed on $PM_{2.5}$ concentration. By preventing large size particles from resuspension, higher wind speed generally increases the dispersion and decreases the accumulation of local primary aerosol [Lim and Turpin, 2002]. Such a trend is also observed in this study. Figures 5 and 6 show the correlation between the wind speed and $PM_{2.5}$ concentration at YRK (Yorkville, GA) site for warm (Summer and Fall) and cold (Winter and Spring) seasons, respectively. The negative correlation between the two variables is apparent for both periods. For the warm seasons, higher concentrations of $PM_{2.5}$ generally occur at low wind speeds. Results for all other sites are presented in Table 6. For all types of measurement sites, two similar trends are shared: 1) Warm seasons are associated with higher background $PM_{2.5}$ concentration, which is consistent with the conclusion obtained from temperature; 2) $PM_{2.5}$ in warm seasons is more sensitive to wind speed than it is in cold season. Such seasonal differences are typical and match earlier analyses for other locations, e.g., Harrison et al. [1997] reported that there is significant and negative correlation between $PM_{2.5}$ and wind speed in summer, but no clear trend is winter at a site in Birmingham, UK. The low R square value in our study also turns out that the correlations between $PM_{2.5}$ and wind speed vary with the location and time period; but overall, wind speed is not the dominant controller for $PM_{2.5}$.

Relative humidity has been considered as a factor affecting total $PM_{2.5}$ mass since secondary organic aerosol (SOA) formation is highly dependent on relative humidity [Seinfeld et al., 2001]. Based on their chamber experiments, Lim et al. [2002] reported

that the extent of effect of humidity depends on the properties (e.g., polarity) of oxidation products involved. With the daily $PM_{2.5}$ concentration only, we find OC_{sec} is anti-correlated with relative humidity and no significant relationship between total $PM_{2.5}$ concentrations are observed on the basis of analysis from measurement at all sites. This corresponds with the results of Jung et al. [2002], who reported that no significant relation was found between $PM_{2.5}$ and relative humidity.

3.3 Source identification

We calculated all the individual trajectories for those days during 2000 when measurements of $PM_{2.5}$ are available at YRK (Yorkville, GA) site. The whole trajectory set is then clustered into seven groups using the algorithm stated earlier. One trajectory is selected from each cluster, which can minimize the average RMSD for all other trajectories within this cluster. Figure 8 illustrates these selected seed trajectories from each cluster. Each seed trajectory is labeled with direction best describing the relative position of its origin to the reception site. The number in the parenthesis shows the percent of the trajectories assigned to a particular cluster. The emission density of $PM_{2.5}$, taken from EPA county-based emission inventory [U.S. EPA, 2000], is also displayed as the background in Figure 8 to provide regional pollutant emission levels that might be loaded into those air parcels when traveling through the region. Clearly, air masses traversing certain regions, such as Georgia and Florida states, are shown in Figure 8 to be areas of highest average emissions of fine particular matter. The average $PM_{2.5}$ concentrations associated with these individual clusters, as well as the frequency of each cluster, for the YRK site are presented in Figure 7.

Air masses approaching YRK site are found most frequently coming from North (N) and Northwest (NW), accounting for a total of 42% of all trajectories calculated. The next frequently occurring categories are Close (C) and Eastern (E), which consist of 17.5% and 16.5%, respectively. The highest PM_{2.5} concentrations, as expected, were associated with trajectories from the northeastern (E) (18.5 µg/m³) and Close (16.5 µg/m³) since both Eastern and Close trajectories originated from high level of PM_{2.5} emission regions. Walker et al. (2001) have demonstrated that substantial ammonia emissions in North Carolina can contribute to considerable increase of PM_{2.5} level, which may explain the highest mass concentration of air mass from SC, which can be further traced back to NC (Figure 8). This hypothesis is supported by the fact that the ratio of ammonium to total PM_{2.5} mass for air masses from E cluster is higher than those from other clusters. Slow movement of air masses, which is the case for Close cluster, may help load the pollutants into those air masses and thereby cause elevated PM_{2.5} concentration. Clean air masses are found associated with trajectories from Northwest (10.3 µg/m³) and West (12.7 µg/m³). Both NW and W clusters originated from regions with relatively lower level of PM_{2.5} emissions (Figure 7), and the PM_{2.5} concentration in air masses of NW clusters is further reduced by the high speed of those air parcels, which move more quickly than any other clusters of trajectories.

IV. Conclusion

The primary objective of this study was to investigate the chemical characteristics of the major species of PM_{2.5}, and the effects of meteorological parameters on total mass of PM_{2.5} in the southeast of USA. Measurements of fine particulate matter (PM_{2.5}) and its

major chemical components, as well as meteorological data for seven diversely located (urban, rural and coastal) southeast sites, are presented. The analysis shows that $PM_{2.5}$ is higher at urban than at rural sites; and $PM_{2.5}$ in coastal areas is lower than that at inland sites. For all the seven sites, SO_4^{2-} and organic matter (OM) account for most of the $PM_{2.5}$ in the southeast United States. The seasonal average of $PM_{2.5}$ peaks in the summer (16.8 $\mu g/m^3$ in YRK, 16.3 $\mu g/m^3$ in CTR, 13.5 $\mu g/m^3$ in OAK) and drops lowest in the winter at the rural sites (11.3 $\mu g/m^3$ in YRK, 9.5 $\mu g/m^3$ in CTR, 10.7 $\mu g/m^3$ in OAK). For the rural sites, the difference between warm seasons (summer and fall) and cold seasons (spring and winter) is of less magnitude than that at urban sites. For the coastal sites, the seasonal variation is much weaker than for inland sites, including rural sites. For all sites, carbonaceous analysis shows that organic carbon (OC) is well correlated with elemental carbon (EC), implying they are emitted from the same sources. Minimum OC/EC ratio method also indicates that organic carbon consists mainly of secondary OC, i.e., formed in the atmosphere, rather than directly emitted OC. The results obtained in our study suggest that the formation of secondary aerosols due to gas-to-particle conversion is significant in our studied areas.

High temperature favors high $PM_{2.5}$ concentration while wind speed has negative correlation with $PM_{2.5}$ concentration, implying that high $PM_{2.5}$ concentrations occur at low wind speed. The correlations between $PM_{2.5}$ with wind speed and temperature are weaker at coastal sites than that at inland sites. No significant correlation between $PM_{2.5}$ concentration and relative humidity is found in this study. Trajectory-cluster analysis showed that higher concentrations are associated with air masses coming from the East, which indicates the important role of high levels of NH_3 emission in North Carolina on

the formation of fine particular matter. Considerations of meteorology in our analysis are still preliminary; more detailed work combined numerical model simulations might be necessary to get more definite conclusions.

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Site characterization	Site	Latitude(degree, N)	Longitude(degree, W)	Elevation(meters)
Rural	YRK	33.931	85.046	395
	CTR	32.902	87.25	135
	OAK	30.986	87.376	100
Inland urban	JST	33.776	84.413	275
	BHM	33.553	86.816	200
Coastal urban	PNS	30.437	87.256	27
	GFP	30.391	89.05	5

Table1 Coordinate and elevation of sites: three rural, two inland urban sites and two coastal urban sites
(YRK: Yorkville, GA; CTR: Centrevi, AL; OAK: Oak Grove, MS; JST: Jefferson, GA; PNS: Pensacola, FL; GFP: Gulfport, MS; BHM: N.Birmingham, AL)

Authors	Location	$\text{NH}_4^+/\text{SO}_4^{2-}$	Comment
Moyers et al. (1977)	Tucson, Arizona	1.5	Average
Pierson et al. (1980)	Allegheny Mountains	0.5-2.3 0.87	Summer Average
Tanner et al. (1979)	New York City	1.9 1.2-1.5	February August
Stelson et al. (1981)	Greater Los Angeles, CA	2.244	Summer
Kellus et al. (1991)	Newton, Connecticut	1.72	Summer average
Aneja et al. (1998)	Continental, Eastern NC	1.70	Summer
Wang et al. (2002)	Urban sties, NC	1.55-2.33	Average
	Lenoir, NC	1.87-2.02	
	Caswell, NC	1.36-1.84	
This result (2000+2001)	Rural, SEARCH	2.11	Average
	Urban Inland, SEARCH	3.22	
	Urban Coast, SEARCH	2.09	

Table 2. Observed Molar $\text{NH}_4^+ / \text{SO}_4^{2-}$ ratios monitored for the continental aerosol in the US.

	Sites	No. of Sample	EC($\mu\text{g}/\text{m}^3$)	OC($\mu\text{g}/\text{m}^3$)	OC/EC	Correlation r^2
Rural	YRK	256	0.64	3.06	4.78	0.78
	CTR	296	0.61	3.10	5.08	0.80
	OAK	297	0.53	2.75	5.19	0.83
	JST	694	1.55	4.02	2.59	0.79
Urban	BHM	266	2.02	4.61	2.28	0.72
	PNS	270	1.06	3.23	3.05	0.83
	GFP	269	0.75	2.55	3.40	0.84

Table 3. Comparison of Elemental Carbon (EC) and Organic carbon (OC) concentration for fine particles at the seven sites in the Southeast US

	Sites	OC _{pri} (ug/m ³)	OC _{sec} (ug/m ³)	OC _{sec} /OC	OC _{sec} /PM _{2.5}
Rural	YRK	1.657	1.403	45.8%	10.14%
	CTR	1.564	1.536	49.5%	11.31%
	OAK	1.506	1.244	45.2%	10.01%
Urban	JST	2.084	1.936	48.2%	11.36%
	BHM	2.700	1.910	41.4%	9.46%
	PNS	1.798	1.432	44.3%	9.78%
	GFP	1.491	1.059	41.5%	8.30%

Table 4. Levels of secondary organic carbon (OC_{sec}) of PM_{2.5} estimated from minimum OC/EC ratio method

Site	Types	Linear Regression	# of samples	R Square
YRK	Rural	$Y = 0.27x + 8.1$	393	0.1486
CTR	Rural	$Y = 0.38x + 5.0$	443	0.1876
OAK	Rural	$Y = 0.21x + 7.0$	417	0.086
JST	Inland urban	$Y = 0.25x + 12.0$	598	0.0773
BHM	Inland urban	$Y = 0.25x + 13.0$	369	0.0614
PNS	Coastal urban	$Y = -0.003x + 12.2$	515	0.0006
GFP	Coastal urban	$Y = 0.03x + 10.6$	383	0.0025

Table 5. Linear Regression between Fine PM Mass and Temperature at Southeast United States, 2000 and 2001.

Site	Types	Seasons	Linear Regression	Number of Samples	R Square
YRK	Rural	Warm	$Y = -2.3x + 19.6$	183	0.1481
		Cold	$Y = -1.3x + 15.5$	221	0.1123
CTR	Rural	Warm	$Y = -4.2x + 23.4$	185	0.1696
		Cold	$Y = -2.4x + 16.3$	223	0.172
OAK	Rural	Warm	$Y = -3.4x + 18.7$	209	0.1353
		Cold	$Y = -0.2x + 10.7$	216	0.0018
JST	Inland Urban	Warm	$Y = -4.9x + 26.6$	296	0.1763
		Cold	$Y = -3.4x + 22.4$	314	0.3396
BHM	Inland Urban	Warm	$Y = -7.8x + 30.9$	189	0.287
		Cold	$Y = -4.3x + 23.4$	166	0.282
PNS	Coastal Urban	Warm	$Y = -1.3x + 13.4$	222	0.0382
		Cold	$Y = -0.9x + 13.2$	285	0.0521
GFP	Coastal Urban	Warm	$Y = -2.2x + 17.4$	200	0.0807
		Cold	$Y = -0.6x + 11.5$	181	0.0273

Table 6. Linear Regression between Fine PM Mass concentration ($\mu\text{g}/\text{m}^3$) and Wind Speed (m/s) at Southeast United States, 2000 and 2001.

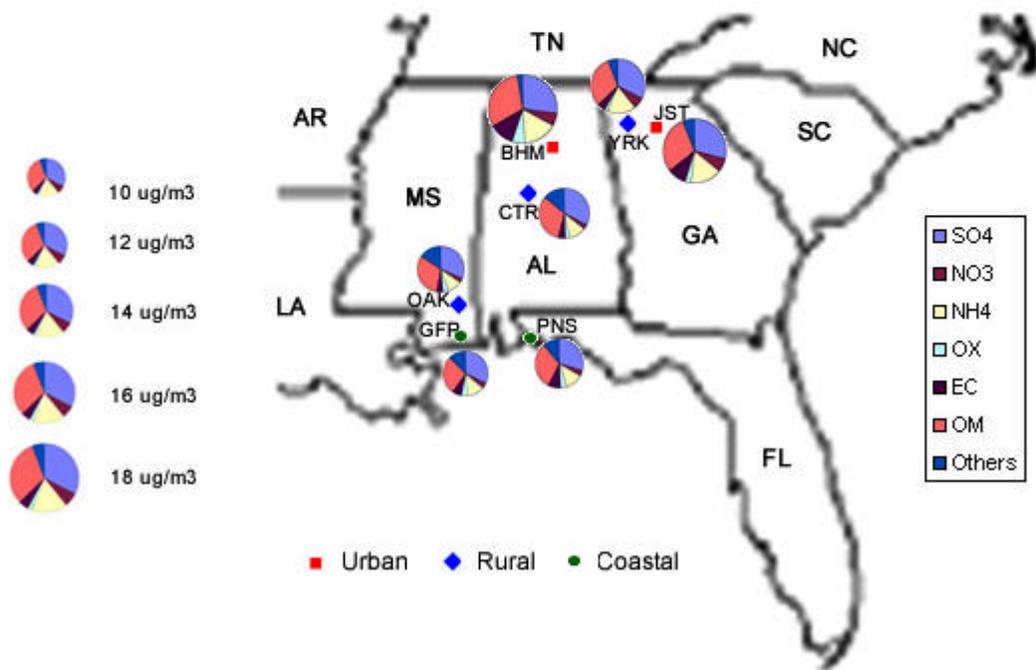


Figure 1. Monitoring network site locations and relative composition of major species of at each site of Southeast U.S.
 (YRK: Yorkville, GA; CTR: Centrevi, AL; OAK: Oak Grove, MS; JST: Jefferson, GA; PNS: Pensacola, FL; GFP: Gulfport: MS; BHM: N. Birmingham, AL)

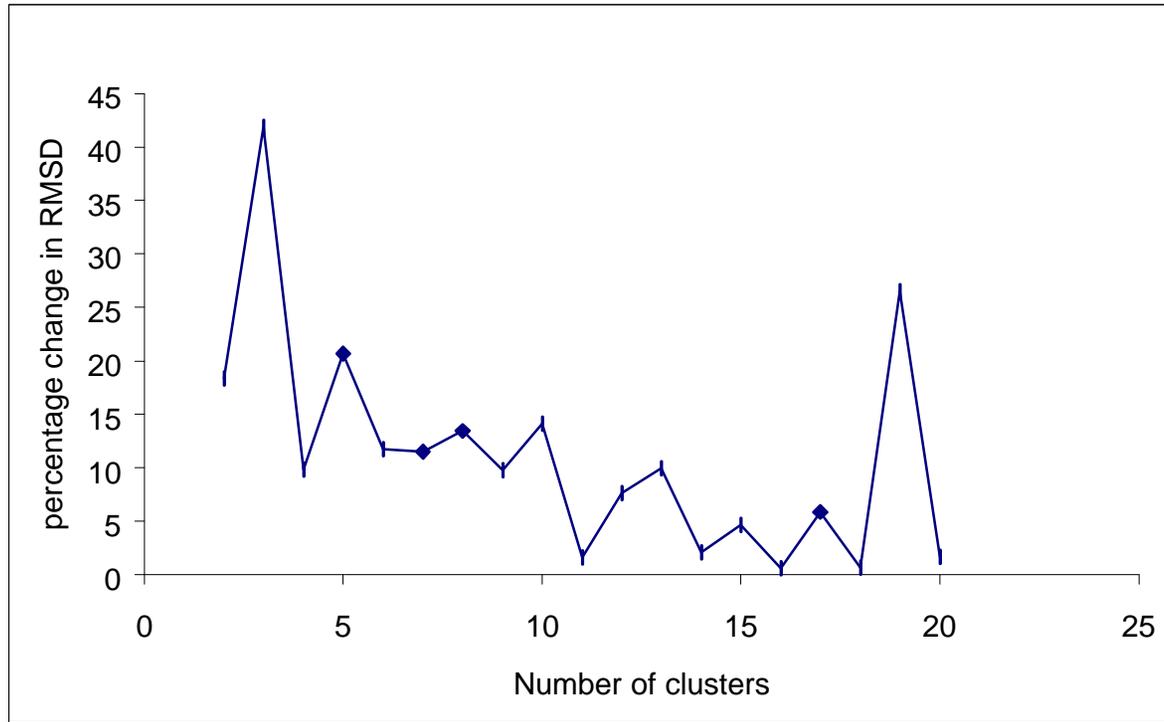


Figure 2. Percent change in the total root mean square deviation (TRMSD) with decreasing number of clusters at YRK (Yorkville, GA)

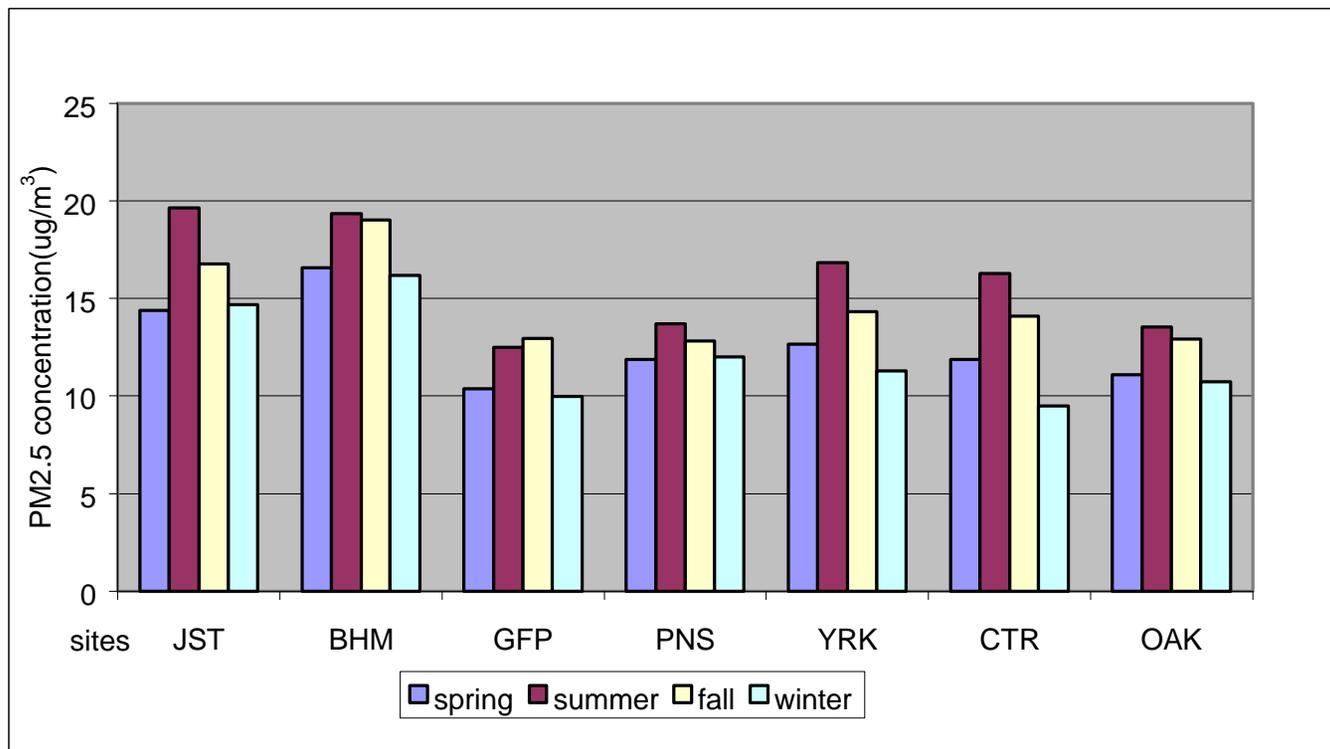


Figure 3 Seasonal variation of PM_{2.5} mass concentration ($\mu\text{g}/\text{m}^3$) in southeast of USA

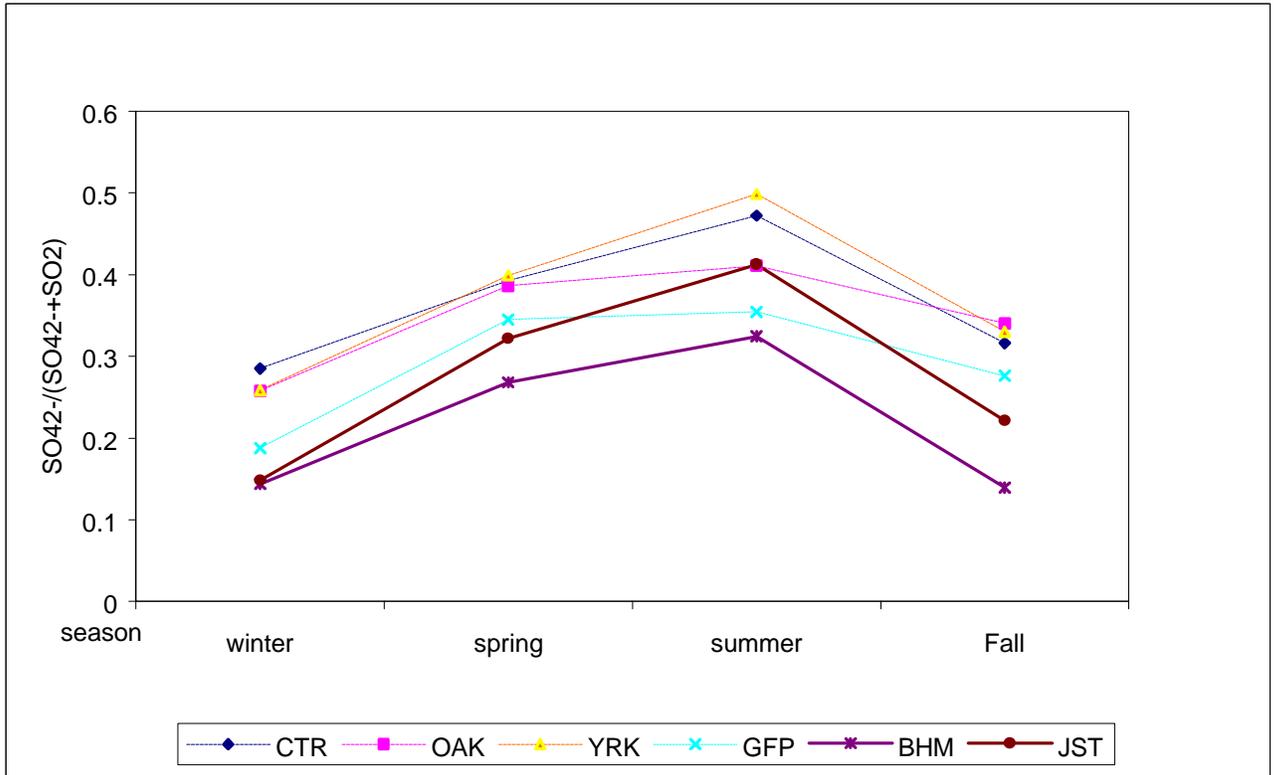


Figure 4 Seasonal conversion ratio of sulfate to total sulfur at three rural sites

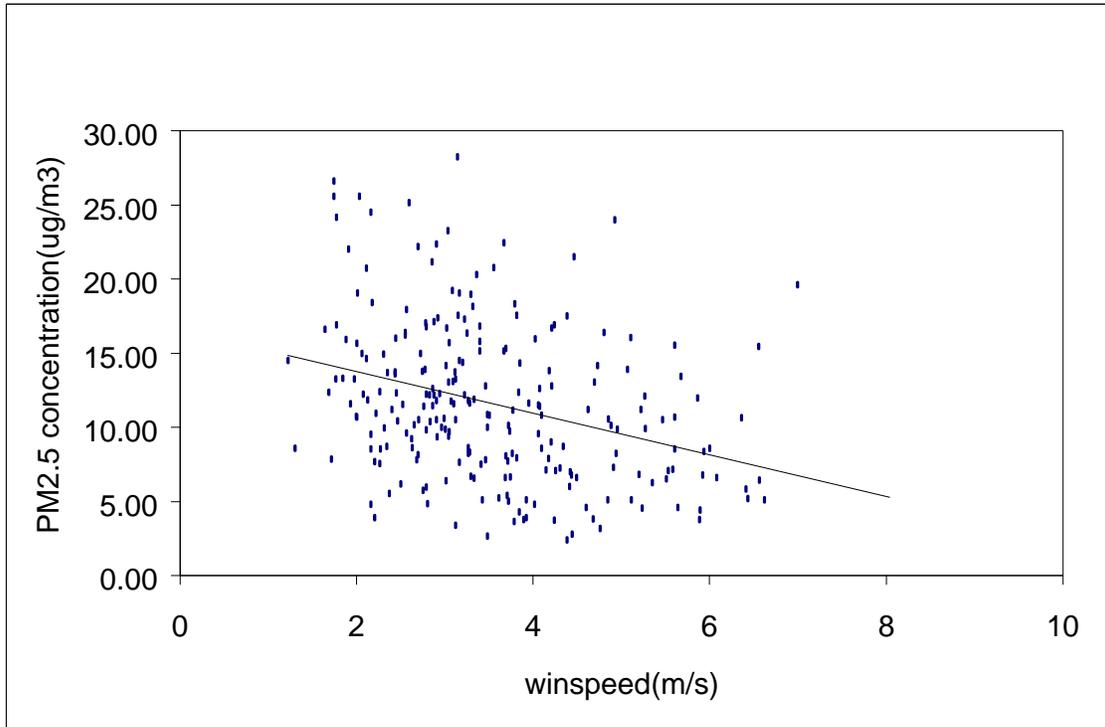


Figure 5 Relationship between PM_{2.5} mass concentration($\mu\text{g}/\text{m}^3$) and wind speed at YRK(Yorkville, GA) at cold seasons (spring and winter)

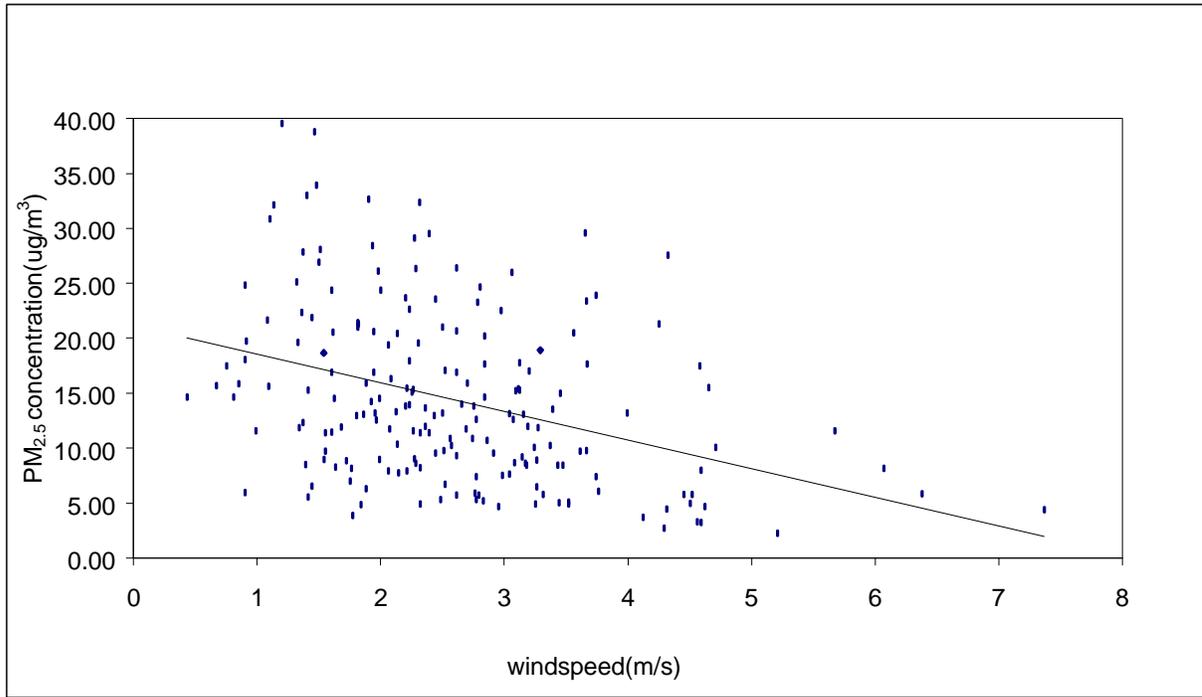


Figure 6 Relationship between PM_{2.5} mass concentration($\mu\text{g}/\text{m}^3$) and wind speed at YRK (Yorkville, GA) in warm seasons (summer and fall)

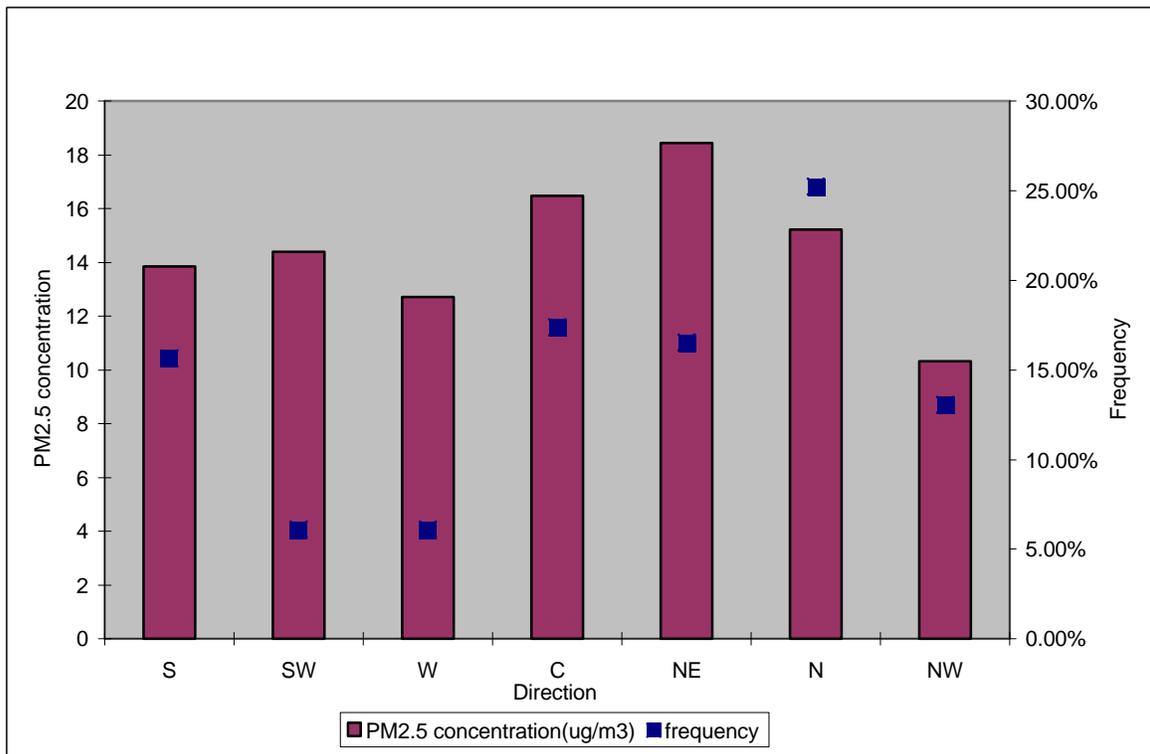
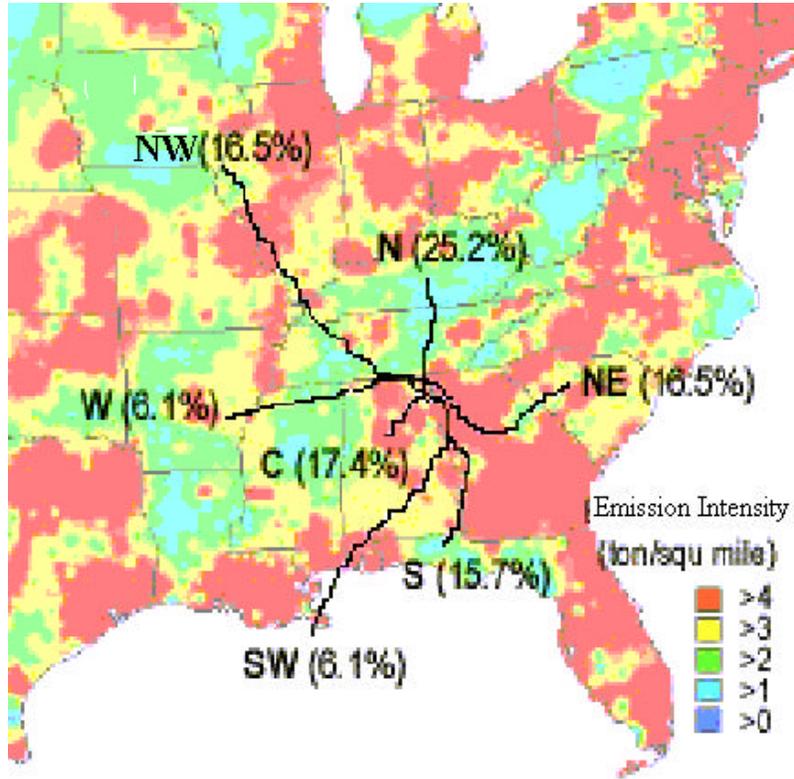


Figure 7. Cluster plot, frequency, and average PM_{2.5} mass concentrations by cluster

Figure 8. Average back-trajectories for the seven clusters at YRK (Yorkville, GA) site, during 2000



**III. Chemical Characterization of Fine Particulate Matter (PM_{2.5})
in North Carolina: Observations and Modeling Analysis**

Abstract:

Daily PM_{2.5} samples have been monitored and analyzed at five sites located in North Carolina (NC) during 2002. Three of these sites consisting of Forsyth County site, Wake County site and Mecklenburg County site are associated with typical urban settings; whereas two others consisting of Lenoir County site and Caswell County site represent rural and agricultural environment. Chemical analysis showed that the major component in NC is organic matter (OM); the major soluble component is sulfate (SO₄²⁻) and then ammonium (NH₄⁺) and nitrate (NO₃⁻). Secondary organic carbon (7.22 µg/m³) constitutes about 47-68% of the total organic carbon and 15-23% of the total PM_{2.5} mass. Back trajectories analysis has been used to address the origin of the air masses containing the particulates. We found that air masses with low PM_{2.5} concentration mainly originated from the marine environment or continental environment with strong subsidence from upper troposphere where the PM content is lower than that in the surface layer. Air masses with high concentrations of PM_{2.5} are largely continental sources of low elevation. The secondary organic carbon (OC) formed through gas-to-particle conversion is estimated from the minimum ratio between OC and elemental carbon (EC). The results show that the formation of secondary organic aerosols (SOA) due to gas-to-particle conversion is significant in our studied areas, and this accounts for approximately 50% of total organic aerosols. It suggests that secondary organic aerosols are more abundant at agricultural sites than that at urban sites. Correlation analysis between PM_{2.5} and meteorology indicates PM_{2.5} is more sensitive to temperature compared to other meteorological parameters such as wind speed, humidity, and solar radiation. The regression analysis also shows PM_{2.5} can be well predicted by O₃ and meteorological variables (temperature, wind speed and direction, humidity, solar radiation, pressure and precipitation) at both urban and rural sites. A three-dimensional, regional Eulerian grid model is employed to investigate the sensitivity of atmospheric aerosol formation to the major gaseous precursors viz., SO₂, NO_x, NH₃ and VOCs. Modeling results revealed that reduction of a specific precursor does not only lead to decrease of the corresponding PM_{2.5} component, but also to changes in other components subsequently. Both NH₄⁺ aerosol and NO₃⁻ aerosol are more sensitive to NH₃ in NH₃-limited area, and to NO_x in NH₃-rich areas in winter.

1. Introduction:

Atmospheric aerosol has gained increasing interest over the past decades due to its role in human health, climate and atmospheric chemistry [Schwartz et al., 1996; Andreae and Crutzen, 1997; US Environmental Protection Agency (US EPA), 1999; Menon et al., 2002]. The major soluble components of the $PM_{2.5}$ are sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+), while the major insoluble are organic carbon (OC) and elemental carbon (EC) [Brook et al, 1997; Lee et al., 2001]. Spatial and seasonal trend of particulate matter (PM) have been investigated in previous studies [Malm et al., 1994; US EPA, 1999; Danalatos and Glavas, 1999; Lee et al., 2001; Lin, 2002]. Over the continental US, the largest single component of particulate matter with aerodynamic diameter less than 2.5 μ m ($PM_{2.5}$) in the east is sulfate, while in the Pacific Northwest it is organics, and in Southern California it is nitrate [Malm et al., 1994]. Similar spatial variability of major chemical components has been reported outside the United States. Organics are reported as the dominant constituent of aerosols in many areas of Asia and Europe (e.g., Beijing, China [He et al., 2001]; Sapporo, Japan [Kaneyasu, et al., 1995]; Birmingham, United Kingdom [Harrison et al., 1997]) while sulfates or nitrates are in other areas (e.g., Chongju, South Korea [Lee and Kang, 2001]; Rion, Greece [Danalatos and Glavas, 1999]). The differences in chemical speciation of atmospheric aerosols can be attributed to the diversity of primary sources and atmospheric constituents, along with differences in environmental conditions prevailing at measurement sites. This study presents a detailed discussion of chemical speciation of atmospheric aerosols measured during 2000 at five sites including three urban and two rural locations in the State of North Carolina.

PM_{2.5} has both primary and secondary origins. Aside from the direct emission of particles into the atmosphere (primary), gas-to-particle conversion processes play an essential role in determining the mass and speciation of airborne PM [Meng et al., 1997]. North Carolina, together with the whole Southeast US, is characterized by large organic biogenic emission sources, which can substantially contribute to the formation of secondary organic aerosols [Andreae and Crutzen, 1997; Meng et al, 1997; Pun et al., 2002]. Moreover, North Carolina is associated with much higher ammonia emissions than the surrounding areas [EPA, National Air Pollution and Emission Trend, 2000], as a result of rapid growth of animal industry concentrated in eastern NC [Aneja et al, 2003; Walker et al., 2000]. It has been well established that the amount of ammonia presented in the ambient air plays a critical role in both the mass and chemical compositions of aerosol inorganics [Meng et al, 1997; Warneck, 2000]. In North Carolina, which is rich in both organic and inorganic precursors to aerosol formation, an extensive monitoring campaign has been launched to study the characterizations of atmospheric aerosols. We present both observation-based and modeling analyses of chemical components of fine PM (PM_{2.5}) and their sensitivity to its key gaseous precursors.

2. Sampling Sites and Measurement Technique

2.1 Sampling Sites

Forsyth, Wake, and Mecklenburg are the three counties where three urban sites are located, while Caswell and Lenoir are the counties where the two agricultural sites are located. All of these five sites are continually monitored by Division of Air Quality in NC (DAQ) and are briefly described below:

(I) The Forsyth County site (36.11N, 80.23W), at an elevation of 287 m above sea level, is located on Hattie Avenue, in Winston-Salem, NC. This is an urban site and located in center of the city with a population of 131,885.

(II) The Mecklenburg County site (35.24N, 80.79W), at an elevation of 232 m above sea level is an urban cite, and is located at Garinger High School, on Eastway Drive, Charlotte, NC, with a population of 314,447 in the city.

(III) The Wake County site (35.856N and 78.574W), at an elevation of 100m above the sea level, is located at Millbrook middle school on Spring Forest Road in Raleigh. As a suburban area with population of 150,255, it is 13km away from Raleigh downtown.

(IV) The Caswell County site (36.307N, 79.467W), at an elevation of 241m above sea leave, is located at Cherry Grove recreation area. This area is surrounded by several coal-fired power plants. Among all the power plants, the one that is most close to the site is Roxboro plant, which is also the one with the biggest power generating capacity [EIA, 2003].

(V) The Lenoir County site (35.231N, 77.569W), at an elevation of 29m above sea level, is located at Lenoir Community College on the corner of highways 70 East and 58 South in Lenoir. Lenoir county is one of the six most concentrated animal farm counties, having an average hog population density ~ 528 hogs/km² [NCDA, 1998] (the shaded area in Figure 1). The average hog population density for the remaining coastal plain is ~ 65 hogs/km² [Walker et al., 2000]. Besides the large hog population density, the area also contains approximately 68% of the Coastal Plain's domestic turkey population. Ammonia emissions from the six-county shaded area in Figure 1 account for about 36%

of total statewide NH₃ emissions [Aneja et al., 2000]. These factors make this site a strong source of NH₃ emission relative to the remaining Coastal Plain.

2.2 Sampling Rate and Instruments

PM_{2.5} speciation samples in 2002 were collected every six days at all sites except at Mecklenburg county site where samples are collected every three days. Hourly measurement of PM_{2.5} mass is also conducted at Mecklenburg county site. Both PM_{2.5} mass concentration and speciation data are reported as daily averages in our analysis except as noted.

Tapered Element Oscillating Microbalance (TEOM), provided by Rupprecht and Patashnick Inc., with a sharp cut cyclone is deployed as continuous monitor for PM_{2.5} sampling. TEOM series 1400a monitor uses exchangeable Teflon coated with borosilicate filter. It incorporates an inertial balance that directly measures the mass collected on an exchangeable filter cartridge by monitoring the corresponding frequency changes of a tapered element. The TEOM mass transducer does not require recalibration because it is specially designed and constructed from non-fatiguing materials. In the process of monitoring, moisture is removed by heating the sample to 50°C. The minimum detection level is 0.11 g/m³. The speciation monitors used are called SASS Teflon monitors made by Met-One Inc. A Sharp Cut Cyclone (SCC) with a flow of 6.7 liters/min is integrated in every sampling canister to remove particles larger than 2.5µm aerodynamic diameters. SASS also incorporates convective solar shield in order to maintain cassettes to less than 5°C over ambient temperature.

A Nylon filter with a nitric acid denuder is used to measure nitrate, sulfate, ammonium, sodium, and potassium for the chemical speciation analysis of samples collected. Ion chromatography (Dionex system) is used to analyze the concentrations of anion (like SO_4^{2-} , NO_3^-) and cation species (like NH_4^+ , K^+ , Na^+). The effluent used for anion analysis is a 2.7 mM Na_2CO_3 / 0.3 mM NaHCO_3 solution while a 22 mN H_2SO_4 solution is used for cation eluent. The measurement method is selective and sensitive, allowing measurement to below 0.05 ppm in the filters extracts. Duplicate injections show a relative percent difference of better than 5% above about 0.05 $\mu\text{g}/\text{mL}$. Analysis of quality control check samples shows a recovery of better than 95%.

It should be recognized that different methods used for carbonaceous species determination may bring different results. Particulate black carbon and organic carbon concentrations used in this study are measured using Thermal-optical Carbon Aerosol Analyzer on the basis of thermal desorption/ oxidation of particulate carbon to CO_2 , which is then reduced to methane and subsequently measured using a flame ionization detector (FID). The analysis sequence is initialized in a non-oxidizing atmosphere (helium) with a 10-second purge followed by four temperature ramps to a maximum of 900°C . A cooling blower then comes on and the temperature drops to 600°C before oxygen is added. Detailed description of the procedure about carbonaceous species measurement has been given by Peterson et al. [2002]. The temperature is held at this point until the transmittance or reflectance returns to the initial point before the sample was heated at all. This point determines the distinction between OC and EC, that is, all of the carbon measured up to this point is OC while all of the carbon measured after this

point is EC. Total Carbon is equal to EC plus OC. The precision is 0.19 at 1 µg C and 0.01 at 10 to 72 µg C.

3. Methodology

3.1 Regression Analysis

It has been well established that atmospheric pollution depends strongly on weather conditions [Pérez et al., 2000]. Watkins (2000) reported that ozone concentration, and meteorology factors such as specific humidity, daily average temperature, and wind speed, are most significant in explaining variance in PM_{2.5} concentration. But these variables are found associated with certain regional meteorological conditions. Besides the influence of meteorological conditions, PM_{2.5} is also thought to closely interact with the atmospheric constituents in the ambient air. After Meng et al. [1997] theoretically explored the relationship between PM_{2.5} and O₃, Parkhurst et al. [1999] and Lim and Turpin [2002] have attempted to link O₃ and PM_{2.5} by simply plotting O₃ versus PM_{2.5} using measurement data. With the daily PM_{2.5} data obtained from these five sites, Pearson correlation and multiple linear regression analysis have been employed in this study to identify the relationship between PM_{2.5} and both ozone and meteorological variables. Backward regression in SAS version 8.01 is used for subset selection analysis. The backward elimination technique begins by calculating *F* statistics for a model, including all of the independent variables. Then the variables are deleted from the model one by one until all the variables remaining in the model produce *F* statistics significant at the SLSTAY= level specified in the MODEL statement (default

level 0.10 is used in our model statement). At each step, the variable showing the smallest contribution to the model is deleted [SAS online].

3.2 Backward Trajectory Analysis

Backward trajectories of air masses can assist in the interpretation of pollution concentrations, indicating possible source regions for the pollutants presented at certain measurement site [Miller, 1981; Ulman and Saxena; 1997; Danalatos and Glavas, 1999]. Back trajectory analysis is performed using the HYSPLIT 4 model [Draxler, 1997] developed by the National Oceanic and Atmospheric Administration's Air Resource laboratory (NOAA/ARL). The actual operation routines are explained and demonstrated by Draxler et al. [1992, 1997] and will not be discussed here. This model was run from the World Wide Web at <http://www.arl.noaa.gov/ready/hysplit4.html> (Hysplit4, 1997) for a set of days during which PM_{2.5} samples were collected at the five sites. Back trajectories were initialized at 11:00 PM of local time, and at an elevation of 500m above the ground level. The residence time of sulfate aerosol, which is the primary component of fine PM present at our measurement sites, has been estimated as "several days" [Charlson et al., 1992]. So the 48-hour back trajectories are applied to determine air mass history because of the substantial errors inherent in depicting air mass movement beyond 3 days [Bahrman and Saxena, 1998].

3.3 CMAQ modeling

The modeling system used in this study, the U.S. EPA's Models-3/Community Multiscale Air Quality (CMAQ) model, has been described elsewhere [Byun and Ching, 1999; Binkowski and Roselle, 2003]. CMAQ is a comprehensive three-dimensional

Eulerian grid model. In the current application, emissions of CO, VOCs, and NO_x are specified temporally and spatially in Models-3/CMAQ. The anthropogenic emissions inventory used is the Ozone Transport Assessment Group (OTAG) inventory for 1995. Biogenic emissions are calculated using the US EPA Biogenic Emission Inventory System 2 (BEIS2) [Geron et al., 1994]. Modeling domain (Figure 2) was chosen based on the results of back trajectory analysis. The selected domain reflects a balance of sufficient representation to emission sources and precise description of the local processes. As Figure 2 shows, the subdomain of this modeling system consists of 72×75 cells using 36-km horizontal resolution. The vertical domain, extending from the surface to 100 mb, is discretized using 23 layers of variable resolution. The Air Quality Model (AQM) was driven using meteorological fields from the Mesoscale Meteorological 5 (MM5) model [Grell et al., 1994], which was exercised in a four-dimensional data assimilation mode using analysis nudging with re-initialization every 5 days.

The gas-phase chemical mechanism used in the AQM was the Regional Acid Deposition Model Mechanism (Version 2) [Gery et al., 1989; Stockwell et al., 1990] with isoprene chemistry enhancement (RADM2-CI4). The RADM2 mechanism is a lumped species type that uses a reactivity-based weighting scheme to adjust for lumping. An aerosol extension, AE2 in this study, is added to gas phase chemistry to address gas and aerosol interactions. The aerosol component of CMAQ has been described [Binkowski and Roselle, 2003] and evaluated [Mebust et al., 2003]. Aqueous chemistry is also added to original chemistry mechanism to simulate aqueous phase chemical interactions.

4. Results and Discussion

4.1 Chemical Analysis

Examining PM_{2.5} mass data monitored at the five sites reveals that the annual National Ambient Air Quality Standard (NAAQS) for PM_{2.5}, which is 15µg/m³ for annual average, is exceeded at all sites except site Lenoir. High annual average concentrations are dominated by elevated concentrations during summer time. But no exceedance of the 24-hour NAAQS for PM_{2.5} (65µg/m³) was founded at those five sites during the entire measurement campaign.

As illustrated in Figure 3, PM_{2.5} mass concentration in summer reaches the highest among the four seasons during 2002 at all sites. The concentrations of PM_{2.5} among the three urban sites are close to each other, which may be attributed to the comparable precursor pollutant emission intensity in those urban areas. Using the analysis of variance (ANOVA) statistical method, the yearly average of PM_{2.5} mass concentration shows no significant difference ($p = 0.99$) among the three urban sites, although there does exist significant difference between the two rural sites, namely, Caswell county site and Lenoir county site ($p = 0.02$). The annual average of PM_{2.5} mass concentrations at the five sites as a whole, however, displays significant differences among them ($p = 0.018$). PM_{2.5} is higher in the urban Wake, Forsyth, and Mecklenburg sites than that in Lenoir, which is an agricultural site. It is interesting to note that another rural site in this study, Caswell site, is associated with PM_{2.5} mass concentration much higher than that all urban sites during each season. This might result from the coal-fired power plants located near the Caswell site. Besides direct emissions of primary particulate matter, power plants also emit gas precursors such as SO₂ and NO_x, which lead to formation of secondary aerosols [Bredl, 2003]. On the other hand, it was reported that power plant plumes may cause frequent

enhancements of ground level O₃ mixing ratios during pollution episodes [St. John and Chameides, 2000], which can help promote gas-to-particle conversion by acting as a major precursor to OH radical that oxidizes most gaseous pollutants.

Figure 1 shows the chemical compositions of PM_{2.5} monitored during 2002 at the five sites. OC values are multiplied by a factor of 1.4 to account for the unmeasured hydrogen and oxygen in the organic materials [He et al., 2001; Lin, 2002]. The fraction of Organic Matter (OM) (47-50%) with annual average 7.22µg/m³ is the most abundant component at all of the five sites. Sulfate (SO₄²⁻) with annual average 4.63µg/m³ ranks the second with a range of 27-32% varying among individual site. The average fractions of other major species i.e., NH₄⁺ (annual average 1.54µg/m³), NO₃⁻ (annual average 1.04µg/m³), and EC (annual average 0.51µg/m³), constitute 9-11% with, 5-7%, and 1-4% of the PM_{2.5} mass, respectively. Comparison of the chemical compositions among those five sites reveals that the “other” portion of the chemical composition, which includes crustal materials, trace elements, and other unidentified constituents, are much larger at the Caswell site than at the four other sites. The high “other” fraction implies that PM_{2.5} source may be different at this site from that of other sites, largely due to the presence of the coal-fired electric power plants surrounding the Caswell site.

The correlation matrix of all the major species at these five sites is constructed based on the Pearson correlation coefficients obtained from correlation analysis. The results show that similar correlation trends are shared by the three urban sites and similarities exist among two agriculture sites, too. Therefore, only the results of one agricultural site and one urban site are listed here. Table 1 and Table 2 show the

correlation matrices of Lenoir and Mecklenburg sites, respectively. A few associations stand out:

- Total PM_{2.5} is well correlated with SO₄²⁻, NH₄⁺, and OC
- NH₄⁺ correlates much better with SO₄²⁻ than with NO₃⁻
- EC and OC are well correlated with each other at urban sites including Wake, Mecklenburg, and Forsyth; but EC and OC are poorly correlated at rural sites.
- NO₃⁻ shows weak correlation with total PM_{2.5}.

Good correlations between SO₄²⁻ and NH₄⁺ suggest that these species are associated closely in ambient air, and that meteorological conditions and emissions that cause the ionic species to vary cause the total PM_{2.5} mass to vary in the same direction [Lee, 2001]. The poor relationship between NO₃⁻ and NH₄⁺ with PM_{2.5} might be related with the depletion of NO₃⁻ in the fine particles and formation of coarse nitrate. According to previous studies [Song and Carmichael, 1999; Lee et al, 2001], NO₃⁻ in fine particles should evaporate to satisfy charge neutrality in the particles in cases where the equivalent ratio of NH₄⁺ and SO₄²⁻ is as high as 0.8 or more, which is consistent with results of this study.

4.1. 1 Water-soluble ion species:

SO₄²⁻ is the most abundant water-soluble component of PM_{2.5} at all of these five sites (Figure 1). This agrees with most of PM_{2.5} chemical speciation studies [e.g.: Malm et al., 1994; Brook et al, 1997; Lee et al., 2001]. The ranges of concentration at the three urban sites are 0.9-19.1µg/m³ with an average of 4.7µg/m³ at Mecklenburg, 0.9-11µg/m³ with average 4.7µg/m³ at Wake, and 0.6-14.3 µg/m³ with average 4.3µg/m³ at Forsyth. At

the two agricultural sites, i.e. Lenoir and Caswell, SO_4^{2-} range is 0.8-13.7 $\mu\text{g}/\text{m}^3$ with average 5.1 and 0.8-12.8 $\mu\text{g}/\text{m}^3$ with average 5.6 separately. Results of the analysis of variance (ANOVA) on the SO_4^{2-} average value indicate that there is significant seasonal difference (p value is less than 0.05) except at Lenoir site where p value bigger than 0.05 while less than 0.1. NH_4^+ also show strong seasonal variability with sequence as following: summer > fall > spring > winter at all the five sites.

There is a good correlation between the concentrations of NH_4^+ and SO_4^{2-} ions ($R^2 = 0.89$ at Caswell, 0.91 at Forsyth, 0.94 at Lenoir, 0.91 at Wake, and 0.87 at Mecklenburg). Sulfate particles are formed in the atmosphere when sulfur gases, such as sulfur dioxide (SO_2) and hydrogen sulfide (H_2S), are oxidized to sulfuric acid and then combined with NH_3 to create ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$] or ammonium bisulfate (NH_4HSO_4) particles [Warneck, 2000]. They are comparably stable in the atmosphere and are removed by dry and wet deposition. It was reported that some areas in southeast of USA, such as the Great Smoky Mountains National Park in Tennessee, Shenandoah National Park in Virginia, and Dolly Sods Wilderness Area in West Virginia, ammonium to sulfate ratio might be below 1.0, especially in the summertime [SAMI report, 2002]. The average molar ratio of NH_4^+ to SO_4^{2-} is larger than 1.5 at most times at all five sites in NC, especially in winter when SO_4^{2-} is low and NO_3^- is comparably high. This may be attributed to the high NH_3 emissions in NC, which lead to high NH_4^+ concentration in the atmosphere. Except for the Caswell site, average ratio of NH_4^+ to SO_4^{2-} is higher than 2 in winter at the other four sites, but this is not the case for other seasons. Even in the winter, the equivalent ratio of NH_4^+ to the sum of SO_4^{2-} and NO_3^- is still less than one. This suggests that H_2SO_4 has not been completely neutralized by NH_4^+ due to the high

concentration of SO_4^{2-} rather than the weak source strength of NH_3 . So except in winter, NH_4^+ containing particles in NC should mostly exist in the form of $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ but not as nitrates [Lee et al., 2001]. On the other hand, NH_4^+ -containing particles could exist as forms of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 in winter, except for the Caswell site. SO_4^{2-} maximum appearing in summer contrasts with maximum NO_3^- concentration in winter. Figure 4 and Figure 5 show that SO_4^{2-} and NO_3^- have different seasonal trends. These also indicate that at all the rural and urban sites whereas SO_4^{2-} has a maximum value in summer and reaches minimum in winter, NO_3^- reaches its highest in winter and lowest in summer. Higher SO_2 oxidative conditions and low thermal stability of NH_4NO_3 in warm period lead to higher sulfate production and volatilization of nitrate species in summer. Higher winter NO_x levels is another factor that may help to accumulate higher nitrate formation in cold season [Querol et al., 2001].

4.1.2 Carbonaceous Species

Carbonaceous particles consist of a complex mixture of substances containing carbon atoms, usually being classified in two major fractions as OC and EC [Gray and Cass, 1986; Castro et al., 1999]. EC originates predominately from incomplete combustions, while OC can be formed from both primary and secondary (through gas-to-particle conversion) sources. The correlation between EC and OC is given in Table 2. Good correlation is observed between OC and EC at urban sites, suggesting that EC and OC at those sites may be emitted from the same sources [Lee et al., 2001]. But poor relationship is found at Caswell and Lenoir sites, which may be due to the abundant secondary aerosol formation at these agricultural sites. Day et al. [1997], using the

monitored PM_{2.5} data at Great Smoky Mountains National Parks from 1988 through 1994, reported that OC was associated with higher concentration during summer and lower concentration during the winter. The carbonaceous aerosol study carried by Castro et al. [1999] also showed that there is more abundant OC (given by the OC/EC ratio) during summer periods than in winter at several of both urban and rural European locations. The comparison of OC/EC ratio is shown in Figure 6, which suggests that there is increased formation of secondary OC in summer because of more favorable conditions for gas/particle conversion of VOCs as a result of photochemical activity. The relatively higher EC concentration in winter may be attributed to increased emissions and more frequent occurrence of stable atmospheric conditions during cold seasons [Lee et al., 2001]. Higher OC/EC ratios are found at Lenoir site, resulting from the lower contribution of local primary emissions (traffic emissions) in rural site [Lim and Turpin, 2002]. Due to the low EC concentration during that period, OC/EC ratio is much higher in summer at Lenoir site.

The minimum OC/EC ratio method is employed to estimate the secondary organic carbon (OC_{sec}) and primary organic carbon (OC_{pri}) [Turpin et al., 1991; Castro et al., 1999; Lim and Turpin, 2002;].

$$OC_{sec} = OC_{tot} - EC \times (OC/EC)_{min}$$

where (OC/EC)_{min} is the minimum ratio observed over the entire measurement period. Detailed information about the method and related assumption has been elucidated by Castro et al. [1999] and will not be explained here. The calculated results of secondary OC show that secondary OC constitutes approximately 68% of total particulate OC at the Lenoir site and 47-55% at other four sites [Table 3]. The results are in agreement with

estimations made in many other locations. For instance, Turpin and Huntzicker [1991 and 1997] reported ratios of secondary OC to total organic carbon ranging between 40-80% during summer episodes in Los Angeles area. Castro et al. [1999] observed values larger than 50% in summer in Birmingham, U.K. and Oporto, Portugal. Higher OC_{sec}/OC is consistent with higher OC/EC ratio at Lenoir, that is, reduced local primary emission leads to more secondary OC compared to primary OC, and low EC as well. Furthermore, it has been reported that VOCs precursors are always present in excess as a result of fresh road transport emissions [Castro et al, 1999], so the probability of gas-to-particle conversion occurring during transport to Lenoir is higher than that in other areas.

4.2. Time Series Analysis:

Hourly PM_{2.5} concentrations are used to do the time series analysis and investigate diurnal and seasonal variation of PM_{2.5}. Unfortunately, except at Mecklenburg county site, no hourly data from other four sites is monitored, so only the results of PM_{2.5} measurement at Mecklenburg site are shown in Figure 7. Figure 7 reveals there is a peak or maximum value occurring between 6:00 and 8:00 in the morning around sunrise time, which is related to the morning rush hour automobile traffic. Besides that, PM_{2.5} level tends to increase slightly from late afternoon to early evening, leading to a secondary peak between 20:00 and 21:00. Similar daily trends have been found in central and southeastern Ohio reported by Jung et al. [2002] and in Santiago, Chile reported by Pérez et al. [2000]. The concentration of PM_{2.5} mass is attributed to both the exhaust of the heavy traffic and the diurnal evolution of the planetary boundary layer (PBL) [Querol et al., 2001]. Increasing PBL height during the day will lead to more active dispersion of

aerosols and decrease of the PBL height at night will help enhance $PM_{2.5}$ concentration by preventing the dispersion of aerosols. The most possible explanation for the peak in the morning is simply rush hour traffic and relatively low mixing height at this time. Though the second peak appears in the evening after the rush hour, it begins to form around five and six clock in the afternoon when the heavy traffic usually occurs, but mixing height is at its maximum. The mixing height, the surface layer winds, and turbulence decrease sharply due to cooling of the surface [Pérez et al., 2000], which lead to the secondary maximum in the evening. Reduced surface wind speed after sunset is another factor that can lead to $PM_{2.5}$ accumulation in the evening. The increase in the particle concentration isn't immediate, but occurs over a period of several hours following the decrease in wind speed [Noble, 2003].

4.3 Identification of sources

In order to further examine the effect of possible source regions for $PM_{2.5}$ concentration in our study areas, the air mass origin was determined using 48 hours back trajectories obtained from the hybrid single-particle Lagrangian integrated trajectory (HY-SPLIT) model. There is no specific standard or definition for high $PM_{2.5}$ or low $PM_{2.5}$, so we set the high value days and low value days respectively based on the actual daily averaged values at different sites. A high $PM_{2.5}$ day is defined when the concentration at the site on that day higher than 40% of the site's own annual average, and a low $PM_{2.5}$ day is defined when $PM_{2.5}$ mass concentration is less than $10 \mu\text{g}/\text{m}^3$ for the particular site. Figures 8 and Figure 9 represent the back trajectories for the days with high $PM_{2.5}$ and low $PM_{2.5}$, respectively, at Lenoir site. In order to take account for the

effect of precipitation, we removed all the low $PM_{2.5}$ days with precipitation at Lenoir site. Figures 10 and Figure 11 give the plots for the days with high $PM_{2.5}$ and low $PM_{2.5}$ respectively at the urban Mecklenburg site. These figures indicate that the actual path of the air masses is particularly important. As shown in the Figure 9 and Figure 11, a large part of air mass loaded with low $PM_{2.5}$ come from the marine areas. There are some trajectories coming from west or northwest direction over continental region, but most of them originated from higher levels in the atmosphere around 2000m ~ 4000m above sea level, where particle concentrations are low [Warneck et al., 2000]. On the other hand, for the days with high $PM_{2.5}$ mass concentrations, air masses most likely originated from southwest direction or northwest direction with low altitude source points. Especially at Mecklenburg county site, at which we have more daily data available, trajectories from northwest with low $PM_{2.5}$ originated from altitudes higher than 2000m. A summary about of the vertical distribution of aerosol particles over the continents of the Northern Hemisphere shows that both the mass concentration and the production of new particles decline rapidly with altitude in the lower troposphere [Warneck et al., 2000]. It also indicates that sea salt aerosol over the ocean carries less particulate matter than continental aerosol, which means that a marine air mass will carry lower particle load. One conclusion from our source analysis is that at Lenoir county site low $PM_{2.5}$ concentrations may be due to its short distance from the sea and high probability of marine air masses coming to this site. To get more detailed information, we also attempted to separate the air trajectories coming from the west continental sector into northwest and northeast directions, but due to limited data, no further distinctions could be made.

4.4. Regression Analysis

Currently O₃, as one of six criteria pollutants reported for daily air quality index, is being modeled and forecasted well. PM_{2.5} modeling and forecasting is just in its infancy. Few groups have used statistical models to link meteorology and PM_{2.5} [Ryan and Piety, 1999]. After Meng et al. [1994] theoretically explored the relationship between PM_{2.5} and O₃, some work has been started to link O₃ and PM_{2.5} using measurement data [Parkhurst et al., 1999; Lim and Turpin, 2002]. Studies from Cox et al. [2000 & 2001] show that certain parameters, mainly O₃, specific humidity, wind speed, and mixing height a strong association with PM_{2.5} concentration in their study areas. Wind speed can inversely affect PM_{2.5} concentration, since high wind speed tends to decrease the suspended particle per unit volume of air [Harrison et al., 1997]. Decreasing water vapor pressure can drive aerosol total mass into the gas phase [Strader et al., 1999], while increasing atmospheric moisture can aid in particle formation [Finlayson-Pitts and Pitts, 1986; Cox et al., 2000, Hidy et al., 2000]. Different studies have given different relations between PM_{2.5} and humidity, based on the simple regression analysis without considering influence from other factors. Seinfeld et al. [2001] have found that that secondary organic aerosol (SOA) formation is highly dependent on relative humidity, while Jung et al. [2002] have shown there is no significant relationship between PM_{2.5} and RH and studies by Pérez et al. [2000] show a slight negative correlation between them.

The variables used in our regression analysis are: 24 hour average PM_{2.5} concentration ($\mu\text{g}/\text{m}^3$), 24 hour average temperature ($^{\circ}\text{C}$), 24 hour total precipitation (mm), 10 am- 4 pm average relative humidity (RH) (%), 10 am- 4 pm average solar radiation (W/m^2), average O₃ daily concentration (ppbv), 24 hour average wind speed

(m/s), 24 hour average wind direction (degree), and daily average pressure (mb). Daily maximum wind speed and daily maximum temperature may bring different effect on the formation of the particles compared to 24-hour average of wind speed and temperature, so daily maximum wind speed and daily maximum temperature are also considered. One or more meteorological variables or O₃ is missing on some days. Such missing variables are omitted from the model for that day. Pearson correlations between PM_{2.5} mass concentration and meteorology parameters and O₃ at Wake county site and Lenoir county site are estimated and listed in Table 4 and Table 5. The results indicate that O₃ has the best correlation with PM_{2.5}, suggesting that a large fraction of the PM_{2.5} might be photochemical aerosol produced simultaneously with O₃. PM_{2.5} is also significantly correlated with temperature, temperature maximum pressure, precipitation, solar radiation, and relative humidity at Wake site at p=0.05 level, and with temperature, temperature maximum, solar radiation, wind direction, and relative humidity at p=0.05 level at Lenoir site. It is interesting to note that the correlation coefficients for PM_{2.5} and temperature are about the same at the two sites. We also note that daily maximum temperature and PM_{2.5} do have a better correlation than 24-hour average temperature and PM_{2.5}, which suggests that daily maximum temperature may be a better PM_{2.5} predictor than 24-hour average temperature. Backward linear regression was done to quantify the relationship between particulate mass concentration, ozone and meteorological variables. Based on the output information of backward elimination regression, we find that all the independent variables (O₃ and meteorological parameters) create a high R square at both Lenoir site ($R^2 = 0.73$) and Wake site ($R^2 = 0.61$) before backward elimination, which suggest PM_{2.5} can be well predicted by O₃ and the meteorological parameters that we

provided in the model input. The output also gives the result after backward elimination one by one: O₃, wind speed, solar radiation, precipitation, relative humidity and pressure are the variables remaining in the model which produce *F* statistics significant at Wake site at SLSTAY=0.1 level, while O₃, wind speed, and pressure are the variables remaining in the model which produce *F* statistics significant at Lenoir site at SLSTAY=0.1 level. Furthermore, we still have a good R square at both sites: R square is 0.66 at Lenoir site and 0.58 at Wake site after backward elimination. The outputs from backward regression analysis indicate that some variables will be hidden by one or more other variable when all the variables are put together.

To better understand the behavior of PM_{2.5}, when model results are analyzed by season (winter versus summer) and the day of week (weekday versus weekend) might be more desirable [Sorrell, et al., 2003]. Also, PM_{2.5} on the previous day may be included as well [Pérez et al., 2000]. Unfortunately, such a model could not be developed in our study here due to the limited data available.

4.5. Sensitivity of PM_{2.5} to Gaseous Precursors

The sensitivity of PM_{2.5} species to its gas precursors including SO₂, NO_x, and NH₃ is investigated using CMAQ model in this study. The output of model sensitivity results reveals that PM_{2.5} sulfate is most sensitive to NO_x and SO₂ emission, but not to NH₃ in winter. Figures 12 and 13 show the response of maximum hourly PM sulfate levels to three different gas emissions at the rural site in Lenoir county and urban site in Wake county, separately, in winter. Both sites show the similar varying trend that PM_{2.5} sulfate decreases with decreasing SO₂, increases with decreasing NO_x, but remains about

constant with decreasing NH_3 emissions. The modeling analysis of $\text{PM}_{2.5}$ nitrate sensitivity to reduction of three different gas emissions (NO_x , SO_2 , NH_3) shows that the maximum 1– hour $\text{PM}_{2.5}$ nitrate level at Lenoir site is most sensitive to NO_x and then to NH_3 ; SO_2 change doesn't lead to any significant NO_3^- difference in winter (Figure 14). But at the other four sites, PM NO_3^- is more sensitive to NH_3 rather than to NO_x , which is represented by $\text{PM}_{2.5} \text{NO}_3^-$ analysis at site Wake in Figure 15. This difference may be attributed to the intensive NH_3 emissions at Lenoir site [Walker et al., 2000]. This can also be seen in Figure 16 and Figure 17, which show the response of maximum 1– hour $\text{PM}_{2.5}$ ammonium levels to reductions in three different gas emissions in winter. $\text{PM}_{2.5}$ ammonium decreases more rapidly in response to NO_x than NH_3 reduction at Lenoir site; but $\text{PM}_{2.5}$ ammonium decreases more rapidly due to NH_3 than NO_x reduction at other four sites.

Similar sensitivity analysis of modeling results is extended to the whole North Carolina region and the entire Southeast subdomain. Modeling results for southeast domain show that $\text{PM}_{2.5}$ sulfate, $\text{PM}_{2.5}$ nitrate and $\text{PM}_{2.5}$ ammonium show similar sensitivities to reductions in gas precursors as shown by North Carolina results. Variations of NH_3 emissions will result in considerable changes in the total $\text{PM}_{2.5}$ nitrate and the total $\text{PM}_{2.5}$ ammonium, but no significant changes in the total $\text{PM}_{2.5}$ sulfate. In other words, both $\text{PM}_{2.5}$ nitrate and $\text{PM}_{2.5}$ ammonium levels are most sensitive to NH_3 , and $\text{PM}_{2.5}$ sulfate is most sensitive to SO_2 . Finally, modeling results also reveal that total $\text{PM}_{2.5}$ mass concentration may not change so significantly due to the reduction in emission of only one gas precursor: for example, decreasing NO_x can lead to a decrease in $\text{PM}_{2.5}$ nitrate and $\text{PM}_{2.5}$ ammonium similarly, but $\text{PM}_{2.5}$ sulfate will increase which

might compensate for part of the loss of $PM_{2.5}$. Similarly, decreasing SO_2 will lead to a decrease in $PM_{2.5}$ sulfate and $PM_{2.5}$ ammonium, but increasing of $PM_{2.5}$ nitrate might compensate for part of the loss of $PM_{2.5}$.

5. Conclusion:

The chemical analysis of $PM_{2.5}$ at five North Carolina sites shows that organic matter (OM) is the most abundant component of $PM_{2.5}$, the daily average of OM accounts for 45-50% of total $PM_{2.5}$ mass, except at Caswell site due to its unique environment around it. SO_4^{2-} is the major soluble ion of $PM_{2.5}$ and the daily average of SO_4^{2-} is about 30% of $PM_{2.5}$. The ranges of daily average concentrations of NH_4^+ and NO_3^- are 7-11% and 6-9% of $PM_{2.5}$, respectively. At all the five sites, NH_4^+ combines mainly with SO_4^{2-} , except in winter when SO_4^{2-} concentration is relatively low but NO_3^- concentration is high. $PM_{2.5}$ daily concentration is determined by both the traffic emissions and the diurnal evolution of the planetary boundary layer. At three urban sites, OC and EC are well correlated while they are poorly correlated at agriculture sites, which suggest that OC and EC may originate from different sources at the agriculture sites. Secondary OC is significantly higher in summer, which almost accounts for half of the total OC and 10-20% of the total $PM_{2.5}$. Secondary OC formation is more likely at rural sites since time allows chemical transformation and gas-to particle conversion during air mass transport from urban areas.

Back trajectory analysis using HY-SPLIT model reveals that air masses with high $PM_{2.5}$ mostly originate from the continental region and near the surface; air masses coming from the marine sources or higher levels usually carry less fine particles due to

particle concentration declining rapidly with altitude in the troposphere and lower particle concentration over the ocean.

Our regression analysis of $PM_{2.5}$, O_3 and meteorological parameters suggests that O_3 is highly correlated to $PM_{2.5}$. Among the meteorological parameters, relative humidity, temperature and solar radiation are significantly correlated with $PM_{2.5}$ at the two sites where the meteorology variables are available. But some of the correlations may be site dependant. And when we put all factors together, influence from some variables may be hidden by one or more other variables.

Using the emissions (SMOKE) and meteorology (MM5) of 1996 as model input, CMAQ modeling analysis reveals that both $PM_{2.5}$ nitrate and $PM_{2.5}$ ammonium are more sensitive to NH_3 than to NO_x , especially in NH_3 poor areas, but more sensitive to NO_x than to NH_3 at the NH_3 rich sites in eastern NC in winter season. Modeling results also show that reduction of emission of a specific precursor does not only lead to decrease of the corresponding $PM_{2.5}$ component, but it may also lead to subsequent increase or decrease in other components. Modeling results for the whole domain of the southeastern U.S. show that, both $PM_{2.5}$ nitrate and $PM_{2.5}$ ammonium are most sensitive to NH_3 , and then to NO_x and SO_2 . Both SO_2 and NO_x emissions are important in determining the $PM_{2.5}$ sulfate in winter.

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Table 1 Pearson correlation coefficient among major species of PM_{2.5} at the Lenoir County site

Species	PM _{2.5}	NH ₄ ⁺	SO ₄ ²⁻	NO ₃ ⁻	EC	OC	Others
PM _{2.5}	1						
NH ₄ ⁺	0.72	1					
SO ₄ ²⁻	0.63	0.97	1				
NO ₃ ⁻	0.36	0.24	0.09	1			
EC	0.15	0.02	-0.06	0.27	1		
OC	0.87	0.46	0.40	0.33	-0.12	1	
Others	0.45	-0.10	-0.20	0.13	0.24	0.26	1

Table 2 Pearson correlation coefficient among major species of PM_{2.5} at the Wake County site

Species	PM _{2.5}	NH ₄ ⁺	SO ₄ ²⁻	NO ₃ ⁻	EC	OC	Others
PM _{2.5}	1						
NH ₄ ⁺	0.82	1					
SO ₄ ²⁻	0.76	0.95	1				
NO ₃ ⁻	0.28	0.02	-0.15	1			
EC	0.26	-0.01	-0.17	0.69	1		
OC	0.82	0.45	0.33	0.41	0.56	1	
Others	0.55	0.34	0.37	0.01	-0.22	0.18	1

Table 3 Levels of secondary organic carbon (OCsec) of PM_{2.5} estimated from minimum OC/EC ratio method

Site	OCpri (̂ g/m ³)	OCsec (̂ g/m ³)	OCsec/OC	OCsec/PM _{2.5}
Caswell	2.37	3.46	0.55	0.15
Lenoir	1.22	3.06	0.68	0.23
Forsyth	2.14	3.02	0.57	0.19
Mecklenburg	2.70	2.71	0.47	0.17
Wake	2.35	3.04	0.52	0.18

Table 4 Pearson Correlation Coefficients at Wake County Site
 Prob > |r| under H0: Rho=0
 Number of Observations

	PM _{2.5}	O ₃	Temperature	Temperature maximum	Pressure	Precipitation	Solar radiation	WD	WS	WSmax	RH
PM _{2.5}	1	0.59	0.37	0.44	-0.224	-0.294	0.314	0.04	-0.244	-0.254	-0.36
		<0.0001	0.0078	0.0014	0.0111	0.0373	0.0265	0.7981	0.1044	0.0906	0.0099
	52	52	51	51	52	51	51	46	46	46	51

Table 5 Pearson Correlation Coefficients at Lenoir County Site
 Prob > |r| under H0: Rho=0
 Number of Observations

	PM _{2.5}	O ₃	Temperature	Temperature maximum	Pressure	Precipitation	Solar radiation	WD	WS	WSmax	RH
PM _{2.5}		0.47	0.37	0.43	-0.22	-0.20	0.50	0.35	-0.25	-0.17	-0.48
		0.0087	0.0079	0.0020	0.1266	0.1717	0.0006	0.0139	0.0859	0.2546	0.0005
		30	51	49	51	48	44	49	49	49	49

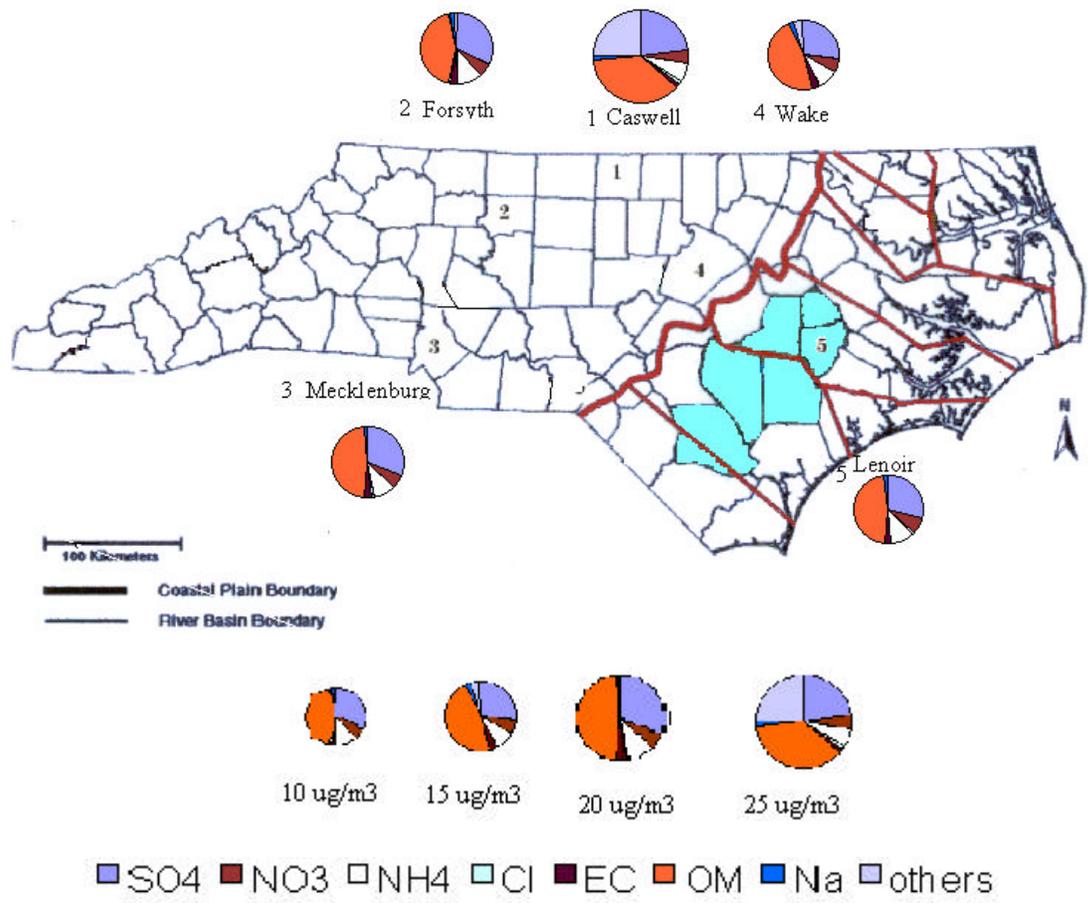


Figure 1: Research areas including 5 sites in NC. The shaded area represents the region defined as having an average hog population density of ~ 528 hogs/km² (i.e. ammonia rich environment). (1) Caswell County (36.307N, 79.467W), (2). Forsyth County (36.111N, 80.227W), (3) Mecklenburg (35.24N, 80.786W), (4) Wake County (35.856N, 78.574W), (5) Lenoir County (35.231N, 77.569W)

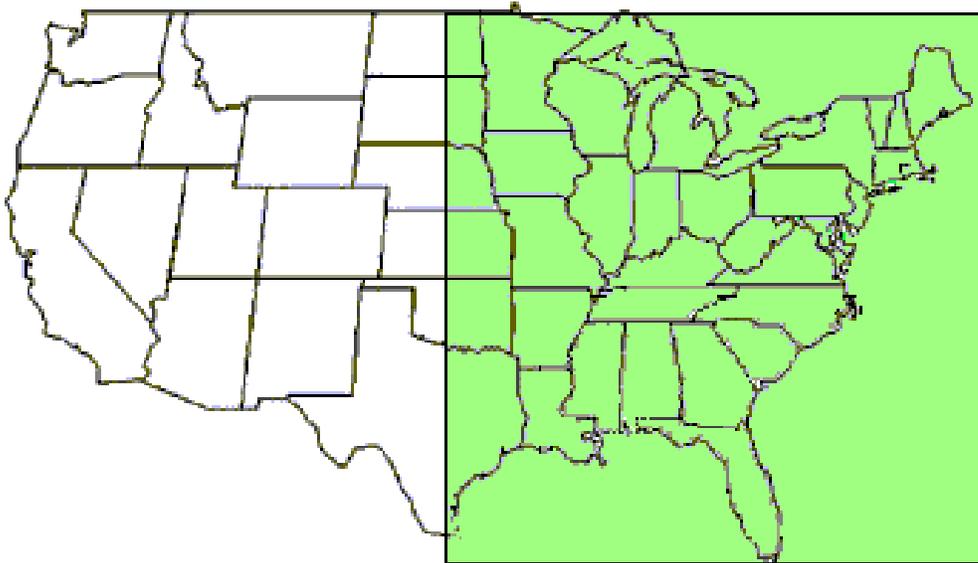


Figure 2. Model domain used in Model 3/CMAQ analysis. The shaded area is defined as the subdomain of the model system. Model resolution is:

- 36 km grid resolution
- 72*75 horizontally
- 23 layers vertically

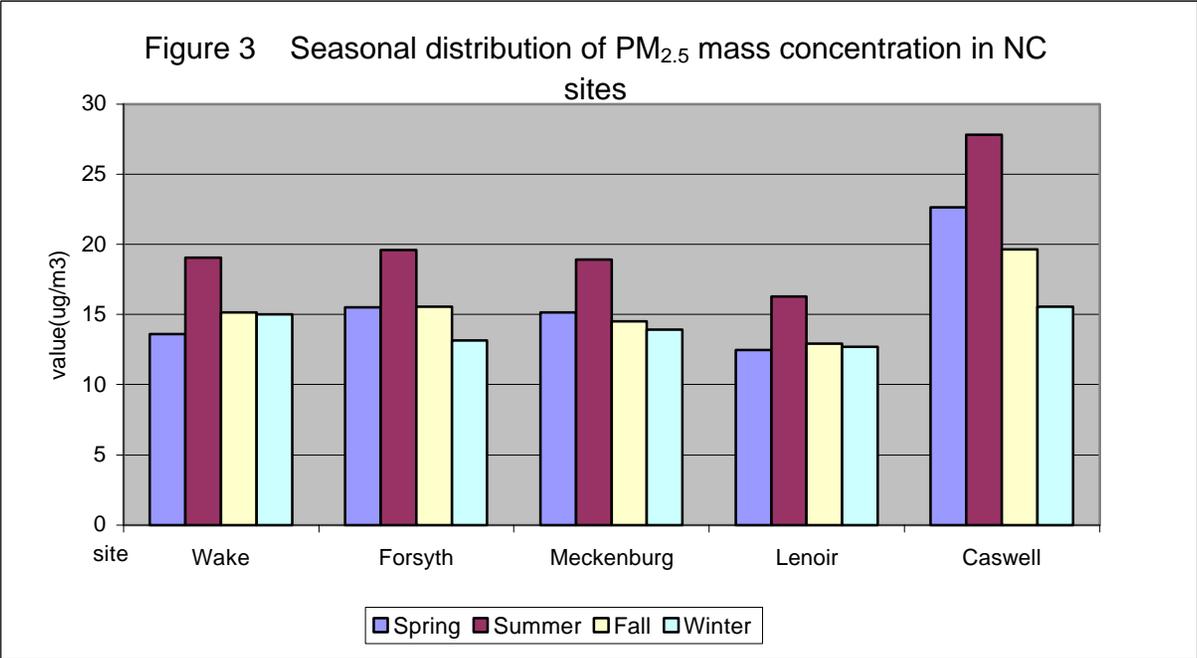
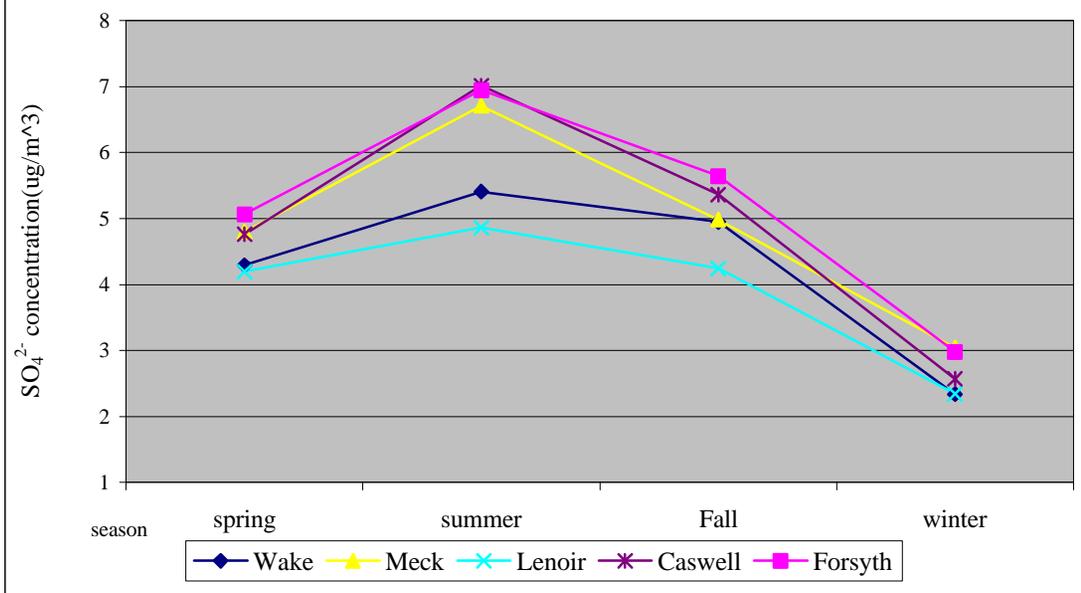


Figure 4 Seasonal variation of sulfate (SO_4^{2-}) mass concentration at the five NC sites



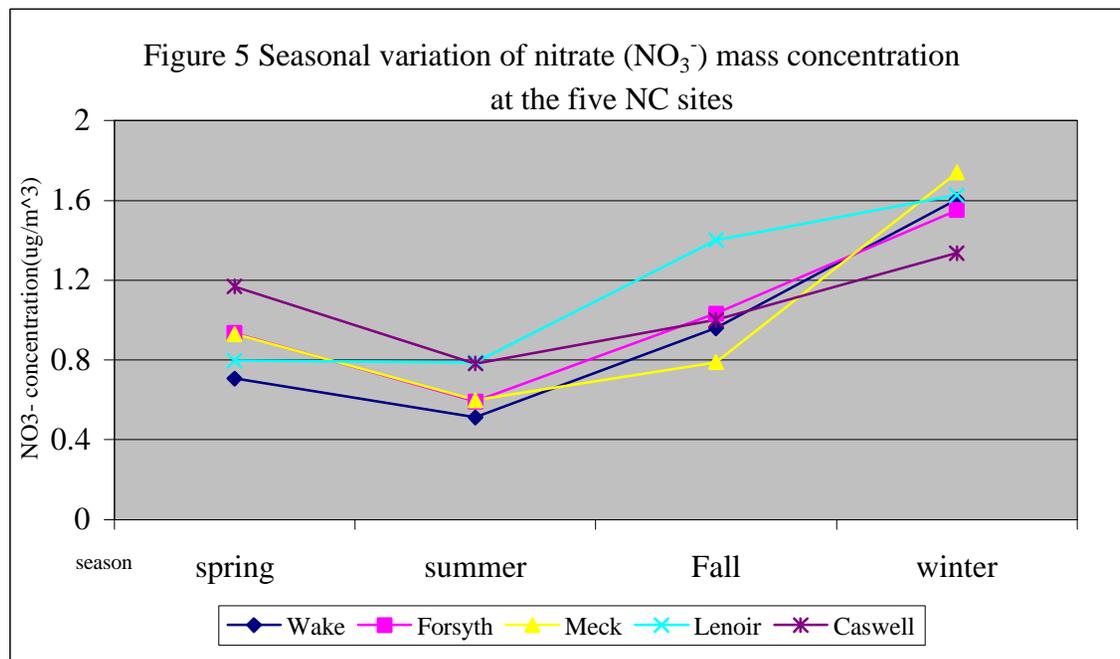


Figure 6. OC/EC (organic carbon/elemental carbon) in summer and winter at the five sites

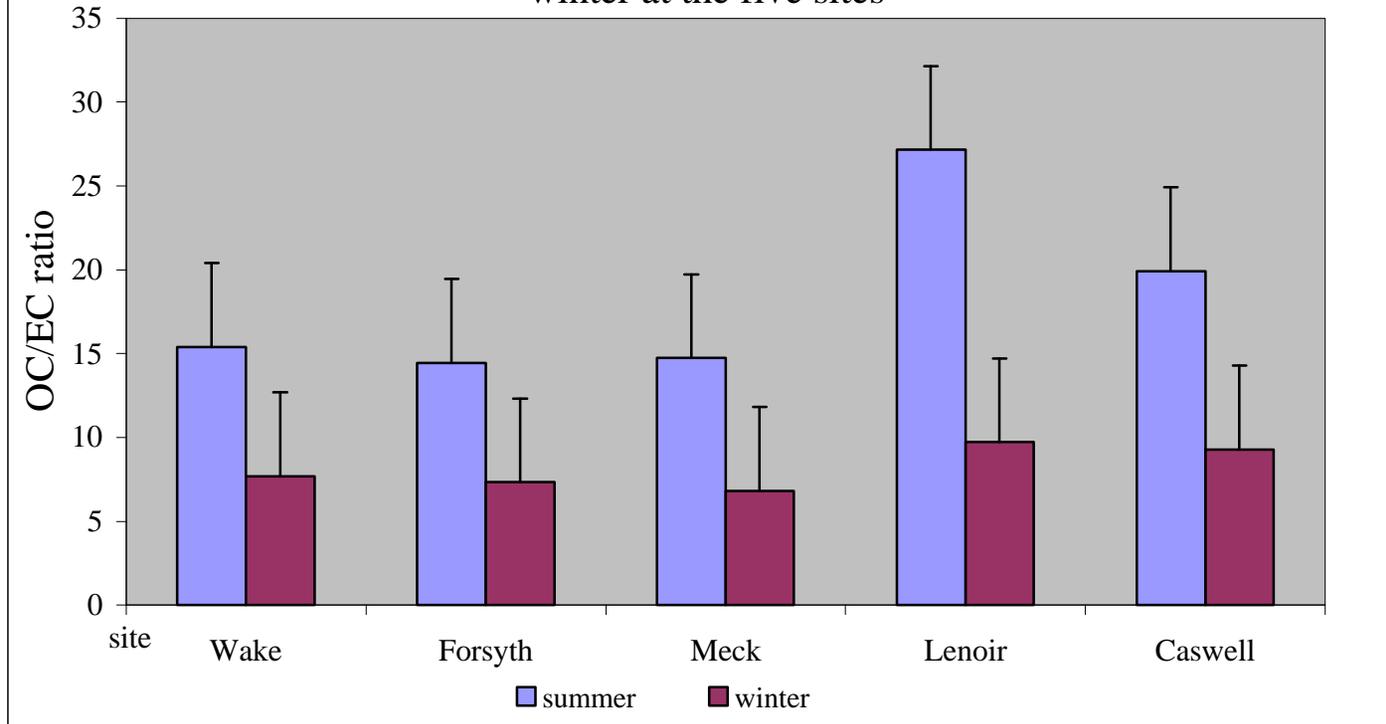
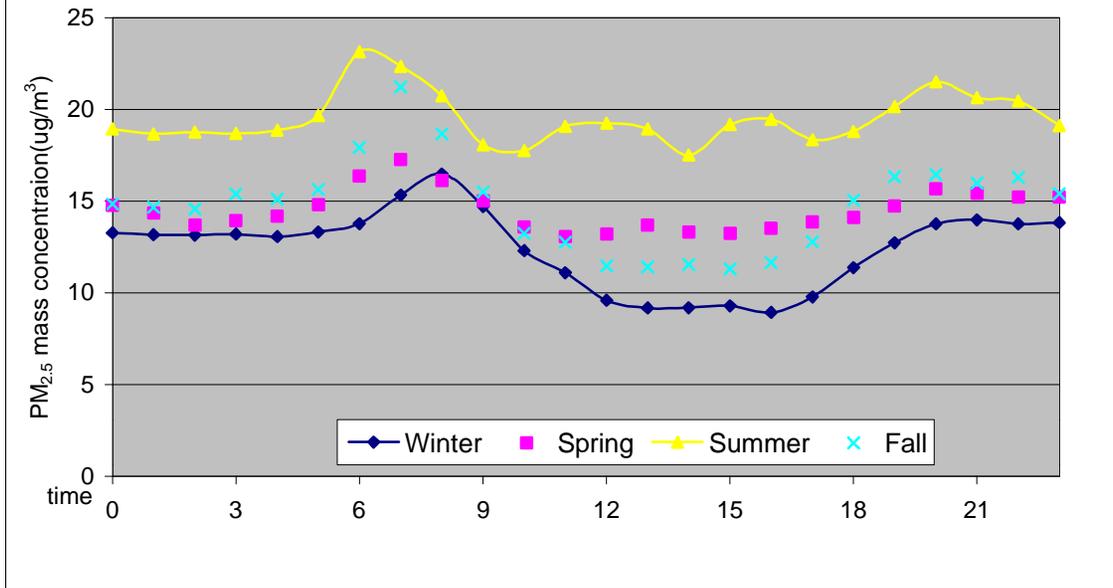


Figure 7 Hourly average PM_{2.5} mass concentration in different seasons at the Mecklenburg site



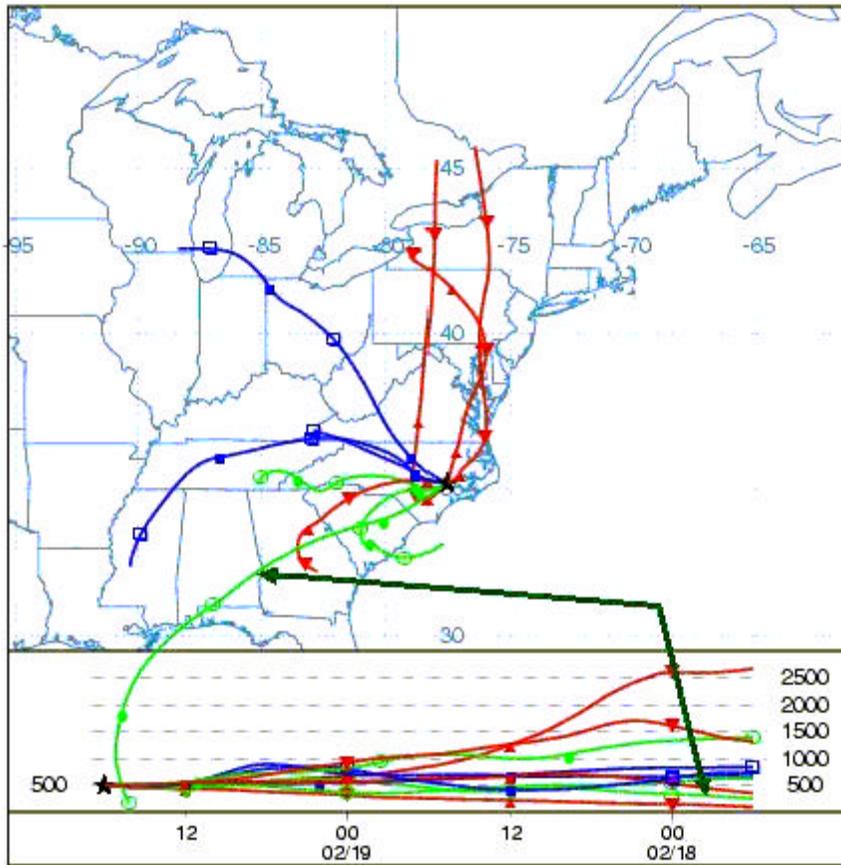


Figure 8. HYSPLIT backward trajectories analysis results for the days with high daily average $PM_{2.5}$ mass concentration at the Lenoir during 2002

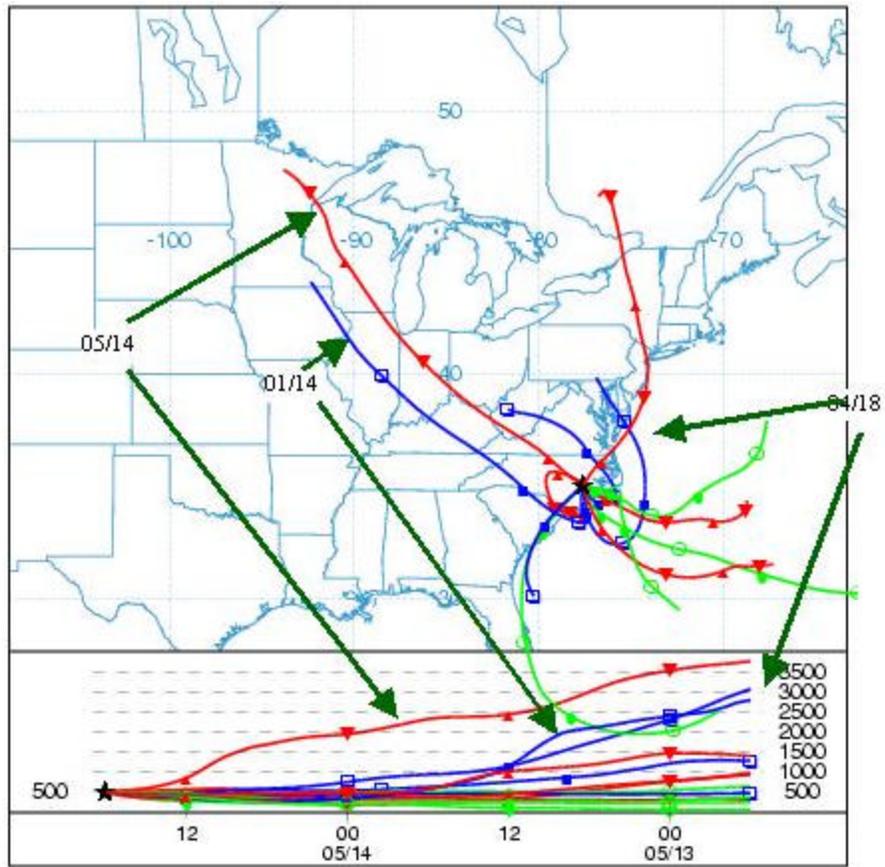


Figure 9 HYSPLIT backward trajectories analysis results for the days with low daily average $PM_{2.5}$ mass concentration at the Lenoir during 2002

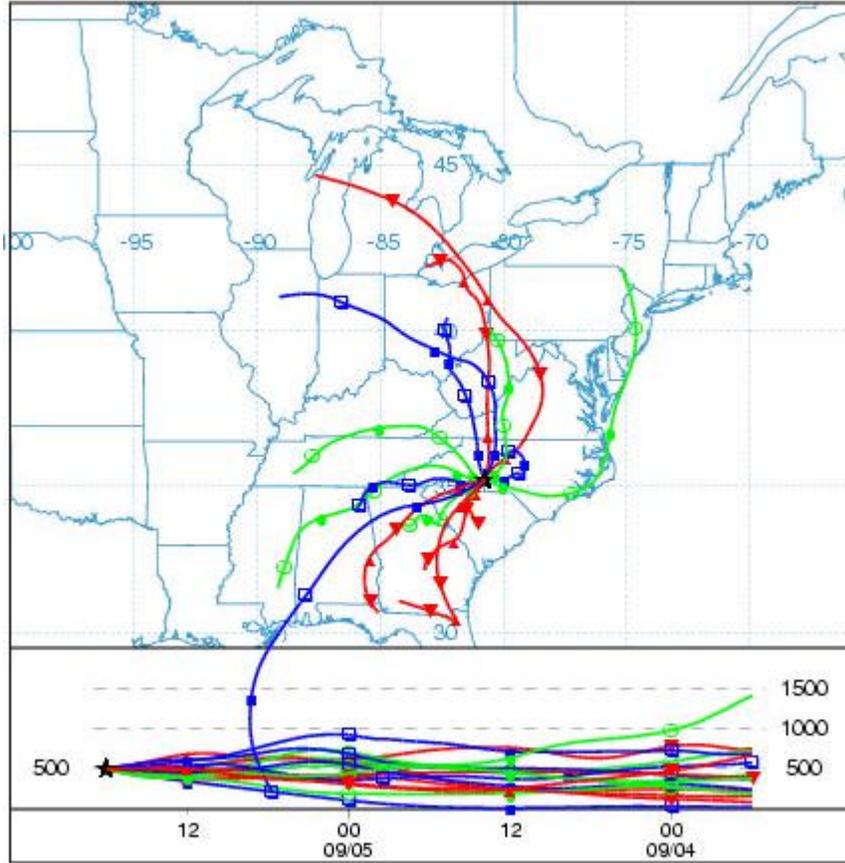


Figure 10. HYSPLIT backward trajectories analysis results for the days with high daily average $PM_{2.5}$ mass concentration at the Mecklenburg site during 2002

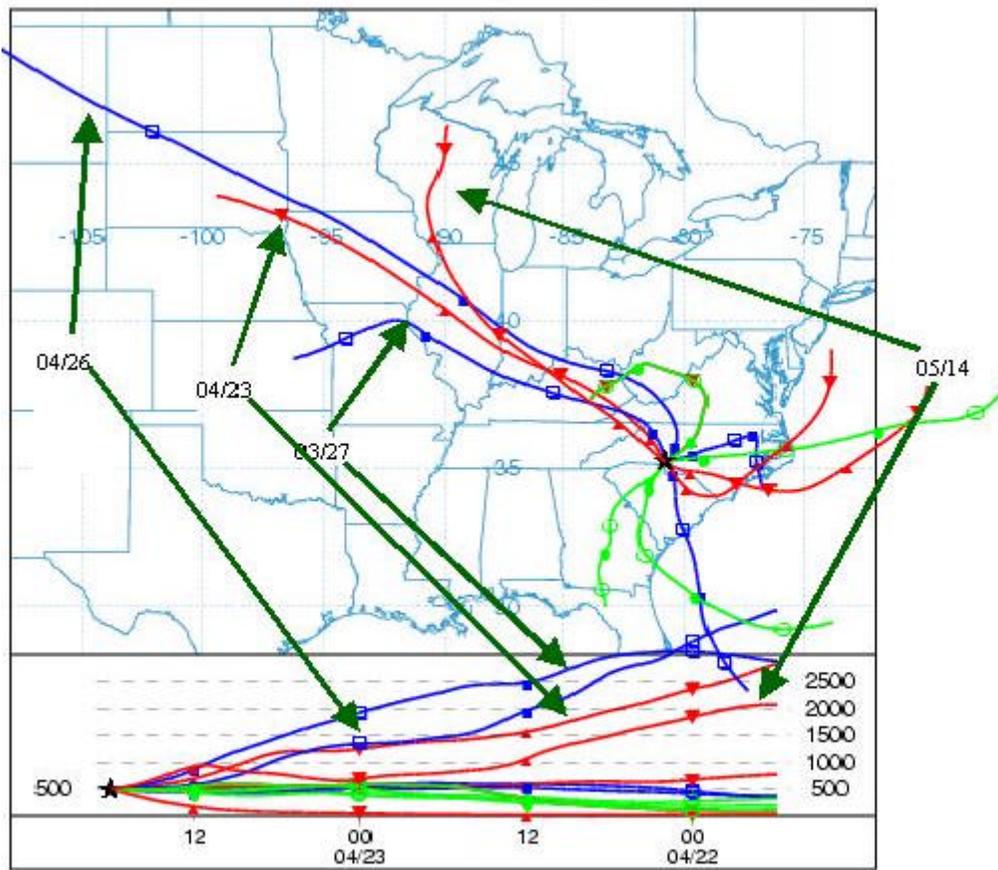


Figure 11 HYSPLIT backward trajectories analysis results for the days with low daily average PM_{2.5} mass concentration at the Mecklenburg site during 2002

Figure 12 PM sulfate versus NH₃, SO₂, NO_x emission reduction at the Wake site during winter

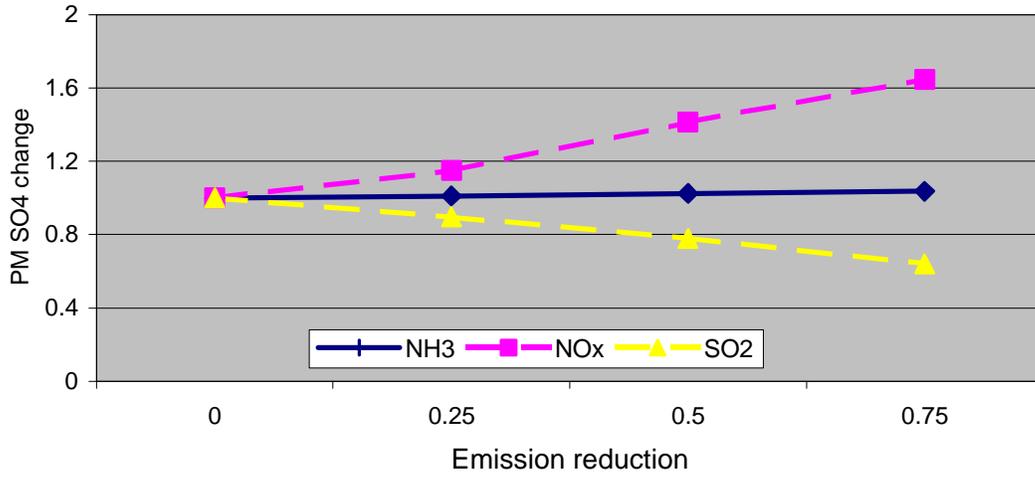


Figure 13 PM sulfate versus NH₃, SO₂, NO_x emission reduction at the Lenoir site during winter

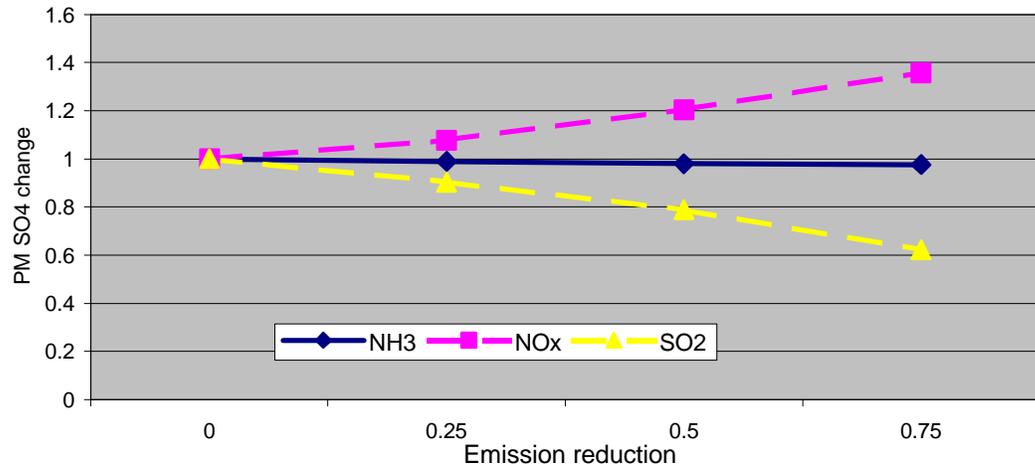


Figure 14 PM_{2.5} nitrate versus NH₃, SO₂, NO_x emission reduction at Lenoir site during winter

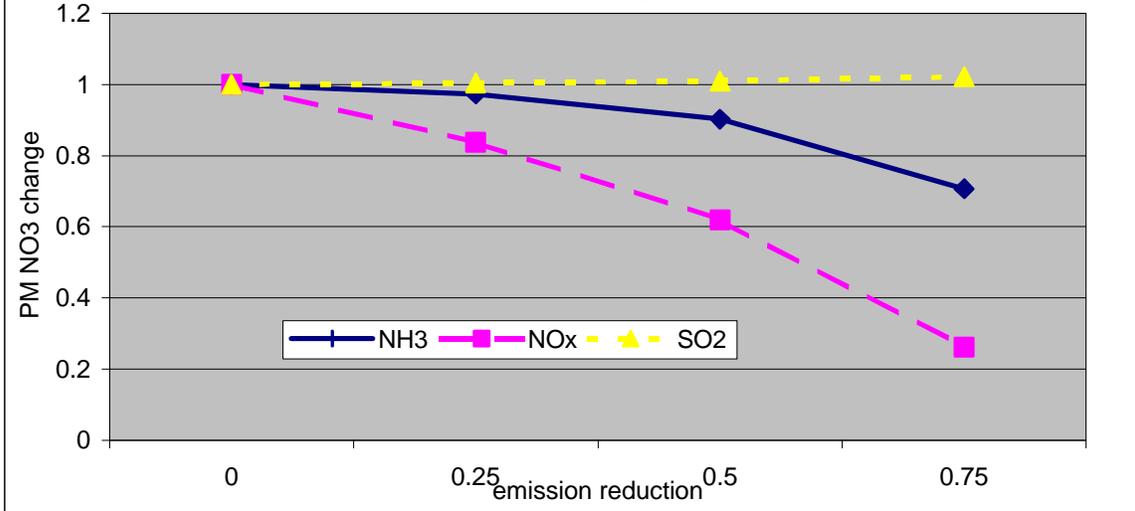


Figure 15 PM_{2.5} nitrate versus NH₃, SO₂, NO_x emission reduction at the Wake site during winter

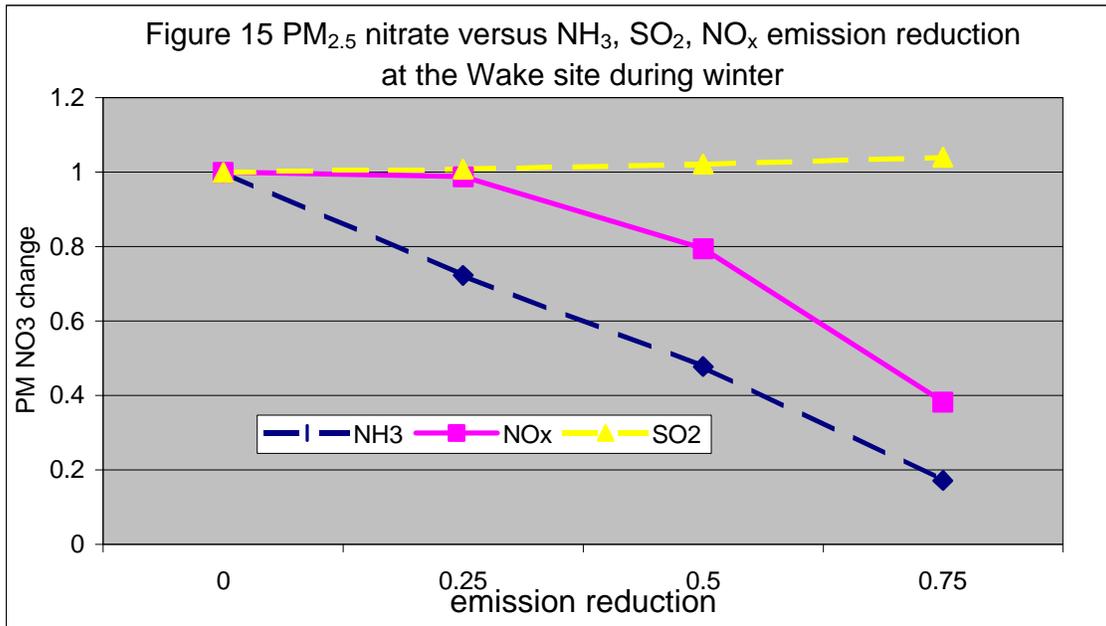


Figure 16 PM_{2.5} ammonium versus NH₃, SO₂, NO_x emission reduction at the Lenoir site during winter

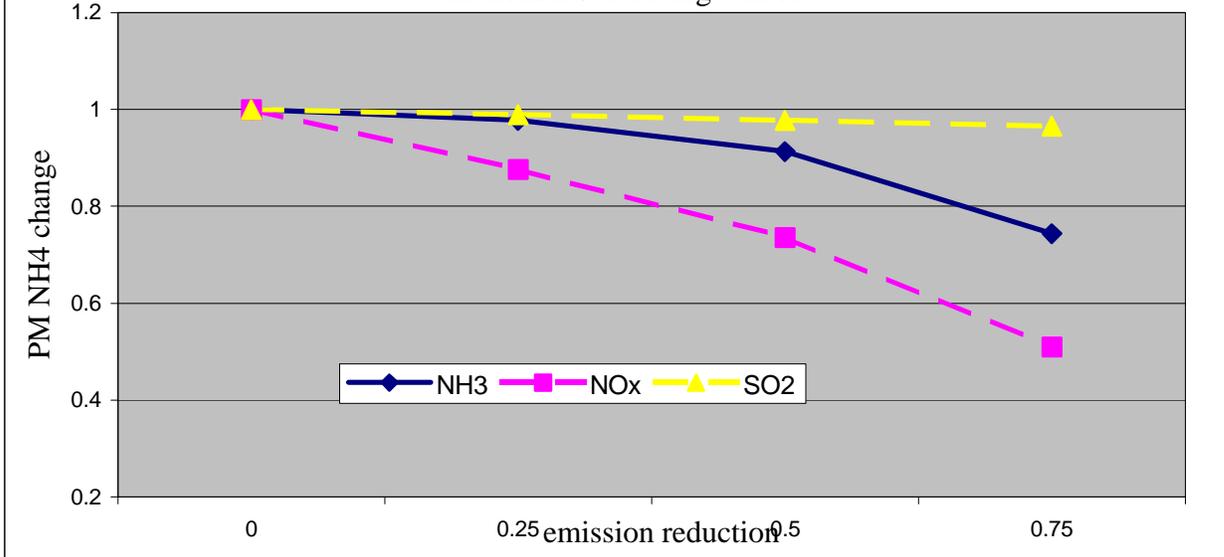
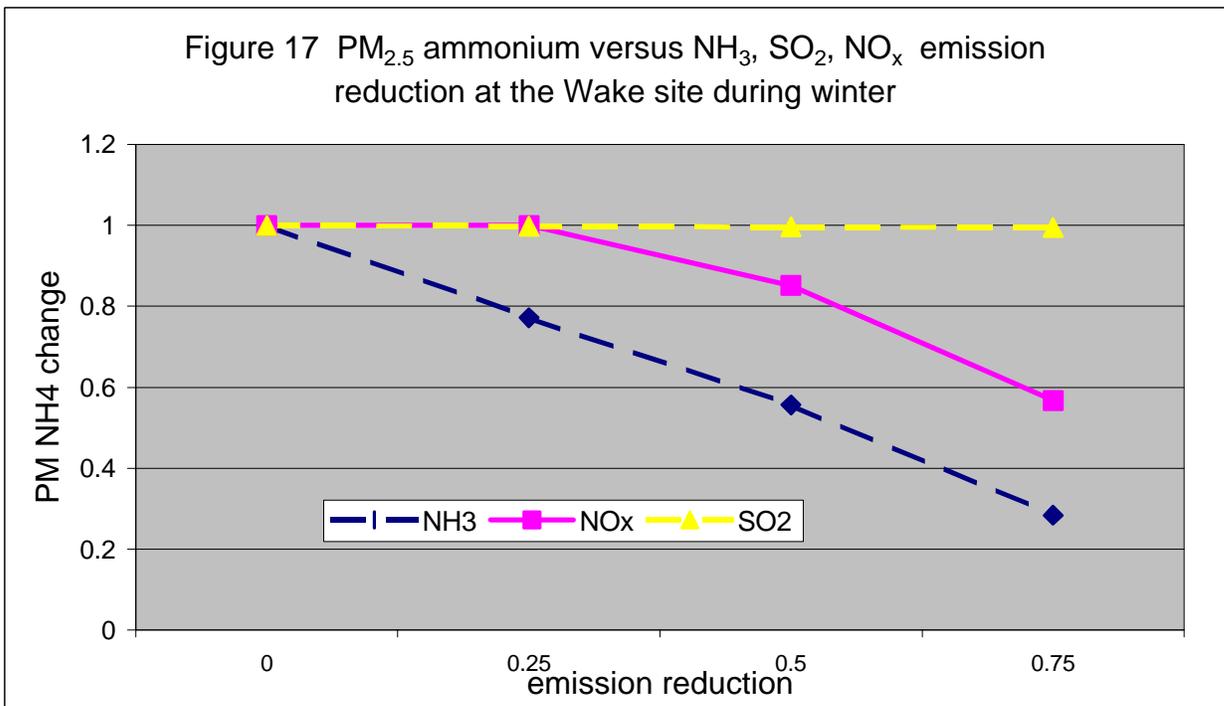


Figure 17 PM_{2.5} ammonium versus NH₃, SO₂, NO_x emission reduction at the Wake site during winter



IV. Overall Conclusion

The primary objective of this study was to investigate the characteristics of the major species of PM_{2.5} and the influence of meteorology on the total mass of PM_{2.5} in the southeastern USA. Measurements of fine particulate matter (PM_{2.5}) and its major chemical components, as well as meteorological data for diversely located (urban, rural and coastal) southeast sites, are presented. Examining PM_{2.5} mass concentration data monitored at a number of selected sites reveals that the annual National Ambient Air Quality Standard (NAAQS) for PM_{2.5}, which is 15µg/m³ for annual average, is exceeded at all urban inland sites. High annual average concentrations are usually dominated by elevated concentrations during summer time. But no exceedance of the 24-hour NAAQS for PM_{2.5} (65µg/m³) was founded at any of the five sites during the entire measurement campaign. The analysis also shows that PM_{2.5} concentration is higher at urban sites than at rural sites; and PM_{2.5} concentrations at coastal urban sites are lower than those at inland urban sites.

The major components in PM_{2.5} are identified as SO₄²⁻, NO₃⁻, NH₄⁺, EC and OC in the studying areas. Irrespective of rural, urban or coastal area, organic matter is the main insoluble component of PM_{2.5}, while SO₄²⁻ is the main soluble ion of PM_{2.5}. The conversion of SO₂ to SO₄²⁻ is higher in summer than during other seasons due to high temperatures in summer. In this study, at all of the selected monitoring sites in the southeast U.S., the daily average concentrations of total PM_{2.5} varied from 12.1 to 13.8 µg/m³ in rural and from 11.4 to 17.8 µg/m³ in urban locations. For the sites in North Carolina, three urban sites have the comparable daily average values ranging between 15.6 and 16.0 µg/m³, while the two rural sites have much different values (13.6 and 21.4

$\mu\text{g}/\text{m}^3$) due to their different environments. At all the sites, NH_4^+ correlates with SO_4^{2-} well and the ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ reveals that NH_4^+ combines mainly with SO_4^{2-} , except in winter when SO_4^{2-} concentration is relatively low but NO_3^- concentration is high. Data analysis results suggest that particle nitrate is limited by the availability of ammonia during most time in the southeast since most NH_4^+ combines with SO_4^{2-} to form sulfate aerosol, but not enough NH_4^+ combines with NO_3^- to form nitrate aerosol.

Organic carbon (OC) and elemental carbon (EC) monitored at various southeastern sites are well correlated at both urban and rural locations. However, in North Carolina OC and EC are well correlated only at urban sites, but not at two agriculture sites, which means that at the latter sites OC and EC may not be emitted from the same sources. The minimum OC/EC ratio method is employed to estimate the secondary organic carbon (OCsec) and primary organic carbon (OCpri). The results obtained in our study suggest that the formation of secondary aerosols due to gas-to-particle conversion is significant in our studied areas. Secondary OC is significantly higher, especially in summer when OCsec accounts for around half of the total OC and around 10-20% of the total $\text{PM}_{2.5}$. Secondary OC is more likely present at rural sites, because more transport time allows chemical transformation and gas-to-particle conversion during air mass transport from urban areas.

Back trajectory-cluster analysis for the YRK (Yorkville, GA) site in Georgia shows that higher concentrations are associated with air masses coming from the northeast, which points out the important role of large NH_3 emissions from animal farms in eastern North Carolina on the formation of fine particulate matter. Back trajectories analysis is also used to do the source analysis for sites in NC. We found that air masses

with low $PM_{2.5}$ concentration mainly originated from the marine environment or from the continental environment with strong subsidence from the upper troposphere where the $PM_{2.5}$ content is lower than in the planetary boundary layer. Air masses with high concentration of $PM_{2.5}$ are largely from continental sources of low elevation.

Besides the primary and secondary formation processes, $PM_{2.5}$ daily concentration in the ambient atmosphere can be affected by many other factors, such as the behavior of the active oxidant, the diurnal evolution and structure of the planetary boundary layer, and synoptic meteorological conditions. Regression analysis on $PM_{2.5}$ with meteorology and O_3 shows that meteorological parameters (wind speed, temperature, and humidity) and O_3 are highly related to $PM_{2.5}$. Temperature is the main meteorological factor, which favors high $PM_{2.5}$ concentration, while wind speed has negative correlation with $PM_{2.5}$ concentration, which leads to high $PM_{2.5}$ concentrations in weak wind and high temperature conditions, often prevailing during summertime.

Three-dimensional Eulerian grid model employed for investigating the sensitivity of atmospheric aerosol formation to the major gaseous precursors reveals that reduction of a specific precursor does not only lead to decrease of the corresponding $PM_{2.5}$ component, but also to changes in other components (increase or decrease) subsequently. Both NH_4^+ aerosol and NO_3^- aerosol are more sensitive to NH_3 in the NH_3 -limited area, but more sensitive to NO_x at NH_3 rich sites.

This work provided ways for $PM_{2.5}$ chemical characterization, source identification, sensitivity examination, and linear regression for $PM_{2.5}$ with O_3 and meteorological variables. Considerations of meteorology in our analysis are still preliminary; a better regression model needs to be developed to represent the nonlinear

relationship between $PM_{2.5}$, O_3 , and meteorological factors. In order to further understand the sensitivity of the major components of $PM_{2.5}$ to its gas precursor emission in different seasons, sensitivity analysis of $PM_{2.5}$ to NH_3 , SO_2 , and NO_x emission in seasons other than winter is needed, especially for summer during the period when the secondary aerosols formation is active. In addition to anthropogenic emissions, Southeast United States is also characterized by large biogenic emissions of hydrocarbons, which is believed to enhance the formation of secondary organic aerosols (SOA) over the area. This study shows that approximately half of the organics in fine PM originated from secondary formation. It will be interesting to explore the implications of biogenic emissions toward the compliance of the annual $PM_{2.5}$ NAAQS over Southeast United States.