Characterization of Major Chemical Components of Fine Particulate Matter in North Carolina

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ABSTRACT

This paper presents measurements of daily sampling of fine particulate matter (PM_{2.5}) and its major chemical components at three urban and one rural locations in North Carolina during 2002. At both urban and rural sites, the major insoluble component of PM_{2.5} is organic matter, and the major soluble components are sulfate (SO4 $^{2-})$, ammonium (NH4 $^+)$, and nitrate (NO3 $^-)$. NH4 $^+$ is neutralized mainly by SO_4^{2-} rather than by NO_3^{-} , except in winter when SO_4^{2-} concentration is relatively low, whereas NO₃⁻ concentration is high. The equivalent ratio of NH_4^+ to the sum of SO_4^{2-} and NO_3^- is <1, suggesting that SO₄²⁻ and NO₃⁻ are not completely neutralized by NH_4^+ . At both rural and urban sites, SO_4^{2-} concentration displays a maximum in summer and a minimum in winter, whereas $\mathrm{NO_3}^-$ displays an opposite seasonal trend. Mass ratio of NO_3^{-1} to SO_4^{2-1} is consistently <1 at all sites, suggesting that stationary source emissions may play an important role in PM_{2.5} formation in those areas. Organic carbon and elemental carbon are well correlated at three urban sites although they are poorly correlated at the agriculture site. Other than the daily samples, hourly samples were measured at one urban site. PM_{2.5} mass concentrations display a peak in early morning, and a second peak in late afternoon. Back trajectory analysis shows that air masses with lower PM_{2.5} mass content mainly originate from the marine environment or from a continental environment but with a strong subsidence from the upper troposphere. Air masses with high PM_{2.5} mass concentrations are largely from continental sources. Our study of fine particulate matter and its chemical composition in North Carolina provides crucial information that may be

IMPLICATIONS

Our study of fine particulate matter and its chemical composition in North Carolina provides crucial information that may be used to determine the efficacy of the new NAAQS for PM fine. Moreover, the gas-to-particle conversion processes provide improved prediction of long-range transport of pollutants and air quality. used to determine the efficacy of the new National Ambient Air Quality Standard (NAAQS) for PM fine. Moreover, the gas-to-particle conversion processes provide improved prediction of long-range transport of pollutants and air quality.

INTRODUCTION

Atmospheric aerosols have gained increasing interest over the past decades because of their importance in climate and atmospheric chemistry¹⁻³ and the adverse impacts on human health.⁴ The major soluble components of particulate matter (PM) with an aerodynamic diameter <2.5 μ m (PM_{2.5}) are sulfate (SO₄²⁻), nitrate (NO₃⁻), and ammonium (NH_4^+) , and the major insolubles are organic carbon (OC) and elemental carbon (EC).5,6 Previous studies on PM reveal that the dominant component of PM_{2.5} is SO_4^{2-} in the Eastern United States, NO_3^{-} in Southern California, and organics in the Northwest Pacific.⁷ Spatial variability in chemical characteristics of PM has been reported elsewhere. Organics are the dominant constituents of atmospheric aerosols in many areas of Asia and Europe (e.g., Sapporo, Japan⁸; Birmingham, United Kingdom⁹; and Beijing, China¹⁰), whereas SO_4^{2-} or NO_3^{-} are dominant in some other areas (e.g., Chongju, South Korea¹¹; and Rion, Greece¹²). Varying chemical speciation of atmospheric aerosols can be attributed to diversity in emission sources and atmospheric constituents and differences in environmental conditions prevailing at measurement sites. This study presents a detailed discussion of chemical speciation of ambient aerosols measured during 2002 at four locations in the state of North Carolina.

North Carolina is of special interest in terms of the environmental setting for PM_{2.5} formation. PM_{2.5} has both primary and secondary origins. Aside from direct emissions of particles into the atmosphere (primary origin), gas-to-particle conversion processes play an essential role in determining the mass and speciation of airborne PM.¹³ The Southeast United States, including North Carolina, is characterized by large biogenic emission sources, which can substantially contribute to the formation of secondary organic aerosols.^{14,15} Moreover, Eastern North Carolina is associated with much higher ammonia emissions than the surrounding areas,¹⁶ as a result of rapid growth of animal industry concentrated in this area.^{17,18} The amount of ammonia present in the ambient air is



Figure 1. Research areas including five sites in North Carolina. The shaded area represents the region defined as having an average hog population density of ~528 hogs per km² (i.e., ammonia rich environment). (1) Caswell County (36.307° N, 79.467° W), (2) Forsyth County (36.111° N, 80.227° W), (3) Mecklenburg (35.240° N, 80.786° W), (4) Wake County (35.856° N, 78.574° W), and (5) Lenoir County (35.231° N, 77.569° W).

critical to determining both mass and chemical compositions of inorganic aerosol.^{13,19} Recognizing the unique environmental characteristics of North Carolina, which is rich in both organic and inorganic precursors to aerosol formation, an extensive monitoring campaign was launched to study the characterizations of atmospheric aerosols. This paper presents both measurements and observation-based analysis of $PM_{2.5}$ speciated data from this monitoring campaign. The data used for this report are available by contacting the Ambient Monitoring Section at the North Carolina Division of Air Quality (available at daq.state.nc.us/contact).

EXPERIMENTAL WORK

Site Description

Three urban sites are located in Forsyth, Wake, and Mecklenburg counties, and the agricultural site is in Lenoir County. Both total $PM_{2.5}$ and its chemical components are monitored at all of the sites. Details of site locations (Figure 1), sampling, and measurement are described below.

First, the monitoring site in Wake County (35.86° N and 78.57° W; U.S. Environmental Protection Agency [EPA] UAR 305925), at an elevation of 100 m above mean sea level (MSL), is located at Millbrook Middle School on

1100 Journal of the Air & Waste Management Association

Spring Forest Road in Raleigh, NC. It is ~13 km from downtown Raleigh, a city with a population of 276,093 (2000 census, the same hereinafter). Second, the monitoring site in Forsyth County (36.11° N, 80.23° W; EPA UAR 185184), at an elevation of 287 MSL, is located on Hattie Avenue of Winston-Salem, NC, a city with a population of 185,776. Third, the monitoring site in Mecklenburg County (35.24° N, 80.79° W; EPA UAR 455597), at an elevation of 232 MSL, is located at Garinger High School, on Eastway Drive, Charlotte, NC, a city with a population of 540,828. Fourth, the monitoring site in Lenoir County (35.23° N, 77.57° W; EPA UAR 0000), at an elevation of 29 MSL, is located at Lenoir Community College on the corner of highways 70 East and 58 South in Lenoir County, a rural county with a population of 59,648. Lenoir County is one of the six counties with most concentrated animal farms in North Carolina, with an averaged hog population density of \sim 528 hogs per km² (the shaded area in Figure 1).20 The averaged hog population density for the remaining coastal plain is ~65 hogs/km².¹⁷ This area also contains $\sim 68\%$ of the domestic turkey population of the Coastal Plain.²⁰ Ammonia emissions from the six counties (shaded area in Figure 1) account for 36% of total statewide NH₃ emissions.²¹ These factors make this site particularly unique among the remaining Coastal Plain and other areas in the Eastern United States.

 $PM_{2.5}$ speciation samples were collected every 6 days in 2002 at three sites, except at Mecklenburg, where samples were collected every 3 days. Continuous electronic hourly measurement of $PM_{2.5}$ mass is also conducted at Mecklenburg. Both $PM_{2.5}$ mass concentration and speciation data are reported as daily average values for days in which air masses are sampled.

Tapered element oscillating microbalance (TEOM)²² with a Sharp Cut Cyclone was deployed as a continuous monitor for PM_{2.5} sampling. TEOM series 1400a monitor uses exchangeable Teflon coated with a 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 nonfatiguing materials. In the process of monitoring, moisture was removed by heating the sample to 50 °C. The minimum detection level was 0.1 μ g/m³. The speciation monitors used are called MetOne SuperSass Teflon monitors from Met-One Inc. A Sharp Cut Cyclone with a flow of 6.7 L/min was integrated in every sampling canister to remove particles $>2.5 \ \mu m$ aerodynamic diameters.

A Nylon filter with a nitric acid denuder was used to measure $\mathrm{NO_3}^-$, $\mathrm{SO_4}^{2-}$, $\mathrm{NH_4}^+$, sodium, and potassium for the chemical speciation analysis of samples collected. Ion chromatography (Dionex system) was used to analyze the concentrations of anion (like SO₄²⁻ and NO₃⁻) and cation species (like NH_4^+ , K^+ , and Na^+). The effluent used for anion analysis is a 2.7-mM Na₂CO₃/0.3 mM NaHCO₃ solution, whereas a 22-mM H₂SO₄ solution was used for cation eluent. The measurement method is selective and sensitive, allowing measurement to <0.05 ppm in the filter extracts. Duplicate injections show a relative percentage difference of >5% above $\sim 0.05 \ \mu g/mL$. Analysis of quality control check samples shows a recovery of >95%. Particulate EC and OC concentrations used in this study were measured using a Thermal-Optical Carbon Aerosol Analyzer on the basis of thermal desorption/oxidation of particulate carbon to CO₂, which is then reduced to methane and subsequently measured using a flame-ionization detector. The analysis sequence was initialized in a nonoxidizing atmosphere (helium) with a 10-sec purge followed by four temperature ramps to a maximum of 900 °C. A cooling blower then came on, and the temperature dropped to 600 °C before oxygen was added. Detailed description of the procedure about carbonaceous species measurement has been given by Peterson et al.²³ The temperature was held at this point until the transmittance or reflectance returned to the initial point before the sample was heated. This point determines the distinction between OC and EC, that is, all of the carbon measured up to this point is OC, whereas 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 of carbon and 0.01 at 10–72 μg of carbon.

Statistical Analysis

The ANOVA is a statistical technique used to test the difference among several group means. It was used in our

study to quantify the seasonal differences among PM_{2.5} species concentrations. This method first hypothesizes that the means of all groups are equal. The hypothesis was evaluated by the output of the tabular form (known as ANOVA table) obtained from statistical computation. After Stataquest computes the ANOVA table, we can determine whether the hypothesis is correct or not by looking at the *P* value. Usually, the null hypothesis is rejected if the critical value *P* is <0.05.

Back-Trajectory Analysis

Backward-trajectory analysis can be used to track the history of air masses in which air pollutants are transported to the measurement site.12,24,25 Back-trajectory analysis is performed using the HYSPLIT 4 model²⁵ developed by the National Oceanic and Atmospheric Administration Air Resource Laboratory. The actual operation routines are explained and demonstrated by elsewhere^{25,26} and will not be discussed here. This model was run for days during which PM_{2.5} samples were collected at the four sites. The three-dimensional motion was obtained using 3-hourly output from the Eta Data Assimilation System for both horizontal and vertical air mass streams. Considering both residence time of SO₄²⁻ aerosol and substantial errors inherent in depicting air mass movement beyond 3 days,27 48-hr back trajectories were applied to determine air mass history in this study.

RESULTS AND DISCUSSIONS

PM_{2.5} Total Mass Concentrations

Our measurement results show that $PM_{2.5}$ concentrations at three urban sites (Wake, Forsyth, and Mecklenburg) exceeded the National Ambient Air Quality Standard (NAAQS)²⁸ for $PM_{2.5}$ during 2002. The primary NAAQS for $PM_{2.5}$ was 15 µg/m³ for an annual average and 65 µg/m³ for a 24-hr average (EPA looks at a 3-yr period for attainment status of the NAAQS).¹⁶ $PM_{2.5}$ mass concentrations at the rural site were lower and did not exceed the annual standard for $PM_{2.5}$. The average concentration in summer was >15 µg/m³ at both urban and rural sites. No exceedance of the 24-hr NAAQS for $PM_{2.5}$ (65 µg/m³) was found at either urban or rural sites during the entire measurement campaign.

The seasonal average concentrations of PM_{2.5} chemical compositions monitored at these four sites are shown in Figure 1. The "other" portion includes crustal materials, trace elements, and other unidentified constituents. A factor of 1.4 was applied to detect OC concentrations to account for the unmeasured hydrogen and oxygen in the organic materials.^{10,29} Organic matter [(OM) 47–50%], with an annual average of 7.22 μ g/m³, was the most abundant component of PM_{2.5} at all of the sites. SO₄²⁻ ranked second, with an annual average of 4.63 μ g/m³, or 27-32% of total PM_{2.5} mass. Other major species, namely, NH_4^+ (annual average: 1.54 µg/m³), NO_3^- (annual average: 1.04 μ g/m³), and EC (annual average: 0.51 μ g/m³), constituted 9-11, 5-7, and 1-4% of the total PM_{2.5} mass, respectively. As illustrated in Figure 2, PM_{2.5} mass concentrations peaked in summer at all of the sites. The three urban sites had similar levels of PM2.5 concentrations probably because of comparable precursor emissions density at those areas. Using the ANOVA statistical method, it



Figure 2. Seasonal distribution of PM_{2.5} concentration in North Carolina sites (urban: Wake, Forsyth, Mecklenburg; rural: Lenoir). Error bars, standard deviation for each site at different season.

was found that the annual average of $PM_{2.5}$ mass concentrations displayed no significant difference (P = 0.99) among these urban sites. However, there did exist some seasonal variations among the urban sites because of influence of local sources. The seasonal variations were smaller during summertime than wintertime. Compared with that in summer, regional dominance by weather and pollution patterns was decreased, thus resulting in more variation in the measured $PM_{2.5}$ values.

Correlation among Major Components

The association pattern among major PM_{2.5} components can be displayed by a correlation matrix of these components. The correlation matrix is constructed based on the Pearson correlation coefficients obtained from a correlation analysis of related components. Tables 1 and 2 show the correlation matrices of one urban site (Wake) and agricultural site (Lenoir), respectively. The results reveal that there exist stronger component-to-component correlation trends at the urban site, whereas the agriculture site has a significantly different trend. A few associations stand out: (1) total $PM_{2.5}$ is well correlated with SO_4^{2-} , $\mathrm{NH_4^+}$, and OC; (2) $\mathrm{NH_4^+}$ correlates much better with SO_4^{2-} than with NO_3^{-} ; (3) EC and OC are well correlated with each other at all three of the urban sites, but EC and OC are poorly correlated at the rural site; and (4) $NO_3^$ has a rather weak correlation with total $PM_{2.5}$. The weak

Table 1. Pearson correlation coefficient among major species of $\text{PM}_{\rm 2.5}$ at the Lenoir County site.

Species	PM _{2.5}	NH4 ⁺	SO 4 ²⁻	NO_3^-	EC	OC	Others
PM _{2.5}	1						
NH ^{2.5}	0.72	1					
S0, 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		
00	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

correlations between NO₃⁻ and NH₄⁺ and between NO₃⁻ and PM_{2.5} might be attributed to the following: (1) depletion of NO₃⁻ in the fine particles to form coarse-mode NO₃⁻; (2) partitioning of NO₃⁻ acid from the collection media into the atmosphere during higher temperatures¹⁹; and (3) contamination from filter artifacts, which cannot be ignored. According to previous studies,^{11,30} NO₃⁻ in fine particles could evaporate to satisfy charge neutrality in the particles in cases where the equivalent ratio of NH₄⁺ to SO₄²⁻ is as high as \geq 0.8, which is the case this study.

Water-Soluble Ion Species

Data analysis reveals that at both rural and urban sites, SO_4^{2-} had a maximum mass concentration in summer and a minimum in winter, whereas NO_3^- displayed a reverse trend, consistent with observations by Malm et al.⁷ SO_4^{2-} was the most abundant water-soluble component of $PM_{2.5}$ at all of the sites for each season. SO_4^{2-} concentrations at urban sites ranged from 0.6 to 19.1 μ g/m³ with an annual average of 4.7 μ g/m³ at Mecklenburg, 4.7 μ g/m³ at Wake, and 4.3 μ g/m³ at Forsyth. At the agricultural site in Lenoir, the range was from 0.8 to 13.7 μ g/m³, with an annual average of 5.1 μ g/m³.

Results of ANOVA for SO_4^{2-} , NO_3^{-} , and NH_4^+ at these sites are shown in Table 3. The *P* value of SO_4^{2-} indicates that there are considerable seasonal differences

Table 2. Pearson correlation coefficient among major species of $\mathsf{PM}_{2.5}$ at the Wake County site.

Species	PM _{2.5}	NH4+	\$04 ²⁻	$\mathrm{NO_3}^-$	EC	OC	Others
PM _{2.5}	1						
NH_4^+	0.82	1					
S04 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		
00	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. ANOVA table for the major solvable ions of $\text{PM}_{\rm 2.5}$ at North Carolina sites.

Site	\$04 ²⁻	NO_3^-	NH4+
Lenoir	0.879	0.0183	0.2067
Forsyth	0.0209	0.0036	0.1258
Mecklenburg	0.0006	< 0.0001	0.1256
Wake	0.0128	< 0.0001	0.1255

at the three urban sites (P < 0.05) but not at Lenoir (0.05 < P < 0.1). NO₃⁻ displays significant seasonal variations (P < 0.05) at both urban and rural sites, suggesting that particulate NO₃⁻ is more dependent on temperature, which determines the transformation rate of NO_x to the NO₃⁻ particulate phase.³¹ There was no strong seasonal variation in NH₄⁺ concentrations at any site, although a weak trend was observed that NH₄⁺ reached its highest in summer and lowest in winter.

Strong correlation between NH₄⁺ and SO₄² existed at all of the sties (0.96 at Forsyth, 0.97 at Lenoir, 0.95 at Wake, and 0.93 at Mecklenburg). SO_4^{2-} particles are formed in the atmosphere when sulfur gases, such as sulfur dioxide and hydrogen sulfide, are oxidized to sulfuric acid and then combined with NH₃ to form ammonium sulfate or ammonium bisulfate particles. They are fairly stable in the atmosphere and removed by dry and wet deposition. It has been reported that at some Southeast US locations, such as the Great Smoky Mountains National Park, TN, Shenandoah National Park, VA, and Dolly Sods Wilderness Area, WV, the NH_4^+ to SO_4^{2-} ratio is generally <1, especially in the summertime.³² The average molar ratio of NH_4^+ to SO_4^{2-} was >1.5 most of the time at the sites in this study. This may be attributed to higher NH₃ emission density in North Carolina, resulting in a higher level of NH₄⁺ in atmospheric aerosols. The average ratio of NH_4^+ to SO_4^{2-} at these sites was >2 in the winter and was between 1 and 2 in other seasons. However, even during wintertime, the equivalent ratio of $\rm NH_4^+$ to the sum of $\rm SO_4^{2-}$ and $\rm NO_3^-$ was still <1. This suggests that neither acid gas was completely neutralized by $\rm NH_3$, or the anions in particles were neutralized by cations other than $\rm NH_4^+$.

It is interesting to note that, given its much higher NH₃ in the air,¹⁷ Lenoir does not show extremely higher particulate NH₄⁺ than other sites. Aneja et al.¹⁸ have reported that local NH₃ emissions strongly influence ambient NH₄⁺ concentrations, but there exists a level above which NH₃ emission is no longer the primary contributor to further NH₄⁺ formation. They attributed this to the fact that NH₄⁺ aerosol formation is limited by availability of acid gases in the presence of excess NH₃.

Arimoto et al.33 and Yao et al.34 used mass ratio of $\mathrm{NO_3}^{-}/\mathrm{SO_4}^{2-}$ as an indicator of the relative importance of stationary versus mobile sources to sulfur and nitrogen in the atmosphere. Seasonal variation of NO_3^{-}/SO_4^{-2-} mass ratio is shown in Figure 3. The ratio reached its lowest in summer (0.09–0.16) and highest in winter (0.52–0.70). Lenoir had a higher NO_3^{-}/SO_4^{-2-} ratio than the urban sites. The ratio was <1 at both urban and rural sites during all of the seasons. This is consistent with earlier results from several Asian urban site cities (Shanghai and Beijing³⁵; and Nanjing and Changshu³⁴) but different from that in downtown Los Angeles and Rubidoux in Southern California.³⁴ The difference is attributed to the different energy sources involved in sulfur and nitrogen emissions in these areas. The low mass ratios in North Carolina suggest that stationary source emissions were more important than the vehicle emissions in the studied areas, especially during summer time.

Carbonaceous Species

Carbonaceous particles consist of a complex mixture of substances containing carbon atoms, usually classified in two major fractions as OC and EC.^{36,37} EC originates predominately from incomplete combustions, whereas OC is from both primary and secondary (through gas-to-particle conversion) sources. The correlation between EC



Figure 3. Seasonal variation of NO_3^{-}/SO_4^{2-} mass ratio in North Carolina.



Figure 4. OC/EC in summer and winter in North Carolina; Error bars, standard deviation for each site in the summer or winter.

and OC is given in Table 2 for an urban site (Wake County). OC and EC are well correlated at urban sites, suggesting that they may be emitted by similar sources.¹¹ A possible reason for EC and OC being poorly correlated at the rural site is that the rural site had a lack of strong combustion sources, such as automotive exhaust, leading to a lower EC mass concentration. However, there was an abundance of OC in the rural region from biogenic sources with varying emissions strength across the year. Using PM_{2.5} data monitored at Great Smoky Mountains National Park from 1988 through 1994, Day et al.³⁸ reported that OC concentration is higher in summer and lower in winter. A study of carbonaceous aerosol by Castro et al.37 also showed that there is more abundant secondary organic aerosol (derived from OC/EC ratio) during summer than during winter at several European locations. The comparison of the OC/EC ratio measured in this work is shown in Figure 4, with the standard deviation depicted by an error bar. Our results show a higher OC/EC ratio in summer and a lower one in winter, consistent with these earlier works.37-39 Compared with that at urban sites, the OC/EC ratio at Lenoir was relatively higher during the entire monitoring period, resulting from the lower contribution of local primary emissions at the rural site.⁴⁰

Diurnal Behavior of PM_{2.5}

At the Mecklenburg site hourly PM_{2.5} mass concentrations were measured. Diurnal variations of PM_{2.5} measured at Mecklenburg are presented at Figure 5. PM_{2.5} mass concentrations displayed a peak in the early morning, attributed to the morning rush hour traffic. A secondary peak was observed in mid evening between 8:00 p.m. and 9:00 p.m. local time. The diurnal trend was similar to that observed in Central and Southeastern Ohio and in Santiago, Chile.41,42 The secondary PM2.5 peak might be attributed to both exhaust of heavy traffic and diurnal evolution of planetary boundary layer (PBL).43 The second peak starts to form around 5:00 p.m. and 6:00 p.m. when the heavy traffic usually occurs. Decreasing PBL height after sunset and weakened turbulence because of cooling of the surface^{42,44} contribute to elevating PM_{2.5} concentration by preventing the dispersion of aerosols, which leads to the secondary maximum in the evening.



Figure 5. Hourly average of $PM_{2.5}$ mass in different seasons at Mecklenburg.

The increase in the particle concentration is not immediate, but builds up over a period of several hours after sunset.⁴⁵

Back-Trajectory Analysis

Source apportionment is essential to determine where fine PM originates. Origin of air masses containing PM_{2.5} is determined by back-trajectory analysis using the HYSPLIT-4 model as described above. All of the trajectories are classified based on both daily PM2.5 average values and the number of samples collected at different sites. A high-PM_{2.5} day is defined as a day when PM_{2.5} concentration is 40% higher than the annual average and a low-PM_{2.5} day as PM_{2.5} concentration 10 μ g/m³ below the annual average. Data at one agricultural site (Lenoir) and one urban site (Mecklenburg) are selected to represent different environmental settings. Figure 6, a and b, shows the back trajectories for high- and low-PM_{2.5} air masses at Lenoir, whereas Figure 7, a and b, shows the same for Mecklenburg. Considering the effects of precipitation, the low PM_{2.5} days marked with precipitation were screened out. These figures reveal the pathway by which air mass travel exerts an important role in PM_{2.5} present at the receptor site. As shown in Figures 6b and 7b, most air masses containing low PM_{2.5} originate from the marine or coastal environment or over continental regions but originated from high elevation, $\sim 2000-4000$ m above ground level. Previous studies of vertical distribution of aerosol particles over the Northern Hemisphere show that both mass concentration and the production of new particles decline rapidly with altitude in the lower troposphere.¹⁹ On the other hand, most high-PM_{2.5} air masses originate at low elevation in southwest or northwest directions. This is likely because of power plant emission of $PM_{2.5}$ and their precursors.

Results of back-trajectory analysis can be combined with observations to better explain the chemical characteristics of $PM_{2.5}$ at a receptor site. Measurements at Lenoir show that, although the equivalent ratio of NH_4^+ to the sum of SO_4^{2-} and NO_3^- was <1 and there was high



Figure 6. HYSPLIT backward trajectories analysis results for the days with high (left) and low (right) daily average PM_{2.5} mass concentration at the Lenoir during 2002.

 $\rm NH_3$ availability, $\rm PM_{2.5}$ concentrations were significantly lower than that at other sites. Back-trajectory analysis reveals that the Lenoir site was predominantly influenced by air masses originating from the marine environment, which carries abundant sea salt components. The sea salt cations will likely compete with $\rm NH_4^+$ to neutralize acid gas, resulting in an equivalent ratio of $\rm NH_4^+$ to the sum of $\rm SO_4^{2-}$ and $\rm NO_3^- < 1$.

CONCLUSIONS

This paper shows measurements and analysis of fine PM $(PM_{2.5})$ and its chemical composition at three urban and one rural site in North Carolina in 2002. The unique environmental characteristics of North Carolina include strong biogenic emissions and populated animal farms that lead to much higher ammonia emissions than surrounding areas in the Eastern United States. Analysis of



Figure 7. HYSPLIT backward-trajectories analysis results for the days with high (left) and low (right) daily average PM_{2.5} mass concentration at the Mecklenburg site during 2002.

 $PM_{2.5}$ chemical components shows that OM was the most abundant component of $\mathrm{PM}_{2.5}$ and accounted for 45–50% of total $PM_{2.5}$ mass at all of the sites. SO_4^{2-} was the major soluble ion of $PM_{2.5}$ accounting for ~30% of $PM_{2.5}$. NH_4^+ and $\mathrm{NO_3}^-$ accounted for 7–11% and 6–9% of total $\mathrm{PM}_{2.5}$ mass concentrations, respectively. At all of the sites, NH4 combined mainly with SO₄²⁻, except in winter, when $\mathrm{SO_4}^{2-}$ was relatively low, whereas $\mathrm{NO_3}^-$ was high. Examining correlations between $\ensuremath{\text{PM}}_{2.5}$ and its major chemical components shows that total PM2.5 was well correlated with SO_4^{2-} , NH_4^+ , and OC and that NH_4^+ correlated much better with SO_4^{2-} than with NO_3^{-} . For both rural and urban sites, SO_4^{2-} had a maximum mass concentration in summer and a minimum in winter, whereas NO₃⁻ displayed a reverse trend. A low mass ratio of NO₃⁻ to SO₄²⁻ was observed at all of the sites, suggesting that stationary source emissions were more important than the vehicle emissions in the studied areas. The equivalent ratio of NH_4^+ to the sum of SO_4^{2-} and NO_3^{-} is <1. Diurnal variation of PM_{2.5} mass concentrations displayed a peak in the early morning and a secondary peak in late afternoon. OC and EC were well correlated at three urban sites, whereas they were poorly correlated at the agriculture site. Back-trajectory analysis reveals that air masses with high PM_{2.5} mostly originate from low altitude over continental regions. Air masses coming from marine sources or higher levels usually carry less fine particles.

Information on the composition of PM impacting an area and whether it is primary (directly emitted from a source) or secondary (formed in the atmosphere from precursors) can be useful in identifying potential sources and strategies for controlling particle emissions. For example, if the dominant component of PM is secondary OM, control strategies that focus on precursor sources of organic emissions may be most effective. On the other hand, if the primary component of PM is made up of SO_4^{2-} , controlling sources of sulfur dioxide may be more effective. For example, the North Carolina Clean Smoke Stacks Act will reduce emissions of sulfur dioxide from coal-fired power utility plants by 73% by 2013. Because sulfur dioxide is an important cause of fine particle pollution, the Clean Smoke Stack Act is expected to reduce the concentration of fine particles in North Carolina's air. As the act takes affect, the percentage of PM composed of $\mathrm{SO_4}^{2-}$ should decrease. Studies of back trajectories to identify where transported PM comes from are also valuable tools to develop strategies for attaining the NAAQS. Back trajectories can also provide useful support for initiatives such as North Carolina's 126 petition requesting neighboring states to control their emissions that affect the quality of North Carolina's air.

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