NOTE: The information in these synthesis papers was drawn from project reports and has not necessarily been peer reviewed.

Appendix E: Synthesis of EMEP Research Findings

I. Air Quality and Related Health Research associated with Particulate Matter, Ozone, and Co-Pollutants

II. Ecosystem Response to Deposition of Sulfur, Nitrogen, and Mercury

III. Crosscutting Environmental Science, Energy, Technology and Policy Research

I. Summary of Findings From EMEP-Supported Projects Related to Air Quality and Health Research associated with the Particulate Matter, Ozone, and Co-Pollutants

Preface

This summary, which focuses on air quality and health effects, was prepared by NYSERDA staff to assist with program evaluation efforts and to facilitate discussions at the upcoming evaluation and planning meeting with EMEP Program Advisors and Science Advisors. Conclusions drawn from this effort will assist in determining research needs related to the EMEP program and help focus future research solicitations.

Introduction

In 1997, EPA set daily and annual standards for particulate matter in two size categories: PM_{10} (less than 10 um in diameter) and $PM_{2.5}$ (less than 2.5 um in diameter). For PM_{10}, the 24-hour standard is set at 150 ug/m^3, and the annual standard is 50 ug/m^3. For $PM_{2.5}$, the 24-hour standard is 65 ug/m^3, and the annual standard is 15 ug/m^3. The current standard for ozone (O_3) is based on a maximum concentration of 0.08 parts per million over an eight-hour period.

Atmospheric concentrations of ozone and fine particulate matter ($PM_{2.5}$) in parts of New York State and other regions of the northeastern United States continue to reach or exceed levels set in the National Ambient Air Quality Standards (NAAQS).

Recent $PM_{2.5}$ designations by EPA identify the New York City area (New York, Kings, Queens, Bronx, and Richmond counties), Long Island (Nassau and Suffolk counties), and Orange, Westchester, and Rockland counties as "non-attainment" for annual $PM_{2.5}$.

EPA has proposed new standards at the level of 35 ug/m^3 and 15 ug/m^3 for 24-hour and annual $PM_{2.5}$, respectively. They also propose removing fine $PM_{2.5}$ from the PM_{10} standard to create a "thoracic" coarse particle standard in the size range of $PM_{10-2.5}$. This new $PM_{10-2.5}$ standard would have a 24-hour limit of 70 ug/m^3.

The Environmental Monitoring, Evaluation, and Protection (EMEP) Program's multi-year plan (2002) identified ozone and $PM_{2.5}$ as important energy-related environmental management challenges facing New York State. It set general research objectives to:

1. develop and evaluate the effectiveness of pollution control strategies;
2. quantify local sources and regional transport of fine particles and their precursors to develop more equitable pollution control strategies; and
3. assess the relationships between health effects and $PM_{2.5}$, ozone, and co-pollutants to support development of control strategies to effectively mitigate health impacts.

Through a series of competitive solicitations targeted at critical research gaps identified in the EMEP research plan, 20 research projects focusing on ozone, $PM_{2.5}$, and co-pollutants were selected and funded by the EMEP Program. The total cost of this research was $20.2 million. The contribution of EMEP funds in these research projects was $9.2 million.

The EMEP approach to ozone, $PM_{2.5}$, and co-pollutant research can be simplified into several policy-relevant questions:

How can we improve measurement of $PM_{2.5}$ and its components?

What are the components of $PM_{2.5}$ in the New York region?

Where are the source regions and source types contributing to $PM_{2.5}$ in New York?

Are there specific components in the $PM_{2.5}$ /co-pollutant complex causing adverse health effects?

What are the implications for air-quality management of $PM_{2.5}$ and ozone?

1. How do we improve measurement of $PM_{2.5}$ and its components?

Ambient aerosols are heterogeneous, comprising particles from numerous sources that may then be modified by atmospheric or chemical processes, resulting in varying properties. For example, hygroscopic particles may adsorb water vapor if there is elevated relative humidity. Likewise, semivolatile compounds on a particle's surface may desorb during the heat of the day or condense at night. Understanding how temperature, pressure, and relative humidity affect particle behavior is important to designing particle samplers and interpreting aerosol measurement data.

Federal Reference Method (FRM)
The ambient air standard is based on measurement of $PM_{2.5}$ using a Federal Reference Method (FRM). Under the FRM procedure, a filter is preconditioned under a defined temperature and humidity and then weighed. Using hardware with well-defined specifications, a sample is collected on the filter over 24 hours at ambient temperature and humidity. The filter is then weighed under the same defined temperature and humidity conditions as during the preconditioning. The weight difference divided by the volume of sampled air yields the average 24-hour mass concentration. Due to the conditions of the FRM, it is only an indicator of $PM_{2.5}$ in the air. It does not precisely represent the mass of $PM_{2.5}$ as it exists and is breathed under ambient conditions.

1.1 Instrumentation Development
With EMEP support, Rupprecht & Patashnick Co. developed three instruments to improve continuous monitoring of ambient air, thereby addressing the limitations of the FRM noted above. These instruments are based on the use of the Tapered Element Oscillating Microbalance (TEOM) inertial mass measurement method. The goals of these efforts were 1) to increase correlation with measurements made using the FRM and 2) to develop a continuous measurement system that more closely represents the mass of fine particles found in ambient air.

To achieve the first goal, a sample equilibration system (SES) was developed to reduce the moisture content of the sampled ambient air stream, so that the temperature of the TEOM filter could be reduced from 50ºC to 30ºC, closer to the typical ambient collection temperature of the FRM. The SES retrofit to the TEOM allowed a lower operation temperature and retained a greater fraction of the collected semivolatile compounds, resulting in a greater degree of correlation with the non-temperature-constrained FRM samples.

To achieve the second goal, a new measurement concept – the Differential TEOM Mass Monitoring System, or Differential TEOM – was developed and tested. In this system, an electrostatic precipitator (ESP) is inserted between the sample inlet and the TEOM mass sensor. The ESP is cycled on and off to selectively remove particles from the sample stream. Mass measurements made with the ESP on are subtracted from those made with the ESP off, to track the gain or loss of semivolatile materials on the filter. This technology is able to resolve issues with measuring adsorption and evaporation of the sample collected by the monitor, providing a more detailed time-series record of $PM_{2.5}$ mass. As a follow-up to the Differential TEOM project, a simpler filter-based version of the monitor, the Filter Dynamics Measurement System (FDMS) was developed. Since its release, the FDMS has received approval from the California Air Resources Board for both PM_{10} and $PM_{2.5}$ sampling and is beginning to be used in sampling networks.

1.2 Instrument Comparison

The FDMS was designed to capture both the volatile and nonvolatile components of aerosol mass. The beta attenuation monitor (BAM) also measures both volatile and non-volatile $PM_{2.5}$ components. Schwab et al. (2006) made comparisons of the FDMS, TEOM, and BAM with the FRM in the field at Queens and Pinnacle State Park. The BAM and FDMS measurements were approximately 25% higher than the FRM measurements at Queens. The FDMS measurement was about 9% higher than the FRM at Pinnacle State Park. The FRM mass was higher than the standard TEOM measurements. The FRM captures a fraction, but not all, of the volatile components of the aerosol mass, raising serious questions about how representative are the FRM measurements of ambient PM.

Carbon

As part of a larger research effort on the source apportionment of organic particles, the Speciation Trends Network (STN) measurement of elemental carbon (EC) and organic carbon (OC) in PM will be compared to an independent analysis. This is another measurement in which the value is operationally defined by the sampler and analysis methodology rather than representing the species present in ambient air.

Particulate Mercury

New rules will soon be going into effect for Hg emissions, creating a need for both monitoring and research measurement to characterize and understand sources, sinks, and transformation processes of Hg. An added challenge is the various forms of Hg in the atmosphere: Hg, Hg (2+) or Reactive Gaseous Mercury (RGM), particulate mercury, and Hg in wet deposition. A comparison of manual measurements of gaseous mercury is being performed with an automated Tekran 2537A in the laboratory and at a field site in Postdam, NY. This project will likely be the basis of a Hg monitoring network in New York State. Based on the lessons learned in this project, the New York State Department of Environmental Conservation (NYSDEC) has submitted a proposal to EPA for expansion of Hg monitoring in New York State.

1.3 Stationary Source Testing: Oil- and Gas-Fired Combustion Systems

A dilution sampling technology and test method for $PM_{2.5}$ emissions and speciation measurements was developed for oil- and gas-fired combustion systems. A compact, lightweight dilution sampler was developed and tested in controlled and field conditions. Seven stationary sources were tested in a field program, including gas-fired boilers and steam generators, gas-fired combined cycle and cogeneration power plants, gas fired heaters, No. 6 oil-fired boilers, and diesel engines. The measurements were used to develop emissions factors and speciation profiles for PM, especially organic aerosols for use in source-receptor and source-apportionment analyses.

The study concluded that dilution source sampling can be an effective method of measuring PM2.5 emissions from stationary sources. Measurement of PM2.5 emissions is, however, highly method dependent. Emissions tests using different methodologies (e.g., dilution vs. filterable + condensable methods) can produce significantly different results and emission factors. In tests with gaseous fuels (refinery gas and natural gas), filterable + condensable methods yielded PM2.5 emission factors that were one to two orders of magnitude greater than determined using dilution methods. In field and pilot tests with No. 6 fuel oil, conventional stack sampling of filterable + condensable PM2.5 produced PM2.5 emission factors that were between 25% and 60% less than those determined using dilution sampling methods. These tests underscore the need for a consistent measurement method for PM2.5 – established at the national level – combined with a concerted effort to improve PM2.5 emissions inventories and emission factors. Specific findings are presented below.

$PM_{2.5}$ Mass
The $PM_{2.5}$ mass emission rates are extremely low. The $PM_{2.5}$ mass concentrations are near ambient levels in some cases, and these concentrations are very difficult to measure with conventional samplers and sampling techniques. However, the dilution sampler technique can achieve lower detection limits than traditional sampling methods and are more representative of gas-fired sources. The $PM_{2.5}$ emissions from No. 6 oil-fired sources and diesel engines are well above the minimum detection levels of this method.

$PM_{2.5}$ Speciation
For gas-fired sources, dilution sampling results indicate that the majority of $PM_{2.5}$ is OC. However, as a portion of the OC is volatile in nature, these measurements are highly uncertain. Sulfate, EC, NH_4^+, and other ions and elements are minor emissions components for gas-fired sources. Sulfate is the dominant $PM_{2.5}$ species for the oil-fired boiler tested, while EC dominates the diesel engine. The speciation profile for the oil-fired boiler also showed some elements, consistent with the ash content of the fuel, that may provide a distinctive signature.

Particle Size
The test results for gas-fired units indicate that nearly all of the $PM_{2.5}$ in the stack is smaller than 0.1 um. Exploratory ultrafine (0.1 um and smaller) particle measurements reveal peak number concentrations at a size of approximately 20 nm, indicating the predominance of particles formed by nucleation, and that ultrafine particles account for approximately one-third of the total mass for fine particles.

Particle size and composition measurements for the No. 6 oil-fired boiler test show that approximately 76% of the particle mass is represented by particles smaller than 0.32 um and that the majority of these are SO_4 related. This is reasonable, considering the elevated sulfur content of the fuel compared to the other sources tested in this program.

The diesel engine test was conducted with and without a diesel particulate filter (DPF). Ultrafine particle number concentration peaks at 60 and 80 nm, and both total PM and ultrafine particles were significantly reduced by the DPF. Studies by others have suggested that addition of a DPF may not reduce fine particles uniformly, but this was not observed in these tests.

<u>*Supporting EMEP Projects:*</u>
Development and Demonstration of a Continuous Ambient Particulate Monitor (R&P 6400 Series), Harvey Patashnick, No. 5060

Development and Demonstration of an Innovative Instrument for Ambient Particulate Matter Mass Measurement Standard, Patashnick, No. 6183

Enhanced Measurements of Oxidants, Fine Particles and Precursors, Demerjian et al., No. 4918

Chemical Composition of Fine Organic Particles from Urban Regional Background Locations in New York State, Monica Mazurek, No. 7616

Impact of In- and Out-of-State Power Plants on Semivolatile Pollutants in NYS, Hopke et al., No. 6083.

Fine/Ultrafine Particulate Emissions Profiles, Glen England et al. No. 6230.

2. What is in $PM_{2.5}$ in the New York region?

Particle composition information is necessary for several reasons. It is needed to identify the relationship between PM toxicity and health effects; to apportion PM primary and secondary mass to sources, thereby informing regulatory control strategies; and to evaluate air quality models.

Numerous research efforts funded through EMEP are working to identify and characterize the annual, seasonal, and diurnal composition of $PM_{2.5}$ in New York State. Figure 1 shows the location of nine sampling sites in New York State where aerosol and co-pollutant studies were conducted under EMEP. These locations include both urban (Queens, Bronx, and Manhattan (2 sites)) and non-urban sites (Stockton, Pinnacle, Sterling Forest, Whiteface Mountain, and Potsdam). In addition, some studies also use data from sites in adjacent states (Chester, NJ, Elizabeth, NJ, and Westport, CT), which represent locations upwind or downwind from New York City. By understanding the relationship of $PM_{2.5}$ composition to upwind source contributions and photochemical activity of precursor gases, PM mitigation strategies can be developed.

2.1. Composition

Annual Composition
The PM Technology Assessment and Characterization Study in New York (PMTACS-NY or "Supersite") research program was designed to address a series of policy-relevant questions. One of the objectives was to measure the temporal and spatial distribution of the $PM_{2.5}$/co-pollutant complex. Figure 2 shows the annual composition of $PM_{2.5}$ in New York City. The largest fraction is carbon based (36%), followed by sulfate (30%), nitrate (15%), and ammonium (15%), with 5% trace metals and water.

Spatial Variation of Composition
Composition of $PM_{2.5}$ at New York City (average of New York Botanical Garden, South Bronx, and Queens College measurements), Rochester, Pinnacle State Park, and Whiteface Mountain includes carbon, nitrate, sulfate, and ammonium at all of the sites, but there is a systematic change in the distribution of these components from the urban to the rural and remote locations (Schwab et al., 2004). Nitrate is highest in the large urban (NYC) and small urban (Rochester) sites, and significantly lower in the rural and remote locations. Sulfate is proportionately highest at Pinnacle State Park, presumably due to its proximity to the Ohio River Valley source region, and lowest in New York City.

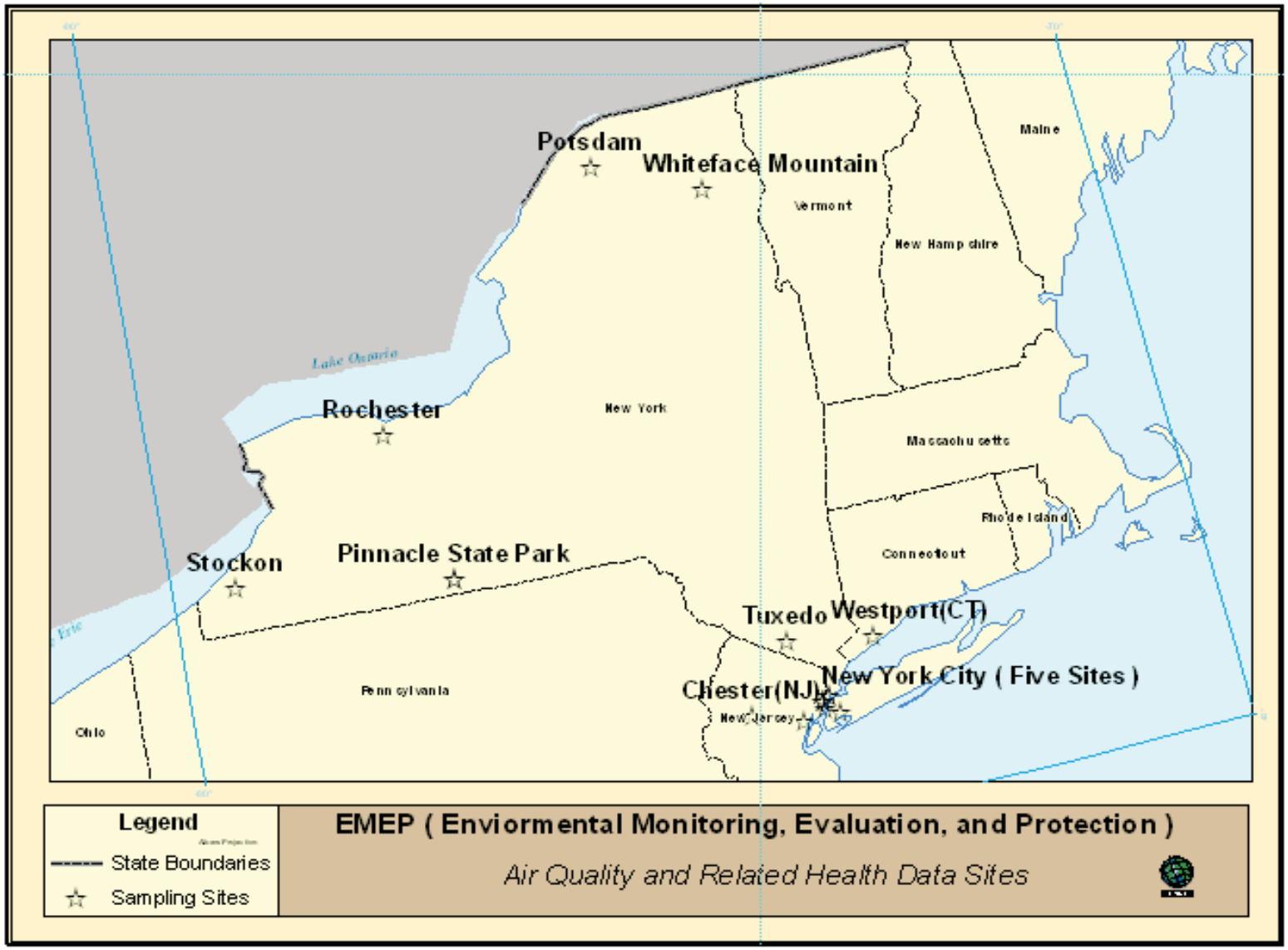

Figure 1. EMEP sampling sites.

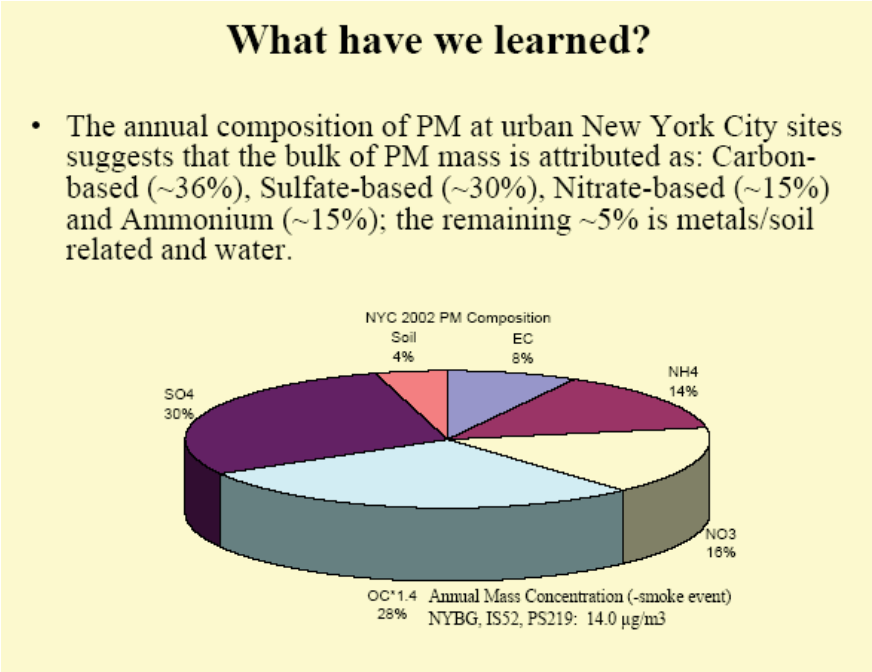

Figure 2. Annual composition of $PM_{2.5}$ in New York City.

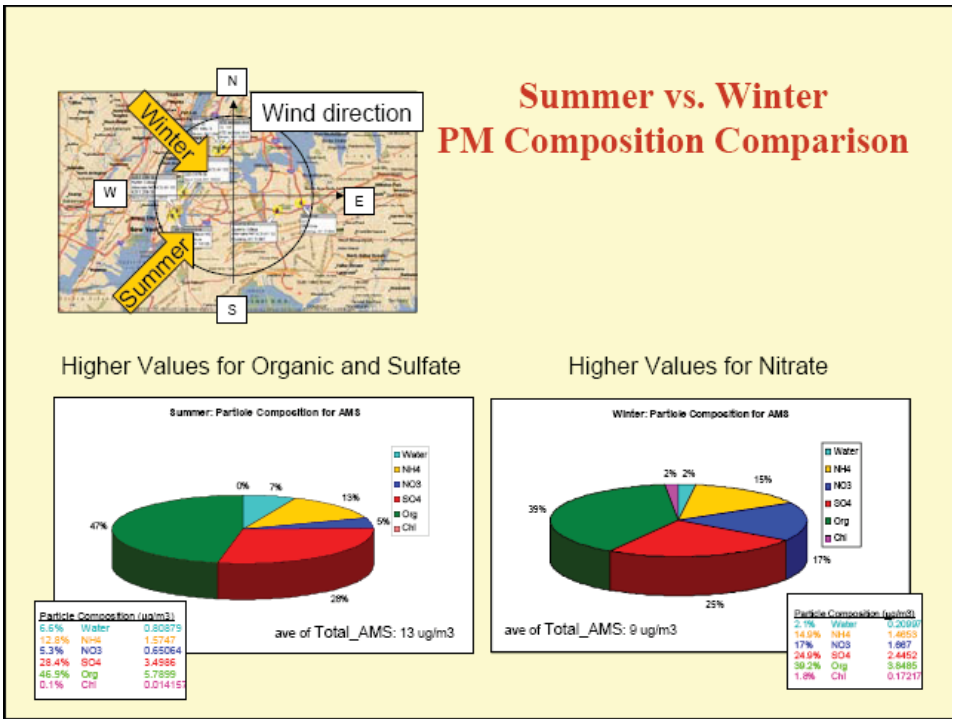

Figure 3. Composition of $PM_{2.5}$ by month, 9/00-10/02. (Demerjian et al., 2005)

Seasonal Composition
The composition of $PM_{2.5}$ changes with the seasons (Figure 3). During summer, wind is generally from the southwest, a region with many coal sources. $PM_{2.5}$ collected during summer has high amounts of sulfate (28%) and organic PM (45%), and fewer nitrates (5%).

In winter, there is less photochemistry and the wind is generally from the northeast, an area of fewer regional sources relative to the southwest. During this season, there is less $PM_{2.5}$ mass, but with a higher proportion of nitrate (17%) and higher mass of nitrate compared to summer.

2.2 Temporal Trends

Day of the Week
Luttinger et al. (2006) examined $PM_{2.5}$ components for day-of-week trends. They found a trend of lower mean concentrations on Sundays, increasing through the week to Thursdays for PM_{10}, elemental carbon (EC), and NOx. A day-of-week trend was not observed for $PM_{2.5}$, OC, or SO_2.

Diurnal Patterns
Three-hour sample averages of organic carbon showed little diurnal variation, possibly increasing slightly during the course of the day. Conversely, $PM_{2.5}$, PM_{10}, and, to a lesser degree, elemental carbon showed daily peaks in the morning hours (6-8 a.m.). These trends were consistent between the Bronx and Manhattan. The diurnal variation for average hourly $PM_{2.5}$ for two years of data collected in the Bronx and Manhattan is given in Figure 4 (Luttinger et al., 2006).

An aerosol mass spectrometer (AMS) was deployed in Queens during PMTACS-NY in summer 2001 (Drewnick et al., 2004). The AMS measures non-refractive mass only and so misses trace element species. It provided 10-minute mass concentration for sulfate, nitrate, ammonium, chloride, and total organics for a five-week period.

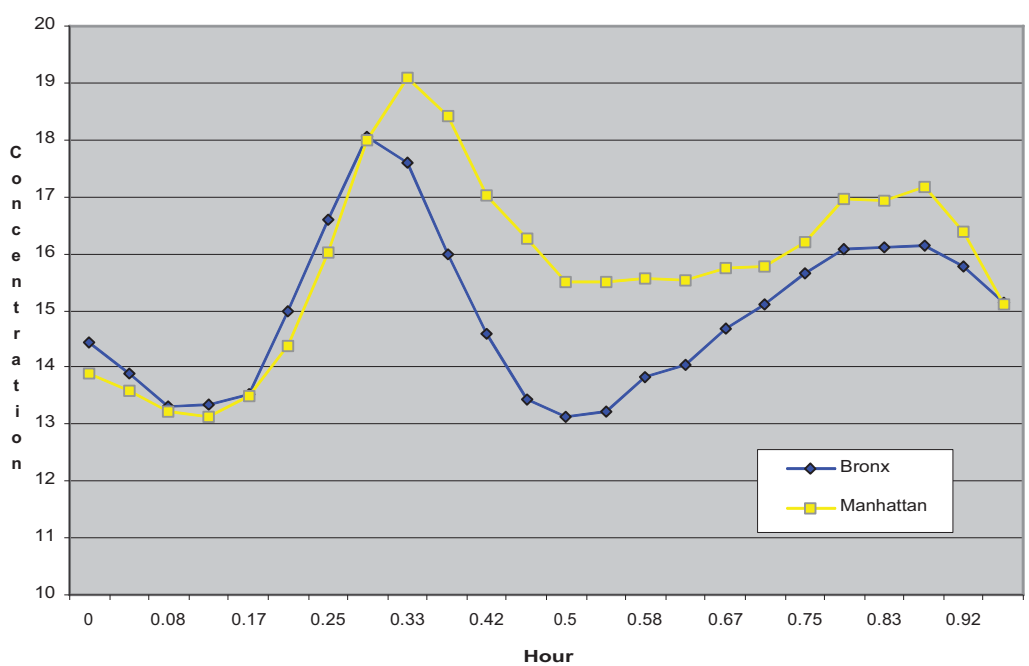

Figure 4. Diurnal Variation of $PM_{2.5}$ in the Bronx and Manhattan (Luttinger et al., 2006).

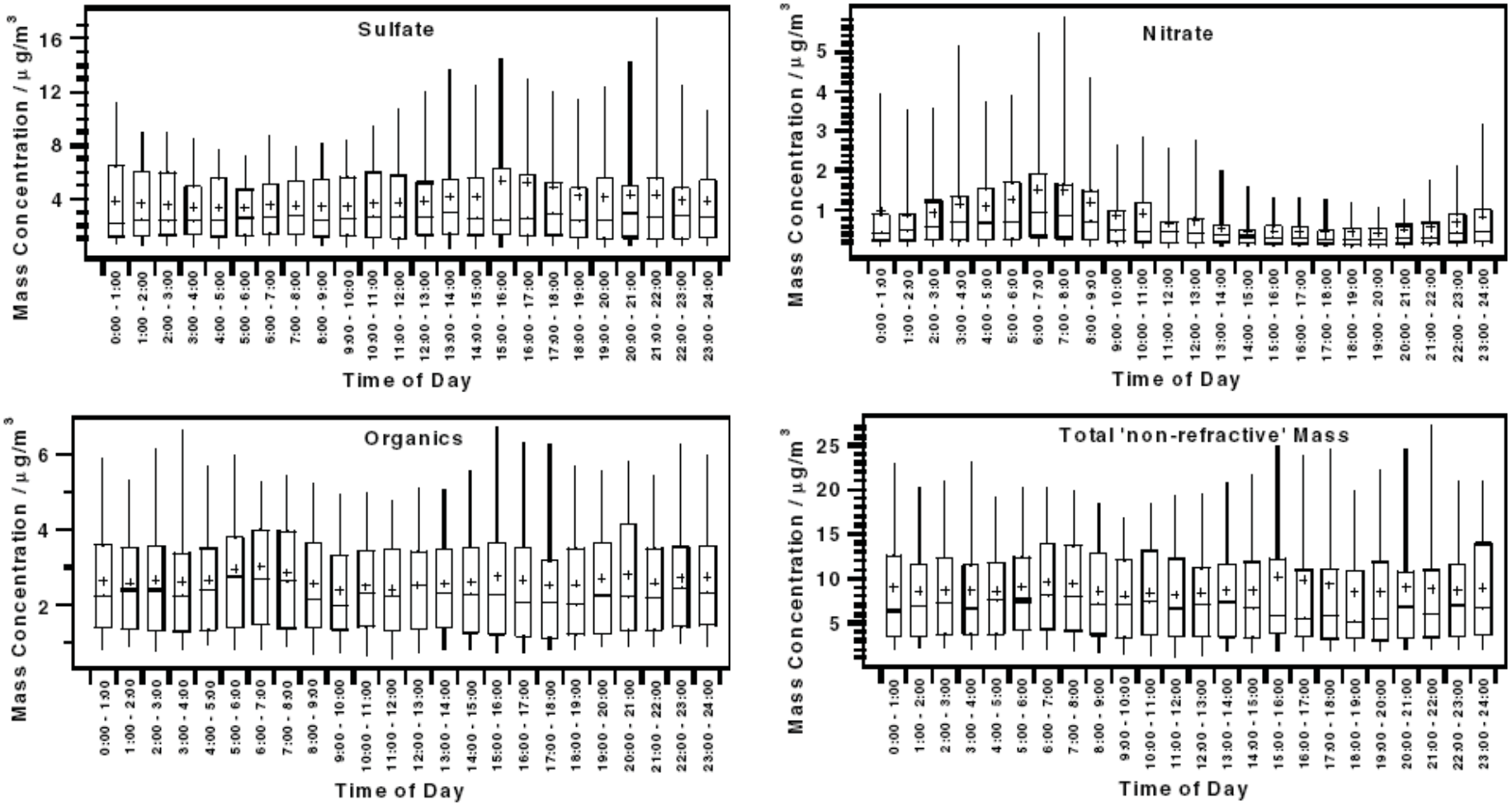

Figure 5. Average diurnal patterns for sulfate, nitrate, total organics, and total nonrefractory mass concentrations, measured during PMTACS-NY 2001. The boxes indicate the 25th percentile, the median, and the 75th percentile. The whiskers indicate the 5th and 95th percentiles. The means are printed as crosses.

Figure 5 shows the diurnal patterns for sulfate, organics, nitrate, and total non-refractive mass. The sulfate measurements show almost no diurnal pattern, indicating that observed sulfate was primarily due to regional transport rather than local production. In contrast, the nitrate particle concentration has a clear diurnal pattern peaking around 6-7 a.m. and decreasing to a minimum in the late afternoon. During the night it increases until early morning, with a small secondary maximum around midnight. The nighttime signal for nitrate is likely ammonium nitrate, formed by a very temperature-sensitive equilibrium. The observation is consistent with the observed summertime diurnal temperature pattern.

The mass concentration of total organic particulate shows a measurable diurnal pattern. There is a maximum from 5:00 to 8:00 a.m., again from 15:00 to 18:00, and later from 19:00 to 22:00. Using mass signals from the AMS to identify "fingerprint" markers, the organic aerosol particles were separated into photochemically generated aerosols and traffic-related hydrocarbons. Figure 6 shows the diurnal pattern for traffic-related particles and photochemical markers. The traffic-related particles have a maximum during the high-traffic periods. The photochemically generated particles show a maximum during the afternoon. From the data, it appears that organic particles measured in New York City are associated with both traffic and photochemical processes, although they are not yet resolved quantitatively.

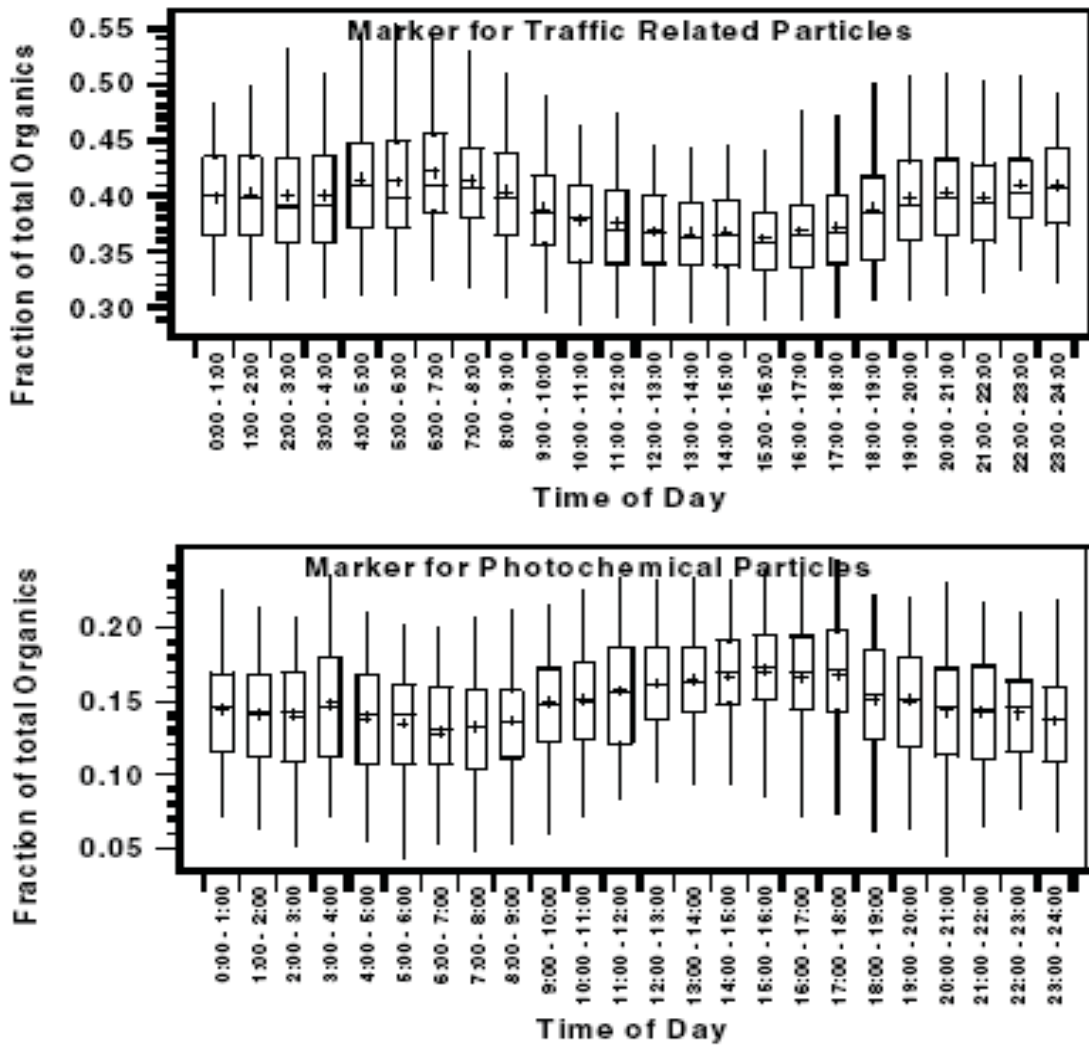

Figure 6. Average diurnal patterns of the fraction of organic particles, identified as markers for traffic aerosol and for photochemical aerosol. Unlike the diurnal pattern of the total organic mass concentration, these fractions both show a distinct diurnal pattern.

2.3 Co-Pollutants

Particulate matter results from both primary emissions of particles and secondary particle formation resulting from photochemical reaction or condensation of precursor gases such as SO_2. New York State is located downwind of major SO_2 sources in the Midwest and frequently receives transported SO_2 and aerosols containing sulfate (SO_4). Conversion of gaseous SO_2 to aerosol sulfate occurs during transport via a photochemical reaction. Figure 7 shows mean monthly SO_2 and sulfate concentrations measured in Manhattan (Bari et al., 2003). The SO_2 and sulfate show opposite seasonal patterns. The concentration of SO_2 is more than a factor of 2 higher in winter than in summer, while sulfate is approximately twice as high in summer as in winter. Bari et al. (2003) attribute the higher concentration of sulfate in summer to the increased rate of photochemical oxidation of SO_2 and to longer periods of meteorological stagnation in summer, allowing more time for reaction. The sum of gaseous SO_2 and particulate sulfate (in ppb) shows a maximum in winter. This may be due to increased SO_2 emissions from space heating in New York City or to meteorological conditions favoring lower mixing heights. Bari et al. also compared the percentage of total sulfur present as sulfate for each month (Figure 7b). The sulfate fraction is much higher in summer (19%) compared to winter (5-7%).

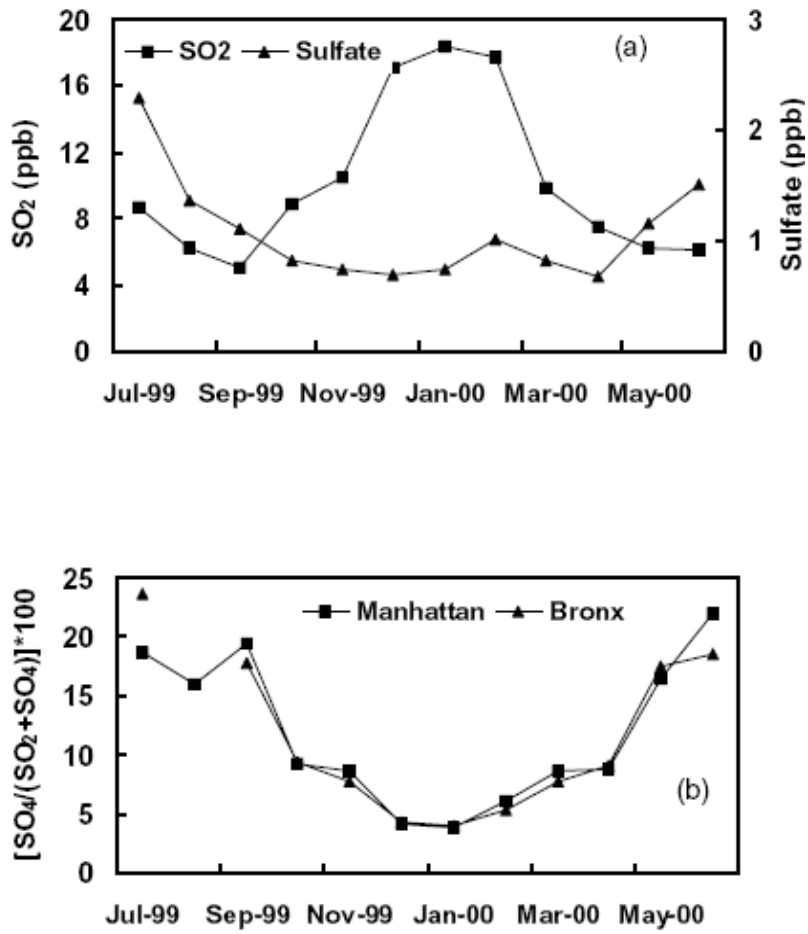

Figure 7. (a) Monthly mean concentration of SO_2 and sulfate; and (b) Monthly mean percentage of total sulfur present as sulfate.

The diurnal pattern for SO_2 (Figure 8) from two years of hourly data collected in Manhattan and at the Bronx shows an increase beginning at about 4 a.m. and peaking at 7 a.m., returning to overnight levels by noon. This pattern is the same for both locations, although SO_2 concentrations are slightly higher in Manhattan than at the Bronx location. This pattern likely reflects morning rush hour, increased use of home heating oil for domestic hot water and space heating, and atmospheric mixing from aloft.

<u>*Supporting EMEP Projects:*</u>
Enhanced Measurements of Oxidants, Fine Particles and their Precursors, Kenneth Demerjian et al., No. 4918

Fine Particle Constituents and Acute Asthma in Urban Areas, Daniel Luttinger et al., No. 6484

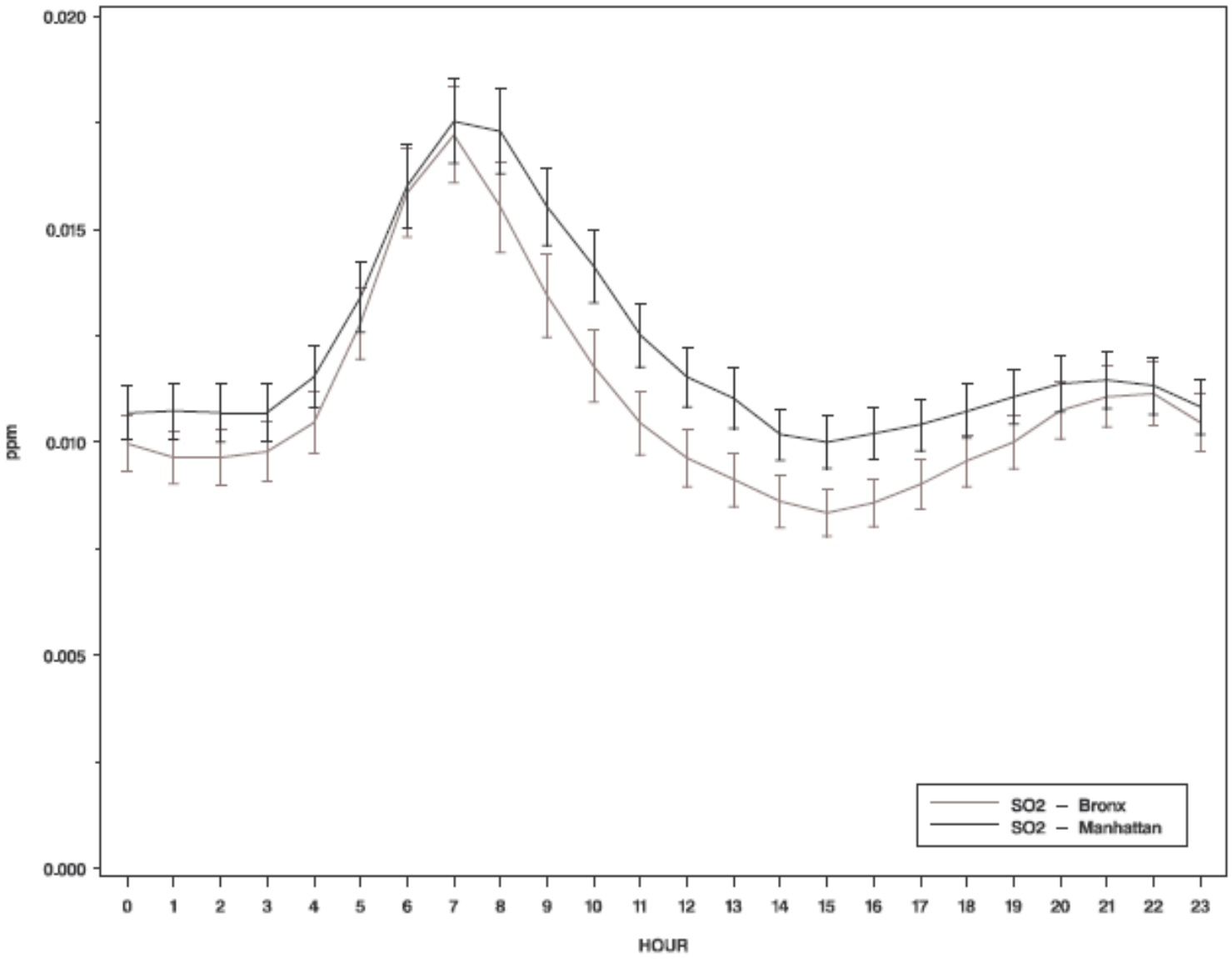

Figure 8. Averages by hour of day for sulfur dioxide. (Luttinger et al.)

3. What are the source regions and source types contributing to PM2.5 in New York?

Considerable effort has gone into understanding where the $PM_{2.5}$ components come from. The techniques described below range from sector analysis of mass concentrations with air trajectories to sophisticated source-apportionment modeling, to ambient real-time photochemistry intensives. Some methods can determine source types by markers, such as those from motor vehicles, soil, and sea salt, but cannot determine the source region. Other methods can identify whether components are of local origin or transported from a greater distance, but these methods have more difficulty identifying exact source types.

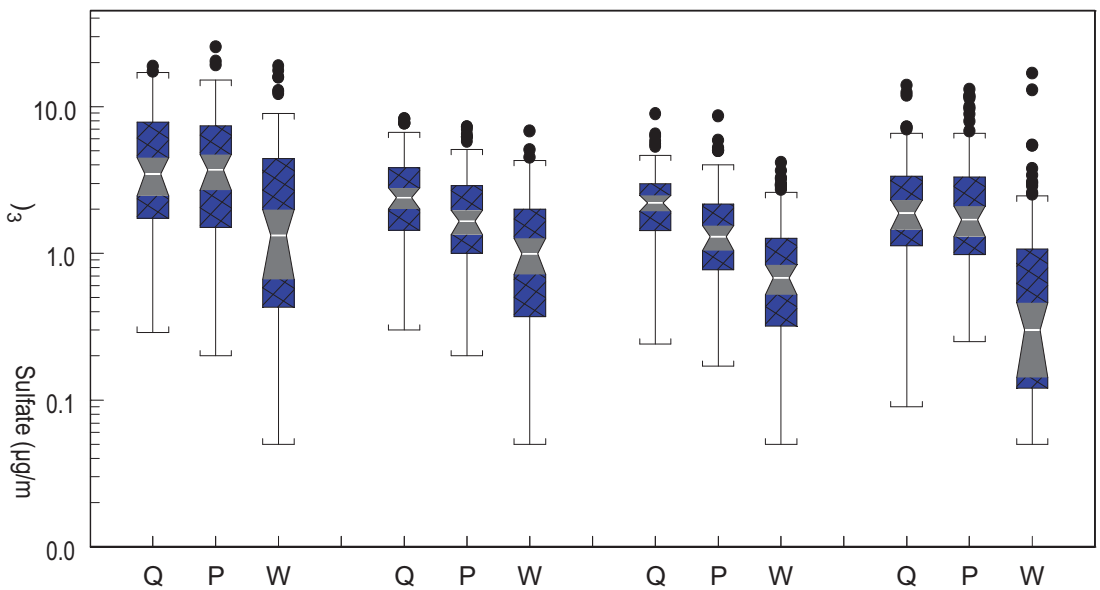

Figure 9. Box plots of daily sulfate at Queens, Pinnacle State Park, and Whiteface Mountain for quarters starting in the third quarter of 2001.

3.1 Local versus Transported Components

In order to develop effective air quality plans, it is necessary to know whether PM is transported from within a region or from a distant source. The Northeast is affected by local sources as well as transported aerosols and precursor gases from upwind sites in the Midwest. In summer, when winds are primarily from the west and southwest, SO_2 and $PM_{2.5}$ are transported into New York State.

Figure 9 shows box plots of the quarterly statistics of daily sulfate measurements at Whiteface Mountain, Pinnacle State Park, and Queens College (Dutkiewicz et al., 2004). Whiteface Mountain and Pinnacle State Park are in rural areas with few local sources. Conversely, the Queens site is in an urban location with many local sources. Although the sites are separated geographically, the concentrations of sulfate are similar due to long-range transport of aerosols impacting all three sites similarly.

Figure 10a shows a radial plot of sulfate as a function of the 12-sector directions superimposed on a map of the Northeast. Figure 10b is the same, but normalized to the frequency of the air masses and expressed as a percent. The radial plots illustrate the importance of source regions to the west and southwest. The highest sulfate at all three sites is focused toward the Ohio River Valley and the area around the Great Lakes. Moderately high concentrations at Pinnacle and Queens are also associated with air flow through the Mid-Atlantic states.

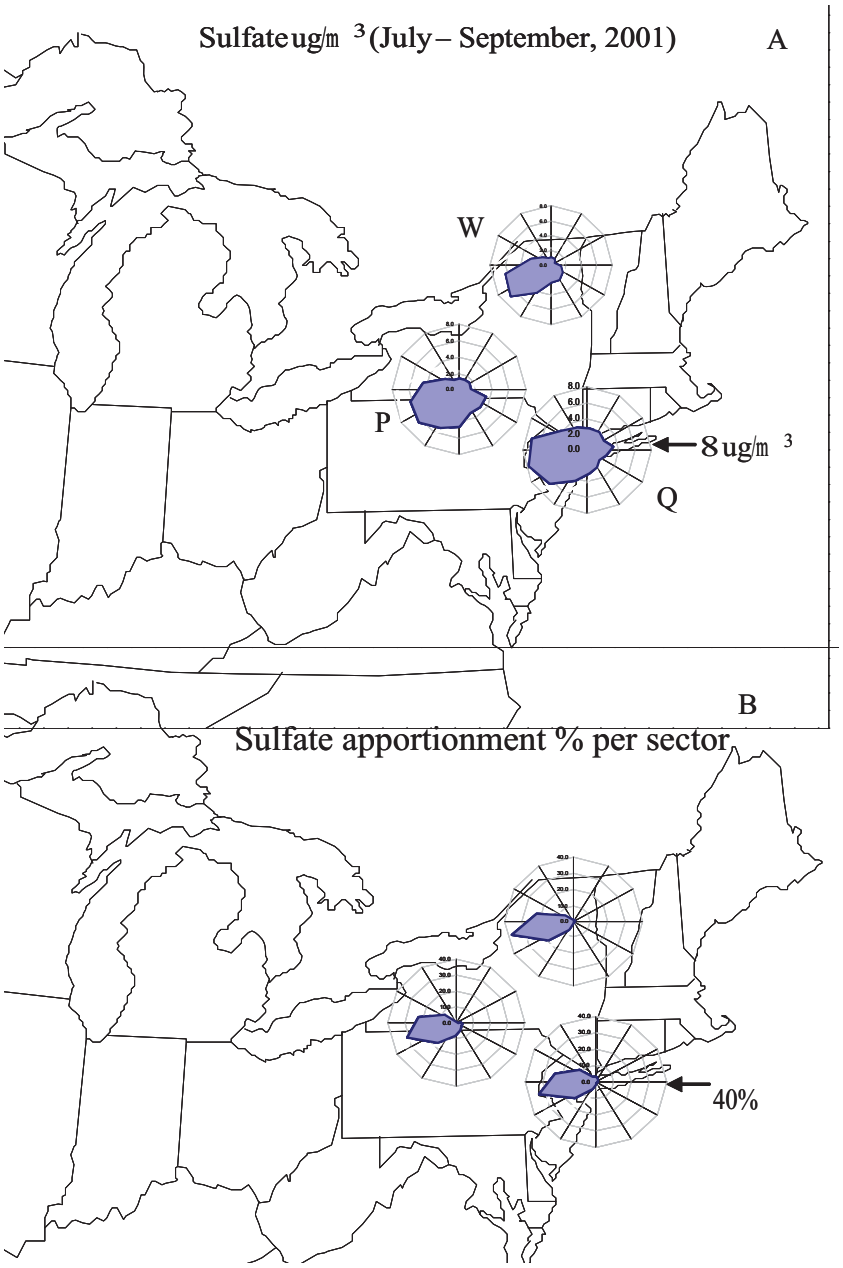

Figure 10. Radial plots of sulfate.

Bari et al. (2003) also used sector analysis to evaluate local and transported contributions to NYC aerosols at the Manhattan and Bronx sampling sites. In this method, "local" sources were considered to be those within 150 km of the sampling site. Sectors 12 through 4 on a clock, including any sources due north, in New England, and on Long Island, were assumed to be the background values. Because of this, local values should be considered as upper estimates. For all seasons, the majority of the transported component was from the Midwest. They found that 30% of annual $PM_{2.5}$ was transported to NYC from outside. The largest amount of transport occurred during summer. In addition, the annual amount of SO_4 transported from the Midwest was 43%, with the remaining 57% found to be of local origin. Conversely, they found that only 14% of SO_2 was transported into NYC, with 86% due to local sources (Figure 11).

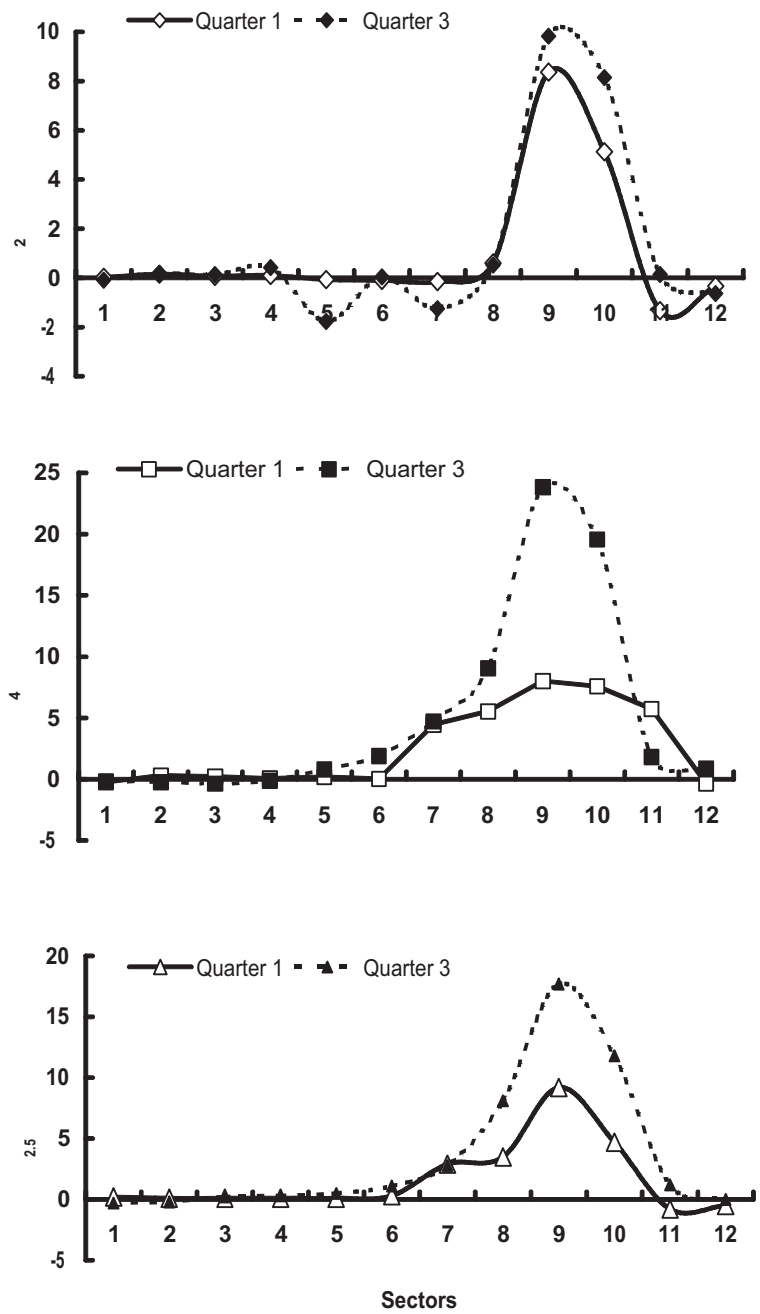

Figure 11. Quarterly transported component (%) after subtracting background for SO_4, SO_2, and $PM_{2.5}$ at Manhattan during first and third quarter 1999.

Dutkiewicz et al. (2004) evaluated the local versus transported components to New York City using the sector analysis approach, as well. Using data from Queens College (Supersite 2001-2002), the Bronx, and Manhattan (DOH, 1999-2000), they found sulfate concentration measured at the three sites to be highest when the wind was from the Midwest, and the effect was largest in summer. The same pattern for all three sites indicates a large effect from transported SO_4 (Figure 12). By separating the Queens data into warm and cold seasons, they estimated the local sulfate component in $PM_{2.5}$ to be 1.75 ug/m^3 during the cold season and 2.4 ug/m^3 during the warm season.

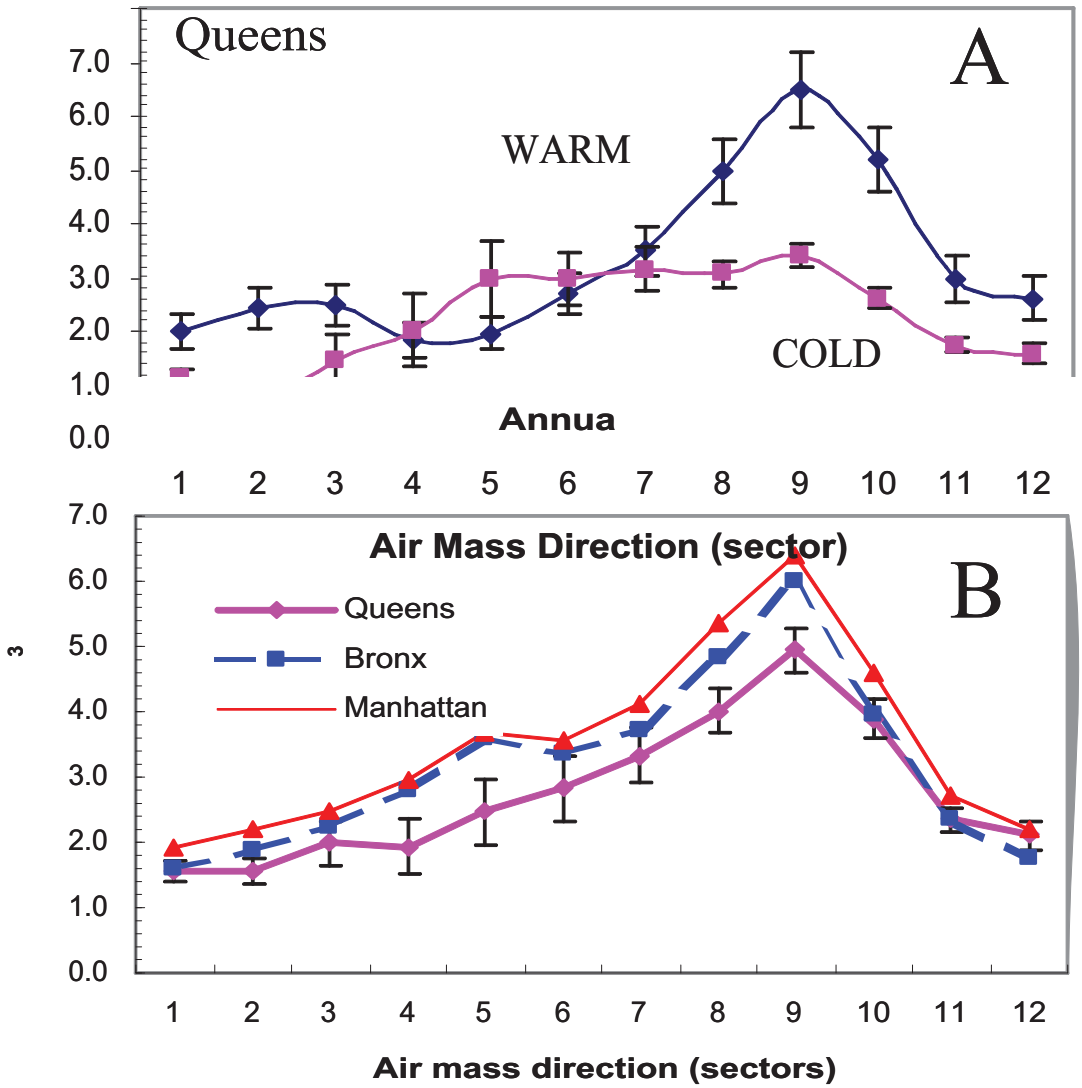

Figure 12. Top: Sulfate concentrations versus 12 sector directions for Queens in warm and cold (Oct.-Mar.) periods. Bottom: Annual sulfate concentrations versus the 12 sector directions for Queens, Manhattan, and Bronx. (Dutkiewicz et al., 2004)

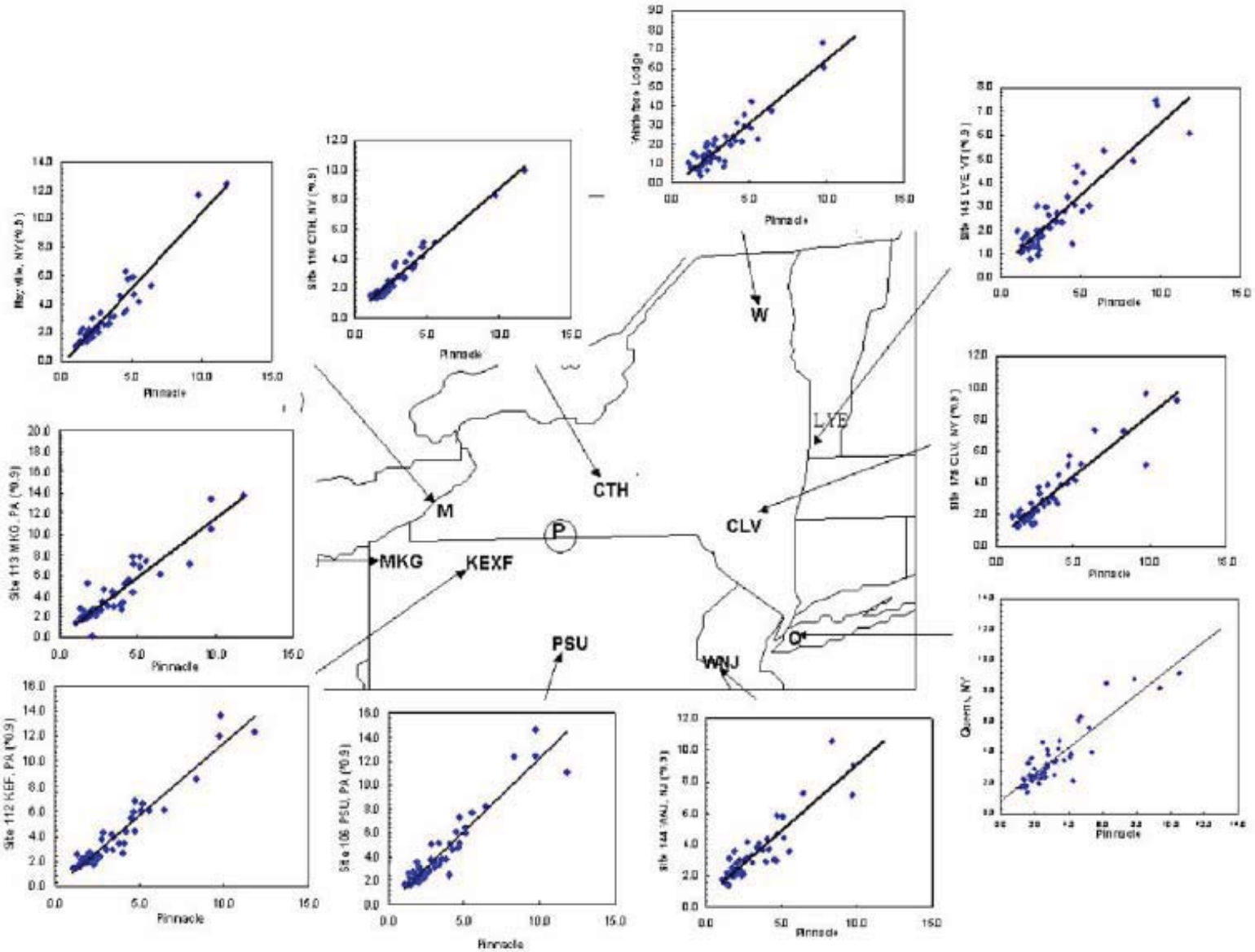

Figure 13. Scatter plots of weekly sulfate at each site versus concentrations at Pinnacle over the period July 2001 through June 2002. Lines are the result of linear regression fits to the data.

Dutkiewicz et al. (2004) determined local and transported sulfate using an alternative approach as well. Figure 13 shows scatter plots of sulfate measured in week-long CASTNet samples from 10 sites in and around New York State relative to sulfate measured at Pinnacle. The slopes of the sites west (upwind) of Pinnacle are greater than 1.0, indicating that they have a greater regional sulfate component than Pinnacle. Their intercept is close to zero, suggesting that their local sulfate is similar to Pinnacle. All of the sites east (downwind) of Pinnacle have slopes less than 1. This is consistent with a smaller regional sulfate component. The intercepts differ from site to site due to the local sulfate component. The lowest is at Claryville, NY (0.46), and the highest is in Queens (0.84), suggesting that the local sulfate component for Queens is 0.84 relative to that at Pinnacle. Adding this to the 0.8 ug/m^3 determined for Pinnacle based on air-mass trajectories yields a local sulfate concentration of 1.6 ug/m^3. This is comparable to the local background determined for Queens in the cold season (1.8 ug/m^3) but not for the warm season (2.4ug/m^3).

The nearest site to Queens is at Washington Crossing, NJ. This agricultural-urban site is in western NJ, 100 km southwest of Queens. The slope is similar to that for Queens, but the intercept is slightly lower at 0.64 ug/m^3. This local sulfate also affects the upwind Queens site.

Qin et al. (in press) also investigated local versus transported components of $PM_{2.5}$ in NYC. They used 2002–2003 Speciation Trends Network (STN) data for four urban sites: Elizabeth, NJ, the New York Botanical Gardens in the Bronx, IS52 in the Bronx, and Queens College. Comparison of the major $PM_{2.5}$ components were in good agreement, which is understandable since the $PM_{2.5}$ measured in NYC should have some common sources. The $PM_{2.5}$ at Chester, NJ, was reasonably well correlated with the NYC sites as well. Chester, NJ, approximately 100 km upwind of NYC, was selected as a background site. They found that 69-82% of PM $_{2.5}$ may be transported to New York City, with 18-31% from local sources. They also found that 93-100% of sulfate was transported, 54 to 65% of nitrate was transported, and 71-86% of NH_4^+ was transported.

Lall and Thurston (2005) used Sterling Forest, NY, a site 50 miles northwest of NYC, as a background site for the Hunter College site in Lower Manhattan. Using positive matrix factorization (PMF), they found that transported aerosols contributed more than 40% of the total $PM_{2.5}$ measured at Hunter College. In addition, more than 80% of the New York City sulfate mass and 30% of the OC was transported from outside. Conversely, the EC fraction in Manhattan is almost completely local (more than 90% of local origin).

Demerjian et al. (2005) estimated summer PM sulfate photochemical production using ambient measurements and reaction kinetics (OH + SO_2), which indicated a mean production rate of 0.14 ug/m^3/h, or 3.38 ug/m^3/day. These results indicate that 15-60% of observed PM sulfate at Queens College in July 2001 could have been generated by photochemical oxidation processes and was most likely of local origin.

Summary of Local versus Transported Components

A summary of the percent of transported $PM_{2.5}$ and aerosol sulfate is given in Table 1. The sulfate values range from approximately 40-100%. Those studies of seasonal transport found that 48-85% of sulfate was transported into New York City during summer. During winter, this value was lower, at 39-79%. The wide range of values is due to the various approaches taken in interpreting the aerosol measurement data. A careful analysis of these results and associated assumptions is necessary in order to apply findings to policy formulation.

The lowest values were determined using sector analysis. In this approach, sectors to the north and east (sectors 12-4) were assumed to be background. The observed SO_4 from these regions was subtracted from that measured in the other sectors to determine the transported component. Because this approach does not account for SO_2 sources in New England and Long Island, it minimizes the transported component. In addition, due to the six-hour trajectories used, this method assumed that all sources within 160 km were local.

In contrast, the methods that determined a higher percent of transported aerosols subtracted the sulfate measured at sites upwind, either Chester, NJ, or Sterling Forest, NY. These sites are 100 km and 80 km from New York City, respectively, well within the 160-km local radius used in the sector analysis. While they are frequently upwind sites, there may be times when they are affected by regional stagnation events and urban pollution to the east. These methods probably overestimate the amount of transported sulfate.

Despite the range of values, all of these studies suggest that a large fraction of aerosol sulfate and $PM_{2.5}$ in New York City is not from local sources and not under the control of New York State air-quality planners.

Table 1. EMEP estimates of $PM_{2.5}$ and sulfate transported into New York City.

Method Used	Estimated percent of PM2.5 transported into NYC(%)	Estimated percent of PM sulfate transported into NYC(%)	Citation
Sector analysis (local is within 160 km)	31 %	44-45 % annual	Bari et al. (2003)
Correlation of sites in northeast and sector analysis	--	48-65 % summer 39-44 % winter	Dutkiewicz et al. (2004)
Photochemical experiments	--	>50 %	Demerjian et al
Subtraction of upwind site and (Sterling Forest)	56 % summer 33 % winter	85 % summer 79 % winter	Lall and Thurston in press
Subtraction of upwind site (Chester)	69-82%	93-100 %	Qin et al. In press

<u>*Supporting EMEP Projects:*</u>
Enhanced Measurements of Oxidants, Fine Particles and their Precursors, Kenneth Demerjian et al., No. 4918

Fine Particle Constituents and Acute Asthma in Urban Areas, Daniel Luttinger et al., No. 6484

Analysis of PM Data in NY Using Advanced Source Apportionment Methods, Philip Hopke et al., No. 7919

Source Apportionment of Fine Particles in New York City, George Thurston et al., No. 6084

3.2 Identification of Source Types

Knowing whether important components of $PM_{2.5}$ are local or distant is only part of the information needed to develop air-quality management strategies. Knowing which source types are important and their relative contributions is also necessary.

New York City

Li et al. (2004) used the six-hour $PM_{2.5}$ data for SO_4 and trace metals; 10-minute aerosol mass spectrometer data for NO_3, NH_4, Cl, and OC; and 15-minute data for Na and K collected during the July 2001 intensive at the Queens College site to identify contributing sources by PMF. These sources and their relative contributions are summarized in Table 2.

Table 2. $PM_{2.5}$ sources identified at Queens College during July 2001 and relative contribution to PM mass determined by source apportionment analysis (Li et al., 2004).

Factor	Source	Major Constituents	Average Mass (ug/m3)	% Contribution to Total Mass
1	Secondary sulfate	SO_4, some OC	7.63	47
2	Secondary nitrate	NO3, some OC	1.28	8
3	Motor vehicles	OC, Zn, Pb	0.52	3
4	Road dust	Al, Ca, Fe, K	4.13	25
5	Sea salt	Cl, Na	1.73	11
6	Oil combustion	Ni, V	1.08	6

By far the largest contributor to $PM_{2.5}$ mass was secondary sulfate, contributing approximately 50% of the total. Road dust was next, comprising approximately 25% of the $PM_{2.5}$. However, due to an irregular pattern during the last two weeks of sampling, the authors suggest that this may have been affected by local construction activities.

Upstate New York

Some techniques can combine meteorology and aerosol data to give a better understanding of source locations. Aerosol data collected at Potsdam and Stockton during the summers of 2000 and 2001 include $PM_{2.5}$, BC, trace elements, and PAHs. The data were analyzed by PMF to identify possible source types (Liu et al., 2003). Six sources were identified as common to both sites: secondary sulfate, secondary nitrate, soil, wood smoke, zinc smelter, and copper smelter. A nickel smelter was also identified as a source for $PM_{2.5}$ at Potsdam (Figure 14). The results were also combined with potential source contribution function (PSCF) modeling, which includes air mass trajectories, to identify likely source regions. Results showed the Ohio River Valley to be the source region for secondary sulfate and secondary nitrate. The soil source region identified was the agricultural area in Ohio. Wood smoke was from the Great Lakes region. A copper source was located in Ontario, a zinc smelter was identified in Quebec, and nickel smelter sources were likely from Ontario and Quebec. Zhou et al. (2004) used the PMF results (Liu et al., 2003) to determine sources by two additional models: residence-time weighted concentrations (RTWC) and quantitative transport bias analysis (QTBA). The results of the methods were consistent with each other and located clearly defined sources well. As in the Liu et al. study (2003), the Midwest was identified as the potential source area for secondary sulfate.

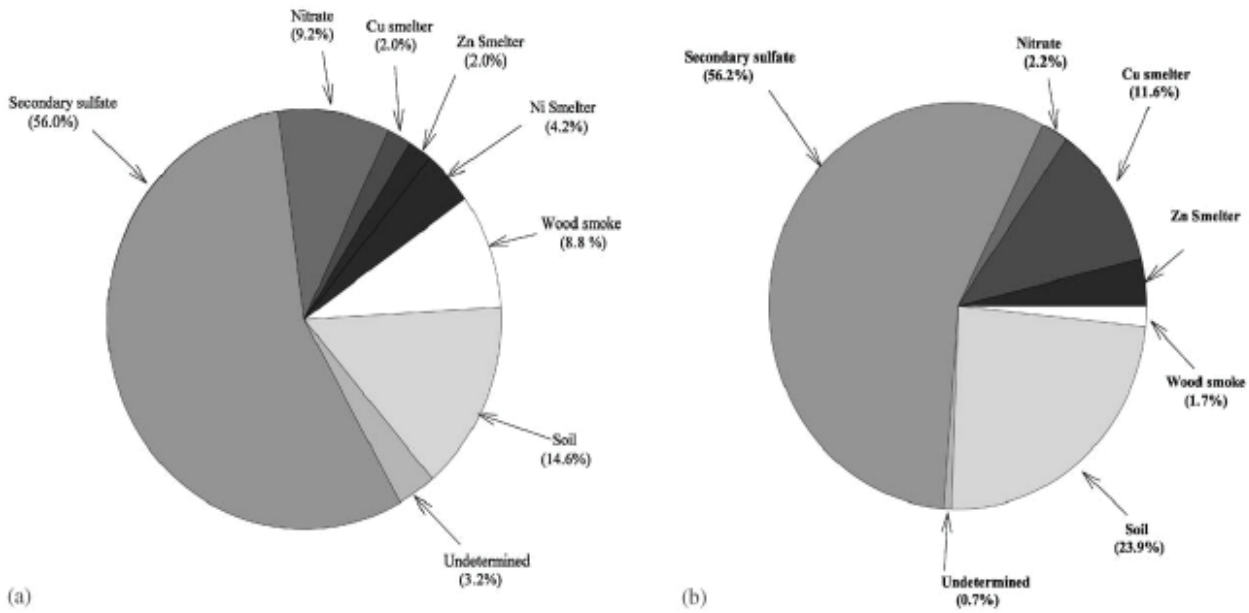

Figure 14. Source apportionment at Potsdam and Stockton. (Liu et al.)

Qin et al. (2005b) used data from four speciation trend network sites in the NYC metropolitan region and analyzed it by PMF to identify secondary sulfate, secondary nitrate, soil dust, aged sea salt, oil combustion, spark ignition, highway vehicle, and diesel as contributing to NYC aerosol (Table 3). A comparison of these findings to the EPA Emissions Inventory for primary $PM_{2.5}$ reveals some discrepancies. For example, the $PM_{2.5}$ source apportionment analysis did not identify a contribution from wood combustion, while it is estimated by the EPA Emissions Inventory to be 17% of primary PM emissions. This analysis also found soil to contribute 6-11% of the $PM_{2.5}$ in NYC, whereas the Emissions Inventory estimates 38-57% of primary $PM_{2.5}$ from fugitive dust. In addition, coal was not identified explicitly, but it is probably included in the secondary sulfate source. The receptor modeling analysis indicates that motor vehicle exhaust is a greater contributor to $PM_{2.5}$ (8-22%) than in the Emissions Inventory estimates. Finally, oil combustion was determined to contribute 4-11% of $PM_{2.5}$, much higher than the EPA Emissions Inventory estimate of 1.3-1.5%. A comparison is given in Table 3.

Table 3. Comparison of source apportionment identification of sources in NYC to those primary emissions in the EPA Emissions Inventory (adapted from Qin et al., in press).

Source Type	NYC Sites % of Total Mass Contribution by Source Category	EPA Emissions Inventory % of Total Mass
soil	6-11	38-57
oil combustion	4-11	1.3-1.5
spark ignition	8-22	3.9-5.3
diesel	approx. 3	approx. 14*
sea salt	3-7	3-5
wood burning	not identified	18

* combines both on-road and non-road

Hopke et al. (preliminary results) have also determined sources of $PM_{2.5}$ using PMF at Rochester, Buffalo, Pinnacle State Park, and Whiteface Mountain using 1-in-3- or 1-in-6-day data from STN or IMPROVE networks. The results are given in Table 4. At each location, secondary sulfate is the major contributor to $PM_{2.5}$, ranging from 36-58%.

Table 4. Average source contributions to $PM_{2.5}$ mass concentration determined by PMF source apportionment at Buffalo, Rochester, Pinnacle, and Whiteface Mountain, NY in ug/m3 and (%).

Sources	Buffalo	Rochester	Pinnacle	Whiteface Mountain
secondary sulfate	5.16 (36.1)	5.44 (43.8)	6.22 (58.2)	4.29 (53.4)
secondary nitrate	2.12 (14.8)	2.59 (20.8)	0.91 (8.5)	0.55 (6.8)
gasoline vehicle	2.76 (19.3)	1.64 (13.2)	1.81 (17.0)	1.55 (19.3)
highway/industry	1.60 (11.2)	--	--	0.47 (5.9)
road salt/sea salt	0.79 (5.5)	0.87 (7.0)	0.51 (4.8)	0.59 (7.3)
diesel emissions	0.68 (4.8)	1.37 (11.1)	0.57 (5.3)	0.35 (4.4)
highway/railroad	0.64 (4.5)	--	--	--
airborne soil	0.54 (3.8)	0.50 (4.0)	0.29 (2.7)	0.24 (3.0)
metal processing	--	--	0.37 (3.5)	--

Supporting EMEP Projects:
Enhanced Measurements of Oxidants, Fine Particles and their Precursors, Kenneth Demerjian et al., No. 4918

Analysis of PM Data in NY Using Advanced Source Apportionment Methods, Philip Hopke et al., No. 7919

Impact of In- and Out-of-State Power Plants on Semivolatile Pollutants in New York State, Philip Hopke et al., No. 6083.

3.3 Organic Components and Source Identification

The organic fraction of $PM_{2.5}$ in NYC is a substantial fraction (Figure 2), contributing 28% of the mass. This fraction is composed of many different compounds, only 15% of which have been identified (NARSTO, 2003). Identifying the various organic classes will be essential to determining sources and subsequent changes in the atmosphere. There is both a primary and secondary organic particle contribution.

Demerjian et al. (2005) compared OC:EC ratios by day of the week and found a higher ratio on the weekend on Canal Street (a major diesel truck route) due to decreased diesel traffic on the weekend. This was not observed at the Queens College site.

A study of the composition of the organic fraction in aerosols is being performed by Mazurek et al. using samples collected in and around New York City. The sites represent upwind and downwind sites as well as urban and rural sites. They were collected as part of the Speciation of Organics for Source Apportionment of $PM_{2.5}$ in the New York City Area (SOAP) project. This analysis identifies mass concentrations for 63 organic molecular marker compounds that will be used in new modeling for source apportionment. The findings for markers of motor vehicles, cooking oil, and photochemical oxidation products are given in Table 5.

Table 5. Preliminary results of organic marker spatial variability in the New York Metropolitan region.

Source Type	Marker	Spatial Variability	Seasonal Variation
motor vehicles	hopanes	highest in urban, lowest in rural	--
cooking oil	n-alkanoic acids C10-C30	highest in urban areas	highest in winter
photochemical oxidation product	C2-C10 diacids	highest in urban areas	highest spring and summer

The project results will be used in a chemical mass balance modeling effort with the EPA National Exposure Research Laboratory. However, initial model results indicate that more work is needed to improve the emissions inventory of fine PM in the NYC airshed, especially with respect to commercial and domestic food cooking.

As detailed in the recent NARSTO Emissions Inventory Assessment (NARSTO, 2005), there is a great need for more detailed inventories including fine particulates and their precursors. This study was able to identify three large classes of molecular markers.

<u>*Supporting EMEP Projects:*</u>
Enhanced Measurements of Oxidants, Fine Particles and their Precursors, Kenneth Demerjian et al., No. 4918

Chemical Composition of Fine Organic Particles from Urban Regional Background Locations in New York State, Monica Mazurek, No. 7616

3.4 Particle Size and Source Identification

Beyond total mass, the physical size of particles is important. Size determines whether a particle will settle out of the air or remain suspended. Size also gives important information about atmospheric processing and source types.

Hopke et al.(2005) measured particle number concentrations and size distributions in Rochester, NY, during 2002 (Figure 15). The Rochester ultrafine particulate data set is one of the longest records in the U.S. The smallest ultrafine particles (UFPs), from 11 to 50 nm, accounted for 70% of the total number concentration. The particles in the range of 50 to 100 nm accounted for approximately 20%. Hopke et al.(2005) found that the mean number concentration in winter months tended to be higher than values in summer. In addition, diurnal patterns emerged. Particles in the range of 11 to 50 nm typically had two peaks, one at about 8 a.m. that was associated with CO in the winter. The emissions were likely directly emitted from vehicles during the morning rush hour.

Nucleation and Growth

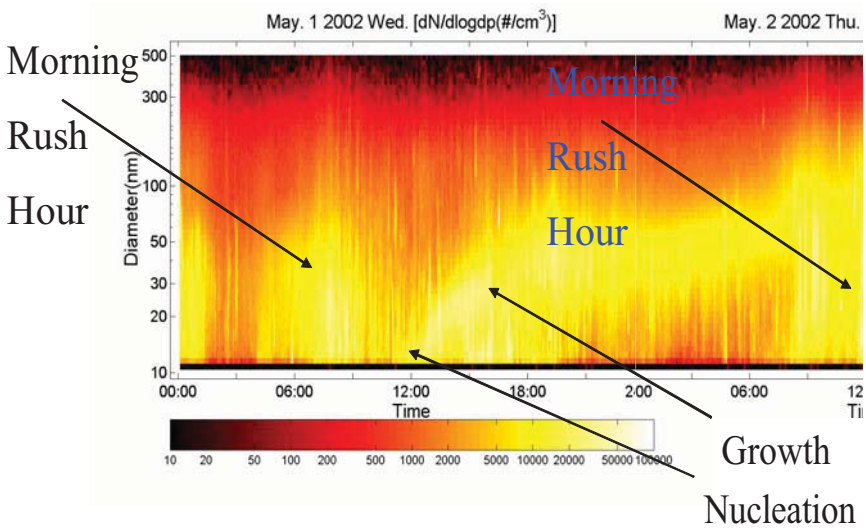

Figure 15. Particle number concentration and size distribution, Rochester, NY. (Hopke et al., 2005)

The second peak was between noon and 6 p.m. and was associated with nucleation events, which had a sharp increase of particles in the 11 to 50 nm range. This was most often observed in spring and summer, when photochemical activity is at its peak. In addition, peaks of SO_2 were observed during the nucleation events when the wind direction was from the northwest, where large local SO_2 emission sources are located. A subsequent study at this site (Jeong et al., 2006) also observed regional nucleation events. Ogulei et al. (in press) used receptor modeling to identify source types contributing to air quality in Rochester, NY. Using particle number concentrations, gaseous species, and meteorological variables, they identified ten different sources during three different seasons (Figure 16). Using this approach they were able to identify residential/commercial heating separately from other sources, such as diesel trucks. This is a significant advancement over other source apportionment techniques.

Particle counting and sizing measurements in the Supersite program showed little evidence of nucleation events in Queens, NY, suggesting preferential condensation of secondary semi-volatile products on existing aerosol surfaces. Only under very clean urban and rural aerosol background conditions, such as at Whiteface Mountain, was there some evidence of possible nucleation.

Drewnick et al. (2004) measured chemically speciated mass distributions during summer 2001 at Queens College. They found ammonium, nitrate, and sulfate particles consist primarily of a single mode at 400, 439, and 477 nm, respectively. In contrast, the organic particles typically had two modes (78 and 359 nm). The similar results for nitrate and sulfate indicate that they are internally mixed. In addition, this is supported by similar distributions even during hourly averages. The lower mode for ammonium indicates that it is associated not only with nitrate and sulfate particles but also with organic particles.

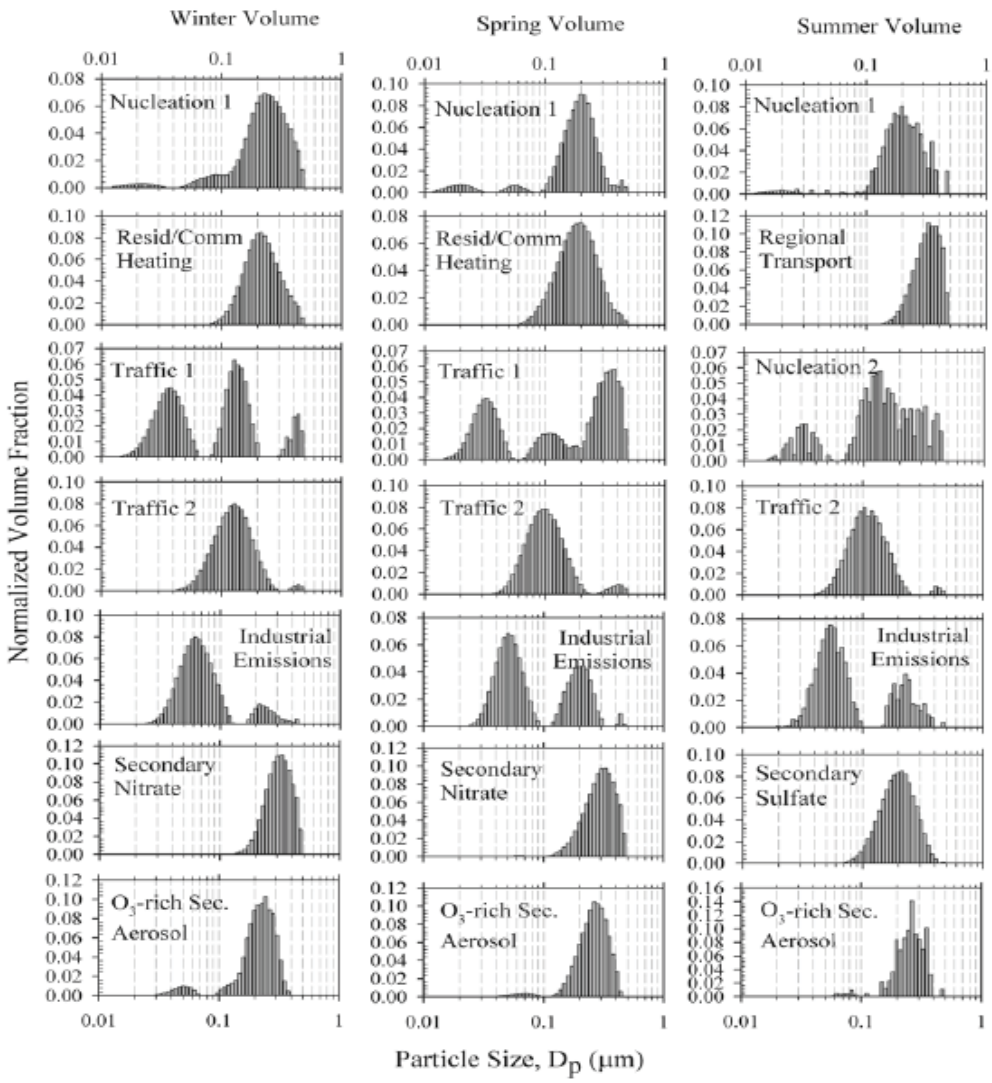

Figure 16. Particle volume profiles of resolved sources.

The organic-particle size distributions are substantially different. The accumulation mode diameter peak occurs at a significantly smaller particle diameter than nitrate, sulfate, and ammonium. In addition, during almost all time intervals, a smaller diameter mode is observed. This small mode and the relatively small diameter of the accumulation mode are indicative of relatively young aerosol, locally produced by the high volume of traffic in the area of the measurement site. This traffic-related organic aerosol is not internally mixed with the more aged ammonium sulfate and ammonium nitrate aerosol.

Research by Demerjian et al. (briefing) observed a seasonal variation in particle size. Figure 17 compares the summer and winter composition of UFP for measurements made in summer 2001 and winter 2004 at Queens College. In winter, there are smaller mean modes (200 nm), and the UFP bimodal distribution is masked. Once again, the organics are in greater abundance, but in winter the nitrate increases and is greater than the sulfate.

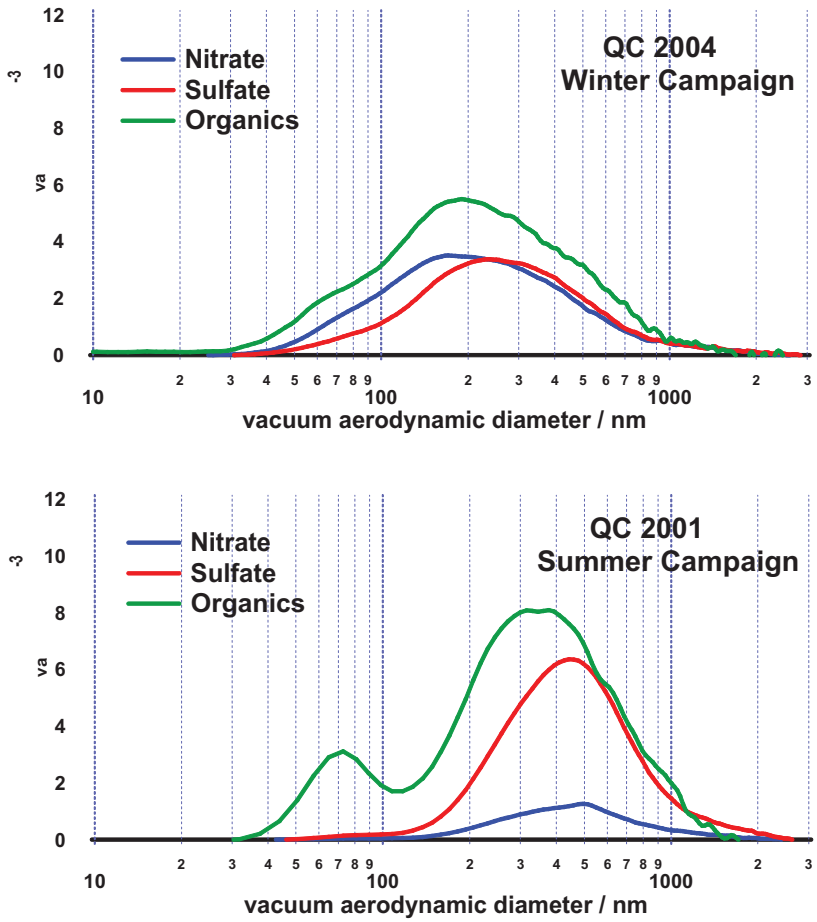

Figure 17. Summer and winter composition of UFP particle by size.

Diurnal patterns of size distributions of nitrate, sulfate, and organic PM were calculated by averaging all size distributions measured over each specific hour of the day (1:00, 7:00, 13:00, and 19:00) during the summer campaign (Figure 18; Drewnick et al., 2004). Diurnal patterns for sulfate, nitrate, and organic particle size distributions show little change of mode during the day, suggesting that most of this aerosol mass is transported to the measurement site from a different region. The most significant pattern was found in the small particle mode (less than 120 nm). This fraction showed a large maximum during the morning

rush hour, when the most traffic was experienced on the highways around the site. Smaller maxima were observed for the afternoon and evening traffic. These results suggest that the appearance of the intense small-particle mode in the size distribution of the organic particles is caused by heavy traffic on the highways.

Demerjian et al. (2005) further investigated summertime secondary organic aerosol (SOA) as a function of oxidant season. Estimates of photochemical production of SOA from direct measurement of OH and VOC are consistent with estimates from aerosol mass spectrometer analyses that attribute organic carbon $PM_{2.5}$ to hydrocarbon-based organic aerosol (HOA) and oxidized organic aerosol (OOA) species. The estimates suggest summertime contributions of SOA production from photochemical reactions in Queens can account for 40% of the observed organic carbon PM. Determining how much of the VOCs are of biogenic or anthropogenic origin will be important for estimating benefits of VOC controls such as diesel particulate filters. It also illustrates that reducing photochemical oxidants in general is important, not just with respect to ozone production but secondary PM formation as well, and that a multi-pollutant approach is needed in air-quality management considerations.

Supporting EMEP Projects:
Enhanced Measurements of Oxidants, Fine Particles and their Precursors, Kenneth Demerjian et al., No. 4918

Monitoring Particle Size Distribution in Rochester, Philip Hopke et al., No. 6820

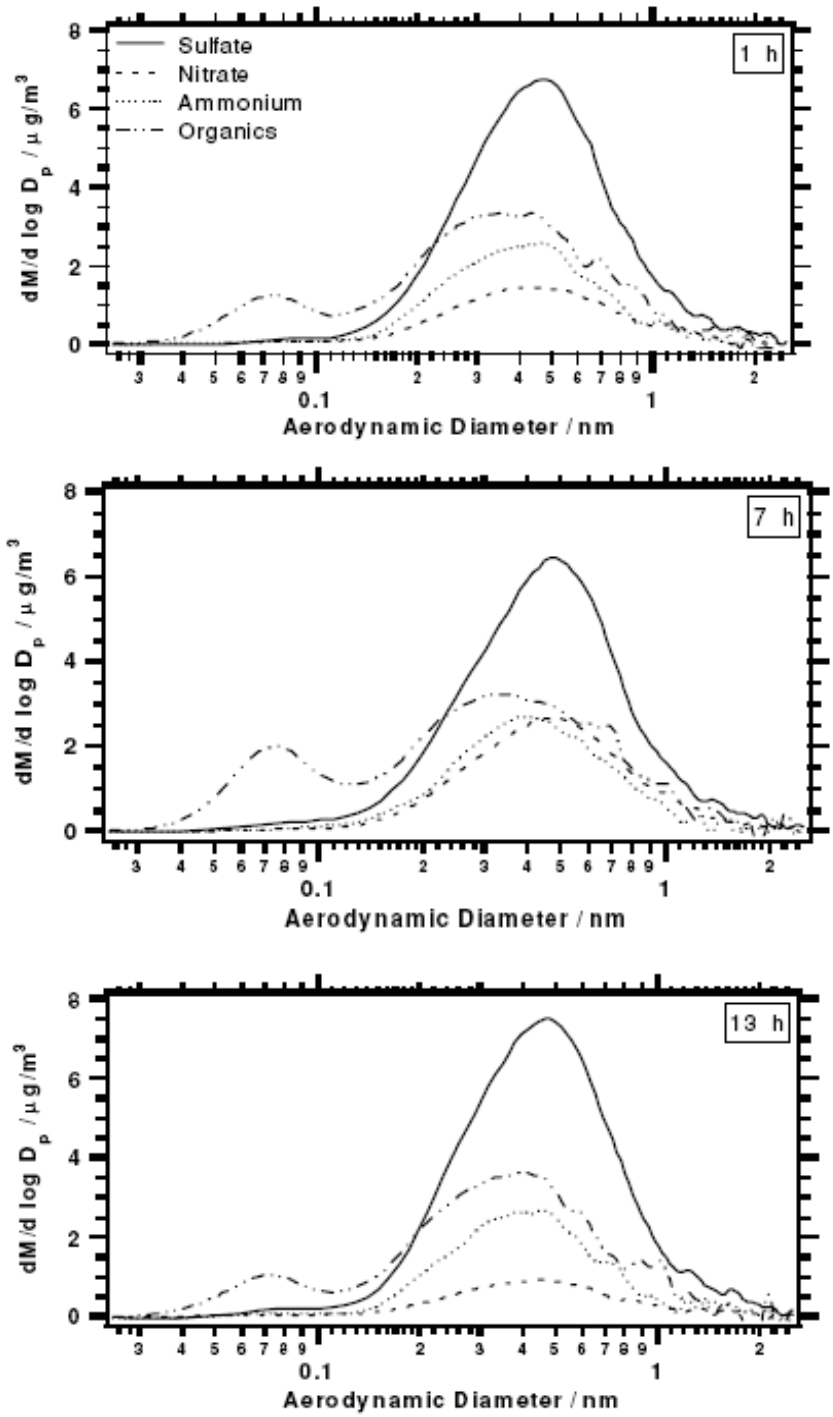

Figure 18. Diurnal patterns of the size distributions of sulfate, nitrate, and organics.

4. Are there specific components in the $PM_{2.5}$/co-pollutant complex causing adverse health effects?

Epidemiological studies have found associations between increasing PM mass concentrations and respiratory symptoms, respiratory and cardiovascular disease, and mortality. The National Ambient Air Quality Standard for PM is mass-based. The U.S. EPA has five PM Health Centers investigating the mechanisms by which PM causes adverse effects on human health. Among the hypotheses being tested are those focusing on particle size or composition. Larger particles can be removed in the nose, whereas smaller particles can travel deeper into the lungs. In addition, it is possible that PM components with different chemical composition have varying health effects. The bulk of the EMEP investment in health effects research has focused on exploring the role of UFPs. This has leveraged significant investment by EPA in a PM Health Effects Center at Rochester.

4.1 Ultrafine Particles

Research by Utell et al. investigated the effects of inhaling ultrafine particles in healthy subjects as part of the $8 million U.S. EPA PM Health Center program at the University of Rochester Medical Center. The researchers developed a UFP-exposure system that generated carbon particles that were diluted by filtered air and breathed through a mouthpiece by healthy subjects. Ultrafine-particle deposition was determined by the difference in numbers of particles exhaled from those inhaled. In addition, blood components were measured to monitor inflammation. The results showed that there were high pulmonary deposition rates, which increased with exercise. The smallest particles had the highest deposition rate. Blood oxygen saturation decreased in females after exposure to 25 ug/m^3 UFPs. There were a number of cardiac effects in addition to pulmonary effects, including signs of alteration of cardiac repolarization.

While these changes were small, they could affect heart function in people with severe cardiac disease. The Rochester PM Health Center will continue to investigate the effects of UFPs by monitoring a sensitive population's response to changes in ambient UFP concentration. Seventy-five subjects will be recruited from a cardiac rehabilitation program. These subjects will not be exposed to carbon particles generated in the exposure system described above; rather, they will simply breathe ambient air. There will be UFP monitors measuring the UFP concentration in the rehabilitation center as well as in ambient air of the general region where participants live. Some additional in-car and in-home measurements will also be performed. Ultrafine particles in Rochester, NY, were characterized by Hopke et al. (NYSERDA publication 05-04, 2006) who found traffic, coal-fired power plants, nucleation of particles from precursors, and particle growth as important influences on UFP number concentration.

Supporting EMEP Projects:
Clinical Studies of Exposure to Ultrafine Particles, Mark Utell et al., No. 4913

Ultrafine Particles and Cardiac Responses: Evaluation in a Cardiac Rehabilitation Center, Mark Utell et al. No. 8650.

4.2 Source Apportionment and Health Effects

In May of 2003, NYSERDA sponsored the "Workshop on Source-Apportionment of PM Health Effects," with the objectives: 1) to ascertain if quantitative relationships can be observed between apportioned source contributions and human mortality using particle composition and mortality data from two different cities; and 2) to ascertain if different receptor modeling methods significantly affect the contribution/mortality relationships.

Seven research groups participated and used various methods to apportion the $PM_{2.5}$ mass samples from Washington, D.C., and Phoenix, AZ. The methods ranged from simple mass regressions to more intricate factor analysis methods (Thurston et al., 2005; Hopke et al., 2005). The apportionments were then evaluated for their associations with daily mortality for each city (Mar et al., 2006; Ito et al., 2006).

The source apportionments by the various groups identified the same major source types with similar key tracers. The results of mortality-to-source-apportionment comparisons indicated that between-source variation in relative risk was statistically significant, while between-analysis variation was not. This indicates that variations in research group and/or choice of source apportionment method had only a relatively small effect on variations in the cardiac mortality relative-risk estimates derived for these cities. Across the two cities, the most consistently associated $PM_{2.5}$ source category with adverse health effects was sulfate-associated mass.

Although further research is needed in defining tracer profiles for sources with less-well-defined compositional characteristics in order to allow more exact quantitative source-specific mass toxicity evaluations, these results provide substantiation that present-day $PM_{2.5}$ source apportionment methods can provide valuable insights into the source components that contribute to $PM_{2.5}$–health-effects associations.

Supporting EMEP Projects:
Workshop on Incorporation of Receptor Models into PM and Adverse Health Effects Study, Philip Hopke et al., No. 7607.

4.3 Asthma in New York City

The New York State Department of Health, along with the New York State Department of Environmental Conservation, undertook a two-year sampling campaign (January 1999 through November 2000) of certain hazardous air pollutants, criteria pollutants, and bioaerosols in two New York City neighborhoods, located only five miles apart. The neighborhoods have different rates of hospital admissions for asthma and different socioeconomic status characteristics. The study was to assess whether ambient air quality differed in the two New York City locations and to evaluate the effects of various air contaminants on exacerbation of acute asthma symptoms.

The statistical analyses comparing ambient air between the Bronx and Manhattan sites were conducted using a paired t-test adjusted for autocorrelation. Comparisons were made on a seasonal basis (quarterly) and for the entire study period. Mean levels of fine PM, particulate acidity, particulate sulfate, particulate nickel, acid gases, ammonia, sulfur dioxide, and nitrogen oxides were significantly higher in Manhattan than in the Bronx over the entire study period. Mean levels of ozone, ragweed pollen, and grass pollen were significantly higher in the Bronx. For the most part, even when there were differences in concentrations between the two sites, the differences were small, less than 1.6-fold.

Using emergency department (ED) visit data and air quality parameters described above, the magnitude of the relationship between daily asthma ED visits and air pollution and bioaerosol concentrations across the two communities were compared. In addition, lag dependency of the asthma response, age and sex stratification, and whether effects were evident for control outcomes (i.e., ED visits for causes not likely to be related to air quality) were explored. The Poisson regression analysis was used to test effects of 14 key air contaminants on daily ED visits with control for temporal cycles, temperature, and day-of-the-week effects. The core analysis utilized the average exposure for the 0- to 4-day lags. Sensitivity analyses examined different lag effects.

Mean daily rates for asthma ED visits were over 8-fold higher in the Bronx study area than in the Manhattan area. The reason for this was beyond the scope of this study. Concentrations of pollutants were generally similar in the two communities with mean levels slightly higher in Manhattan in most cases. Among the 14 key pollutants examined individually in regression analyses, five had statistically significant effects on asthma ED visits in the Bronx, including daily 8-hour maximum ozone, mean daily nitrogen dioxide (NO_2), sulfur dioxide (SO_2), $PM_{2.5}$, and maximum one-hour $PM_{2.5}$. No statistically significant pollution effects were observed in the Manhattan community.

The findings of this study suggest that $PM_{2.5}$, SO_2, ozone, and NO_2 had statistically detectable impacts on acute asthma ED visits in a community with a relatively high baseline rate of acute asthma exacerbations. It is of particular interest that the more robust health impacts were observed with the daily maximum $PM_{2.5}$ concentrations compared to the 24-hour mean, suggesting that peak exposures may have larger health impacts. These associations with health effects in the Bronx occurred at ambient air levels that are below the current short-term NAAQS. Based on the results of this study, the New York State Department of Health has recommended that the U.S. EPA consider the findings in this study identifying respiratory health effects associated with SO_2 concentrations below current standards during their five-year review of the SO_2 NAAQS. It also gives evidence for considering the effects of short-term $PM_{2.5}$ excursions in future reviews of the $PM_{2.5}$ NAAQS. In addition, when community-based asthma interventions are planned with respect to air pollution messages, higher priority should be given to communities with larger asthma burdens.

Supporting EMEP Projects:
Fine Particle Constituents and Acute Asthma in Urban Areas, Daniel Luttinger et al., No. 6484

4.4 Water-Soluble Metals

The metals in PM are present only in trace amounts but may be bio-available when inhaled as small particles. No EMEP-funded health study is currently using this data, but the toxicity of water-soluble metals in ambient PM is a topic of current research nationally. Table 6 shows the solubility of various trace metals collected in daily samples at the Queens College site from July 2001-2002 (Dutkiewicz et al., unpublished). As anticipated, the anthropogenic elements are highly soluble, while the elements associated with the crustal components are insoluble.

Supporting EMEP Projects:
Enhanced Measurements of Oxidants, Fine Particles and their Precursors, Kenneth Demerjian et al., No. 4918

Table 6. Solubility of Trace Elements in $PM_{2.5}$ from Queens, NY.

element	mean solubility (%)	method*	regression coef. (r^2)	number
Zn	90 ±1.3	R	0.93	174
V	88 ±0.8	R	0.95	332
Pb	88 ±1.0	R	0.94	309
Mg	88 ±1.2	R	0.89	239
Mn	84 ±1.0	R	0.91	254
As	84 ±1.0	R	0.88	236
Co	73 ±1.2	R	0.90	156
Sb	71 ±0.8	R	0.91	298
Se	70 ±0.8	R	0.93	260
Ni	64 ±0.9	R	0.86	192
Fe	62 ±1.1	R	0.70	242
Ca	47 ±14	M	NA	12
Cd	12 ±7	M	NA	5
Al	11 ±8	M	NA	13
Cr	5 ±4	M	NA	6

* R = regression slope ; uncertainty= standard error
M = mean: uncertainty = standard deviation

5. What are the implications for air quality management of $PM_{2.5}$ and ozone?

To answer this, we must understand how particles form and evaluate the reliability of the emissions inventories that are used to determine major sources. These emissions inventories are key to air quality management. For $PM_{2.5}$ we need to know both primary composition and precursor emissions, as well as size distributions. For example, researchers lack detailed information on the carbon component, yet it makes up 36% of the PM mass in New York City.

5.1 Particle Formation in Vehicle Exhaust

Research by Yu et al. is investigating the possible mechanisms that determine how particles are formed and grow in motor vehicle exhaust. They are focusing on two theories: ion-mediated nucleation (chemiion theory) and H_2SO_4-H_2O binary homogeneous nucleation. They are also investigating the role of organic compounds in growing nucleated particles. Much of this work is being done by developing theoretical models, but some involves laboratory experiments with the NYSDEC's Automotive Emissions Laboratory.

Chemiions can be observed at high concentrations during vehicle acceleration but are much lower during idling or steady speed. Nucleated ions can explain some of the nucleated particles but do not address particle formation at very high concentrations. This study is investigating the role of binary nucleation, which can produce significant particle formation. It is also looking at the effect of particle formation when the S content of fuel is much lower, as with ULSD.

This study modeled particle formation and growth to investigate the role of organic compounds in a plume. Researchers found sulfuric acid vapor contributing to particle growth to about 3-4 nm, but organic compounds, such as from unburned fuel and lubrication oils, dominate the growth of the nucleated nanoparticles to around 10-20 nm.

Supporting EMEP Projects:
Formation and Transformation of Particles in Motor Engine Exhaust, Fangqun Yu, et al., No. 7618

5.2 Bus Technology Emissions Testing

Over the past 10 years, there has been an increase in the number of technologies available to improve emissions from heavy-duty vehicles. These strategies range from alternative-fuel technology to emissions-control technologies for use with existing diesel vehicles.

In 1996, the voters of New York State passed the Clean Air/Clean Water Environmental Bond. Among many resulting environmental programs was the Clean Fuel Bus Program, designed to provide financial incentives for public transportation authorities to begin procuring buses operating on alternative fuels. Such technologies included compressed natural gas (CNG), electric, and hybrid-electric buses. In 2000, the Metropolitan Transportation Authority began a year-long demonstration of diesel retrofits requiring ultra-low-sulfur diesel, a specialty fuel at the time that will be widespread in the fall of 2006.

The New York State Department of Environmental Conservation evaluated the durability and performance of these technologies in a chassis-dynamometer emissions test program. Performance evaluations of the particle filters showed they were durable and reduced CO, HC, and PM by more than 90% (Lanni, 2001). In addition, carbonyls were reduced by more than 99%, and more than 80% of PAH and N-PAH reduction was achieved (Lanni, 2001).

For CNG buses, the reduction of PM was approximately the same as a diesel bus with a continuously regenerative diesel particulate filter (CRDPF) using ultra-low-sulfur diesel (ULSD): more than 90% (Lanni et al., 2003). CO was higher for CNG buses than for buses with CRDPF. Similar SO_2 emissions were

observed from the two bus types; however, the buses with CRDPF had much higher SO_4-PM. The CRDPF emissions had a high NO_2/NOx ratio (50%) due to high NO_2 emissions. The ratio in emissions from CNG buses was equal to those from diesel buses without a CRDPF.

As part of the EMEP-funded PMTACS program, a mobile lab was set up for chase studies of the buses while in use. NOx emissions from diesel and CNG buses were comparable (Shorter et al., 2005), while the hybrid-electric buses produced about half the NOx emissions. In buses operating on ULSD and retrofitted with a CRDPF, NO_2 was approximately one-third of the NOx emitted, while for buses running on ULSD without a CRDPF, NO_2 was about 10% of the NOx. Researchers also found that SO_2 emissions from buses using ULSD were 16 times lower than those using conventional fuel (Herndon et al., 2005). Emissions of formaldehyde and methane from in-use CNG buses were approximately 15 times greater than those from diesel-powered buses (Herndon et al., 2005).

Characterization of Diesel Emissions
As part of the PMTACS bus-chase studies, an aerosol mass spectrometer (AMS) was used to study non-refractory PM_{10}. They found that the mass spectra of the non-refractory diesel aerosol components measured by AMS were dominated by lubricating-oil spectral signatures. The different processing of fuel and lubricating oil result in diesel fuel being enriched in n-alkanes, while the lubricating oil contains relatively more cycloalkanes and aromatics (Tobias et al., 2001).

Figure 19 shows the chemically resolved size distributions provided by the AMS during a chase event (Canagaratna et al., 2004). The in-plume versus background values were obtained using CO_2 as a tracer. In this figure, the in-plume sulfate distribution at 400 nm is dominated by ambient aerosols, but the smaller mode at 90 nm is dominated by vehicle emissions. The small mode is also prominent in the "in-plume" organic distribution, and comparison to the background organic distribution indicates that this mode is largely due to exhaust aerosol. Evaluation of the diesel chase data revealed that the small organic mode was always present between 80-100 nm. In their ambient measurements in Queens, other AMS measurements showed organic particles with modes at 80 and 360 nm (Drewnick et al., 2004a). The smaller mode was generally correlated with traffic activity levels, and when the small mode was more intense than the large mode, the measured ambient mass spectra resembled that of lubricating oil. The observations suggest that the small organic mode observed in ambient aerosol measurements is a signature of motor-vehicle-related aerosol.

Supporting EMEP Projects:
Enhanced Measurements of Oxidants, Fine Particles and their Precursors, Kenneth Demerjian et al., No. 4918

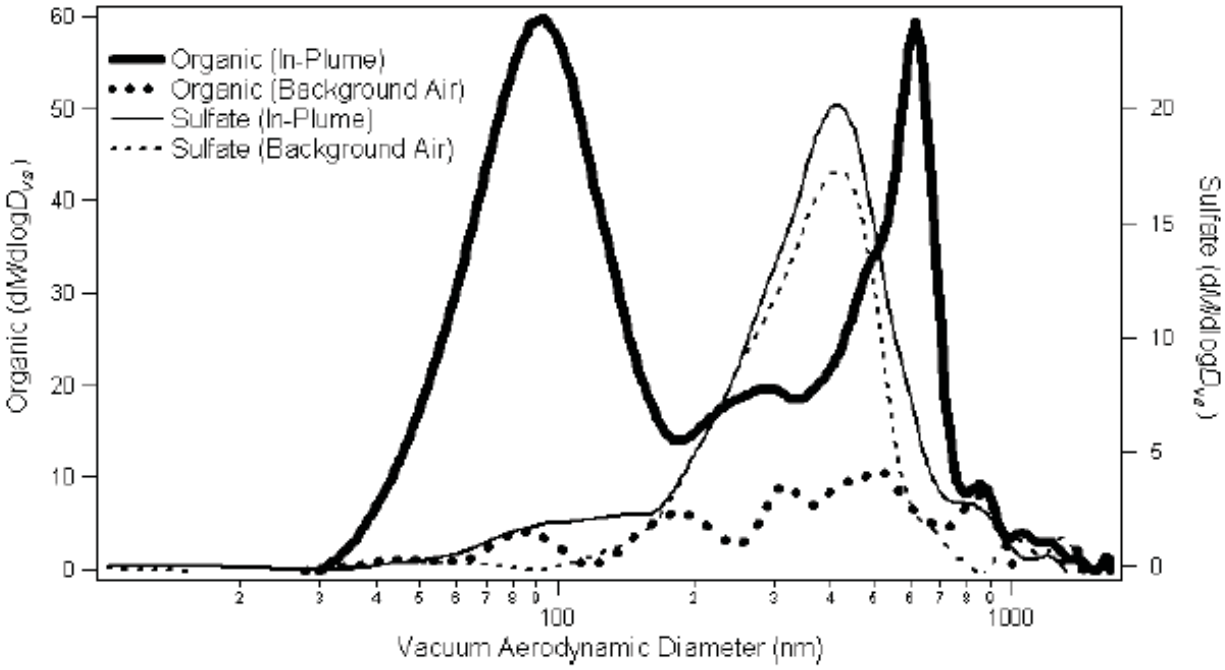

Figure 19. Chemically speciated size distributions measured for an individual vehicle during one chase event. The solid lines correspond to distributions averaged over time periods when the mobile laboratory was sampling the vehicle's exhaust plume. The dotted lines correspond to size distribution averages over time periods corresponding to ambient measurement conditions.

5.3 Ozone

EMEP O_3 research focused on increasing the understanding of long-range transport of O_3 and O_3 precursors. To improve our understanding of the problem of long-range transport of air pollution and source-receptor relationships for trace-level air contaminants, spatiotemporal features of pollutant observations were analyzed through a combination of statistical tools and back-trajectory analysis. Concentrations of O_3 and $PM_{2.5}$ are determined by a complex interplay of emissions (both anthropogenic and natural), chemical transformations (such as the formation of ozone from hydrocarbons and nitrogen oxides in the presence of sunlight), and physical processes (such as atmospheric transport and removal from the atmosphere by wet and dry deposition). To address the problem of attributing these products to specific sources, the concept of an "airshed" for O_3 and $PM_{2.5}$ was used to identify the spatial scale for these pollution problems and to delineate regions exhibiting similarities in their pollution characteristics.

The findings underscore that no state in the Northeast can adequately address pollutant problems alone until region-wide control strategies are implemented for O_3 and $PM_{2.5}$. The probabilistic framework recommended by these studies – aimed at integrating the spatiotemporal information of observations and model predictions and applied to ozone concentrations for demonstration purposes – should be expanded to address multipollutant problems within the "one atmosphere" approach (NYSERDA Report 03-02, 2003).

<u>*Supporting EMEP Projects:*</u>
Analysis of Ozone and Fine Particles in the Northeast, S.T. Rao et. al. No. 4914

Assessing the Effects of Transboundary Pollution on New York's Air Quality, S.T. Rao et. al. No. 6085

5.4 Sector-Specific Emission Control Initiatives

Although not sponsored through EMEP, NYSERDA has a number of emission-control testing and deployment programs designed to provide information on the efficacy of different control strategies and provide real-world improvements in air quality. These program are summarized in Table 7.

Table 7. Controls and emerging technologies: Activities at NYSERDA outside of EMEP.

NYSERDA Program	Description
Clean Air School Bus	**Incentive program for installation of diesel retrofit technology to reduce PM emissions.**
Ferry Emission Reduction	**Demonstration of emission control technologies for use in marine vessels operating in New York Harbor. Program also includes an incentive program for vessel retrofits and repowering.**
Clean Diesel Initiative	**Program will characterize the off-road fleet and range of equipment duty-cycles followed by a technology feasibility demonstration.**
Truck Stop Electrification	**Idle reduction technology demonstration.**
Low Sulfur Heating Oil	**Demonstration of performance and emissions characteristics of using low S heating oil in commercial and residential heating systems.**
Combined Heat and Power	**Emerging technology to improve facility energy efficiency by utilizing waste heat.**

6. Knowledge Gaps and Research Needs Identified Through EMEP Projects

The studies described above have greatly advanced the understanding of PM, ozone, and co-pollutants in New York State. Despite these advances, much more work is needed. The specific areas include better quantification of the local and transported component of PM. This will necessitate better trace-metals measurements than currently achieved through the Speciation Trends Network. Also, more speciation of organics will be needed to understand which sources are contributing to the largest component of PM. Currently, only 15% of this fraction can be resolved. Additional understanding of the real-time chemical transformations such as those obtained with the AMS is also needed.

The detailed atmospheric chemistry needs to be related to specific source types. This will require source profiling of many source types with both more species and better measurements than are currently in the EPA emissions inventory. Size distributions, in addition to detailed chemical speciation, will help resolve different combustion types using the same fuel, such as oil-fired boilers and diesel trucks. The change in sulfur in on-road diesel fuel should provide a tool to resolve these signatures.

Finally, improved use of more accurate emissions data and atmospheric and chemical processing are needed for air quality models. These need to be developed to reflect a probabilistic approach to air quality management.

More specific health research is needed to understand the mechanisms by which pollutants cause mortality and morbidity. This could help prevent unintended consequences as we move forward with air quality management strategies and product development of energy technologies.

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