I. Purpose
The topic of this meeting was airborne organic carbon, which is the second most important contributor to regional haze in the MANE-VU region (after sulfates). Organic carbon particles are even more important in major urban areas as a component of PM$_{2.5}$.

This meeting was intended to help participants:
- Learn more about the sources and impacts of organic carbon particles;
- Understand some of the complexities of measuring and analyzing organic PM;
- Explore linkages between haze and health effects;
- See how OC fits into the modeling of regional haze and PM$_{2.5}$; and
- Be better prepared to identify the next steps for reducing particles and haze.

The following highlights were prepared by Susan Wierman of MARAMA and have not been reviewed by the presenters, so please check with the speakers to confirm before citing their work. These notes represent only my understanding of the presentations.

II. Science and Policy Issues and Health Effects of PM

Overview of Science and Policy Issues
Dr. John Graham, NESCAUM

NESCAUM is completing a report for NYSERDA called an “Assessment of Carbonaceous Fine Particles for New York and the Region.” The report will include a policy-relevant assessment of scientific and technical information with respect to five questions:

1. Do carbonaceous aerosols contribute significantly to high levels of ambient PM$_{2.5}$ in New York State?
2. What proportion of carbonaceous PM$_{2.5}$ present in NY is derived from in-state sources?
3. Does carbonaceous PM$_{2.5}$ present a public health concern?
4. What are the technical options for reducing emissions of carbonaceous aerosols from sources?
5. What are the near-term strategies for reducing emissions of carbonaceous PM for NY and the region?

Dr. Graham indicated that seven source categories were chosen for analysis based on their contribution to EC and OC in ambient PM: commercial meat cooking, residential fuel combustion, light-duty vehicles, heavy-duty trucks and buses, nonroad engines, airports, and marine ports.

Generally, emissions inventories for OC and EC are poor in quality and should be a primary focus in future work. He also noted that further study of atmospheric chemistry and gas-particle partitioning was needed, as were improved emission sampling and analytical methods, calibration standards for the methods, and realistic study conditions.

He did not provide answers to the questions posed but indicated that despite the limitations of existing data and approaches, sufficient certainty exists to support policy decisions.

Fine Particulate Matter and Human Health
Ron White, Johns Hopkins University School of Public Health

Mr. White reviewed health effects associated with PM and noted that while some information is being developed about the health effects of components of PM, he considers it unlikely that EPA will set a standard for individual species of PM anytime soon. He explained that there is no threshold below which there is no health effect, and that effects have been shown to occur at levels below the current PM standards.

In response to a question, he indicated that in order to reduce health effects it might be especially important to control wood smoke, which clearly sends people with asthma to the emergency room, and diesel emissions and oil burning, which have metal components that are of concern.

An important point he made was that it has been demonstrated that reductions in PM$_{2.5}$ are associated with health benefits. The “six cities study” and the follow-up assessment (which looked at data for Portage, WI, Topeka, KS, Louisville, KY, Kingston, TN, Watertown, MA, and Steubenville, OH) was one of the primary epidemiological studies that formed the basis for the fine particle health standard. Pollution levels declined, and there was a resulting reduction in mortality.

The women’s health study (1994-98, about 66,000 older women in 36 cities) showed an increased risk of death due to increase in PM$_{2.5}$. The increase was shown both between and with cities. The within-city effect was higher than between cities. For each 10 µg/m$^3$ increase in PM$_{2.5}$, death from cardiovascular disease increased by 76% for older women and by around 15% for the population in general.
Johns Hopkins University did a study of about 11.5 million people over the age of 65 in 204 counties. Heart failure was associated with increased PM. Respiratory infection was increased two days after the high PM exposure.

There are differences between the eastern and western US, with higher risks in the east for cardiovascular outcomes and higher respiratory problems in the west. Each 10 µg/m$^3$ improvement in PM concentrations resulted in 10,000 avoided cardio-pulmonary hospital visits. Effects still showed at levels below 35 µg/m$^3$. Substantial national health benefits were estimated for fine PM reductions even at levels below the NAAQS.

A recent study of effects in Seattle showed a decrease in lung function in older adults one day after an increase in PM$_{2.5}$.

Maternal exposure to PM$_{2.5}$ showed an increased likelihood of pre-term birth. Dr. Michelle Bell’s recent study in CT and MA showed an association between low birth weight and maternal exposures to PM.

He mentioned that there is a nice review of various studies of PM health effects in the AWMA Journal, June 2006 by Pope and Dockery.

Recent studies confirm earlier evidence of mortality and morbidity. Longer-term chronic studies find larger effects. Finer exposure resolution seems to show higher impacts. Inter-individual variability makes it extremely unlikely that studies will find a no effect level. There is increasing emphasis on sensitive populations—those with pre-existing cardio-vascular and respiratory disease, diabetics, fetuses, and possibly women.

There is emerging evidence about various PM components and mechanisms of adverse effects. There is limited evidence so far for the role of OCs in fine PM health effects. There may be a more significant role in lung cancer.

### III. Atmospheric Chemistry of Carbonaceous Aerosols

**Effects of Semivolatile Emissions and Photochemical Aging on Urban and Regional Primary and Secondary Organic Aerosol Concentrations**

Prof. Allen Robinson, Carnegie Mellon University

Primary emissions of organic compounds are semi-volatile, and we need to develop a better way to estimate them and use them in models. Low volatility organic vapors are important precursors of secondary organic aerosol particles. The implication is there should be a reduction in estimates of primary aerosol emissions, but an increase in predictions of downwind secondary aerosol. NOx reductions may have unexpected influence on the formation of SOA.
There are many sources of primary organic aerosol emissions, but there are also gas phase emissions from those same sources, and these gasses can also be converted into particles through photochemistry.

In general, while there are exceptions, studies around the world have shown that most organic aerosol is SOA, though primary sources are more important in urban than rural areas. In rural areas, organic aerosol is almost entirely oxygenated organics (SOA).

It's difficult to identify the source of SOA. In source apportionment studies, unapportioned OC dominates summer aerosol.

Models assume primary OA is not volatile and non-reactive, and that SOA is formed from highly reactive compounds. Secondary reactions and low-volatility compounds are ignored.

Particle formation occurs in a plume of gaseous organic emissions, and the particle concentration can be measured by dilution sampling. This is the estimate of primary OC emissions. Some components are known, but many are unknown.

Concentration and exhaust temperature both have impacts on how emissions react in the atmosphere and whether they are present as gasses or particles. Temperature and concentration have competing effects. (Higher temperatures favor gasses, higher concentrations favor particle formation.) In the winter, there will be greater concentrations of particles in emissions.

In dilution sampling, a sample of emissions is diluted only up to about 50%, and at this level concentrations are still high though temperatures come down to ambient levels. As additional dilution air is added, the concentration drops. At high concentrations, most emissions are in the particle phase, but as gas is added, an increasing amount convert to the gas phase. This has been demonstrated with experiments both with diesel emissions and woodsmoke. Isothermal dilution causes the organic PM to evaporate.

This means that there will be a bias toward high emissions of direct OC from dilution sampling, which would affect the accuracy of modeling. Models also do not represent the gas to particle conversions downwind and any subsequent phase changes. Concentrations of OC should decrease at first as dilution is allowed, but with aging, there will be increased formation of secondary aerosol downwind.

He believes that to properly model SOA formation one must include emissions of and atmospheric reactions of low-volatility organic compounds. Low volatility organic vapors are an important source of atmospheric aerosol.

His lab has created an aging model to reflect that gaseous organic compounds move gradually into a particle phase as they age in appropriate conditions. Using their model decreases concentrations of organic aerosol in cities and increases rural concentrations.
IV. Sources of Carbonaceous Aerosols—in General

**What do Molecular Markers Tell Us about the Sources of Organic Carbon?**
Dr. Monica Mazurek, Rutgers

Molecular markers are concentrations of specific chemicals that are present in PM and are used in source apportionment analysis as indicators of specific types of sources.

Chemical analysis with a GCMS is used to identify the presence of various chemicals. The general pattern of high concentrations of some chemicals and low concentrations of others present in a sample of PM can be compared to the pattern of concentrations known to be associated with various types of sources. Chemical Mass Balance is one technique for identify sources affecting PM concentrations.

Approximately 500 markers of various sources have been identified. For example, hopanes and steranes are markers of petroleum sources. More source profiles are needed, and her group has been developing some.

Long-term field studies are important. Multi-season and multi-year data provide much better insights into PM.

**Source Apportionment of Particulate Matter in Atlanta**
Dr. Mei Zheng, Georgia Institute of Technology

Dr. Zheng and her colleagues investigated ambient fine particle data from Atlanta in order to identify major sources of PM$_{2.5}$, assess seasonal variation, compare various methods, consider the impact of fires, and determine how much organic carbon was due to combustion of fossil fuels as opposed to other sources.

An analysis of data from July 2001 and January 2002 indicated that organic matter was a much larger percent of total fine particle mass in winter than in summer. Average concentrations of both OC and EC were higher in winter than in summer. OM was 20% of PM$_{2.5}$ in summer and 54% of PM$_{2.5}$ in winter.

On average, based on carbon dating studies, about 40% of OC is modern and about 60% is from combustion of fossil fuels. Modern carbon is important for both carbon associated with primary sources and carbon from unknown sources (the unexplained fraction of total carbon or TC). Urban sites exhibit more fossil-derived carbon than rural sites.

Using Chemical Mass Balance methods with data on molecular markers to apportion mass to likely source categories showed that wood combustion and gasoline exhaust
were dominate sources of organic matter in the winter. Unexplained (secondary?) carbon dominated summer concentrations.

Comparing results from CMB, CMAQ modeling, and PMF source apportionment showed some differences in results for various sources.

Both source apportionment methods (CMB and PMF) indicated that the contribution from gasoline-powered motor vehicles was much larger in winter 2002 than in summer 2001, while the CMAQ model predicted basically the same levels in the winter as in the summer.

For wood combustion, CMAQ predicted higher concentrations in winter. PMF identified a much larger and more episodic contribution from wood combustion in both summer and winter than did either CMB or CMAQ.

CMAQ predicted higher impacts from diesel exhaust than were identified by CMB, though in summer there was pretty good agreement between CMAQ and PMF estimates of diesel contributions.

In general, there was much more day-to-day variation reflected in the receptor analysis results than in CMAQ results.

Levoglucosan is an indicator of smoke from fires. Analysis of Atlanta data showed a dramatic increase in levoglucosan concentrations during periods affected by prescribed fires.

Concentrations of total PM and of EC and OC were higher at a monitoring site next to a highway than they were at a rooftop site away from roads.

**Contribution of SOA to Ambient PM$_{2.5}$ Organic Carbon in Eastern US Locations**

Dr. Tadeusz Kleindienst, EPA

The objective of this EPA project is to use both lab and field studies to find tracer compounds representative of the major SOA precursors. Their focus is isoprene, alpha-pinene, beta caryophyllene, and toluene. The first three would be indicators of vegetative sources; toluene would indicate human activity.

EPA’s Conclusions:
Secondary organic aerosol from isoprene, monoterpenes, sesquiterpenes, and aromatics (e.g., toluene) contributes substantially to organic carbon in PM$_{2.5}$ in the eastern US, mainly during the summer.

The aromatic contribution (indicative of anthropogenic contribution) is higher than typically predicted in air quality models. Even though the anthropogenic contribution is lower than the biogenic contribution, it is higher than shown in models.
Organic carbon in PM$_{2.5}$ was found to range from 2 to 5 µgC/m$^3$ throughout the year, with primary sources dominating in the winter and SOC dominating during the summer. Changes in the primary and secondary contributions can be offsetting, reducing seasonal differences.

EPA found estimates of SOC contribution from biogenic HC precursors to be substantially greater than anthropogenic HC precursors in the eastern US. These results were consistent with SOC contributions to the organic carbon measured in laboratory mixtures and with carbon-14 measured in laboratory experiments and from field studies.

There is further work to do, including combining CMB analysis for primary compounds and mass fractions for secondary compounds to see the degree of consistency between SOA and “other OC” from the CMB analysis.

**Fossil vs Contemporary Carbon at 12 Rural and Urban Sites in the US**

Dr. Bill Malm, National Park Service & Colorado State University

Analysis of samples for $^{14}$C allows scientists to distinguish between carbon that is due to the combustion of fossil fuels and carbon that is from more modern sources, such as combustion of wood, meat cooking, or evaporation of chemicals from pine, oak or other vegetation. Fossil fuels are so old that the radioactive $^{14}$C they once contained has decayed to form other substances. Modern carbon is still radioactive.

The Park Service conducted a study at 12 sites, installing a high volume sampler near an existing IMPROVE monitor and then analyzing filters to assess the fraction of Carbon that was fossil versus modern. Modern carbon was termed “biogenic,” recognizing that there are both natural and anthropogenic sources of modern carbon. Sites in the MANE-VU region included Brigantine (NJ) and Proctor Maple (VT).

They also looked at the ratio of elemental carbon to total carbon for the fossil and modern carbon and compared that to results of various other studies that had identified EC:TC ratios associated with various categories of sources. Secondary organic aerosol would have an EC:TC ratio of zero. Both fossil and biogenic EC:TC ratios tended to be smaller in the summer than in the winter, probably because there was more SOA in the summer.

Based on this analysis, they concluded that biogenic (modern) carbon accounts for 80-95% of the total carbon at rural sites, 70-80% of total carbon at near-urban sites, and 50% of total carbon at urban sites.

They concluded that urban fossil carbon is primarily due to local sources during the winter and summer, and summer biogenic carbon is regionally distributed (i.e., primarily due to transport). About 40-50% of the winter urban excess (above rural concentrations) is biogenic carbon, and not all biogenic carbon is “natural.”
They concluded that 42% or more of the summertime organic carbon is secondary, and 32% or more of the summertime fossil carbon is secondary.

They identified the following sources of carbonaceous aerosols:

- Primary biogenic sources: smoke, pollen, soil, cooking
- Secondary biogenic sources: smoke, vegetation
- Primary fossil sources: combustion (mobile, off-road, oil/gas/coal-fired stationary sources)
- Secondary fossil sources: combustion sources (as above), evaporative loss

V. Sources of Carbonaceous Aerosols—Transportation

New York Vehicle Chase Study: Emission Characterization and Hot Spot Assessments
Prof. Kenneth Demerjian, State University of New York at Albany

Prof. Demerjian reported on work funded by EPA, NYSERDA, and NY DEC to monitor the effectiveness in improving air quality of CNG power and diesel filter traps on busses in the MTA system in NY City.

The study used both stationary monitoring sites alongside roadways and an instrumented mobile lab deployed to chase and sample exhaust from specific vehicles.

The mobile van used in the chase studies included sophisticated equipment designed to provide short-term analyses of concentrations of various gasses and PM. An aerosol mass spectrometer provided particle composition.

About 130 busses were sampled. 27 had been retrofitted with CRT filters. 56 were CNG-fueled. 90 other vehicles were also sampled.

The dirtiest vehicle measured was a smoking automobile, with PM emissions 10 times more than the dirtiest bus.

The diurnal pattern in ambient PM organic measurements was consistent with other precursor emissions and indicates that a substantial portion of organic PM emissions can be attributed to mobile sources.

Organic PM in the plume from the busses is much greater than background levels and appears to be related to combustion of lube oil in the engine.

This study demonstrated that on-road vehicle emissions can be measured using a chase van.
CNG powered busses and those equipped with CRT diesel particulate filters showed significant reductions in PM emissions as compared to their standard diesel counterparts.

In use emissions seem to be much more variable than values indicated by dynamometer testing.

CNG powered buses have significant formaldehyde emissions that will require additional controls (e.g., oxy-catalyst).

The ratio of NO2:NOx emissions from buses equipped with CRT diesel particle filters is significantly different, and this may have to be addressed.

Ultra low sulfur fuels have significant direct benefits with respect to PM, total hydrocarbons, CO and SO2 emissions.

Roadside monitoring indicated the proportion of particles in the very small size range was higher than previously expected. This was consistent with results from California studies.

The roadside measurement study indicated that plumes from diesel and gasoline powered vehicles are distinguishable. Roadside measurements may help improve inventories and have value in surveillance monitoring for gross emitters.

Particulate Matter Exhaust Emissions from Light-Duty Gasoline Vehicles in Kansas City
Gene Tierney, US Environmental Protection Agency, Office of Transportation Air Quality

EPA conducted a major study ($4 million) of PM emissions from gasoline vehicles. This is the most comprehensive program focused on light-duty gasoline PM emissions ever conducted. EPA will use the results to help improve its new models of vehicle emissions (MOVES).

Issues not addressed by this study include effect of aging on emissions from new vehicles, regional variations, heavy-duty vehicle emissions, and the effect of new standards on future emissions.

The Kansas City study represents a large sample from one place at one time for a single driving cycle. It was done under ambient conditions, testing a variety of vehicles on a dynamometer and on the road.

The strengths of this study were to identify the proportion of the fleet representing high emitters and to study PM emissions of a random sample in order to judge the distribution of emissions in the fleet. Other pollutants were also sampled; this presentation concentrated on PM.
Temperature, vehicle speed, and vehicle deterioration are not considered in the MOBILE model.

The study was conducted in 2004-2005 on about 500 light duty cars and trucks 1968-2005 MY, including both winter and summer testing (about ½ vehicles in each season). About 50 vehicles were tested both in summer and in winter.

Cars tested were selected in a stratified random sample to obtain a representative sample by socio demographics and fleet composition. It was hard to recruit enough older vehicles. Sample size for newer cars was larger than the goal.

One reason Kansas City was chosen was that it did not have an I/M program, and another study was already underway to identify vehicle ownership by socio-economic factors.

The study used Portable Emissions Measurement Systems (PEMS). The vehicles were driven on surrounding roads. Dynamometer tests were also conducted.

The dynamometer protocol used was LA92 cycle (not same as the standard cycle). Measurements were taken in three bags and second-by-second. Toxics were sampled on a subset of vehicles. Oil samples were taken from each, though funds were not available for analysis; the samples are in a freezer.

All vehicles were preconditioned before dynamometer testing in order to flush out the artifacts of vehicles not driven aggressively.

Preliminary results: PM emissions are higher in winter than summer, higher from older vehicles than newer vehicles, higher from trucks than cars, and a small number of vehicles produce higher proportion of emissions, but many were not identified as “smokers.” Except for new vehicles, emissions were higher than predicted by the MOBILE model.

It’s not clear whether older vehicles have higher emissions due to deterioration or due to improvements in technology.

The average winter temperature was 45F, with the min about 20F (not a very cold winter). PM emissions in this and other studies indicated that PM emissions double for about a 20F drop in temperature.

There were cars that had higher emissions than others. 50% of the PM emissions came from about 13% of the vehicles. In summer, of 14 vehicles emitting over 5 mg/mi, most were older than 1996 and only 2 had barely visible smoke at idle. Significantly smoking vehicles were seen in winter. Most were MY 1997 or older, and only 11% of vehicles tested in winter were identified as smokers at idle. (That is, you can’t tell a high emitter by looking for smoke.)
Why is winter PM higher? It may be related to temperature related phase transitions—particles more likely to form in colder temperature, evaporation to gasses in higher temperature. It may also be due to changes in fuels, oils, or operation of the vehicles. More investigation is needed.

**Emissions from Ships**  
**Dr. James Corbett, University of Delaware**

Freight is an important multimodal transport function, and international shipping is an important part of the picture. Ships are more heterogeneous than onroad vehicles. Ships follow defined routes, which shift seasonally and in order to avoid adverse weather.

About 60% of the power production on ships is via two-stroke marine engines. Tests indicate that the particle mass is dominated by volatile organics, that conditions favor formation of a larger number of smaller particles, that dirtier marine fuels emit higher total PM, and that NOx emissions are also high.

Marine diesel is different from fuel used on land. The fuel has a very high sulfur content. Particle pollution results from ash, nickel, and other contaminants in the fuel. Lube oil consumption leads to organic emissions. Black carbon is generated in the flame. Engines operate at slow speed and so have high residence time, with a 2 meter stroke. Marine diesel fuel quality has declined since the 1940s as other refinery products have improved.

Shipping emissions are expected to increase, even if international agreements result in a North American Sulfur Emission Control Area, because there is expected to be a tremendous growth in shipping.

Dr. Corbett’s work addresses emissions in shipping lanes, not emissions while idling in port. These emissions are important contributors to global CO$_2$ inventories. Emissions inventory estimates contain significant uncertainty. There are different estimates of ship traffic from two major sources, each of which is biased toward different types of ships (container vs other ships). Slowing down ships reduces emissions.

He recommended using inventories in upper and lower bound estimates to check whether the inventory matters. If it matters, then work on improving it.

His group is working on an inter-modal model that assesses shifts between air, sea, or land transport based on optimizing time, cost, or CO2 emissions.

Interestingly, Dr. Corbett is a former ship’s engineer.
VI. Other Emissions that Contribute to Organic Particles

Nonparametric Regression of Continuous BC, EC, and OC in Detroit
Dr. Donna Kenski, LADCO

Dr. Kenski used data on EC, OC, and BC from monitors in Dearborn, MI to demonstrate a technique for identifying major local sources contributing to high levels of PM$_{2.5}$.

Detroit continues to exceed the PM$_{2.5}$ NAAQS at the Dearborn monitoring site and a few other sites, and Detroit is predicted to continue to be in nonattainment even after implementation of the CAIR rule. Detroit is similar to Cleveland, St. Louis, and Indiana, with large point sources, most of which are steel mills. The Dearborn monitor is next to a school and residential area that is next to a big steel mill.

There is continuous speciation data for the Dearborn site, including Aethalometers, TEOMs and continuous EC/OC with co-located meteorological instruments. There are Aethalometers at 4 sites. Sulfate, nitrate, and OC are the largest portion of PM at sites in and around Detroit. OC and soil are much higher at Dearborn than at other sites, and EC is slightly higher.

Nonparametric regression regresses concentration on wind direction and speed to locate areas associated with peak concentrations. Ron Henry was the first to use this with air quality data and has been very helpful to Donna in her use of the technique. It’s a kernel density estimate weighted by the number of observations. It gives something like a moving average but with a smoothing parameter. It is also similar to a modified trajectory analysis. It compares the concentration at a point at one time with concentrations at other points at a previous time.

Used with BC data from Aethalometers the technique was able to identify sources including both a rail terminal, a bridge with major traffic backups, a cement manufacturing plant, and an industrial area including a steel mill. Combining data from all three monitoring sites identified the area that had the most impact on all three jointly, which was the industrial complex.

The Sunset instrument was provided continuous EC data and helped identify hot spots. The OC data also was analyzed, though she did not expect to see the same result since it has a secondary fraction, but the OC data also pointed out the hotspot in the industrial area.

When data are available, the results are stable over different seasons. There needs to be a lot of data to use this technique.

Like other trajectory models, there are limitations to the technique. She does not see much benefit in using the technique for total PM$_{2.5}$ data. The reasons the technique
does not pick out local sources using PM$_{2.5}$ data are not clear. It may be due to the influence of secondary sources or that there are uncertainties in the PM$_{2.5}$ data.

One of the advantages of this method over other trajectory analysis methods is that it provides more information about uncertainties in the results. She will be doing further work to investigate this, compare it with other methods, and apply it to other areas and data.

The method appears useful to identify distinct local sources of BC and EC and, at least in this case, primary OC also.

**The Contribution of Biomass Combustion to Ambient Particulate Organic Carbon**

Prof. Jeff Collett, Colorado State University

Biomass combustion is an important contributor to PM in urban and rural settings. Wild and prescribed fires are especially important in the western US. Residential wood combustion is a major contributor to winter PM episodes in some urban areas.

OC is a large fraction of total PM$_{2.5}$ mass in Oregon, Montana, and northeastern California and Northwestern Nevada, probably due to fires impacting these areas.

Molecular markers are tracers of source impacts. Ideally, they are representative of a unique source, stable in the atmosphere, present at detectable concentrations, and are primary aerosols.

Wood is composed of cellulose (45%), hemicellulose (30%), and lignin (25%). Each leads to different chemicals that are potential markers of woodsmoke. Levoglucosan is one that is frequently used.

To test for levoglucosan, a high volume sampler is used with subsequent chemical analysis of filters. It’s a fairly expensive and labor-intensive process. Typically, people collect a lot of filters and then analyze composite samples. A new technique makes routine measurement more practical. It’s currently being applied in a LADCO study.

His group conducted a study in Yosemite in summer 2002. The study lasted about 8 weeks, with daily sampling. Levoglucosan, Retene, and Vanillin were used as markers of fire impacts and agreed fairly well with each other. However, the markers were not high during all periods of high PM that was thought to be due to smoke. There was a large unexplained fraction, which was thought to be secondary PM formed downwind of the fires. These days also had high values of other biogenic markers.

Prof. Collett’s lab has been developing a revised method for filter analysis using an anion exchange column and water-based extraction to analyze for marker compounds. Their goal is a high time resolution very portable system.
Source profiles for fires may need work. Estimates using markers do not always agree with measured PM.

Most published source profiles are for residential wood combustion. Prescribed or wildfires appear to have a different (lower) percentage of levoglucosan. The forest service and others are working on studies to address issues such as variations due to flaming vs smoldering, etc.

Dr. Collett noted that we need a better handle on the formation of SOA in smoke plumes.

Analysis of the Baltimore Supersite Data
Prof. John Ondov, University of Maryland, College Park

Prof. Ondov posed the question, “Can local stationary source control reduce ‘urban excess’ concentrations?” During the study period (February - December 2002), PM$_{2.5}$ concentrations averaged 15.8 $\mu$g/m$^3$, barely above the federal standard. The maximum was 198 $\mu$g/m$^3$, during the Canadian smoke episode. Concentrations exceeding the 24-hr standard were rare.

There were 31 times when the concentration was greater than 30 $\mu$g/m$^3$. 50% were considered traffic-related, 42% due to sulfate haze, and 8% were affected by smoke from Canadian fires.

Short-term data and a number of organic markers helped point to likely sources of higher levels. Speciation data was very important to the analysis.

Features of episodes dominated by traffic included morning peaks in OC associated with rush hour, but further analysis is indicating that other sources (biomass combustion, meat cooking, and secondary terpene oxidation products) also contributed, and more work is needed.

Only about 3% to 5% of the OC measured by the Sunset instrument was able to be identified.

Hot spots need to be analyzed in terms of meteorology and local topography rather than making generalizations.

Their analysis suggests that secondary OC is 50% of total particulate OC. Wood combustion and meat cooking may have contributed oxygenated OM to measured OC, but it is doubtful that these sources could have accounted for so much OC. He thinks more investigation of the unidentified mass might help.
VII. Monitoring Organic Particles

Overview of Commercially Available “On-Line” Aerosol Carbon Field Instruments
George Allen, NESCAUM

Mr. Allen used the term “on-line” to refer to continuous or semi-continuous instruments. He focused on practical methods for routine monitoring that did not require constant attention from an operator and provide data with 1 minute to 3 hour resolution.

The Sunset Labs Model 3 or 4 is the most widely-used on-line aerosol carbon analyzer. It collects aerosol on a quartz filter followed by a thermal analysis.

Hourly black carbon measurements from an aethalometer at the South Bronx site were highly correlated with the elemental carbon measured by the Sunset instrument. However, from April to October BC was 30% higher than EC, while from November to March BC was equal to or less than EC. NESCAUM is working on methods to resolve these differences.

Mr. Allen also noted that Aerosol Mass Spectrometry is used in research programs to provide information on size-resolved single particle OC composition. It is a complex and expensive technique. There are two commercial systems. Neither gives a quantitative measure of total OC mass.

LIDAR and Satellite Monitoring of Ambient Particulate Matter
Prof. Ray Hoff, University of Maryland–Baltimore County

Satellite sensors can provide horizontal data coverage, and ground- and space-based LIDAR can measure aerosols in the vertical dimension. Satellites and LIDAR provide measurements of aerosol optical depth, which is a measure of light scattering in the column of air sensed by the instrument.

This data can help fill gaps between ground-based monitors, provide improved understanding of pollution events, help assess model performance, and track impacts of pollution control programs.

The MODIS satellite provides aerosol optical depth and ground imagery within about a year of the overpass.

It’s important to know the height in the atmosphere of the aerosol seen by the satellite in order to properly interpret the concentration. The LIDAR measurements can help provide that information.

Prof. Hoff is participating in an EPA study to link satellite data with ground based measurements and air quality modeling to assess and demonstrate the potential of
these techniques to track the impacts of the implementation of the CAIR program. The vision is to link datasets to help build connections between health data and emissions information through air quality surface and satellite data. The case study is being undertaken in the Baltimore area.

An interesting point from his talk was that some plumes (e.g., smoke from fires) loft up and are not measured by ground level monitors but can be seen in satellite photos and data.

UMBC has a website that provides information: http://alg.umbc.edu. This includes US Air Quality (The Smog Blog) http://alg.umbc.edu/usaq

There are several LIDAR instruments at UMBC. http://alg.umbc.edu/REALM provides information on their sites as well as a number of other sites in the eastern US as far back to 2004. It provides a visual picture of the data which those interested can obtain from the scientists running the particular sites.

In January there will be a workshop at UMBC to discuss visualization tools.

VIII. Modeling of Aerosols

Regional Haze and Earth System Science
Prof. Russ Dickerson, University of Maryland–College Park

Prof. Dickerson identified some new air quality issues for the Eastern US:

- The IPCC report on Climate Change predicts more hot spells in the summer, heavier rain in winter.
- Changes in aerosol concentrations can have impacts on local climate, for example, atmospheric stability and cloud microphysics.
- EPA has formed a Committee on Integrated Nitrogen, which will consider air, land, and water issues. The main source of atmospheric ammonia is agriculture.
- EPA is also considering tighter secondary air quality standards.

Based on UMCP aircraft monitoring and studies, aerosol light scattering correlates with ozone and behaves like a secondary pollutant. However, it is not clear that air quality models are accurately representing sulfate chemistry. Data from aircraft sampling indicate that CMAQ overestimates the amount of SO₂, as does the model GOCART. Their analysis indicates that the models are overestimating the lifetime of SO₂ in the atmospheres. This may be related to cloud chemistry. It's important for accurate estimation of sulfate formation.
Carbon Analyses in the VISTAS Region for PM$_{2.5}$ and Haze
Patricia Brewer, VISTAS

In the Southeast, areas with the poorest visibility are in the same general areas as PM nonattainment areas.

Sulfate dominates the 20% haziest days as well as the 20% clearest days at VISTAS Class I areas.

Estimates of natural conditions show that POM would be a larger fraction than sulfate.

VISTAS conducted a monitoring study from April 2004-May 2005 with the objective of identifying sources of organic carbon. They used high volume samplers with PM$_{2.5}$ heads and quartz filters at five sites to collect carbon for analysis with GC/MS to support source-receptor analysis. In addition to four Class I areas, data was collected in Raleigh, NC. Analysis of $^{14}$C was conducted for some samples.

The modern carbon fraction was seldom less than 50% and usually greater than 70%. The percent of modern carbon was higher at forested than coastal or urban sites. At the urban site, higher TC and higher PM$_{2.5}$ accompanied a lower modern carbon percent. There was no clear seasonal trend in modern carbon data (possibly because wood burning emissions are higher in the winter, and vegetative emissions are higher in the summer).

Tracer analysis and chemical mass balance analysis are ongoing. There are a lot of uncertainties. Much of the material is from unidentifiable sources.

Modern carbon, either from wood burning or natural sources, is more important than fossil carbon at Class I areas, based on preliminary results.

Continuous data was collected in 2003-2004 to assess diurnal patterns—summer afternoon peaks were shown, as well as an early morning nitrate peak in urban areas, and early morning and afternoon peaks in BC in urban areas.

Air quality modeling work is ongoing to support both PM and regional haze SIPs. Model performance evaluation indicates that sulfate is in the right ballpark, nitrate is sometimes over-predicted in winter but generally OK. (This implies a need to look at ammonia.) OC levels are about a factor of 2 under-predicted (even more at STN than at IMPROVE sites). CMAQ is considered sufficient for regulatory application: sulfite is most important and has the best performance, performance is acceptable for nitrate, soil, and EC, though performance was initially unacceptable in the summertime for OC.

For OC, the model was 100% underpredicting measured levels. They worked with Ralph Morris to enhance the CMAQ SOA module, and the model is now within acceptable levels.
The greatest potential for future visibility improvement is to reduce SO$_2$ from utilities and other point sources. VISTAS states are major contributors to VISTAS Class I areas. MANE-VU, CENRAP, and MRPO state emissions are important for VISTAS Class I areas close to those regions.

**New York State Preliminary PM$_{2.5}$ Modeling**  
**Dr. Gopal Sistla, NY State Department of Environmental Conservation**

Five modeling centers are coordinating both PM and ozone modeling for the northeast, including NY, MD, NJ, VA, and NESCAUM. Rutgers and the University of Maryland are participating.

Preliminary PM modeling was compared to 2002 monitoring data from FRM, STN, and IMPROVE sites in the Ozone Transport Retion (OTR) plus the remainder of Virginia. July 6-9 data was excluded due to forest fire impacts. There are 264 FRM sites, 50 STN, and 21 IMPROVE sites in the OTR+

Results indicated that CMAQ was generally over-estimating PM during cold months and under-estimating PM during the summer. There was excellent agreement during the mid-August episode.

Dr. Sistla’s further evaluation focused on the NY metropolitan area, which is a nonattainment area for PM$_{2.5}$. 56 FRM monitors at 46 locations and 9 STN monitors at 8 locations were used in the evaluation for this area. Two counties in CT, 10 in NY and 10 in NJ are included in the nonattainment area. Sulfates, nitrates, and ammonium were over-estimated, as was elemental carbon and soil mass.

Organic carbon was generally over-estimated except very much under-estimated in the summer. CMAQ predicts that 80 to 90% of OM is in the primary fraction.

EPA’s methodology for calculating SIP design values and relative reduction factors requires calculations for each species and for various seasons. Data substitution for missing data has not yet been completed.

There is a significant amount of work left to do to post-process model results once the modeling is completed to meet EPA’s requirements.

Preliminary results indicate that modeling will show attainment in 2009 at all monitors in the NYC metro area.

**MANE-VU PM and Visibility Modeling**  
**Dr. Gary Kleiman, NESCAUM**

NESCAUM is the lead for regional haze modeling in the MANE-VU region, so their analysis of modeling results focuses on IMPROVE monitoring sites at Class I areas rather than on nonattainment areas.
MANE-VU has used both the CMAQ platform and other sulfate tagging and apportionment tools (REMSAD, CALPUFF, q/D, % time upwind).

Work products include: the MANE-VU Contribution Assessment report, 2018 projections, 2018 pollution apportionment, and (coming soon) 2018 reasonable progress projections.

CMAQ under-estimates sulfate to some extent at Class I areas, mostly in the summertime. Within the MANE-VU region, correlations are very good for CMAQ. REMSAD correlations are not quite as good.

CMAQ generally over-estimates nitrate except in May through August.

CMAQ yields about a 75% under-estimate of OC in the summer months, but this is primarily in the VISTAS region. In the MANE-VU region, performance is better.

Sulfate affecting MANE-VU Class I areas comes from states within and outside MANE-VU. There will be dramatic reductions in SO2 emissions by 2018, which will result in dramatic reductions in sulfate mass. The most significant reductions will occur in the southern part of the MANE-VU region, since that is closest to the areas with large sources which will be controlled.

Most MANE-VU Class I sites will achieve more than uniform progress in visibility improvement. Dr. Kleiman noted that the next question is, “what’s reasonable progress?” To assist in that decision, NESCAUM is conducting a sensitivity run to evaluate the impacts of additional control measures to address the impacts of low sulfur heating oil, additional controls on EGUs, BART, and possibly other measures. Results from the 2018 reasonable progress projections should be available soon.