Appendix G-1

Conceptual Model

The Nature of the Fine Particle and Regional Haze Air Quality Problems in the MANE-VU Region:
A Conceptual Description

Prepared for the Ozone Transport Commission

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Executive Summary

Scientific evidence has established a solid link between cardiac and respiratory health risks and transient exposure to ambient fine particle pollution. The same fine particles that are capable of penetrating deep into the lungs are also in the size range that is most efficient at absorbing and scattering visible light, thus impairing visibility. The emission sources, atmospheric chemistry, and meteorological phenomena that influence ambient concentrations of fine particle pollution can act on scales that range from hundreds to thousands of kilometers. Fine particles are not exclusively a secondary pollutant; primary fine particle pollution from local sources can have a significant effect on ambient concentrations in some locations. Fine particles are also not exclusively a summertime pollutant. There are important differences between the meteorological and chemical dynamics that are responsible for high fine particle levels during summer and winter.

In 1997, the U.S. Environmental Protection Agency (USEPA) issued a national ambient air quality standard (NAAQS) for fine particles with an aerodynamic diameter of 2.5 micrometers or less. In 1999, the USEPA followed up with the Regional Haze Rule that enforces a national visibility goal laid out in the Clean Air Act. This will ultimately restore natural visibility to 156 national parks and wilderness areas across the country (called “Class I” areas). To address these Clean Air Act requirements, states will have to develop State Implementation Plans (SIPs) detailing their approaches for reducing fine particle pollution to meet the health-based fine particle NAAQS. They also must develop plans that address the degradation of visibility that exists in various parts of the Northeast (referred to as the Mid-Atlantic/Northeast Visibility Union (MANE-VU) region). As part of this process, the USEPA urges states to include in their SIPs a conceptual description of the pollution problem in their nonattainment and Class I areas. This document provides the conceptual description of the fine particulate and regional haze problems in the MANE-VU states consistent with the USEPA’s guidance.

Scientific studies of the regional fine particle problem have uncovered a rich complexity in the interaction of meteorology and topography with fine particle formation and transport. Large scale high pressure systems covering hundreds of thousands of square miles are the source of classic severe fine particle episodes in the eastern United States, particularly in summer. These large, synoptic scale systems create particularly favorable conditions for the oxidation of sulfur dioxide (SO_2) emissions to various forms of sulfate which, in turn, serves to form – or is incorporated into – fine particles that are subsequently transported over large distances. These synoptic scale systems move from west to east across the United States, bringing air pollution emitted by large coal-fired power plants and other sources located outside MANE-VU into the region. This then adds to the pollution burden within MANE-VU on days when MANE-VU’s own air pollution sources are themselves contributing to poor air quality. At times, the high pressure systems may stall over the East for days, creating particularly intense fine particle episodes.

In the winter, temperature inversions occur that are effective at concentrating local primary particle emissions at the surface overnight and during early morning hours. This pollution can then be mixed into regionally transported particle pollution (aloft) later in the morning when convection is restored. Additionally, the lower temperature in the winter can shift the chemical equilibrium in the atmosphere slightly toward the production of nitrate particle pollution relative to sulfate formation. As a result, nitrate can become a significant fraction of measured fine particle mass in parts of the eastern U.S. during winter months.

Primary and secondary emissions of carbon-containing compounds (e.g., diesel exhaust, biogenic organic carbon emissions, and anthropogenic volatile organic compound emissions) all contribute to a significant presence of carbonaceous aerosol across the MANE-VU region, which can vary from urban to rural locations and on a seasonal basis. In addition, short range pollution transport exists, with primary and precursor particle pollutants pushed by land, sea, mountain, and valley breezes that can selectively affect relatively local areas. With the knowledge of the different emission sources, transport scales, and seasonal meteorology in various locations adjacent to and within MANE-VU, a conceptual picture of fine particle pollution and its impacts emerges.

The conceptual description that explains elevated regional $PM_{2.5}$ peak concentrations in the summer differs significantly from that which explains the largely urban peaks observed during winter. On average, summertime concentrations of sulfate in the northeastern United States are more than twice that of the next most important fine particle constituent, organic carbon (OC), and more than four times the combined concentration of nitrate and black carbon (BC) constituents. Episodes of high summertime sulfate concentrations are consistent with stagnant meteorological flow conditions upwind of the MANE-VU region and the accumulation of airborne sulfate (via atmospheric oxidation of SO_2) followed by long-range transport of sulfur emissions from industrialized areas within and outside the region.

National assessments have indicated that in the winter, sulfate levels in urban areas are higher than background sulfate levels across the eastern U.S., indicating that the local urban contribution to wintertime sulfate levels is significant relative to the regional sulfate contribution from long-range transport. A network analysis for the winter of 2002 suggests that the local enhancement of sulfate in urban areas of the MANE-VU region ranges from 25 to 40% and that the long-range transport component of $PM_{2.5}$ sulfate is still the dominant contributor in most eastern cities.

In the winter, urban OC and sulfate each account for about a third of the overall $PM_{2.5}$ mass concentration observed in Philadelphia and New York City. Nitrate also makes a significant contribution to urban $PM_{2.5}$ levels observed in the northeastern United States during the winter months. Wintertime concentrations of OC and nitrate in urban areas can be twice the average regional concentrations of these pollutants, indicating the importance of local source contributions. This is likely because winter conditions are more conducive to the formation of local inversion layers which prevent vertical mixing. Under these conditions, emissions from tailpipe, industrial and other local sources become concentrated near the Earth's surface, adding to background pollution levels associated with regionally transported emissions.

From this conceptual description of fine particle pollution formation and transport into and within MANE-VU, air quality planners need to develop an understanding of what it will take to clean the air in the MANE-VU region. Every air pollution episode is unique in its specific details. The relative influences of the transport pathways and local emissions vary by hour, day, and season. The smaller scale weather patterns that affect pollution accumulation and its transport underscore the importance of local (in-state) controls for SO_2, nitrogen oxides (NO_X) and volatile organic compound (VOC) emissions. Larger synoptic scale weather patterns, and pollution patterns associated with them, support the need for SO_2 and NO_X controls across the broader eastern United States. Studies and characterizations of nocturnal low level jets also support the need for local and regional controls on SO_2 and NO_X sources as locally generated and transported pollution can both be entrained in low level jets formed during nighttime hours. The presence of land, sea, mountain, and valley breezes indicate that there are unique aspects of pollution accumulation and transport that are area-specific and will warrant policy responses at the local and regional levels beyond a one-size-fits-all approach.

The mix of emission controls is also important. Regional fine particle formation is primarily due to SO_2, but NO_X is also important because of its influence on the chemical equilibrium between sulfate and nitrate pollution during winter. While the effect of reductions in anthropogenic VOCs is less well characterized at this time, secondary organic aerosol (SOA) is a major component of fine particles in the region and reductions in anthropogenic sources of OC may have a significant effect on fine particle levels in urban nonattainment areas. Therefore, a combination of localized NO_X and VOC reductions in urban centers with additional SO_2 and NO_X reductions from across a larger region will help to reduce fine particles and precursor pollutants in nonattainment areas as well improve visibility across the entire MANE-VU region.

1. INTRODUCTION

1.1. Background

Fine particle pollution is a persistent public health problem in the Mid-Atlantic/Northeast Visibility Union (MANE-VU) region. Because of its physical structure, fine particulate matter ($PM_{2.5}$) can bypass conductive airways and deliver exogenous materials, such as reactive organic chemicals that adsorb onto the particle core, into the deep lung.[1] Studies of particulate matter (PM) in urban areas have found associations of short- (daily) and long-term (annual and multiyear) exposure to airborne PM as well as $PM_{2.5}$ with cardiopulmonary health outcomes. These effects include increased symptoms, hospital admissions and emergency room visits, and premature death (Pope *et al.* 2004).

In addition to health implications, visibility impairment in the eastern United States is largely due to the presence of light-absorbing and light-scattering fine particles in the atmosphere. The United States Environmental Protection Agency (USEPA) has identified visibility impairment as the best understood of all environmental effects of air pollution (Watson, 2002). A long-established physical and chemical theory relates the interaction of particles and gases in the atmosphere with the transmission of visual information along a sight path from object to observer.

The Clean Air Act requires states that have areas designated “nonattainment” of the fine particle national ambient air quality standard (NAAQS) to submit State Implementation Plans (SIPs) demonstrating how they plan to attain the fine particle NAAQS.[2] The Clean Air Act also contains provisions for the restoration and maintenance of visibility in 156 federal Class I areas.[3] SIPs for dealing with visibility impairment (or regional haze) must include a long-term emissions management strategy aimed at reducing fine particle pollution in these rural areas.

As part of the SIP process for both of these air quality issues, the USEPA urges states to include a conceptual description of the pollution problem. The USEPA has provided guidance on developing a conceptual description, which is contained in Chapter 11 of the document “Guidance on the Use of Models and Other Analyses for

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[1] $PM_{2.5}$ or “fine particles” refer to those particles with a diameter ≤ 2.5 micrometers (μm).

[2] The 1997 $PM_{2.5}$ NAAQS includes a requirement that the three-year average of yearly annual average $PM_{2.5}$ design values must be below 15 $\mu g/m^3$ and a requirement that the three-year average of the 98th percentile 24-hour average concentration must be below 65 $\mu g/m^3$. In October 2006, the USEPA acted to change the daily standard (98th percentile value based on valid 24-hour average concentrations measured at a site) from 65 to 35 $\mu g/m^3$.

[3] The Class I designation applies to national parks exceeding 6,000 acres, wilderness areas and national memorial parks exceeding 5,000 acres, and all international parks that were in existence prior to 1977. In the MANE-VU area, this includes: Acadia National Park, Maine; Brigantine Wilderness (within the Edwin B. Forsythe National Wildlife Refuge), New Jersey; Great Gulf Wilderness, New Hampshire; Lye Brook Wilderness, Vermont; Moosehorn Wilderness (within the Moosehorn National Wildlife Refuge), Maine; Presidential Range – Dry River Wilderness, New Hampshire; and Roosevelt Campobello International Park, New Brunswick.

Demonstrating Attainment of Air Quality Goals for Ozone, $PM_{2.5}$, and Regional Haze" (EPA-Draft 3.2, September 2006) (Appendix A of this report reproduces Chapter 11 of the USEPA guidance document). This report provides the MANE-VU states with the basis for their conceptual descriptions, consistent with the USEPA's guidance. In the guidance, the USEPA recommends addressing 13 questions related to $PM_{2.5}$ and eight questions related to visibility to help define the problem in a nonattainment or Class I area. This report addresses these questions, as well as provides some in-depth data and analyses that can assist states in developing conceptual descriptions tailored to their specific areas.

1.2. PM Formation

Fine particles directly emitted into the atmosphere are called "primary" fine particles, and they come from both natural and human sources. These fine particles commonly include unburned carbon particles directly emitted from high-energy processes such as combustion, and particles emitted as combustion-related vapors that condense within seconds of being exhausted to ambient air. Combustion sources include motor vehicles, power generation facilities, industrial facilities, residential wood burning, agricultural burning, and forest fires.

Fine particles are also comprised of "secondary" fine particles, which are formed from precursor gases reacting in the atmosphere or through the addition of PM to pre-existing particles. Although direct nucleation from the gas phase is a contributing factor, most secondary material accumulates on pre-existing particles in the 0.1 to 1.0 micrometer (µm) range and typically account for a significant fraction of the fine PM mass. Examples of secondary particle formation include the conversion of sulfur dioxide (SO_2) to sulfuric acid (H_2SO_4) droplets that further react with ammonia (NH_3) to form various sulfate particles (e.g., ammonium sulfate $(NH_4)_2SO_4$, ammonium bisulfate (NH_4HSO_4), and letovicite ($(NH_4)_3H(SO_4)_2$). The dominant source of SO_2 emissions in the eastern U.S. is fossil fuel combustion, primarily at coal-fired power plants and industrial boilers. Similarly, secondary $PM_{2.5}$ is created by the conversion of nitrogen dioxide (NO_2) to nitric acid (HNO_3) which reacts further with ammonia to form ammonium nitrate (NH_4NO_3) particles. Nitrate particles are formed from the NO_X emitted by power plants, automobiles, industrial boilers, and other combustion sources. Nitrate production in the northeastern U.S. is ammonia-limited and controlled by the availability of sulfate and temperature, especially along the East Coast.[4] While human sources account for most nitrate precursors in the atmosphere, there are some natural sources, including lightning, biological and abiological processes in soils, and stratospheric intrusion. Large sources of ammonia arise from major livestock production and fertilizer application throughout the Midwest, Gulf Coast, mid-Atlantic, and southeastern United States, in addition to the sources of ammonia associated with human activities.

The carbon fraction of fine PM may refer to black carbon (BC) and primary organic and/or secondary organic carbon (OC). Most black carbon is primary, which is

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[4] Ammonia reacts preferentially with sulfuric acid, and if sufficient excess ammonia is available, it can then combine with nitric acid to form particulate nitrate.

also sometimes referred to as elemental carbon (EC) or soot. Black carbon is the light-absorbing carbonaceous material in atmospheric particles caused by the combustion of diesel, wood, and other fuels. Organic carbon includes both primary emissions and secondary organic PM in the atmosphere. Secondary organic particles are formed by reactions involving volatile organic compounds (VOCs), which yield compounds with low saturation vapor pressures that nucleate or condense on existing particles at ambient temperature. Organic carbon in both the gas and solid phase is emitted by automobiles, trucks, and industrial processes, as well as by many types of vegetation. The relative amounts of organic carbon from different sources remain highly uncertain, and data are needed to be able to assess the relative contribution of primary versus secondary and anthropogenic versus biogenic production.

1.3. PM Impacts on Visibility

Under natural atmospheric conditions, the view in the eastern United States would extend about 60 to 80 miles (100 to 130 kilometers) (Malm, 2000). Unfortunately, views of such clarity have become a rare occurrence in the East. As a result of man-made pollution, the average visual range in the eastern half of the country has diminished to about 15-30 miles, approximately one-third the visual range that would be observed under unpolluted natural conditions.

In general, the ability to see distant features in a scenic vista is determined less by the amount of light reaching the observer than by the contrast between those features and their surroundings. For example, the illumination of a light bulb in a greenhouse is barely discernible on a sunny day but would be highly visible at night. Similarly, a mountain peak is easily seen if it appears relatively dark against the sunlit sky. If, on the other hand, a milky haze "fills" the space between the observer and the mountain peak, the contrast between the mountain and its background is diminished as both take on a similar hue (Figure 1-1).

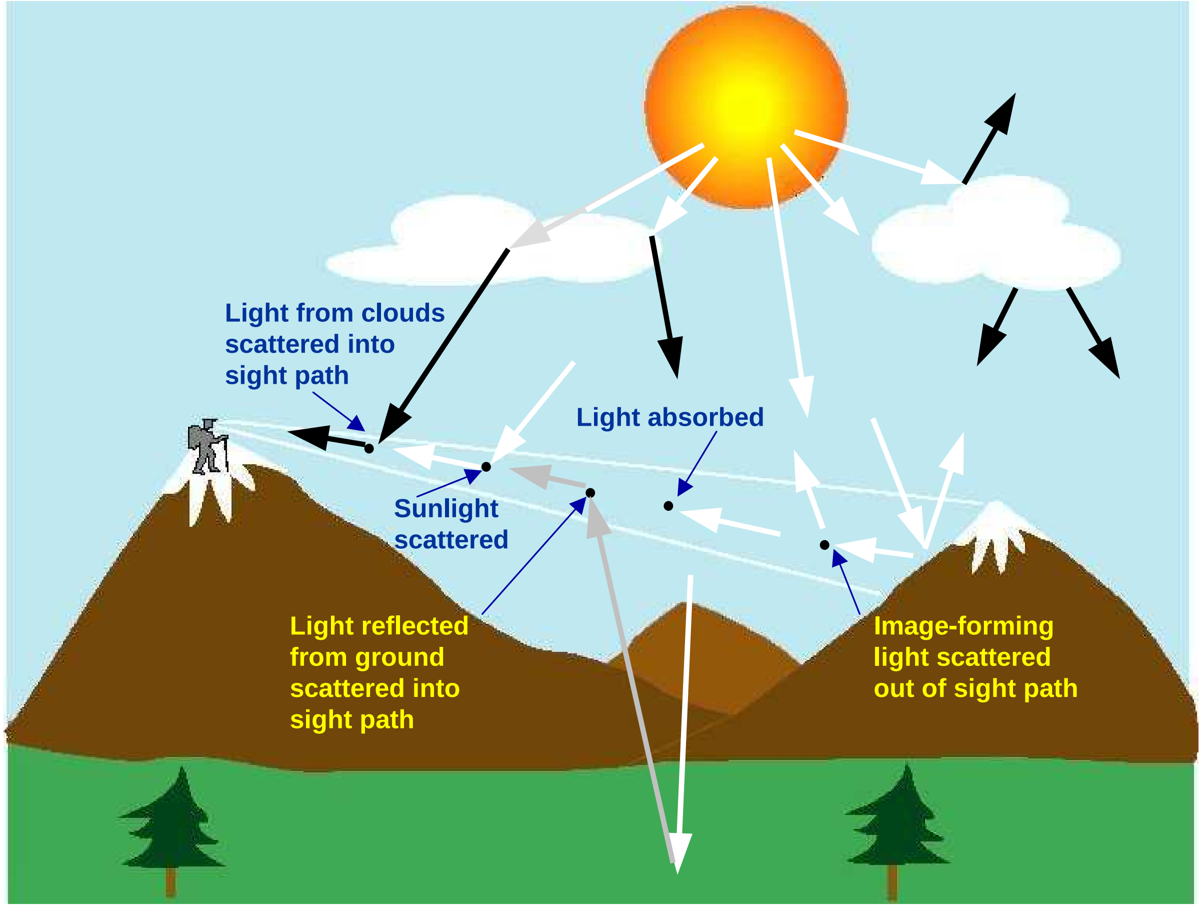
Figure 1-1. View of a good visibility day (left) and a poor visibility day (right) at Acadia National Park, Maine in June 2003.

Source: CAMNET, http://www.hazecam.net

In simple terms, this hazy effect occurs when small particles and certain gaseous molecules in the atmosphere absorb or scatter visible light, thereby reducing the amount of visual "information" that reaches the observer. This occurs to some extent even under natural conditions, primarily as a result of the light scattering effect of individual air molecules (known as Rayleigh scattering[5]) and of naturally occurring aerosols.[6] The substantial visibility impairment caused by manmade pollution, however, is almost entirely attributable to the increased presence of fine particles in the atmosphere.[7]

Figure 1-2 presents a simplified schematic of the way such small particles interact with packets of light or "photons" as they travel from a distant object to an observer. Along the way, particles suspended in the air can deflect or scatter some of the photons out of the sight path. Intervening particles can also absorb photons, similarly removing them from the total amount of light reaching the observer.

Figure 1-2. Schematic of visibility impairment due to light scattering and absorption (adapted from Malm, 2000).



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[5] Because air molecules more effectively scatter light of short wavelengths (i.e., blue light), Rayleigh scattering explains the blue color of the sky.

[6] Atmospheric aerosol is a more general term for fine particles suspended in the atmosphere and refers to any particle (solid or liquid) that is suspended in the atmosphere.

[7] The only light-absorbing *gaseous* pollutant present in the atmosphere at significant concentrations is nitrogen dioxide (NO_2). However, the contribution of NO_2 to overall visibility impacts in the Northeast is negligible and hence its effects are not generally included in this discussion or in standard calculations of visibility impairment.

At the same time, particles in the air can scatter light into the sight path, further diminishing the quality of the view. The extraneous light can include direct sunlight and light reflected off the ground or from clouds. Because it is not coming directly from the scenic element, this light contains no visual information about that element. When the combination of light absorption and light scattering (both into and out of the sight path) occurs in many directions due to the ubiquitous presence of small particles in the atmosphere, the result is commonly described as “haze.”

1.4. $PM_{2.5}$ Design Values in the MANE-VU Region

SIP developers use monitoring data in several important ways to support SIP activities. This section as well as Section 1.5 present measurements from the FRM and IMPROVE network needed in establishing SIP requirements. Following USEPA guidance (40CFR Part 50, Appendix N; USEPA, 2003a; USEPA, 2003b), we use these data to preview the Design Values and Baseline Conditions that SIP developers must consider for each nonattainment area and Class I area.

The current annual fine particle National Ambient Air Quality Standard was established in 1997 at 15 $\mu g/m^3$. To meet this standard, the 3-year average of a site’s annual mean concentration must not be greater than this level. The current daily standard was set at 65 $\mu g/m^3$ at the 98th percentile level. To meet this standard, the 98th percentile value (of valid measurements recorded at a site) must not be greater than this level. No counties in MANE-VU have been designated nonattainment for the daily standard, however, the USEPA has revised the NAAQS with respect to the 24-hr average concentrations and states will have to comply with the new standard (35 $\mu g/m^3$ at the 98th percentile level) within five years of designations (expected in 2010). Fine particle data from the USEPA’s Air Quality System (AQS) database for years 2002 through 2004 were used to determine the attainment status of monitoring sites in MANE-VU.

Table 1-1 shows a summary of areas found to exceed the annual standard (no areas exceed the daily standard). As tabulated, 12 areas fail to achieve the annual standard, with design values ranging from 15.1 to 20.4 $\mu g/m^3$. The nonattainment areas are concentrated in Pennsylvania and the coastal urban corridor. Sulfates and organic carbon represent the largest contributors to these high fine particle levels.

Table 1-1. 2004 $PM_{2.5}$ Design Value for Nonattainment Areas in MANE-VU

State(s)	Nonattainment Area	2004 Annual Design Value	2004 24-hr Design Value
MD	Baltimore	16.3	41
PA	Harrisburg-Lebanon-Carlisle	15.4	41
PA	Johnstown	15.3	40
PA	Lancaster	16.8	42
PA	Liberty-Clairton	20.4	65
MD	Martinsburg, WV-Hagerstown	16.1	39
NY-NJ-CT	New York-N. New Jersey-Long Island	16.8	50
PA-NJ-DE	Philadelphia-Wilmington	15.4	39
PA	Pittsburgh-Beaver Valley	16.5	45
PA	Reading	16.1	42
DC-MD-VA	Washington, DC	15.1	42
PA	York	16.9	43

1.5. Regional haze baseline conditions

The Regional Haze Rule requires states and tribes to submit plans that include calculations of current and estimated baseline and natural visibility conditions. They will use monitoring data from the IMPROVE program as the basis for these calculations. Table 1-2 and Table 1-3 present the five-year average[8] of the 20 percent worst day mass concentrations and 20 percent best day mass concentrations respectively in six Class I areas. Five of these areas are in MANE-VU and one (Shenandoah) is nearby but located in a neighboring regional planning organization (RPO) region.[9] Table 1-4 and Table 1-5 give the corresponding worst day and best day contributions to particle extinction for the six Class I areas. Each of these tables show the relative percent contribution for all six Class I sites. Sulfate and organic carbon dominate the fine mass, with sulfate even more important to particle extinction.

To guide the states in calculating baseline values of reconstructed extinction and for estimating natural visibility conditions, the USEPA released two documents in the fall of 2003 outlining recommended procedures (USEPA 2003a; USEPA 2003b). Recently, the IMPROVE Steering Committee endorsed an alternative method for the calculation of these values. The IMPROVE alternative methods were used, to create Table 1-6, which provides detail on the uniform visibility goals for the 20 percent worst conditions at the six Class 1 areas.

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[8] Great Gulf calculations are based on four years of data (2001-2004).

[9] Note that values presented for Shenandoah, a Class I area in the Visibility Improvement State and Tribal Association of the Southeast (VISTAS) region, are for comparative purposes only. VISTAS will determine uniform rates of progress for areas within its region.

The first column of data in Table 1-6 gives the alternative proposed natural background levels for the worst visibility days at these six sites. MANE-VU has decided to use this approach, at least initially, for 2008 SIP planning purposes (NESCAUM, 2006). The second column shows the baseline visibility conditions on the 20 percent worst visibility days. These values are based on IMPROVE data from the official five-year baseline period (2000-2004) and again were calculated using the IMPROVE alternative approach. Using these baseline and natural background estimates, we derive the uniform rate of progress shown in the third column.[10] The final column displays the interim 2018 progress goal based on 14 years of improvement at the uniform rate.

Table 1-2. Fine mass and percent contribution for 20 percent worst days

20% Worst-day Fine Mass (µg/m³)/% contribution to fine mass					
Site	SO_4	NO_3	OC	EC	Soil
Acadia	6.3/ 56%	0.8/ 7%	3.2/ 28%	0.4/ 4%	0.5/ 5%
Brigantine	11.6/ 56%	1.7/ 8%	5.8/ 28%	0.7/ 3%	1/ 5%
Great Gulf	7.3/ 59%	0.4/ 3%	3.8/ 31%	0.4/ 3%	0.6/ 5%
Lye Brook	8.5/ 58%	1.1/ 7%	3.9/ 27%	0.5/ 3%	0.6/ 4%
Moosehorn	5.7/ 54%	0.7/ 7%	3.4/ 32%	0.4/ 4%	0.4/ 4%
Shenandoah	13.2/ 68%	0.7/ 3%	4.2/ 22%	0.6/ 3%	0.7/ 4%

Table 1-3. Fine mass and percent contribution for 20 percent best days

20% Best-day Fine Mass (µg/m³)/% contribution to fine mass					
Site	SO_4	NO_3	OC	EC	Soil
Acadia	0.8/ 42%	0.1/ 6%	0.8/ 41%	0.1/ 5%	0.1/ 6%
Brigantine	1.8/ 43%	0.5/ 11%	1.5/ 35%	0.2/ 6%	0.2/ 5%
Great Gulf	0.7/ 43%	0.1/ 7%	0.7/ 40%	0.1/ 5%	0.1/ 6%
Lye Brook	0.6/ 44%	0.1/ 11%	0.4/ 33%	0.1/ 5%	0.1/ 7%
Moosehorn	0.8/ 37%	0.1/ 6%	1/ 47%	0.1/ 5%	0.1/ 5%
Shenandoah	1.4/ 45%	0.5/ 16%	1/ 29%	0.2/ 5%	0.2/ 5%

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[10] We calculate the rate of progress as (baseline – natural background)/60 to yield the annual deciview (dv) improvement needed to reach natural background conditions in 2064, starting from the 2004 baseline.

Table 1-4. Particle extinction and percent contribution for 20 percent worst days

20% Worst-day particle extinction (Mm^{-1}) /% Contribution to particle extinction						
Site	SO_4	NO_3	OC	EC	Soil	CM
Acadia	69.2/ 64%	8/ 7%	11.2/ 10%	4.3/ 4%	0.5/ 0%	1.9/ 2%
Brigantine	127.1/ 66%	15.7/ 8%	24.2/ 13%	7/ 4%	1/ 1%	5.4/ 3%
Great Gulf	76.6/ 68%	3/ 3%	14.4/ 13%	3.9/ 3%	0.6/ 1%	3/ 3%
Lye Brook	87.3/ 67%	9.1/ 7%	15.3/ 12%	4.8/ 4%	0.6/ 0%	1.8/ 2%
Moosehorn	58.5/ 60%	6.4/ 7%	11.9/ 12%	4.4/ 5%	0.4/ 0%	2.1/ 3%
Shenandoah	155.5/ 79%	5.8/ 3%	16.1/ 8%	5.7/ 3%	0.7/ 0%	2.5/ 1%

Table 1-5. Particle extinction and percent contribution for 20 percent best days

20% Best-day particle extinction (Mm^{-1}) /% Contribution to particle extinction						
Site	SO_4	NO_3	OC	EC	Soil	CM
Acadia	6.8/ 28%	1.1/ 4%	2.2/ 9%	0.9/ 4%	0.1/ 0%	0.7/ 6%
Brigantine	14.8/ 35%	3.9/ 9%	4.5/ 11%	2.4/ 6%	0.2/ 1%	3.2/ 11%
Great Gulf	5.8/ 27%	1/ 4%	2/ 9%	0.8/ 4%	0.1/ 0%	0.9/ 8%
Lye Brook	4.4/ 23%	1.2/ 6%	1.3/ 7%	0.6/ 3%	0.1/ 0%	0.5/ 6%
Moosehorn	6.7/ 26%	1.1/ 4%	3.1/ 12%	1/ 4%	0.1/ 0%	1.1/ 8%
Shenandoah	11.2/ 36%	4.2/ 13%	2.9/ 9%	1.6/ 5%	0.2/ 1%	1.1/ 5%

Table 1-6. Natural background and baseline calculations for select Class I areas

Site	**20 % Worst Days Natural Background (dv)**	**20% Worst Days Baseline 2000-04(dv)**	**Uniform Rate (dv/yr)**	**Interim Progress Goal 2018 (dv)**	**20% Best Days Baseline 2000-04(dv)**
Acadia	12.54	22.89	0.17	20.47	8.77
Brigantine	12.34	29.01	0.28	25.12	14.33
Great Gulf	12.12	22.82	0.18	20.32	7.66
Lye Brook	11.85	24.44	0.21	21.50	6.37
Moosehorn	12.10	21.72	0.16	19.48	9.15
Dolly Sods	10.45	29.05	0.31	24.71	12.28
James River Face	11.20	29.12	0.30	24.94	14.21
Shenandoah	11.44	29.31	0.30	25.14	10.92

As demonstrated in Table 1-2, the inorganic constituents of fine particles, sulfates and nitrates are the dominant contributors to visibility impairment, accounting for about 80 percent of total particle extinction. Within the MANE-VU sites, the relative split between these two components is ~8 to 1 sulfate to nitrate (at Shenandoah, the average 20 percent worst day contribution of sulfates is even more dominant). Carbonaceous components account for the bulk of the remaining particle extinction, ranging from 12 to nearly 20 percent, mostly in the form of organic carbon. The remaining components add little to the extinction budget on the worst days, with a few percent attributable to coarse mass and around a half percent from fine soil.

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2. A DETAILED LOOK AT FINE PARTICLE POLLUTION AND REGIONAL HAZE IN THE MANE-VU REGION

Developing a conceptual description of fine particle pollution or regional haze requires combining experience and atmospheric-science expertise with multiple data sources and analysis techniques. This includes measured data on ambient pollutant concentrations as well as emission inventory and meteorological data, chemical transport modeling, and observationally based models (NARSTO, 2003). Here, we begin with a conceptual description based on the existing scientific literature and regional data analyses concerning $PM_{2.5}$ and its effect on visibility. This includes numerous review articles and reports on the subject. Subsequent chapters review monitoring data, emissions inventory information, and modeling results to support the conceptual understanding of regional fine particle pollution presented here.

Most past assessments of fine particle pollution and visibility impairment have tended to be national in scope. For purposes of this discussion, we have selectively reviewed the literature in order to present a distinctly eastern U.S. focus. While we already know much about fine particle pollution and visibility impairment and their causes in the MANE-VU region (see NESCAUM, 2001, 2006; NARSTO, 2003; Watson, 2002), significant gaps in understanding remain with respect to the nitrate and organic component of $PM_{2.5}$. While research continues, we have assembled the relevant information that is available to provide an overview of our current understanding of the regional context for $PM_{2.5}$ nonattainment and visibility impairment in the MANE-VU region.

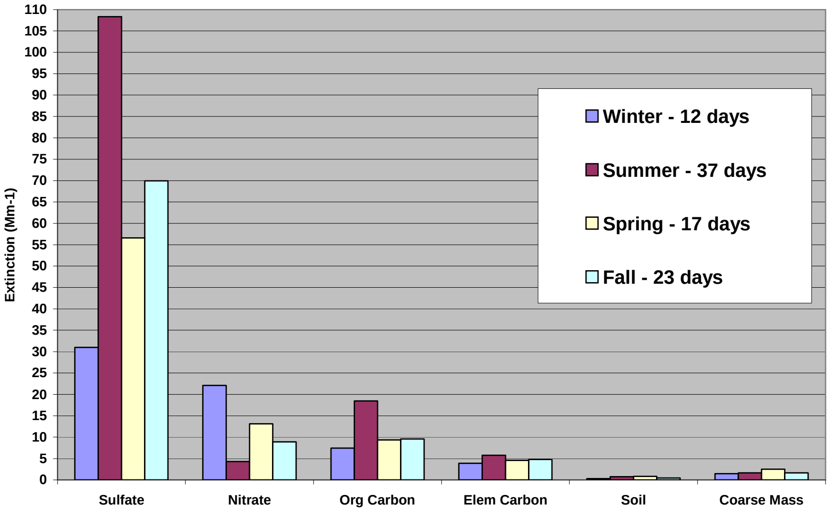
2.1. Chemical composition of particulate matter in the rural MANE-VU region

Sulfate alone accounts for anywhere from one-half to two-thirds of total fine particle mass on high $PM_{2.5}$ days in rural areas of MANE-VU. Even on low $PM_{2.5}$ days, sulfate generally accounts for the largest fraction (40 percent or more) of total fine particle mass in the region (NESCAUM, 2001, 2004b). Sulfate accounts for a major fraction of $PM_{2.5}$, not only in the Northeast but across the eastern United States (NARSTO, 2003).

After sulfate, organic carbon (OC) consistently accounts for the next largest fraction of total fine particle mass. Its contribution typically ranges from 20 to 30 percent of total fine particle mass on the days with the highest levels of $PM_{2.5}$. The fact that the contribution from organic carbon can be as high as 40 percent at the more rural sites on low $PM_{2.5}$ days is likely indicative of the role played by organic emissions from vegetation (so-called “biogenic hydrocarbons”).

Relative contributions to overall fine particle mass from nitrate (NO_3), elemental carbon, and fine soil are all smaller (typically under 10 percent), but the relative ordering among the three species varies with location and season. Figure 2-1 below, reflects the difference between nitrate and organic contributions to rural fine particle concentrations during different seasons (monitoring data for additional sites in the MANE-VU region are in Appendix B).

Figure 2-1. Comparison of contributions during different seasons at Lye Brook Wilderness Area on 20% worst visibility (high $PM_{2.5}$) days (2000-2003).

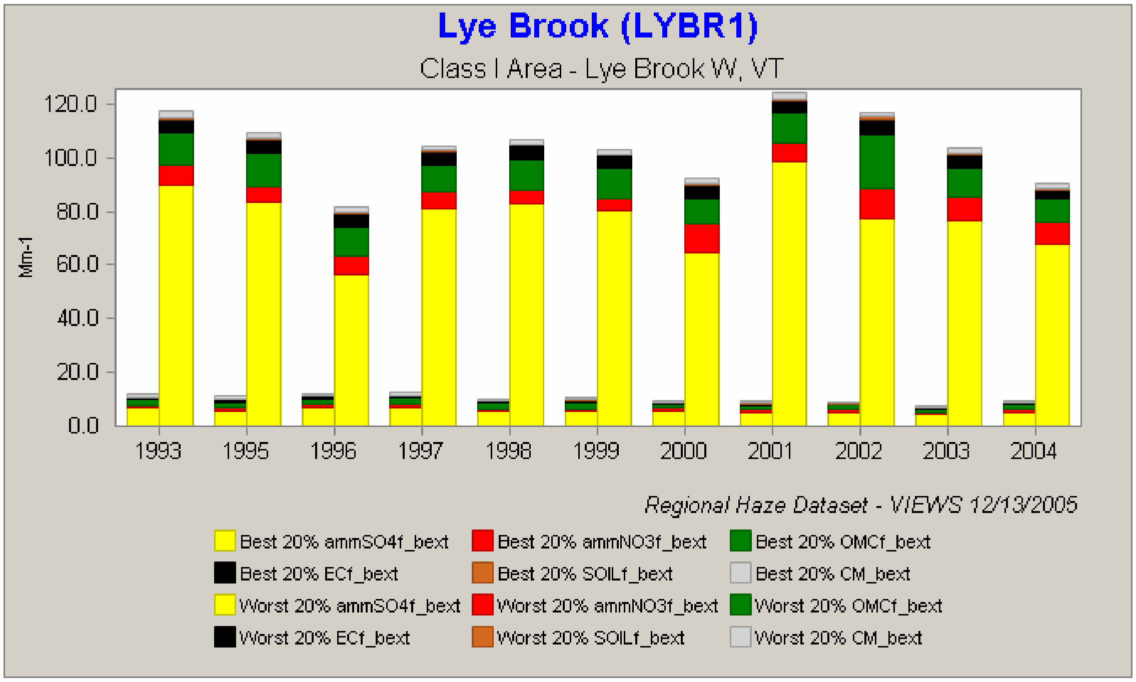


Almost all particle sulfate originates from sulfur dioxide (SO_2) oxidation and typically associates with ammonium (NH_4) in the form of ammonium sulfate ($(NH_4)_2SO_4$). Ninety-five percent of SO_2 emissions are from anthropogenic sources (primarily from fossil fuel combustion), while the majority of ammonium comes from agricultural activities and, to a lesser extent, from transportation sources in some areas (NARSTO, 2003).

Two major chemical pathways produce sulfate from SO_2 in the atmosphere. In the gas phase, production of sulfate involves the oxidation of SO_2 to sulfuric acid (H_2SO_4), ammonium bisulfate (NH_4HSO_4), or ammonium sulfate, depending on the availability of ammonia (NH_3). In the presence of small wet particles (typically much, much smaller than rain drops or even fog), a highly efficient aqueous phase process can oxidize SO_2 to sulfate extremely quickly (~10 percent per hour).

Not only is sulfate the dominant contributor to fine particle mass in the region, it accounts for anywhere from 60 percent to almost 80 percent of the *difference* between fine particle concentrations and extinction on the lowest and highest mass days at rural locations in the northeast and mid-Atlantic states (See Figure 2-2). Notably, at urban locations such as Washington DC, sulfate accounts for only about 40 percent of the difference in average fine particle concentrations for the 20 percent most versus least visibility impaired days (NESCAUM, 2001).

Figure 2-2. Comparison of species contributions on best and worst days at Lye Brook Wilderness Area.



2.2. Rural versus urban chemistry

Contributions to fine particle mass concentrations at rural locations include long-range pollutant transport as well as non-anthropogenic background contributions. Urban areas generally show mean $PM_{2.5}$ levels exceeding those at nearby rural sites. In the Northeast, this difference implies that local urban contributions are roughly 25 percent of the annual mean urban concentrations, with regional aerosol contributing the remaining, and larger, portion (NARSTO, 2003).

This rural versus urban difference in typical concentrations also emerges in a source apportionment analysis of fine particle pollution in Philadelphia (see Chapter 10 of NARSTO, 2003) using two different mathematical models, UNMIX and Positive Matrix Factorization (PMF). This analysis provides additional insight concerning sources of fine particle pollution in urban areas of the densely populated coastal corridor between Washington DC and New England. Specifically, this analysis found the following apportionment of $PM_{2.5}$ mass in the study area:

- Local SO_2 and sulfate: ~ 10 percent
- Regional sulfate: ~ 50 percent
- Residual oil: 4-8 percent
- Soil: 6-7 percent
- Motor vehicles: 25-30 percent

The analysis does not account for biogenic sources, which most likely are embedded in the motor vehicle fraction (NARSTO, 2003). The Philadelphia study suggests that both local pollution from nearby sources and transported "regional" pollution from distant sources contribute to the high sulfate concentrations observed in urban locations along the East Coast on an annual average basis. Summertime sulfate and organic carbon are strongly regional in eastern North America. Typically 75–95 percent of the urban sulfate concentrations and 60–75 percent of the urban OC concentrations arise from cumulative region-wide contributions (NARSTO, 2003). Urban air pollutants are essentially added on top of this regional background. Nitrate plays a noticeably more important role at urban sites compared to northeastern and mid-Atlantic rural monitoring sites, perhaps reflecting a greater contribution from vehicles and other urban pollution sources (NESCAUM, 2001).

It is difficult to discern any significant meaning about the cause of “excess” mass from a single pair of sites. There are many factors that influence the concentrations at a particular site and it is likely that for every pair of sites that shows an urban excess, one could find some pair of locations that might show something similar to an urban “deficit.” While paired sites from an urban and a rural location will *typically* show greater concentrations in the urban location and lower levels of pollution in rural areas, great care must be exercised in the interpretation of any two-site analysis such as the comparisons of speciated components of $PM_{2.5}$ presented here. Nonetheless, such comparisons do provide a general feel for the typical chemical composition of $PM_{2.5}$ in the eastern U.S. and the relative differences in chemical composition between rural and more urban locations. More detailed, “network”-wide analyses (e.g., see NESCAUM 2004b; relevant sections are attached in Appendix C to this report) indicate that the results provided are not anomalous of typical urban environments in the MANE-VU region.

Figure 2-3 and Figure 2-4 compare two urban-rural pairs of speciation monitors: the New York nonattainment area (Elizabeth and Chester, New Jersey) and the Boston metropolitan area (Boston and Quabbin Reservoir, Massachusetts). The first three sites are Speciation Trends locations, while the Reservoir site is part of the IMPROVE protocol network.[11]

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[11] To provide a more direct comparison of the differences between the urban and rural sites, only those days for which both monitors in a pair had data were used. Four seasonal averages were computed for 2002, with seasons defined as winter (January, February, December), spring (March, April, May), Summer (June, July, August) and Fall (September, October, November). July 7 was excluded from the analysis because the Quebec forest fires affecting the region on that day would have dominated the summertime averages. The major fine particle species categories considered included ammonium sulfate, ammonium nitrate, organic carbon, elemental carbon, and soil mass. The traditional assumptions about these constituents were made; all sulfate was fully neutralized and a multiplier of 1.4 was used to account for mass of organic carbon. An “other $PM_{2.5}$ mass” category was created to delineate the difference between gravimetric mass determined from the Teflon filter and the reconstructed mass sum of the individual mass constituents. Where no “other” mass is graphed, the sum of the species either equaled or exceeded the directly measured mass. No adjustments were made to account for the different operational definitions of carbon between the IMPROVE and STN networks. Average blank corrections were applied to all samples. In the case of New York City, both rural and urban monitors were STN. The Boston pair reflects not only inter-site differences, but also differences in definition of organic and elemental carbon. However, the general interpretation of the data differences remains consistent. Based on current understanding, the rural elemental carbon would be even lower than what is shown on the graph if it were made consistent with the STN definition of EC. Likewise, the organic carbon value would increase slightly for the rural value, as the

Figure 2-3. New York nonattainment area (Elizabeth, NJ) compared to an upwind background site (Chester, NJ)

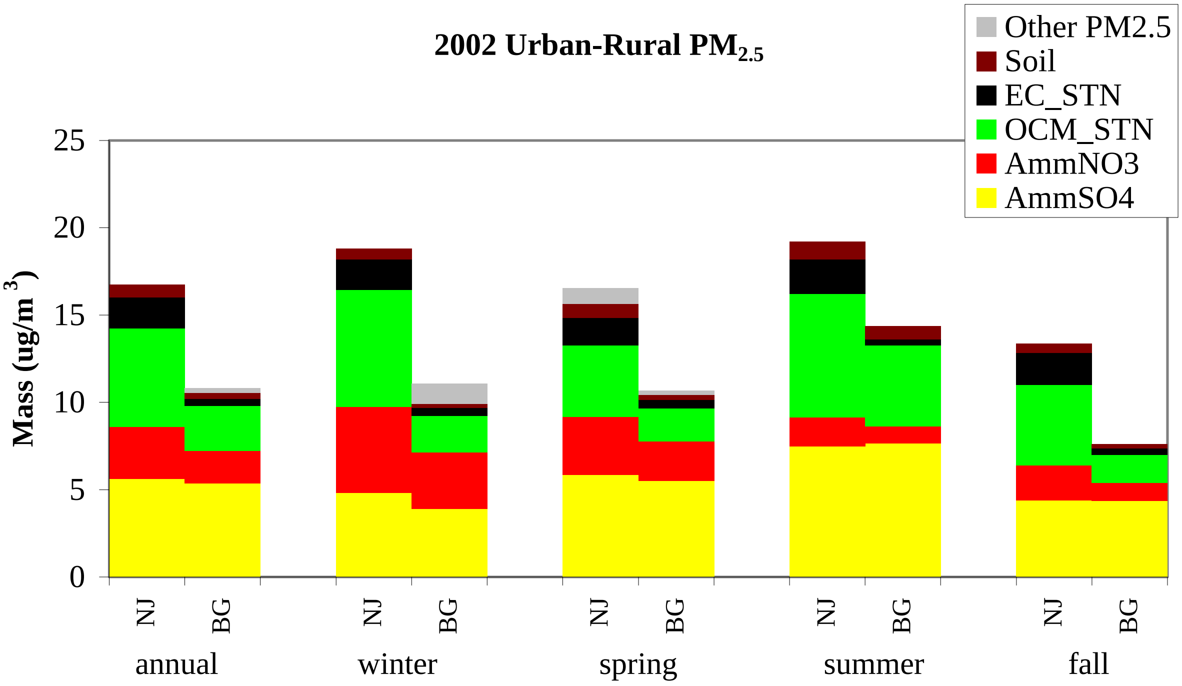
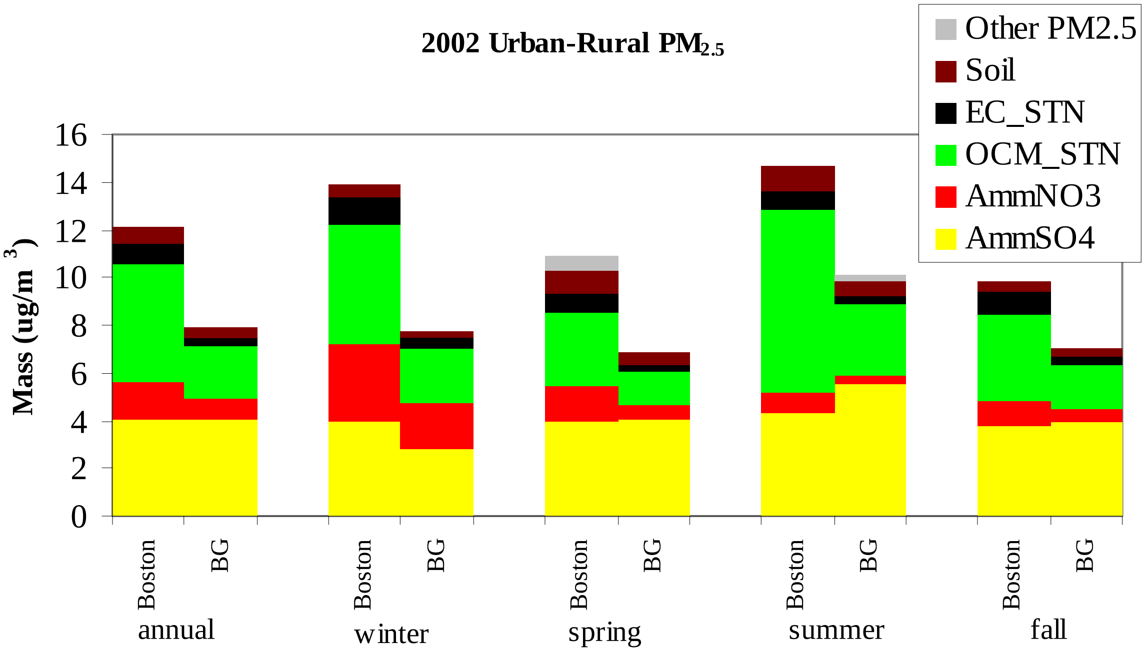


Figure 2-4. Boston urban area (Boston, MA) compared to an upwind background site (Quabbin Reservoir, MA)



EC would be allocated to OC. The urban OC levels are so much greater than those in the rural area that a slight increase in rural OC makes little difference.

The urban-rural differences show consistency for both the New York City nonattainment area and Boston. On an annual scale, the sulfate levels are comparable, with increased mass loading at these urban sites driven primarily by differences in nitrates and carbon with smaller differences in "soil" levels. One interesting aspect of this comparison is the seasonal differences in the urban-rural sulfate split. On an annual basis, sulfate appears to be similar at urban and rural locations (based on these two pair of sites); however, during the colder months, the urban sulfate levels are elevated relative to the rural levels. This behavior is opposite during the summer. During the wintertime, the Northeast urban corridor itself is a substantial source of sulfur emissions. These local emissions can be trapped near the surface during the winter and have a corresponding higher impact on the urban area relative to the rural area.

For both urban and rural areas, the summertime OC levels are significantly greater than wintertime concentrations. Although the oxidation chemistry slows in winter, the cooler temperatures change the phase dynamics, driving more mass into the condensed over the gas phase. This along with more frequent temperature inversions (which limit atmospheric ventilation of the urban boundary layer) can lead to the observed increases in the relative influence of both organic and nitrate levels during winter months. EC, OC, and nitrate all are observed to have higher measured levels in the urban area (but still lower than the comparable summer values measured at the same sites), driven by local sources of these constituents.

2.3. Geographic considerations and attribution of $PM_{2.5}$/haze contributors

In the East, both annual average and maximum daily fine particle concentrations are highest near heavily industrialized areas and population centers. Not surprisingly, given the direct connection between fine particle pollution and haze, the same pattern emerges when one compares measures of light extinction on the most and least visibility impaired days at parks and wilderness areas subject to federal haze regulations in the MANE-VU region (NESCAUM, 2001). An accumulation of particle pollution often results in hazy conditions extending over thousands of square kilometers (km^2) (NARSTO, 2003). Substantial visibility impairment is a frequent occurrence in even the most remote and pristine areas of the MANE-VU region (NESCAUM, 2001).

$PM_{2.5}$ mass declines fairly steadily along a southwest to northeast transect of the MANE-VU region. This decline is consistent with the existence of large fine particle emissions sources (both primary and secondary) to the south and west of MANE-VU. This trend is driven, in large part, by the marked southwest-to-northeast gradient in ambient sulfate concentrations during three seasons of the year as illustrated in Figure 2-5. Wintertime concentrations, by contrast, are far more uniform across the entire region. Figure 2-6 shows that on an annual basis, both total $PM_{2.5}$ and sulfate mass are highest in the southwestern portions of the MANE-VU region (note the different scales for each pollutant). High concentrations of nitrate and organic particle constituents, which play a role in localized wintertime $PM_{2.5}$ episodes, tend to be clustered along the northeastern urban corridor and in other large urban centers.

Figure 2-5. 2002 Seasonal average SO_4 based on IMPROVE and STN data

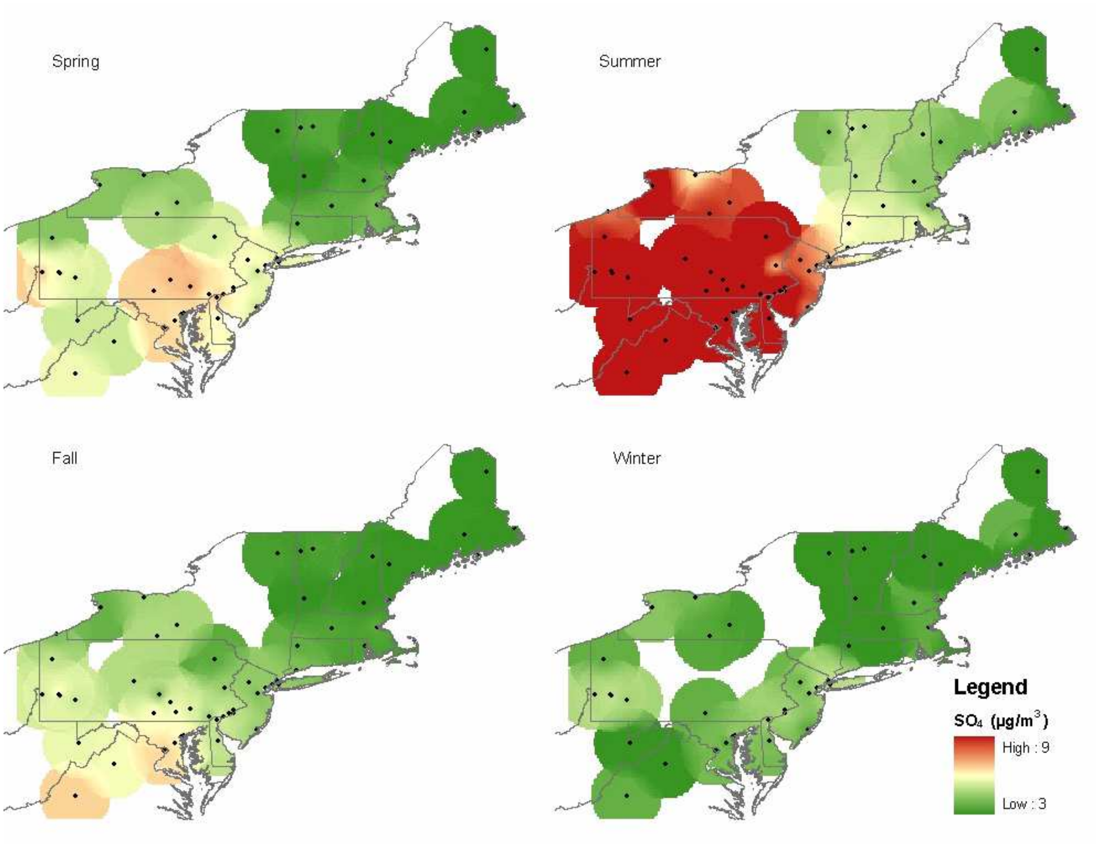
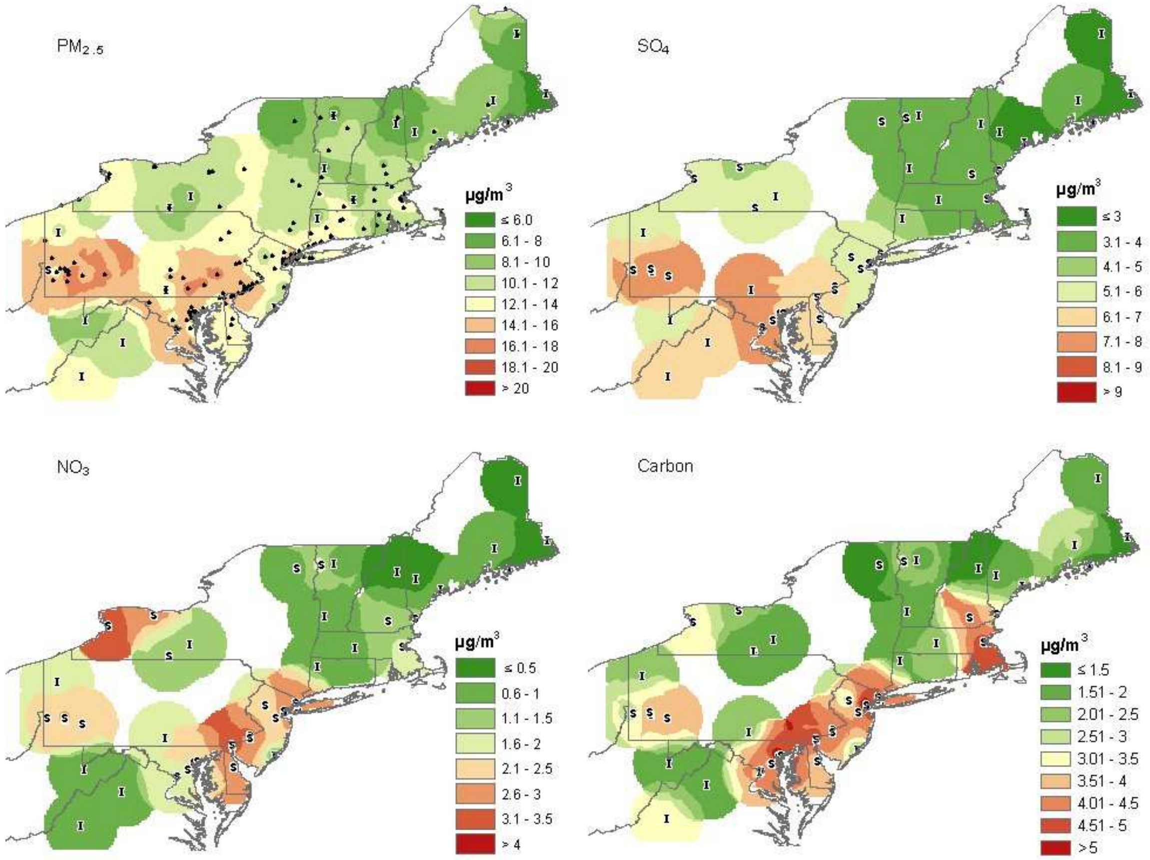


Figure 2-6. 2002 Annual average $PM_{2.5}$, sulfate, nitrate and total carbon for MANE-VU based on IMPROVE (I) and STN (S) data. $PM_{2.5}$ mass data are supplemented by measurements from the FRM network (•).



While these figures provide some preliminary context for identifying sources contributing to the region's particulate matter and visibility problems, they say nothing about the relative efficiency of a state's or region's emissions in contributing to the problem. It is clear that distance from the emissions source matters. Local, nearby sources are exceedingly important and sources within about 200 km are much more efficient (on a per ton emitted basis) at producing pollution impacts at eastern Class I sites such as Shenandoah National Park than emissions sources farther away (USNPS, 2003). In general, the "reach" of sulfate air pollution resulting from SO_2 emissions is longest (650–950 km). The reach of ammonia emissions or reduced nitrogen relative to nutrient deposition is the shortest (around 400 km), while oxides of nitrogen and sulfur — in terms of their impacts with respect to acidic deposition — have a reach between 550–650 km and 600–700 km, respectively (USNPS, 2003).

Monitoring evidence indicates that non-urban visibility impairment in eastern North America is predominantly due to sulfate particles, with organic particles generally second in importance (NARSTO, 2003). This makes sense, given the "long reach" of SO_2 emissions once they are chemically transformed into sulfate and given the ubiquitous nature of OC sources in the East. The poorest visibility conditions occur in highly industrialized areas encompassing and adjacent to the Ohio River and Tennessee Valleys. These areas feature large coal-burning power stations, steel mills, and other large emissions sources. Average fine particle concentrations and visibility conditions are also poor in the highly populated and industrialized mid-Atlantic seaboard but improve gradually northeast of New York City (Watson, 2002).

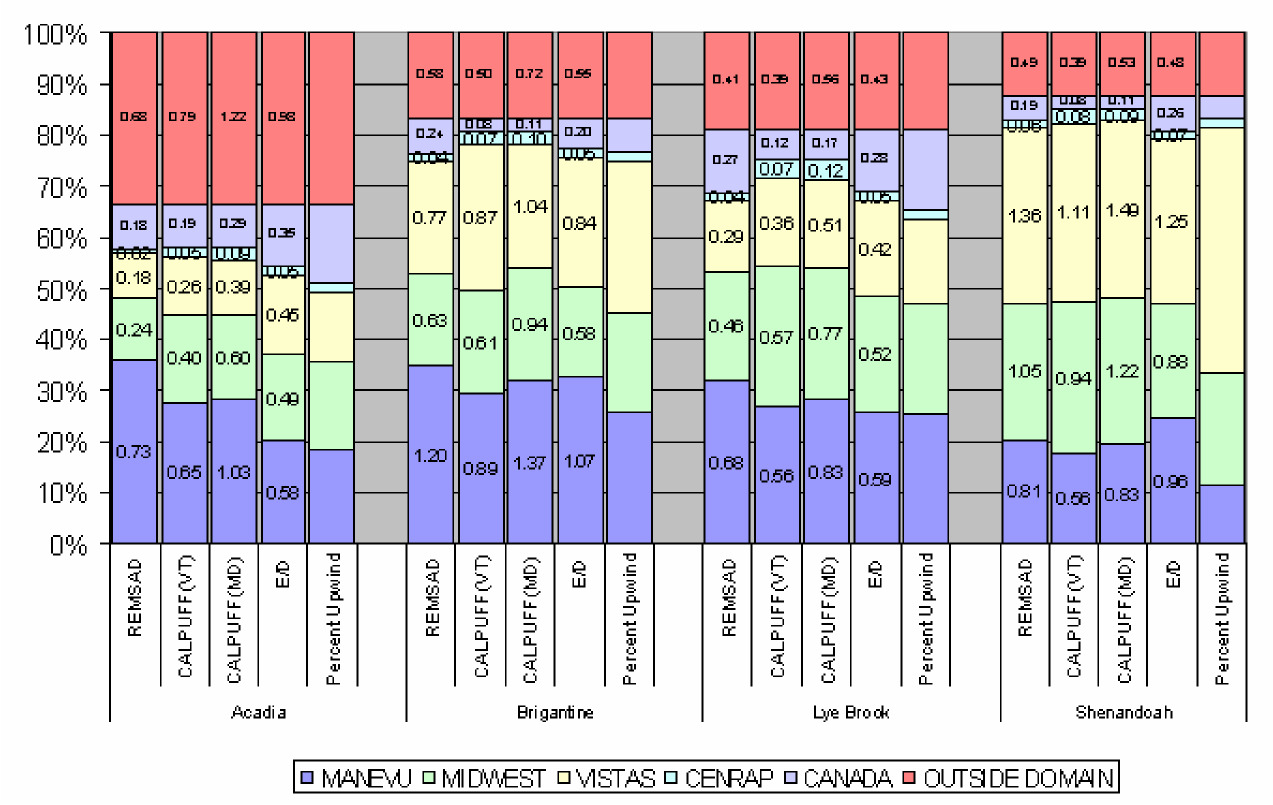
A review of source apportionment and ensemble trajectory analyses conducted by USEPA (2003) found that all back trajectory analyses for eastern sites associated sulfate with the Ohio River Valley area. These studies also are frequently able to associate other types of industrial pollutants (e.g., copper or zinc smelting, steel production, etc.) with known source areas, lending credibility to their performance. Several studies in the USEPA review noted transport across the Canadian border, specifically sulfates from the midwestern United States into Canada, and smelter emissions from Canada into the northeastern United States.

A recent, comprehensive analysis of air quality problems at Shenandoah National Park conducted by the U.S. National Park Service (USNPS, 2003) focused on contributions to particulate pollution and visibility impairment south of the MANE-VU region. In descending order of importance, the Park Service analysis determined that Ohio, Virginia, West Virginia, Pennsylvania, and Kentucky comprise the top five of 13 key states contributing to ambient sulfate concentrations and haze impacts at the park. West Virginia, Ohio, Virginia, Pennsylvania, and Kentucky comprise the top five contributing states with respect to sulfur deposition impacts at the park. Finally, Virginia, West Virginia, Ohio, Pennsylvania, and North Carolina were found to be the top five states contributing to deposition impacts from oxidized nitrogen at the park (USNPS, 2003).

In sum, the Park Service found that emission sources located within a 200 km (125 mile) radius of Shenandoah cause greater visibility and acidic deposition impacts at the park, on a per ton basis, than do more distant emissions sources (USNPS, 2003). When mapping deposition and concentration patterns for all three pollutants using contour lines, the resulting geographic pattern shows a definite eastward tilt in the area of highest impact. This is the result of prevailing wind patterns, which tend to transport most airborne pollutants in an arc[12] from the north-northeast to the east. The Park Service found, for example, that emissions originating in the Ohio River Valley end up three times farther to the east than to the west (USNPS, 2003).

The recent sulfate attribution work completed by MANE-VU (NESCAUM, 2006) finds that a variety of different states contribute to observed sulfate in rural locations across the MANE-VU region, but that in the southwest portions of the region, neighboring RPOs contribute to a more significant degree relative to rural areas in the Northeast. Figure 2-7 shows relative contributions of RPOs to sulfate at three MANE-VU Class I areas and one VISTAS Class I area based on a variety of analysis methods. Figure 2-8 shows the individual state contributions to sulfate at Brigantine Wilderness Area on the New Jersey coast according to tagged REMSAD modeling.

Figure 2-7. 2002 Annual average contribution to $PM_{2.5}$ sulfate as determined by multiple analysis methods for four Class I areas spanning MANE-VU and Virginia



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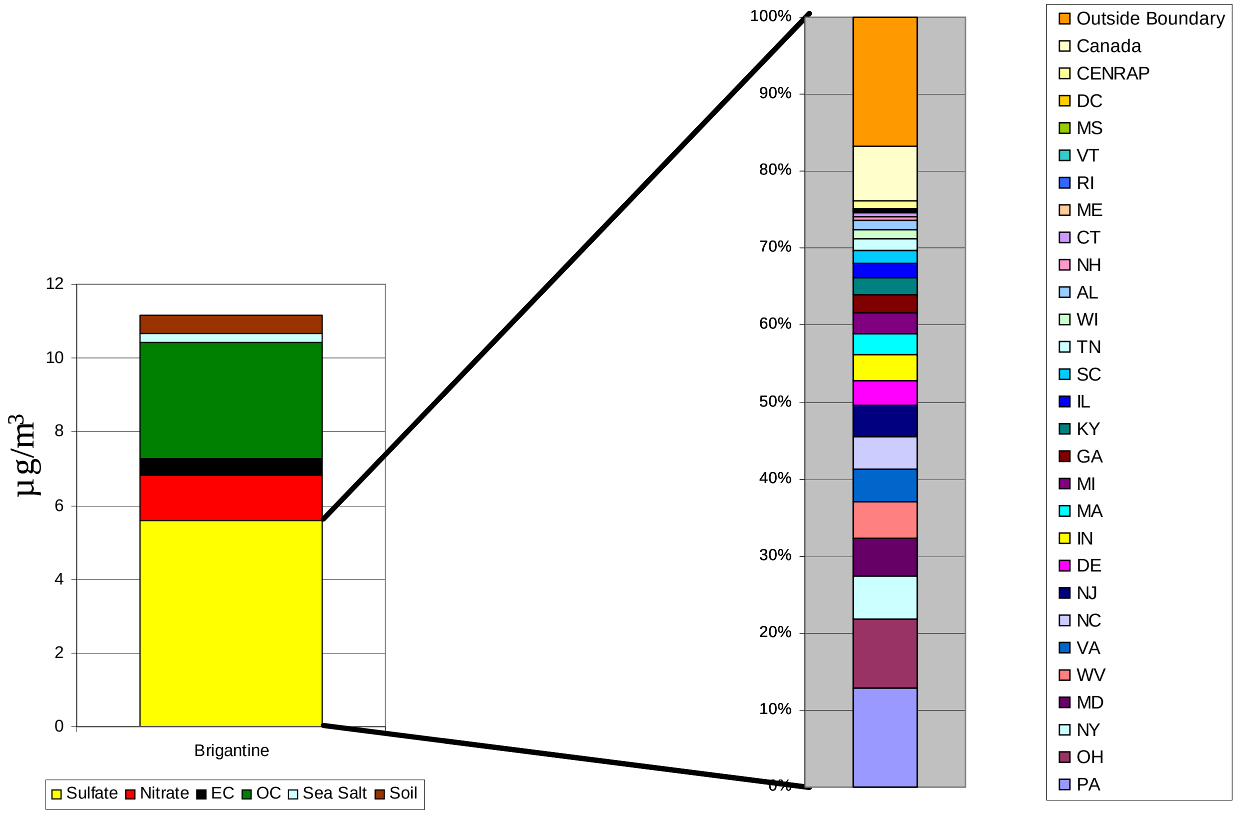
[12] The prevailing winds are eastward to northeast. This leads to greater pollution transport to the east-northeast relative to other directions.

Figure 2-8. 2002 Annual average mass contribution to $PM_{2.5}$ at Brigantine Wilderness in New Jersey (IMPROVE) and sulfate contributions as determined by tagged REMSAD model simulations (NESCAUM, 2006)



2000-2004 average IMPROVE mass

REMSAD 2002 average contributions to sulfate

2.4. CAIR Modeling

The CAIR modeling by the USEPA provides information on the upwind areas (by state) contributing to downwind nonattainment for $PM_{2.5}$ in MANE-VU counties. Table 2-1 presents the upwind states significantly contributing to $PM_{2.5}$ nonattainment in counties within MANE-VU during 2001, according to significance criteria used by the USEPA (USEPA, 2005, from Table VII-3). The states listed in the table as significantly contributing to downwind nonattainment in MANE-VU counties include states outside of MANE-VU, indicating the broad regional scale of the $PM_{2.5}$ transport problem.

Table 2-2 provides the maximum contribution from each state to annual average $PM_{2.5}$ nonattainment in a downwind state (not necessarily restricted to MANE-VU nonattainment counties) based on CAIR modeling.

Table 2-1. Upwind states that make a significant contribution to $PM_{2.5}$ in each downwind nonattainment county (2001 modeling).

Downwind State/County		**Upwind States**									
DE	New Castle	MD/DC	MI	NY	OH	PA	VA	WV			
DC	District of Columbia	NC	OH	PA	VA	WV					
MD	Anne Arundel	NC	OH	PA	VA	WV					
MD	Baltimore City	NC	OH	PA	VA	WV					
NJ	Union	MD/DC	MI	NY	OH	PA	WV				
NY	New York	MD/DC	OH	PA	WV						
PA	Allegheny	IL	IN	KY	MI	OH	WV				
PA	Beaver	IN	MI	OH	WV						
PA	Berks	MD/DC	MI	NY	OH	VA	WV				
PA	Cambria	IN	MD/DC	MI	OH	WV					
PA	Dauphin	MD/DC	MI	OH	VA	WV					
PA	Delaware	MD/DC	MI	OH	VA	WV					
PA	Lancaster	IN	MD/DC	MI	NY	OH	VA	WV			
PA	Philadelphia	MD/DC	MI	OH	VA	WV					
PA	Washington	IN	KY	MI	OH	WV					
PA	Westmoreland	IN	KY	MD/DC	MI	OH	WV				
PA	York	MD/DC	MI	OH	VA	WV					

Table 2-2. Maximum downwind $PM_{2.5}$ contribution ($\mu g/m^3$) for each of the 37 upwind states (2001 data).

Upwind State	**Maximum Downwind Contribution**	**Upwind State**	**Maximum Downwind Contribution**
Alabama	0.98	Nebraska	0.07
Arkansas	0.19	New Hampshire	<0.05
Connecticut	<0.05	New Jersey	0.13
Delaware	0.14	New York	0.34
Florida	0.45	North Carolina	0.31
Georgia	1.27	North Dakota	0.11
Illinois	1.02	Ohio	1.67
Indiana	0.91	Oklahoma	0.12
Iowa	0.28	Pennsylvania	0.89
Kansas	0.11	Rhode Island	<0.05
Kentucky	0.9	South Carolina	0.4
Louisiana	0.25	South Dakota	<0.05
Maine	<0.05	Tennessee	0.65
Maryland/DC	0.69	Texas	0.29
Massachusetts	0.07	Vermont	<0.05
Michigan	0.62	Virginia	0.44
Minnesota	0.21	West Virginia	0.84
Mississippi	0.23	Wisconsin	0.56
Missouri	1.07		

2.5. Seasonal differences

Eastern and western coastal regions of the United States and Canada show marked seasonality in the concentration and composition of fine particle pollution, while central interior regions do not (NARSTO, 2003). While MANE-VU extends inland as far as the Pennsylvania and Ohio border, the majority of $PM_{2.5}$ NAAQS nonattainment areas and Class I areas affected by the Regional Haze Rule cluster along the East Coast and thus typically show strong seasonal influences. Maximum $PM_{2.5}$ concentrations typically occur during the summer over most of the rural Northeast, with observed summer values for rural areas in the region, on average, twice those of winter. In urban locations, summertime and wintertime $PM_{2.5}$ levels are more comparable and whether one season dominates over the other is more of a function of inter-annual variability of meteorology and fire activity (i.e., summertime fire activity can push average $PM_{2.5}$ values higher in some years). As described below, the reason for the wintertime strength of $PM_{2.5}$ levels in urban areas is related to the greater concentration of local pollution that accumulates when temperature inversions are present, significantly boosting the wintertime $PM_{2.5}$ levels. Winter nitrate concentrations are generally higher than those observed in summer and, as mentioned above, urban concentrations typically exceed rural concentrations year-round. In addition, local mobile source carbon grows in importance during wintertime. Hence, in some large urban areas such as Philadelphia and New York City, peak concentrations of $PM_{2.5}$ can occur in winter.

The conceptual descriptions that explain elevated regional $PM_{2.5}$ peak concentrations in the summer differs significantly from those that explain the largely urban peaks observed during winter. On average, summertime concentrations of sulfate in the northeastern United States are more than twice that of the next most important fine particle constituent, OC, and more than four times the combined concentration of nitrate and black carbon (BC) constituents (NARSTO, 2003). Episodes of high summertime sulfate concentrations are consistent with stagnant meteorological flow conditions upwind of MANE-VU and the accumulation of airborne sulfate (via atmospheric oxidation of SO_2) followed by long-range transport of sulfur emissions from industrialized areas within and outside the region.

National assessments (NARSTO, 2003) have indicated that in the winter, sulfate levels in urban areas are almost twice as high as background sulfate levels across the eastern U.S., indicating that the local urban contribution to wintertime sulfate levels is comparable in magnitude to the regional sulfate contribution from long-range transport. MANE-VU's network analysis for the winter of 2002 suggests that the local enhancement of sulfate in urban areas of MANE-VU is somewhat less with ranges from 25 to 40% and that the long-range transport component of $PM_{2.5}$ sulfate is still the dominant contributor in most eastern cities.

In the winter, urban OC and sulfate each account for about a third of the overall $PM_{2.5}$ mass concentration observed in Philadelphia and New York City. Nitrate also makes a significant contribution to urban $PM_{2.5}$ levels observed in the northeastern United States during the winter months. Wintertime concentrations of OC and NO_3 in urban areas can be twice the average regional concentrations of these pollutants, indicating the importance of local source contributions (NARSTO, 2003). This is likely because winter conditions are more conducive to the formation of local inversion layers that prevent vertical mixing. Under these conditions, emissions from tailpipe, industrial, and other local sources become concentrated near the Earth's surface, adding to background pollution levels associated with regionally transported emissions.

It is worth noting that while sulfate plays a significant role in episodes of elevated particle pollution during summer and winter months, the processes by which sulfate forms may vary seasonally. Nearly every source apportionment study reviewed by USEPA (2003) identified secondary sulfate originating from coal combustion sources as the largest or one of the largest contributors to overall fine particle mass in the region. It often accounted for more than 50 percent of PM$_{2.5}$ mass at some locations during some seasons. In a few cases, source apportionment studies identified a known local source of sulfate, but most assessments (in conjunction with back trajectory analysis) have pointed to coal-fired power plants in the Midwest as an important source for regional sulfate. Studies with multiple years of data have also tended to identify a distinguishable chemical "signature" for winter versus summer sources of sulfate, with the summer version typically accounting for a greater share of overall fine particle mass. Researchers have speculated that the two profiles represent two extremes in the chemical transformation processes that occur in the atmosphere between the source regions where emissions are released and downwind receptor sites. We note that while coal combustion is often referred to as the "sulfate source" because of the dominance of its sulfate contribution, coal combustion is often a source of significant amounts of organic carbon and is usually the single largest source of selenium (Se) and other heavy metal trace elements (USEPA, 2003).

Figure 2-9. Moving 60-day average of fine aerosol mass concentrations based on long-term data from two northeastern cities

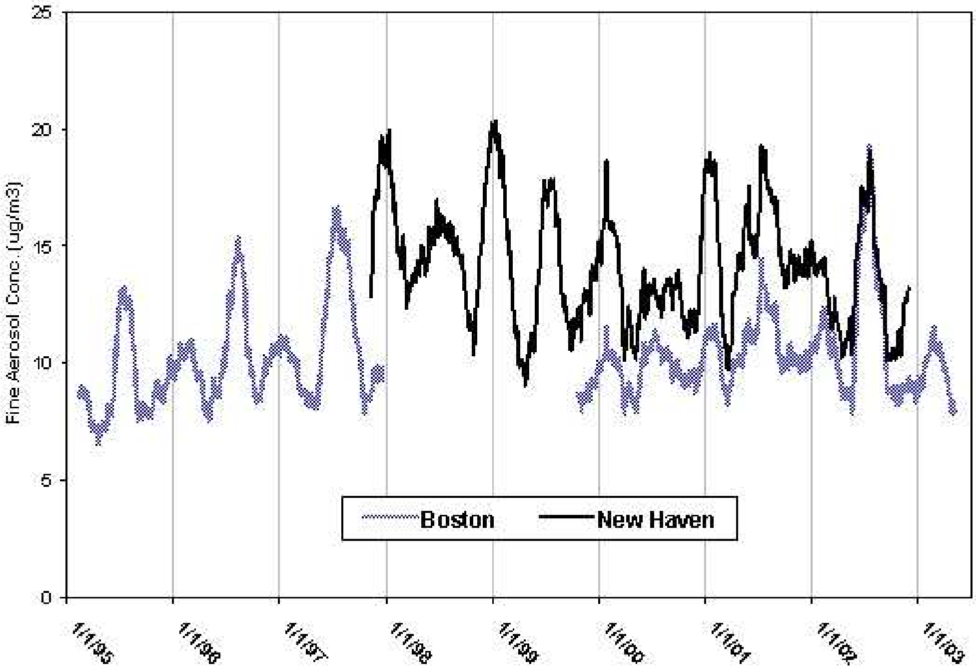
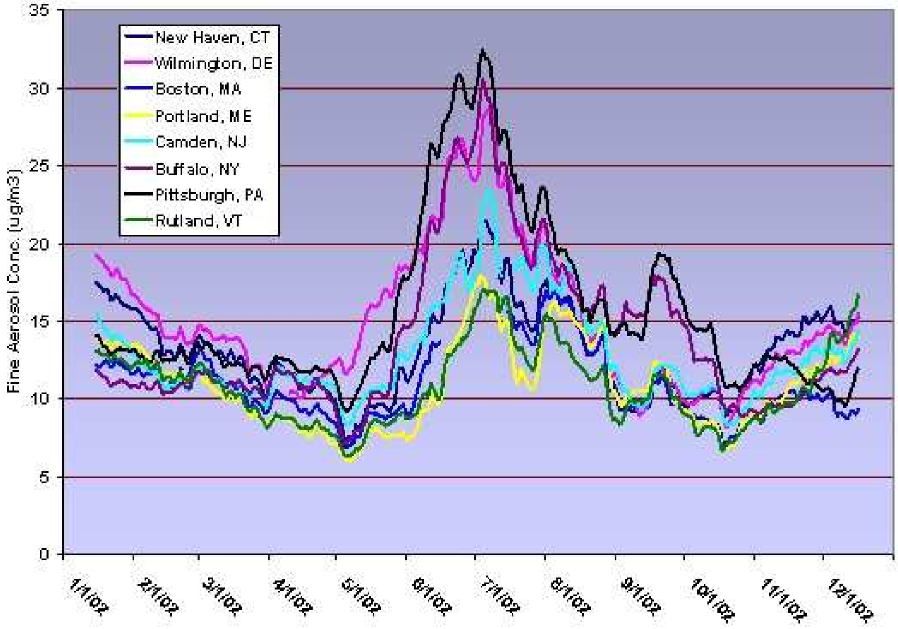


Figure 2-10. The 30-day average $PM_{2.5}$ concentrations from 8 northeastern cities during 2002



In general, fine particle concentrations in MANE-VU are highest during the warmest (summer) months but also exhibit a secondary peak during the coldest (winter) months that can dominate during some years, particularly in urban locations. This bimodal seasonal distribution of peak values is readily apparent in Figure 2-9. The figure shows the smoothed 60-day running average of fine particle mass concentrations using continuous monitoring data from two northeastern cities over a period of several years.

Figure 2-10 also demonstrates this bimodal pattern. Though slightly more difficult to discern in just a single year's worth of data, a "W" pattern does emerge at almost all sites across the region during 2002 with the winter peak somewhat lower than the summer peak at most sites. Urban monitors in Wilmington, Delaware and New Haven, Connecticut have wintertime peak values approaching those of summer.

In the summertime, MANE-VU sites repeatedly experience sulfate events due to transport from regions to the south and west. During such events, both rural and urban sites throughout MANE-VU record high (i.e., >15 $\mu g/m^3$) daily average $PM_{2.5}$ concentrations. Meteorological conditions during the summer frequently allow for summer "stagnation" events when very low wind speeds and warm temperatures (upwind and over MANE-VU) allow pollution levels to build in an air mass as it slowly moves across the continent. During these events, atmospheric ventilation is poor and local emission sources add to the burden of transported pollution with the result that concentrations throughout the region (both rural and urban) are relatively uniform. Generally, there are enough of these events to drive the difference between urban and rural sites down to less than 1 $\mu g/m^3$ during the warm or hot months of the year. As a result, concentrations of fine particles aloft will often be higher than at ground-level during the summertime, especially at rural monitoring sites. Thus, when atmospheric "mixing" occurs during summer[13] mornings (primarily 7 to 11 a.m.), fine particle concentrations at ground-level can actually increase (see Hartford, CT or Camden, NJ in Figure 2-11).

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[13] Here we define summer as May, June, July and August.

Figure 2-11. Mean hourly fine aerosol concentrations during 2002 summer months

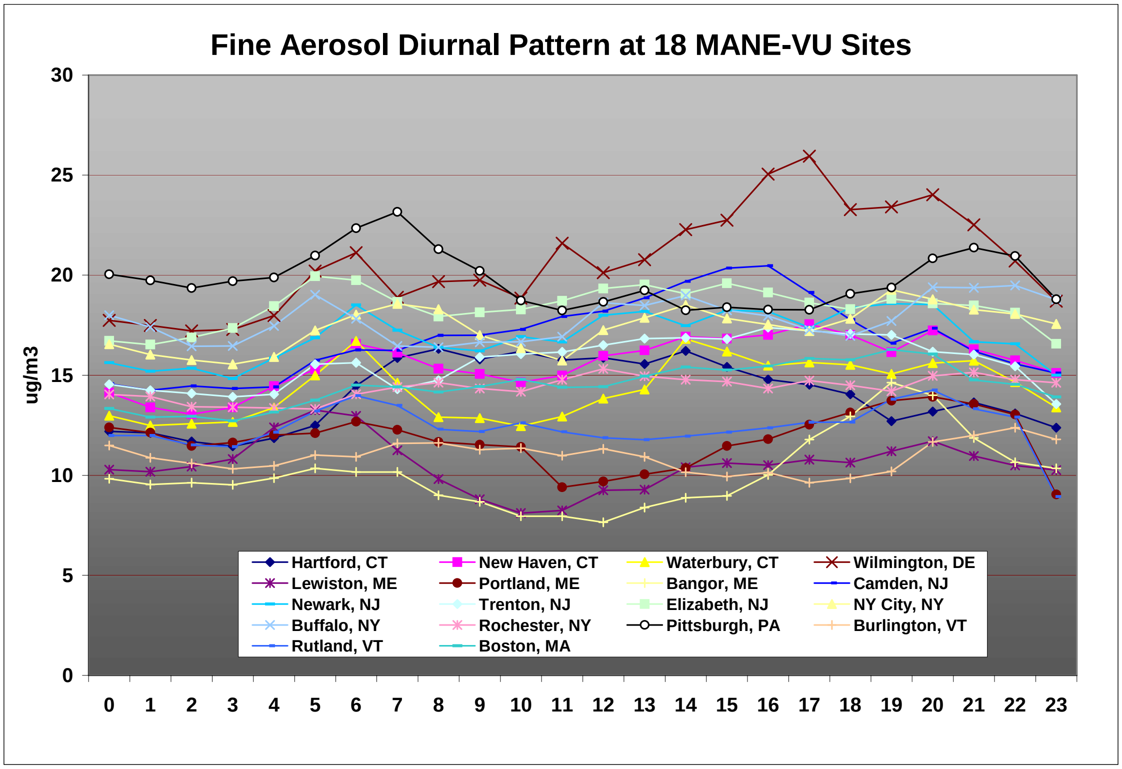
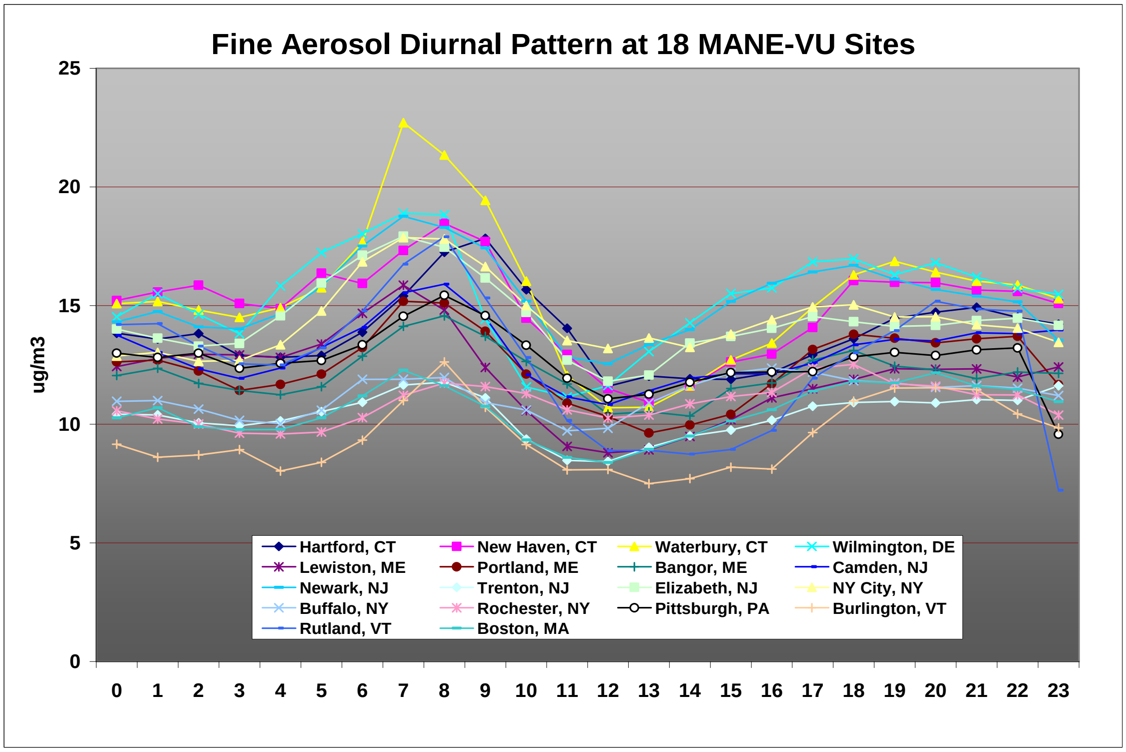


Figure 2-12. Mean hourly fine aerosol concentrations during 2002 winter months



During the wintertime, strong inversions frequently trap local emissions overnight and during the early morning, resulting in elevated urban concentrations. These inversions occur when the Earth's surface loses thermal energy by radiating it into the atmosphere (especially on clear nights). The result is a cold, stable layer of air near the ground. At sunrise, local emissions (both mobile and stationary) begin increasing in strength and build-up in the stable ground layer (which may extend only 100 meters or less above the ground). Increasing solar radiation during the period between 10 a.m. and noon typically breaks this cycle by warming the ground layer so that it can rise and mix with air aloft. Because the air aloft during wintertime is typically less polluted than the surface layer, this mixing tends to reduce ground-level particle concentrations (see Figure 2-12). This diurnal cycle generally drives wintertime particle concentrations, although the occasional persistent temperature inversion can have the effect of trapping and concentrating local emissions over a period of several days, thereby producing a significant wintertime pollution episode.

Rural areas experience the same temperature inversions but have relatively fewer local emissions sources so that wintertime concentrations in rural locations tend to be lower than those in nearby urban areas. Medium and long-range fine particle transport events do occur during the winter but to a far lesser extent than in the summertime. In sum, it is the interplay between local and distant sources together with seasonal meteorological conditions that drives the observed 3–4 $\mu g/m^3$ wintertime urban-rural difference in $PM_{2.5}$ concentrations.

Visually hazy summer days in the Northeast can appear quite different from hazy winter days. The milky, uniform visibility impairment shown in Figure 2-13 is typical of summertime regional haze events in the Northeast. During the winter, by comparison, reduced convection and the frequent occurrence of shallow inversion layers often creates a layered haze with a brownish tinge, as shown in Figure 2-14. This visual difference suggests seasonal variation in the relative contribution of different gaseous and particle constituents during the summer versus winter months (NESCAUM, 2001). Rural and inland areas tend not to experience these layered haze episodes as frequently due to the lack of local emission sources in most rural areas (valleys with high wood smoke contributions are an exception).

Overall (regional) differences in summer versus winter particle mass concentrations and corresponding visibility impairment (as measured by light extinction) are largely driven by seasonal variation in sulfate mass concentrations. This is because winter meteorological conditions are less conducive to the oxidation of sulfate from SO_2 (as borne out by the previously cited source apportionment studies). In addition, seasonal differences in long-range transport patterns from upwind SO_2 source regions may be a factor.

The greater presence of nitrate during the cold season is a consequence of the chemical properties of ammonium nitrate. Ammonia bonds more weakly to nitrate than it does to sulfate, and ammonium nitrate tends to dissociate at higher temperatures. Consequently, ammonium nitrate becomes more stable at lower temperatures and hence contributes more to $PM_{2.5}$ mass and light extinction during the winter months relative to the summer (NESCAUM, 2001).

Figure 2-13. Summertime at Mt. Washington

Clean Day **Typical Haze Event**

Figure 2-14. Wintertime in Boston

Clean Day **Typical Haze Event**

2.6. Summary

The presence of fine particulate matter in ambient air significantly degrades public health and obscures visibility during most parts of the year at sites across the MANE-VU region. Particle pollution generally, and its sulfate component specifically, constitute the principle driver for regional visibility impacts. While the broad region experiences visibility impairment, it is most severe in the southern and western portions of MANE-VU that are closest to large power plant SO_2 sources in the Ohio River and Tennessee Valleys.

Summer visibility impairment is driven by the presence of regional sulfate, whereas winter visibility depends on a combination of regional and local influences coupled with local meteorological conditions (inversions) that lead to the concentrated build-up of pollution.

Sulfate is the key particle constituent from the standpoint of designing control strategies to improve visibility conditions in the northeastern United States. Significant further reductions in ambient sulfate levels are achievable, though they will require more than proportional reductions in SO_2 emissions.

Long-range pollutant transport and local pollutant emissions are important, especially along the eastern seaboard, so one must also look beyond the achievement of further sulfate reductions. During the winter months, in particular, consideration also needs to be given to reducing urban sources of SO_2, NO_X and OC (NARSTO, 2003) .

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3. MANE-VU EMISSION INVENTORY CHARACTERISTICS FOR FINE PARTICLES

The pollutants that affect fine particle formation and visibility are sulfur oxides (SO_X), NO_X, VOCs, ammonia (NH_3), and particles with an aerodynamic diameter less than or equal to 10 and 2.5 µm (i.e., primary PM_{10} and $PM_{2.5}$). The emissions dataset illustrated in this section is the 2002 MANE-VU Version 2 regional haze emissions inventory. The MANE-VU regional haze emissions inventory version 3.0, released in April 2006, has superseded version 2 for modeling purposes.

3.1. Emissions inventory characteristics

3.1.1. Sulfur dioxide (SO_2)

SO_2 is the primary precursor pollutant for sulfate particles. Ammonium sulfate particles are the largest contributor to $PM_{2.5}$ mass on an annual average basis at MANE-VU nonattainment sites. It also accounts for more than 50 percent of particle-related light extinction at northeastern Class I areas on the clearest days and for as much as or more than 80 percent on the haziest days. Hence, SO_2 emissions are an obvious target of opportunity for both addressing $PM_{2.5}$ nonattainment and for reducing regional haze in the eastern United States. Combustion of coal and, to a substantially lesser extent, of certain petroleum products accounts for most anthropogenic SO_2 emissions. In fact, in 1998 a single source category — coal-burning power plants — was responsible for two-thirds of total SO_2 emissions nationwide (NESCAUM, 2001).

Figure 3-1 shows SO_2 emissions trends in MANE-VU states[14] extracted from the National Emissions Inventories (NEI) for the years 1996, 1999 (MARAMA, 2004), and the 2002 MANE-VU inventory. Most of the states (with the exception of Maryland) show declines in year 2002 annual SO_2 emissions as compared to 1996 emissions. Some of the states show an increase in 1999 followed by a decline in 2002 and others show consistent declines throughout the entire period. The upward trend in emissions after 1996 probably reflects electricity demand growth during the late 1990s combined with the availability of banked SO_2 emissions allowances from initial over-compliance with control requirements in Phase 1 of the USEPA Acid Rain Program. This led to relatively low market prices for allowances later in the decade, which encouraged utilities to purchase allowances rather than implement new controls as electricity output expanded. The observed decline in the 2002 SO_2 emissions inventory reflects implementation of the second phase of the USEPA Acid Rain Program, which in 2000 further reduced allowable emissions and extended emissions limits to more power plants.

Figure 3-2 shows the percent contribution from different source categories to overall annual 2002 SO_2 emissions in MANE-VU states. The chart shows that point sources dominate SO_2 emissions, which primarily consist of stationary combustion sources for generating electricity, industrial energy, and heat. Smaller stationary combustion sources called “area sources” (primarily commercial and residential heating)

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[14] The description of MANE-VU state inventories discussed throughout this section does not include the portion of Virginia in the Washington, DC metropolitan area.

are another important source category in MANE-VU states. By contrast, on-road and non-road mobile sources make only a relatively small contribution to overall SO_2 emissions in the region (NESCAUM, 2001).

Figure 3-1. State level sulfur dioxide emissions

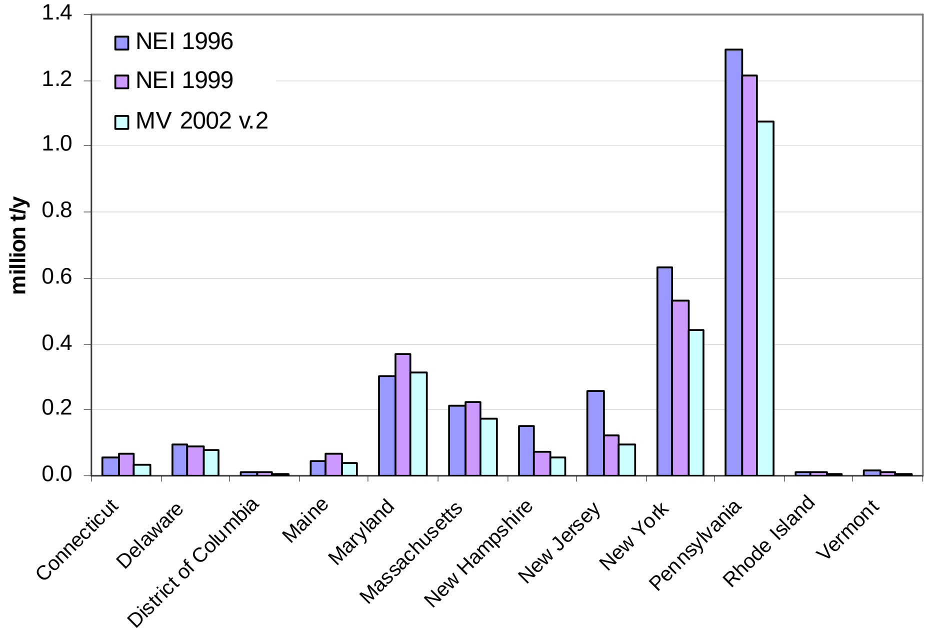


Figure 3-2. 2002 MANE-VU state SO_2 inventories

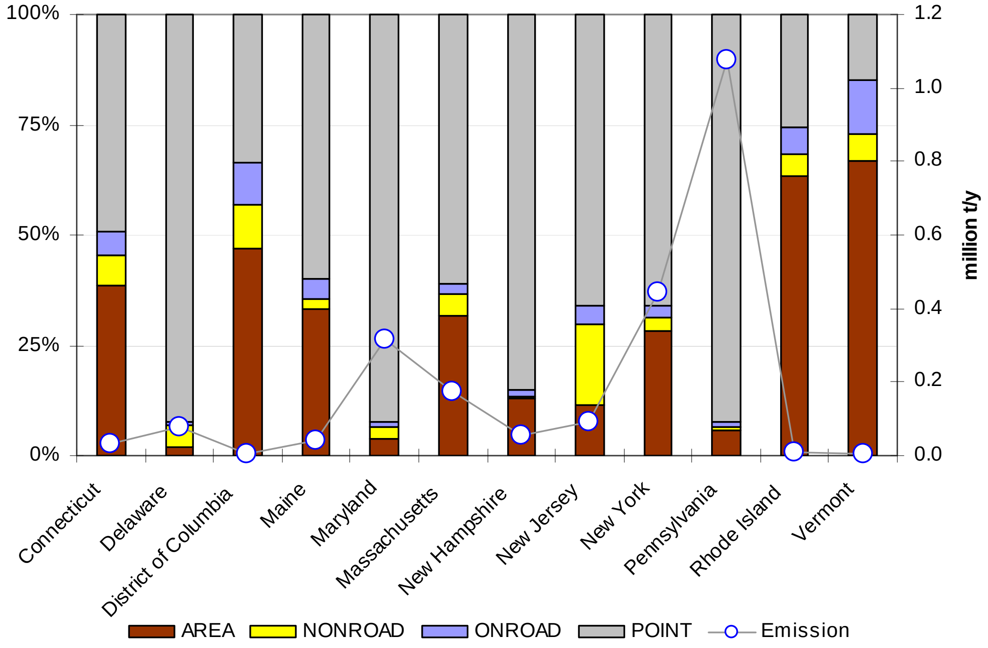


Figure Key: Bars = Percentage fractions of four source categories; Circles = Annual emissions amount in 10^6 tons per year. Note that Version 2 of the MANE-VU inventory was used and the Virginia portion of the Washington, DC metropolitan area is not shown in the figure.

3.1.2. Volatile organic compounds (VOCs)

Existing emission inventories generally refer to VOCs based on their historical contribution to ozone formation. From a fine particle perspective, VOCs (also referred to as hydrocarbons) are of concern because they can react in the atmosphere to form secondary organic aerosol (SOA) as a result of condensation and oxidation processes. The SOA component of fine particles also obscures visibility, but this component has a smaller impact on visibility (on a per unit mass basis) relative to sulfate or nitrate, which have an affinity for water that allows them to significantly "grow" as particles under humid conditions. Nonetheless, organic carbon typically has the second largest visibility impact at most Class I sites next to sulfate, given its large mass contribution.

As shown in Figure 3-3, the VOC inventory is dominated by mobile and area sources. Most VOC emissions in MANE-VU, however, come from natural sources, which are not shown in the figure. Among the human-caused VOC emissions, on-road mobile sources of VOCs include exhaust emissions from gasoline passenger vehicles and diesel-powered heavy-duty vehicles as well as evaporative emissions from transportation fuels. VOC emissions may also originate from a variety of area sources (including solvents, architectural coatings, and dry cleaners) as well as from some point sources (e.g., industrial facilities and petroleum refineries).

Naturally occurring (biogenic) VOC emissions are caused by the release of natural organic compounds from plants in warm weather. Natural, or biogenic, VOCs contribute significantly to fine particle formation. Biogenic VOCs are not included in Figure 3-3, but nationally, they represent roughly two-thirds of all annual VOC emissions (USEPA, 2006). Biogenic emissions are extremely difficult to estimate, as it requires modeling the behavior of many plants as well as their responses to the environment.

With regard to fine particle formation, understanding the transport dynamics and source regions for organic carbon is likely to be more complex than for sulfate. This is partly because of the large number and variety of VOC species, the fact that their transport characteristics vary widely, and the fact that a given species may undergo numerous complex chemical reactions in the atmosphere. Thus, the organic carbon contribution to fine particles in the East is likely to include manmade pollution transported from a distance, manmade pollution from nearby sources, and biogenic emissions, especially terpenes from coniferous forests.

For fine particles derived from organic carbon, the oxidation of hydrocarbon molecules containing seven or more carbon atoms is generally the most significant pathway for their formation (Odum *et al.*, 1997). Recent research, however, suggests that smaller reactive hydrocarbons like isoprene not only contribute significantly to ground-level ozone, which may indirectly impact organic aerosol formation, but also contribute directly to ambient organic aerosol through heterogeneous processes (Claeys et al., 2004; Kroll et al., 2005).

Figure 3-3. 2002 MANE-VU state VOC inventories

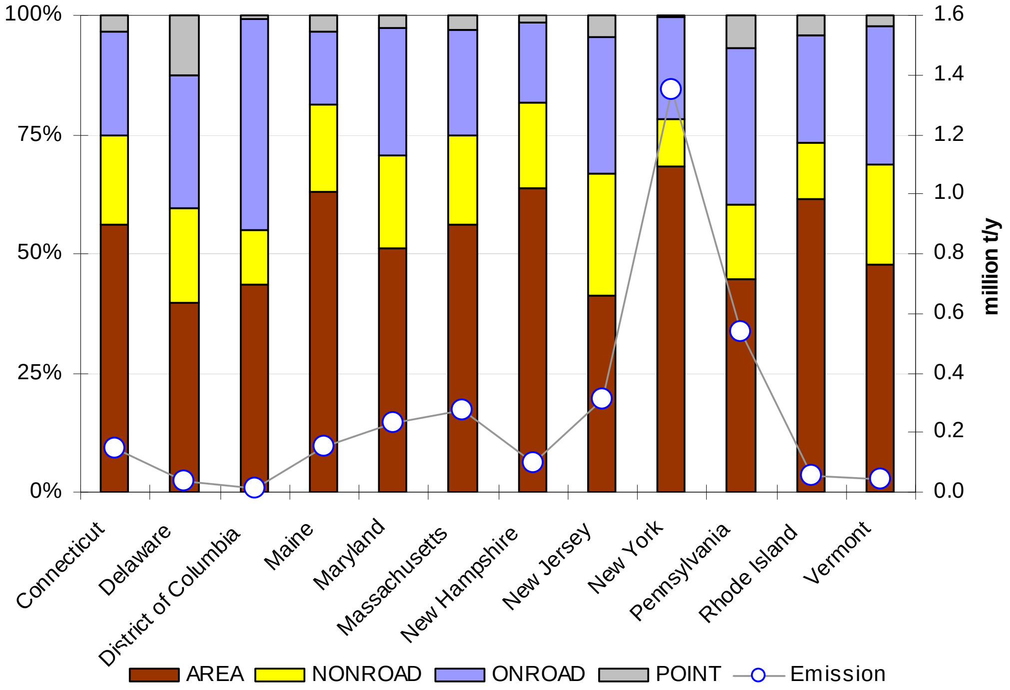


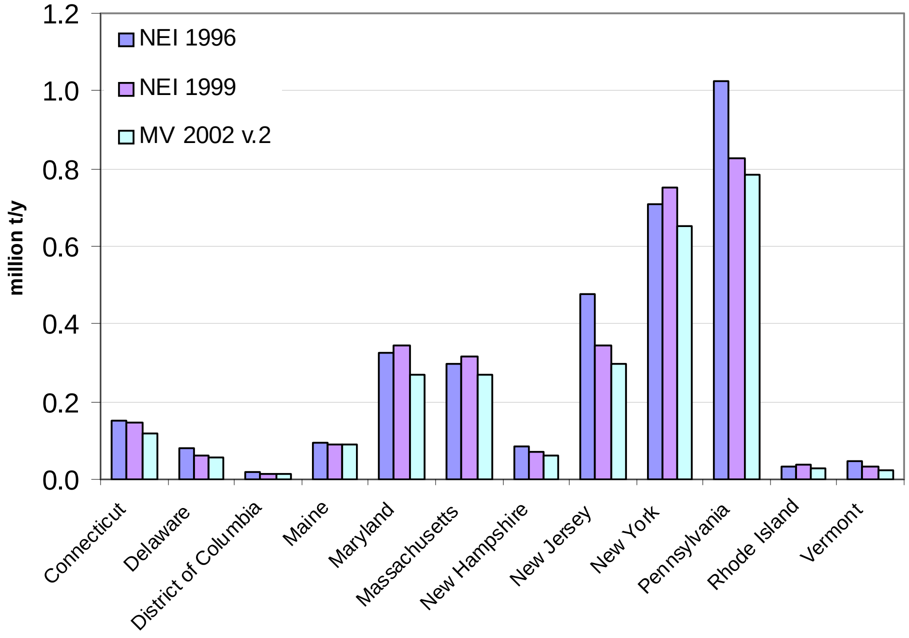
Figure key: Bars = Percentage fractions of four source categories; Circles = Annual emissions amount in 10^6 tons per year. Note that Version 2 of the MANE-VU inventory was used and the Virginia portion of the Washington, DC metropolitan area is not shown in the figure. Biogenic VOCs are not included in this figure.

3.1.3. Oxides of nitrogen (NO_X)

NO_X emissions contribute directly to $PM_{2.5}$ nonattainment and visibility impairment in the eastern U.S. by forming nitrate particles. Nitrate generally accounts for a substantially smaller fraction of fine particle mass and related light extinction than sulfate and organic carbon regionally in MANE-VU. Notably, nitrate may play a more important role at urban sites and in the wintertime. In addition, NO_X may have an indirect effect on summertime visibility by virtue of its role in the formation of ozone, which in turn promotes the formation of secondary organic aerosols (NESCAUM, 2001).

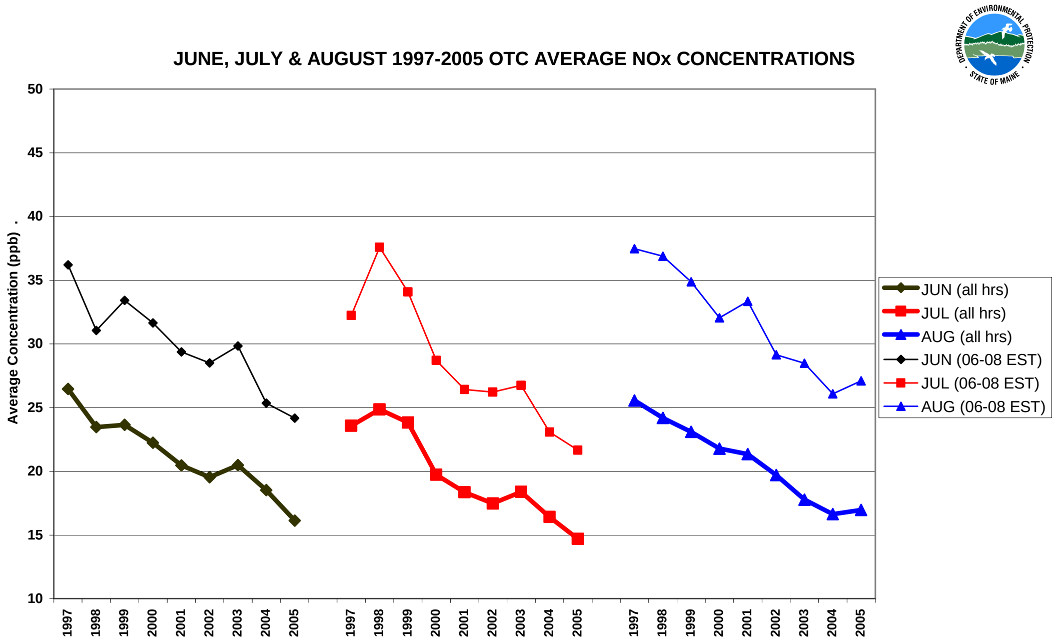
Figure 3-4 shows NO_X emissions in MANE-VU at the state level. Since 1980, nationwide emissions of NO_X from all sources have shown little change. In fact, emissions increased by 2 percent between 1989 and 1998 (USEPA, 2000a). This increase is most likely due to industrial sources and the transportation sector, as power plant combustion sources have implemented modest emissions reductions during the same time period. Most states in MANE-VU experienced declining NO_X emissions from 1996 through 2002, except Massachusetts, Maryland, New York, and Rhode Island, which show an increase in NO_X emissions in 1999 before declining to levels below 1996 emissions in 2002.

Figure 3-4. State level nitrogen oxides emissions



Monitored ambient NO_X trends during the summer from 1997 to 2005 corroborate the downward trend in NO_X emissions seen in the emissions inventories for MANE-VU. As seen in Figure 3-5, the 24-hour (lower trend lines) and 6 a.m.-8 a.m. (upper trend lines) NO_X concentrations indicate decreases in NO_X over this time period in MANE-VU. The NO_X reductions likely come from decreasing vehicle NO_X emissions due to more stringent motor vehicle standards as well as NO_X reductions from MANE-VU NO_X Budget Program and the NO_X SIP Call (mainly power plants).

Figure 3-5. Plot of monitored NO_X trends in MANE-VU during 1997-2005



Note: Upper trend lines correspond to NO_X measured from 0600-0800 EST in the morning. Lower trend lines correspond to NO_X measured over entire day (created by Tom Downs, Maine Department of Environmental Protection).

Power plants and mobile sources generally dominate state and national NO_X emissions inventories. Nationally, power plants account for more than one-quarter of all NO_X emissions, amounting to over six million tons. The electric sector plays an even larger role, however, in parts of the industrial Midwest where high NO_X emissions have a particularly significant power plant contribution. By contrast, mobile sources dominate the NO_X inventories for more urbanized mid-Atlantic and New England states to a far greater extent, as shown in Figure 3-6. In these states, on-road mobile sources — a category that mainly includes highway vehicles — represent the most significant NO_X source category. Emissions from non-road (i.e., off-highway) mobile sources, primarily diesel-fired engines, also represent a substantial fraction of the inventory.

Figure 3-6. 2002 MANE-VU state NO_X inventories

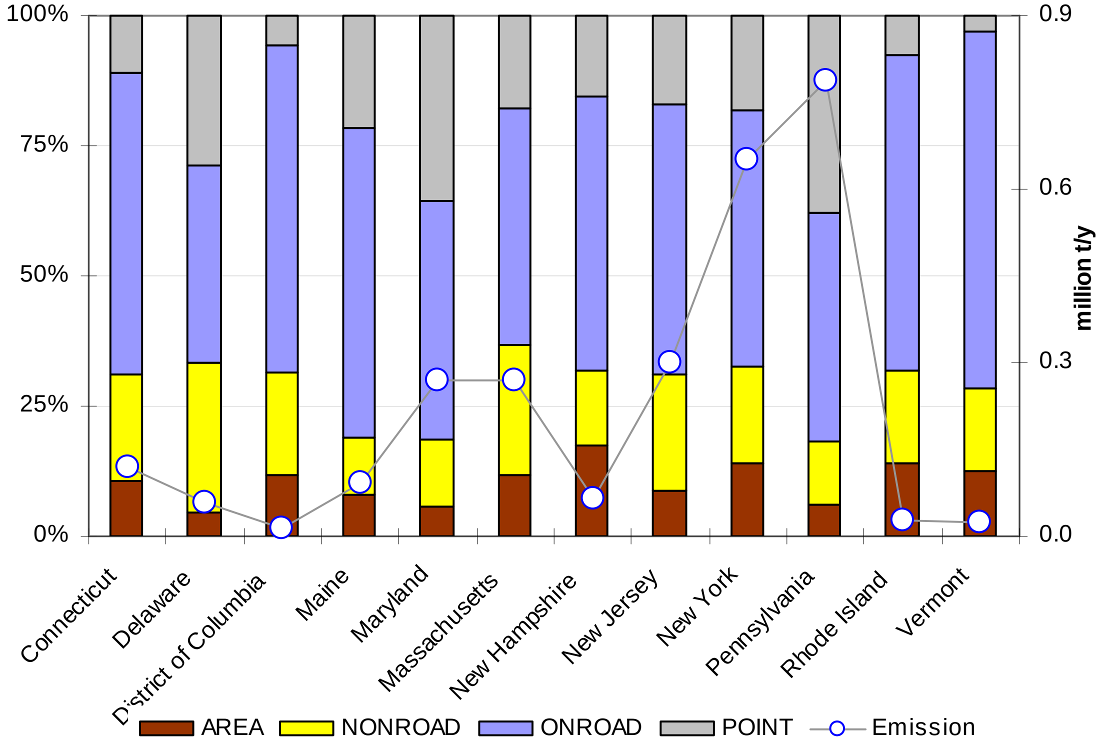


Figure key: Bars = Percentage fractions of four source categories; Circles = Annual emissions amount in 10^6 tons per year. Note that Version 2 of the MANE-VU inventory was used and the Virginia portion of the Washington, DC metropolitan area is not shown in the figure.

3.1.4. Primary particulate matter (PM_{10} and $PM_{2.5}$)

Directly-emitted or "primary" particles (as distinct from secondary particles that form in the atmosphere through chemical reactions involving precursor pollutants like SO_2 and NO_X) also contribute to fine particle levels in the atmosphere. For regulatory purposes, we make a distinction between particles with an aerodynamic diameter less than or equal to 10 micrometers and smaller particles with an aerodynamic diameter less than or equal to 2.5 micrometers (i.e., primary PM_{10} and $PM_{2.5}$, respectively).

Figure 3-7 and Figure 3-8 show PM_{10} and $PM_{2.5}$ emissions for MANE-VU states for the years 1996, 1999, and 2002. Note that, as opposed to the other constituents of PM, the 2002 inventory values for PM_{10} are drawn from the 2002 NEI. Most states show a steady decline in annual PM_{10} emissions over this time period. By contrast, emission trends for primary $PM_{2.5}$ are more variable.

Crustal sources are significant contributors of primary PM emissions. This category includes fugitive dust emissions from construction activities, paved and unpaved roads, and agricultural tilling. Typically, monitors estimate PM_{10} emissions from these types of sources by measuring the horizontal flux of particulate mass at a fixed downwind sampling location within perhaps 10 meters of a road or field. Comparisons between estimated emission rates for fine particles using these types of measurement techniques and observed concentrations of crustal matter in the ambient air at downwind receptor sites suggest that physical or chemical processes remove a significant fraction of crustal material relatively quickly. As a result, it rarely entrains into layers of the atmosphere where it can transport to downwind receptor locations. Because of this discrepancy between estimated emissions and observed ambient concentrations, modelers typically reduce estimates of total $PM_{2.5}$ emissions from all crustal sources by applying a factor of 0.15 to 0.25 before including in modeling analyses.

From a regional haze perspective, crustal material generally does not play a major role. On the 20 percent best-visibility days during the baseline period (2000-2004), it accounted for 6 to 11 percent of particle-related light extinction at MANE-VU Class 1 sites. On the 20 percent worst-visibility days, however, crustal material generally plays a much smaller role relative to other haze-forming pollutants, ranging from 2 to 3 percent. Moreover, the crustal fraction includes material of natural origin (such as soil or sea salt) that is not targeted under USEPA's Regional Haze Rule. Of course, the crustal fraction can be influenced by certain human activities, such as construction, agricultural practices, and road maintenance (including wintertime salting) — thus, to the extent that these types of activities are found to affect visibility at northeastern Class I sites, control measures targeted at crustal material may prove beneficial.

Experience from the western United States, where the crustal component has generally played a more significant role in driving overall particulate levels, may be helpful where it is relevant in the eastern context. In addition, a few areas in the Northeast, such as New Haven, Connecticut and Presque Isle, Maine, have some experience with the control of dust and road-salt as a result of regulatory obligations stemming from their past nonattainment status with respect to the NAAQS for PM_{10}.

Current emissions inventories for the entire MANE-VU area indicate residential wood combustion represents 25 percent of primary fine particulate emissions in the region. This implies that rural sources can play an important role in addition to the contribution from the region's many highly populated urban areas. An important consideration in this regard is that residential wood combustion occurs primarily in the winter months, while managed or prescribed burning activities occur largely in other seasons. The latter category includes agricultural field-burning activities, prescribed burning of forested areas, and other burning activities such as construction waste burning. Limiting burning to times when favorable meteorological conditions can efficiently disperse resulting emissions can manage many of these types of sources.

Figure 3-7. State level primary PM_{10} emissions

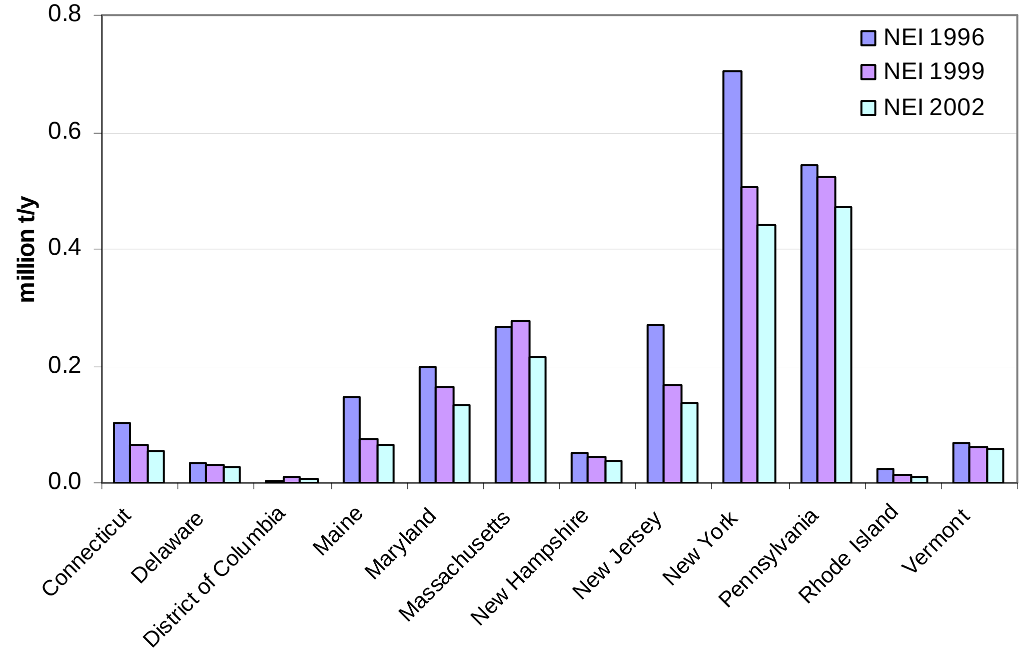


Figure 3-8. State level primary $PM_{2.5}$ emissions

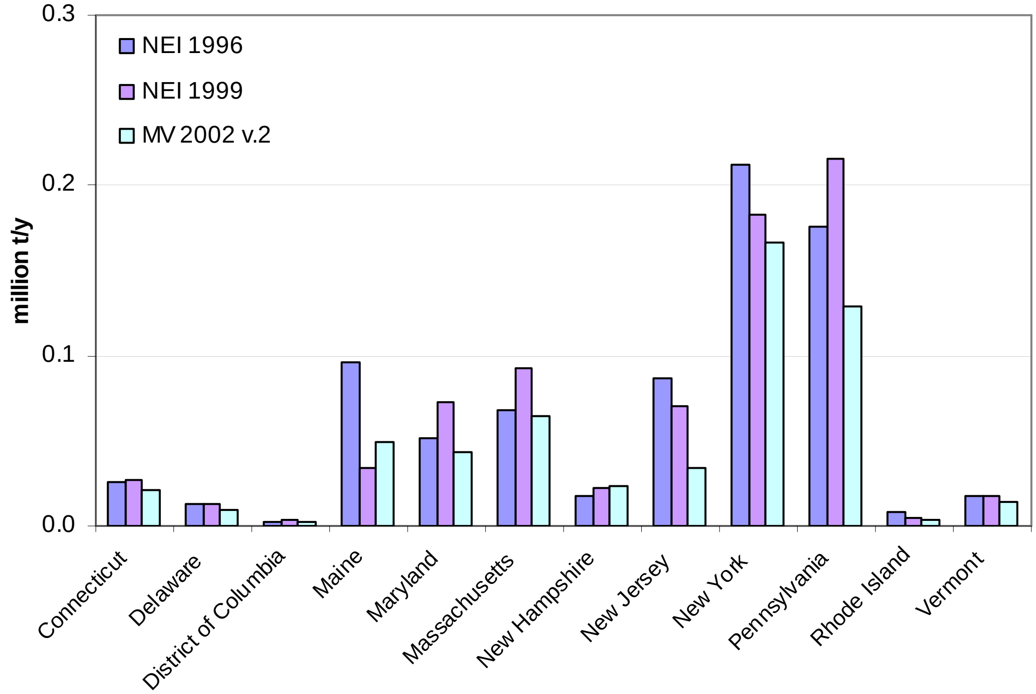


Figure 3-9 and Figure 3-10 show that area and mobile sources dominate primary PM emissions. (The NEI inventory categorizes residential wood combustion and some other combustion sources as area sources.) The relative contribution of point sources is larger in the primary $PM_{2.5}$ inventory than in the primary PM_{10} inventory since the crustal component (which consists mainly of larger or “coarse-mode” particles) contributes mostly to overall PM_{10} levels. At the same time, pollution control equipment commonly installed at large point sources is usually more efficient at capturing coarse-mode particles.

Figure 3-9. 2002 MANE-VU state primary PM_{10} inventories

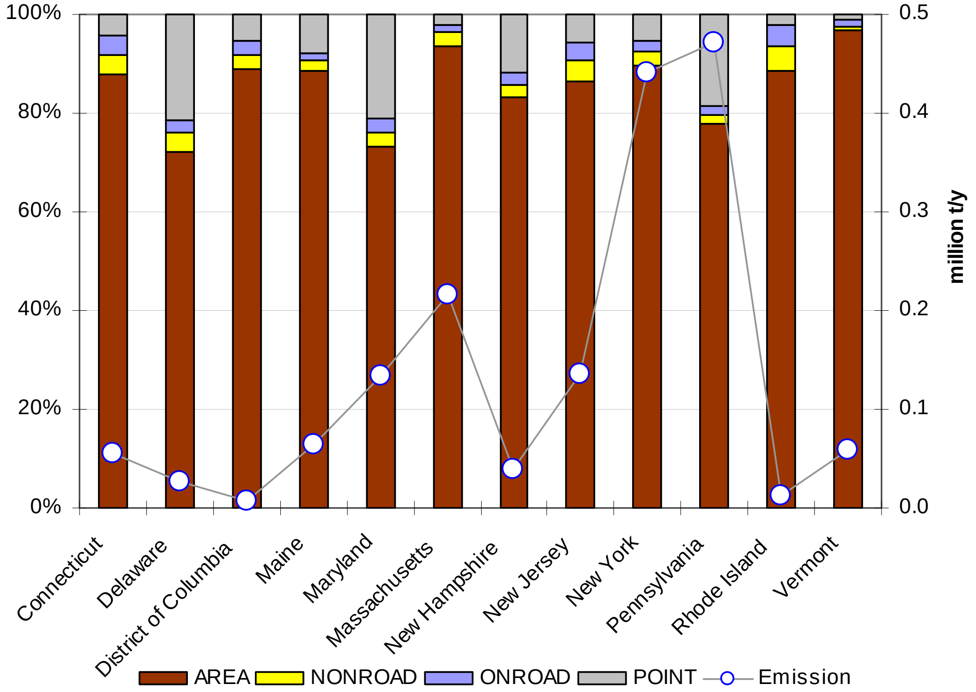


Figure 3-10. 2002 MANE-VU state primary $PM_{2.5}$ inventories

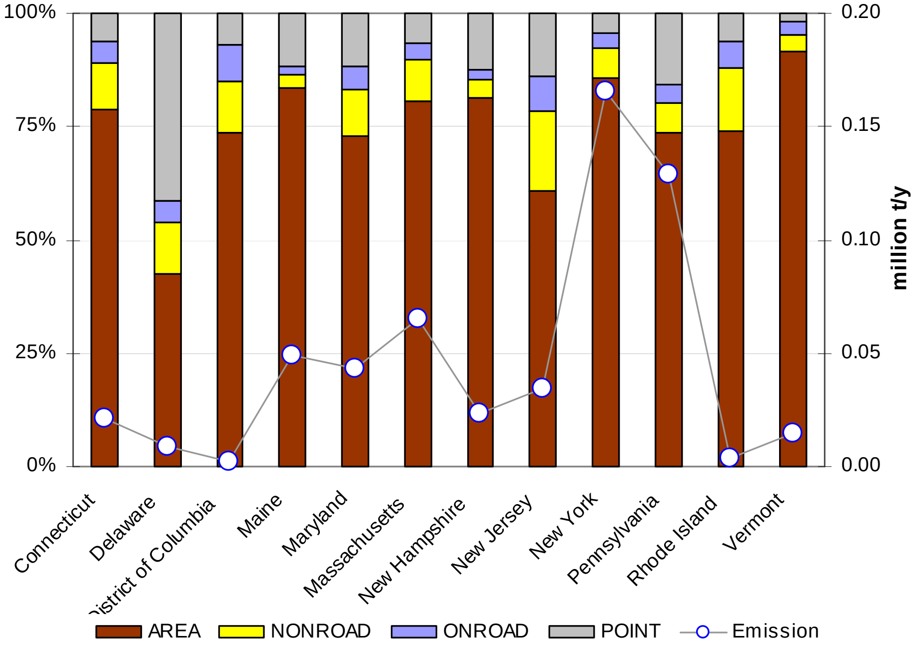


Figure key: Bars = Percentage fractions of four source categories; Circles = Annual emissions amount in 10^6 tons per year. Note that Version 2 of the MANE-VU inventory was used and the Virginia portion of the Washington, DC metropolitan area is not shown in the figure.

3.1.5. Ammonia emissions (NH_3)

Knowledge of ammonia emission sources will be necessary in developing effective regional haze reduction strategies because of the importance of ammonium sulfate and ammonium nitrate in determining overall fine particle mass and light scattering. According to 1998 estimates, livestock and agriculture fertilizer use accounted for approximately 85 percent of all ammonia emissions to the atmosphere (USEPA, 2000b). We need, however, better ammonia inventory data for the photochemical models used to simulate fine particle formation and transport in the eastern United States. Because the USEPA does not regulate ammonia as a criteria pollutant or as a criteria pollutant precursor, these data do not presently exist at the same level of detail or certainty as for NO_X and SO_2.

Ammonium ion (formed from ammonia emissions to the atmosphere) is an important constituent of airborne particulate matter, typically accounting for 10–20 percent of total fine particle mass. Reductions in ammonium ion concentrations can be extremely beneficial because a more-than-proportional reduction in fine particle mass can result. Ansari and Pandis (1998) showed that a one $\mu g/m^3$ reduction in ammonium ion could result in up to a four $\mu g/m^3$ reduction in fine particulate matter. Decision makers, however, must weigh the benefits of ammonia reduction against the significant role it plays in neutralizing acidic aerosol. SO_2 reacts in the atmosphere to form sulfuric acid (H_2SO_4). Ammonia can partially or fully neutralize this strong acid to form ammonium bisulfate or ammonium sulfate. If planners focus future control strategies on ammonia and do not achieve corresponding SO_2 reductions, fine particles formed in the atmosphere will be substantially more acidic than those presently observed.

To address the need for improved ammonia inventories, MARAMA, NESCAUM and USEPA funded researchers at Carnegie Mellon University (CMU) in Pittsburgh to develop a regional ammonia inventory system (Davidson et al., 1999). This study focused on three issues with respect to current emissions estimates: (1) a wide range of ammonia emission factor values, (2) inadequate temporal and spatial resolution of ammonia emissions estimates, and (3) a lack of standardized ammonia source categories.

Figure 3-11 shows that estimated ammonia emissions were fairly stable in the 1996, 1999, and 2002 NEI for MANE-VU states, with some increases observed for Massachusetts, New Jersey and New York. Area and on-road mobile sources dominate the ammonia inventory, according to Figure 3-12. Specifically, emissions from agricultural sources and livestock production account for the largest share of estimated ammonia emissions in MANE-VU, except in the District of Columbia. The two remaining sources with a significant emissions contribution are wastewater treatment systems and gasoline exhaust from highway vehicles.

Figure 3-11. State level ammonia emissions

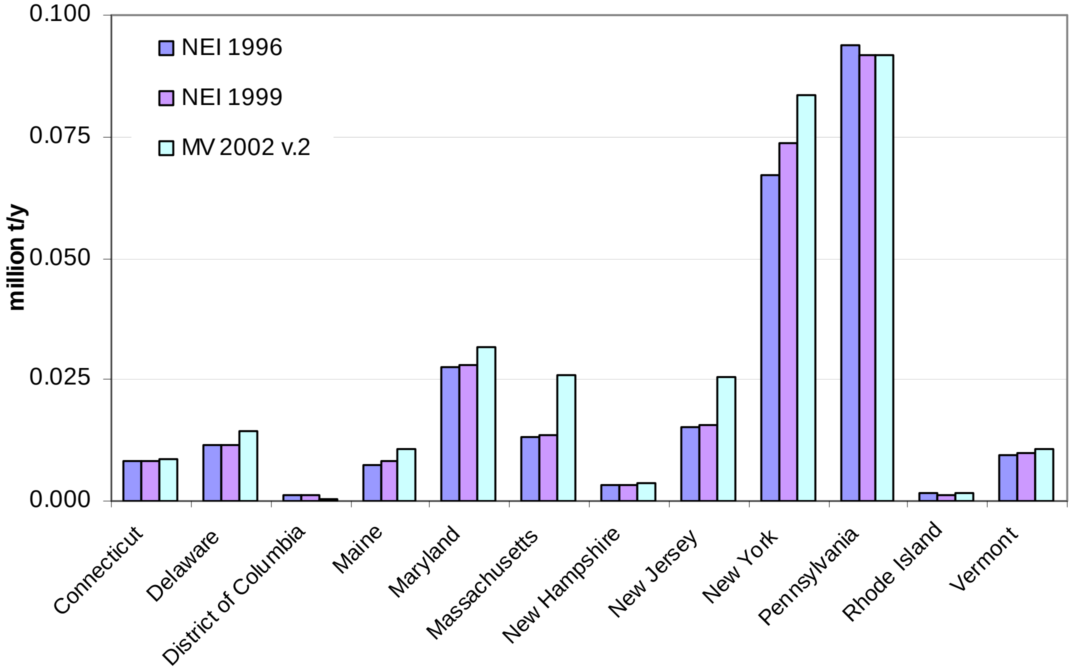


Figure 3-12. 2002 MANE-VU state NH_3 inventories

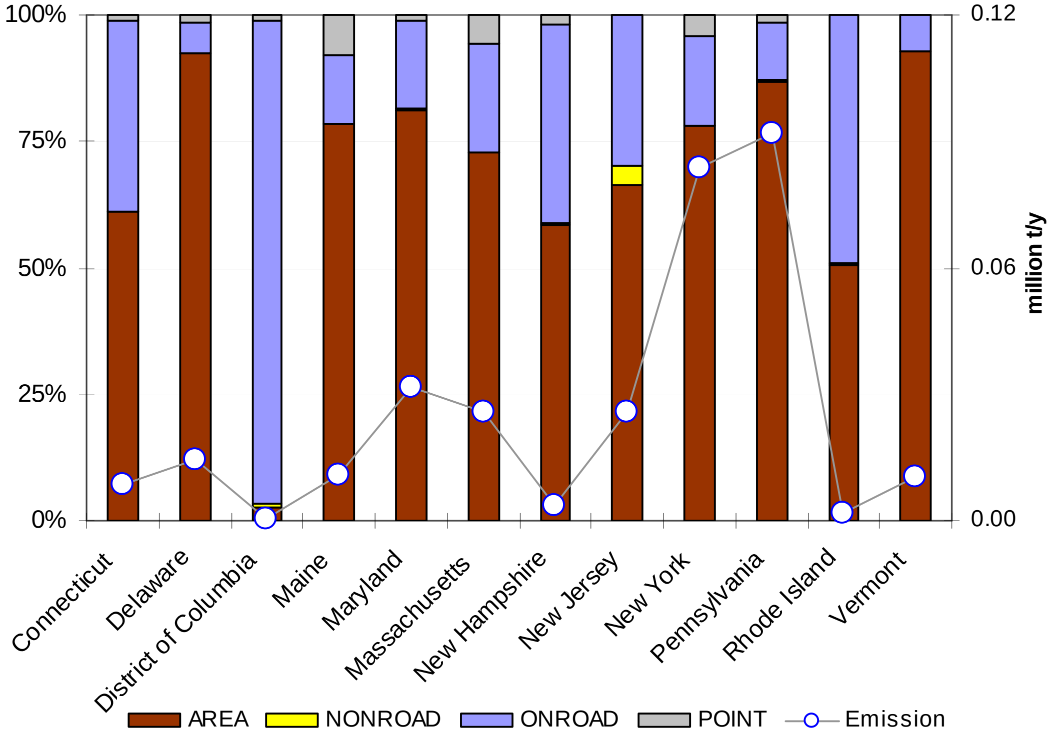


Figure key: Bars = Percentage fractions of four source categories; Circles = Annual emissions amount in 10^6 tons per year. Note that Version 2 of the MANE-VU inventory was used and the Virginia portion of the Washington, DC metropolitan area is not shown in the figure.

3.2. Emissions inventory characteristics outside MANE-VU

SO_2, NO_X and VOC emissions from within MANE-VU are only one component of the emissions contributing to fine particles affecting the MANE-VU region. As regional modeling for the CAIR has shown, emission sources, primarily of SO_2 and NO_X, located outside MANE-VU can significantly contribute to particle sulfate and nitrate transported into the MANE-VU region. Here we present regional emissions information grouped by the three eastern RPOs – MANE-VU, VISTAS (Visibility Improvement State and Tribal Association of the Southeast), and the MWRPO (Midwest RPO). Table 3-1 lists the states in each RPO.

The inventory information is extracted from the USEPA final 2002 National Emissions Inventory (NEI). For consistency, the MANE-VU information here also comes from the 2002 NEI rather than from the MANE-VU Version 2 regional haze emissions inventory described in Section 3.1. The differences between the inventories are not great, as the NEI and the MANE-VU Version 2 inventory are both based on the same inventory information provided by the states.

Table 3-1. Eastern U.S. RPOs and their state members

RPO	State
MWRPO	Illinois
MWRPO	Indiana
MWRPO	Michigan
MWRPO	Ohio
MWRPO	Wisconsin
MANE-VU	Connecticut
MANE-VU	Delaware
MANE-VU	District of Columbia
MANE-VU	Maine
MANE-VU	Maryland
MANE-VU	Massachusetts
MANE-VU	New Hampshire
MANE-VU	New Jersey
MANE-VU	New York
MANE-VU	Pennsylvania
MANE-VU	Rhode Island
MANE-VU	Vermont
VISTAS	Alabama
VISTAS	Florida
VISTAS	Georgia
VISTAS	Kentucky
VISTAS	Mississippi
VISTAS	North Carolina
VISTAS	South Carolina
VISTAS	Tennessee
VISTAS	Virginia
VISTAS	West Virginia

Table 3-2 presents SO_2 emissions by source sector and RPO for the eastern United States. The NO_X emissions by source sector and RPO are presented in Table 3-3 and VOC emissions in Table 3-4. Regionally, SO_2 emissions are more important with respect to regional particle formation and transport. NO_X emissions play an important role in determining the equilibrium between ammonium sulfate and ammonium nitrate formation, especially during winter. VOC emissions contribute to secondary organic aerosol formation.

Table 3-2. SO_2 emissions in eastern RPOs (tons/yr)

RPO	Point	Area	On-road	Non-road	Total
MWRPO	3,336,967	133,415	49,191	82,307	3,601,880
MANE-VU	1,924,573	353,176	39,368	74,566	2,391,683
VISTAS	4,349,437	448,023	83,001	91,307	4,971,769

Table 3-3. NO_X emissions in eastern RPOs (tons/yr)

RPO	Point	Area	On-road	Non-road	Total
MWRPO	1,437,284	184,790	1,290,178	723,844	3,636,096
MANE-VU	680,975	268,997	1,297,357	534,454	2,781,783
VISTAS	2,094,228	266,848	2,160,601	812,615	5,334,293

Table 3-4. VOC emissions in eastern RPOs (tons/yr)

RPO	Point	Area	On-road	Non-road	Total
MWRPO	234,938	1,182,186	660,010	492,027	2,569,160
MANE-VU	93,691	1,798,158	793,541	494,115	3,179,504
VISTAS	458,740	2,047,359	1,314,979	609,539	4,430,617

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Davidson, C., R. Strader, S. Pandis, and A. Robinson. *Preliminary Proposal to MARAMA and NESCAUM: Development of an Ammonia Emissions Inventory for the Mid-Atlantic States and New England*. Carnegie Mellon University, Pittsburgh, PA, January 7, 1999.

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USEPA. *National Air Pollutant Trends, 1900 – 1998*, EPA 454/R-00-002, available online: http://www.epa.gov/ttn/chief/trends/trends98/trends98.pdf, 2000b.

USEPA. *2002 Final National Emissions Inventory (NEI)*, available online: ftp://ftp.epa.gov/EmisInventory/2002finalnei/, 2006 (accessed October 10, 2006) [The 2002 NEI reports national annual emissions for total anthropogenic VOC emissions as 16.8 million tons, and total biogenic VOC emissions as 41.8 million tons].

4. WHAT WILL IT TAKE TO CLEAN THE AIR?

In this chapter we build on the conceptual description of fine particle formation and impacts in the MANE-VU region by looking at a typical fine particle pollution event and the meteorological and chemical conditions which contributed to its formation. As an illustration of how the conceptual elements laid out in Chapter 2 and 3 contribute to a pollution event under real-world circumstances, we examine a pollution event from 2002. We examine this event from two perspectives: (1) the broad spatial patterns of the formation and transport of particle air pollution and (2) the chronological sequence of events at a few discrete points where high temporal resolution monitoring was in place. We then proceed to examine likely emission reduction strategies that should be considered in light of the conceptual understanding of fine particle formation and transport developed in this report.

4.1. Meteorological and Pollution Overview of August 8-16, 2002

Annual and seasonal statistics are useful for understanding the general patterns of air pollution in our region, but it is also instructive to review specific high $PM_{2.5}$ episodes in order to shed more light on the meteorological circumstances under which high ambient concentrations of $PM_{2.5}$ are able to form from emitted precursor pollutants. Here we present an analysis of the high $PM_{2.5}$ and regional haze episode of August 2002 by reviewing surface maps from the period to provide a synoptic overview of major weather systems that were influencing air quality across the Northeast U.S. during that time.

Figure 4-1 through Figure 4-3, respectively, show eight-panel displays of afternoon fine particle concentrations as well as surface weather maps and back trajectories from 12Z (8 a.m. EDT) each day. The following chronology of events combines the meteorological insights with $PM_{2.5}$ concentration information to provide a basic storyline for analysis.

A slow-moving high pressure system centered over the Great Lakes set up northerly flow over MANE-VU on August 8. The high drifted southeast-ward and became extended over several days bringing high temperatures to the region. Calm conditions west of MANE-VU on August 10 were pivotal in the formation of fine aerosol concentrations, which began building in the Ohio River Valley. Over the next four days, concentrations in MANE-VU climbed into the 60-90 $\mu g/m^3$ range over a wide area before being swept out to sea by a series of frontal passages beginning on August 15.

8/8 – A high pressure system over the Great Lakes produces NW-N prevailing surface winds (~4-8 mph) throughout the region. Maximum daily temperatures approach or exceed 80° F.

8/9 – Wind speeds fall off but direction remains NW-N as the high moves into the central portion of MANE-VU. Temperatures rise as cloud cover declines.

8/10 – The high reaches the East Coast and stalls. Temperatures (except in northern-most areas) reach 90° F while surface-level winds turn to more southerly directions. Calm conditions through the morning hours in the lower Ohio River Valley promote creation of haze noted in surface observations.

8/11 – Circulation around the high (now near Cape Hatteras) becomes well established. Peak temperatures are in the low to mid-90's. Morning winds are light-to-calm in the area east of the Mississippi – the area of haze now reaches from Michigan to northern Texas and eastward to West Virginia and eastern Tennessee. A surface-level trough descends from north of the Great Lakes during the day, passes eastward through the Ohio River Valley and stalls over the Allegheny Mountains and southward.

8/12 – Temperatures exceed 90º F throughout MANE-VU except in coastal ME. The area of concentrated haze has pushed eastward and now extends from central ME to central PA. Haze builds throughout the day as circulation forces it to channel NE between the stalled trough and a cold front approaching from the Midwest.

8/13 – Calm conditions prevail as the trough reaches coastal NJ by 8 a.m. Generally clear skies allow temperatures to reach the mid-90's everywhere except in coastal ME. Dew points, which had been rising since 8/8, reach the upper 60's. Peak hourly fine aerosol concentrations are greater than 40 $\mu g/m^3$ everywhere in MANE-VU and exceed 90 $\mu g/m^3$ in some locations. By 8 p.m., showers associated with the approaching cold front have reached into Ohio.

8/14 – By 8 a.m. the trough has dissipated and the high is moving offshore. Dew points remain in the upper 60's and peak temperatures reach into the 90's everywhere and top 100 in several locations. Increased ventilation causes aerosol concentrations to drop throughout the day everywhere except ME where some locations peak above 60 $\mu g/m^3$ after midnight.

8/15 – The approaching cold front and associated showers fall apart during the morning hours. By 8 p.m., a new batch of moderate rain has intruded deeply into the region from the SW and has virtually pushed the haze out of the MANE-VU region.

8/16 – A new high building in over the upper Midwest pushes the remains of the showers out of the Northeast.

Figure 4-1. Spatially interpolated maps of fine particle concentrations August 9 – 16, 2002

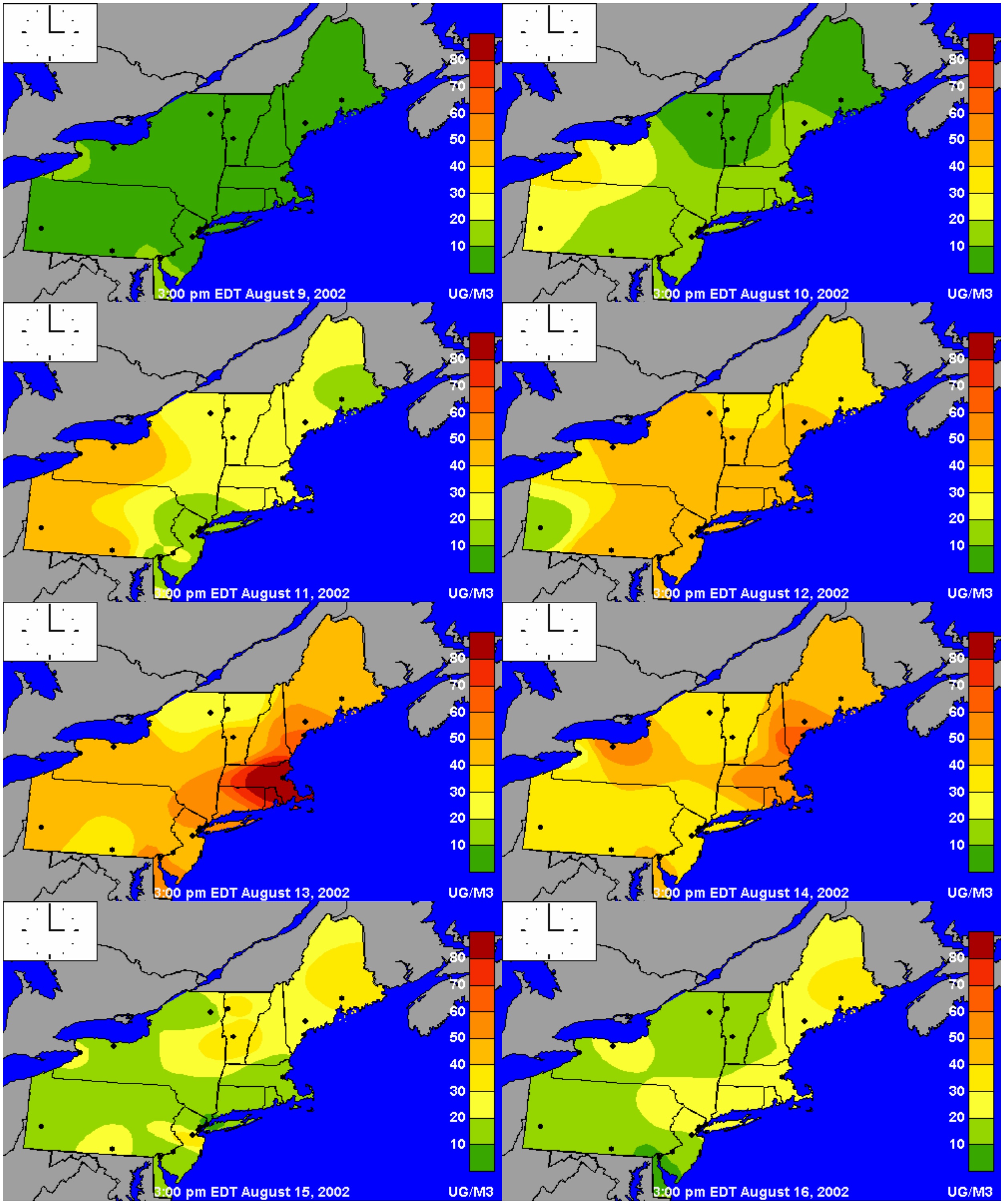
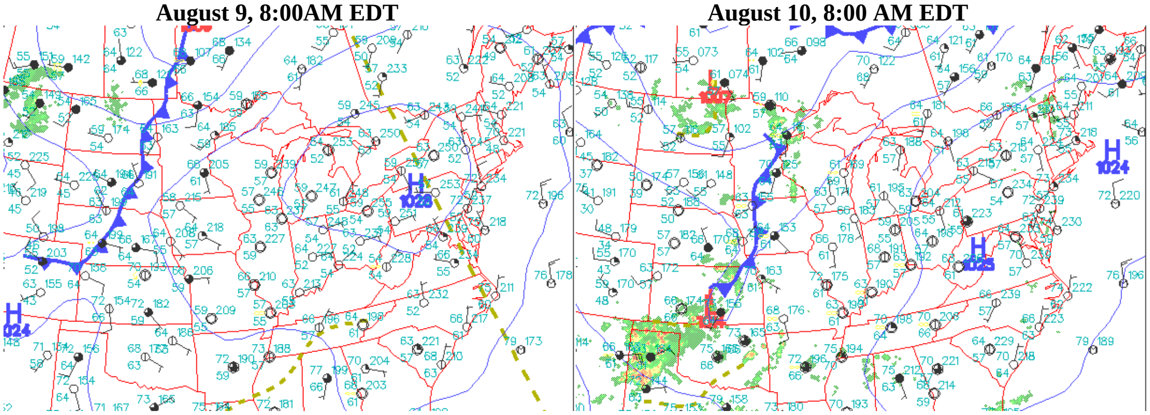
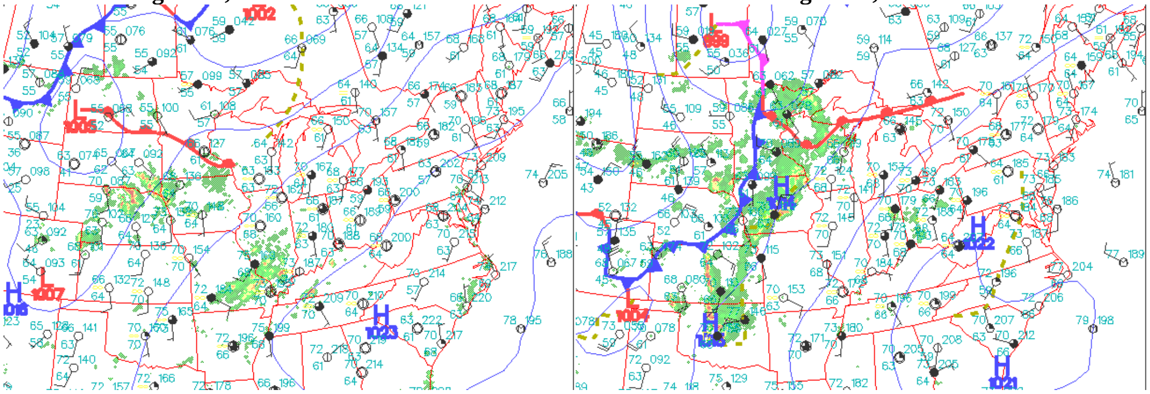


Figure 4-2. Surface weather maps for August 9-16, 2002

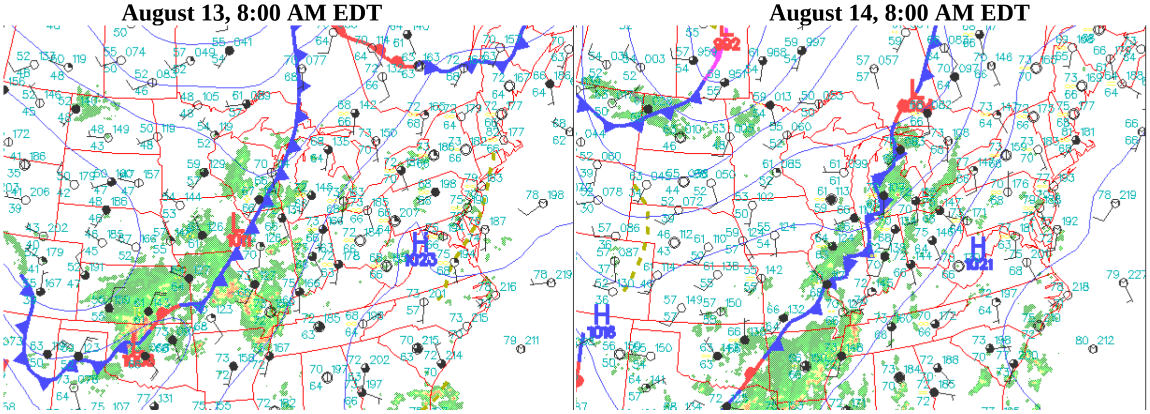
August 9, 8:00AM EDT **August 10, 8:00 AM EDT**



August 11, 8:00 AM EDT **August 12, 8:00 AM EDT**



August 13, 8:00 AM EDT **August 14, 8:00 AM EDT**



August 15, 8:00 AM EDT **August 16, 8:00 AM EDT**

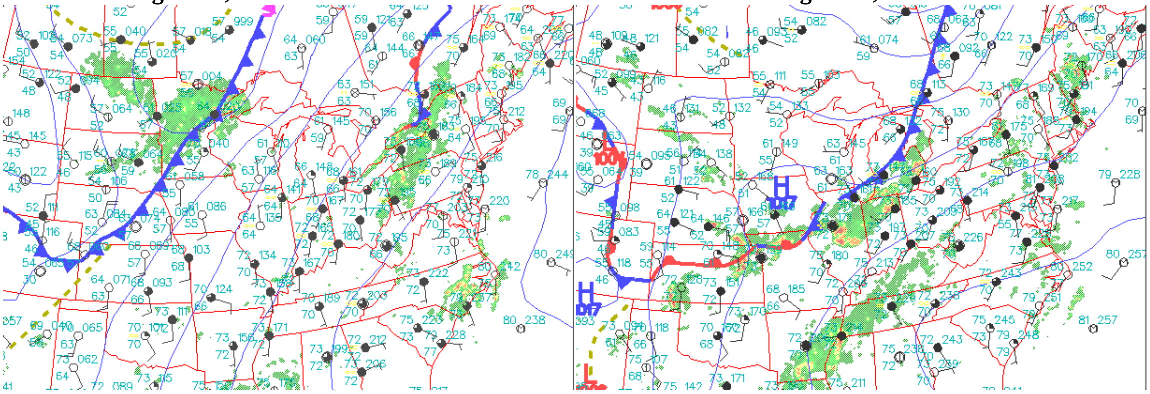
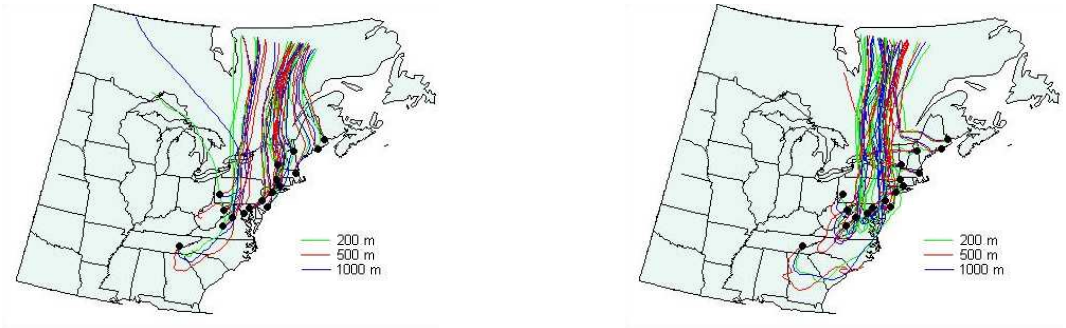


Figure 4-3. HYSPLIT 72-hour back trajectories for August 9-16, 2002

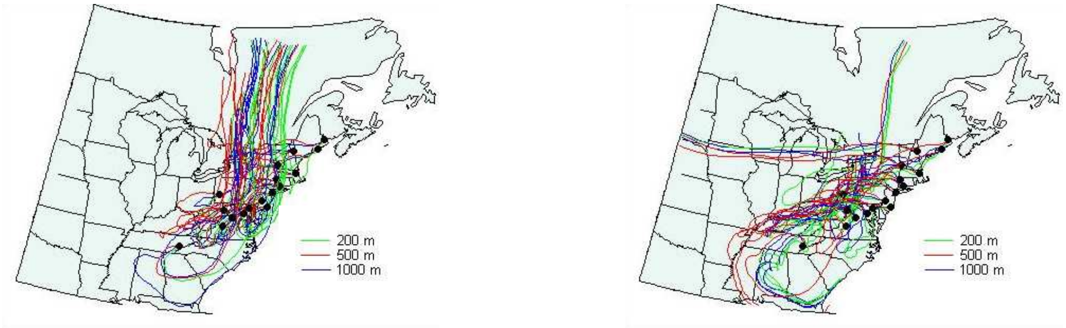
Aug 9, 2002 8 am EDT

Aug 10, 2002 8 am EDT



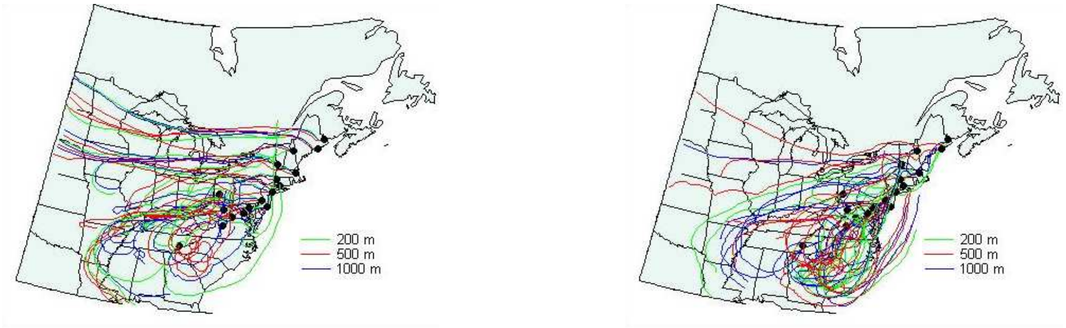
Aug 11, 2002 8 am EDT

Aug 12, 2002 8 am EDT



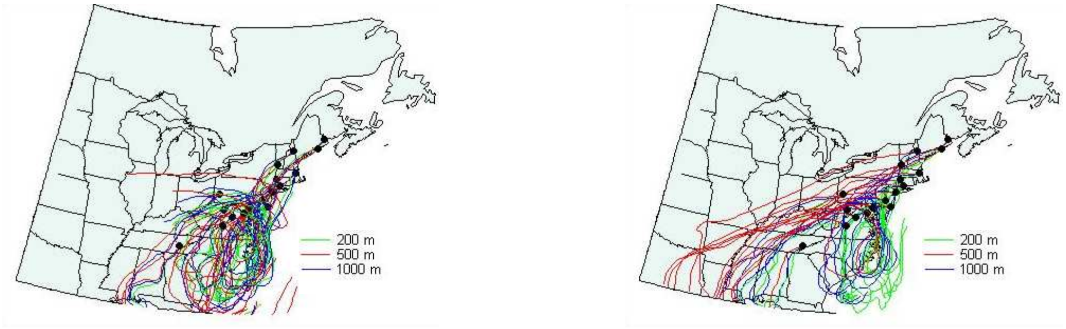
Aug 13, 2002 8 am EDT

Aug 14, 2002 8 am EDT



Aug 15, 2002 8 am EDT

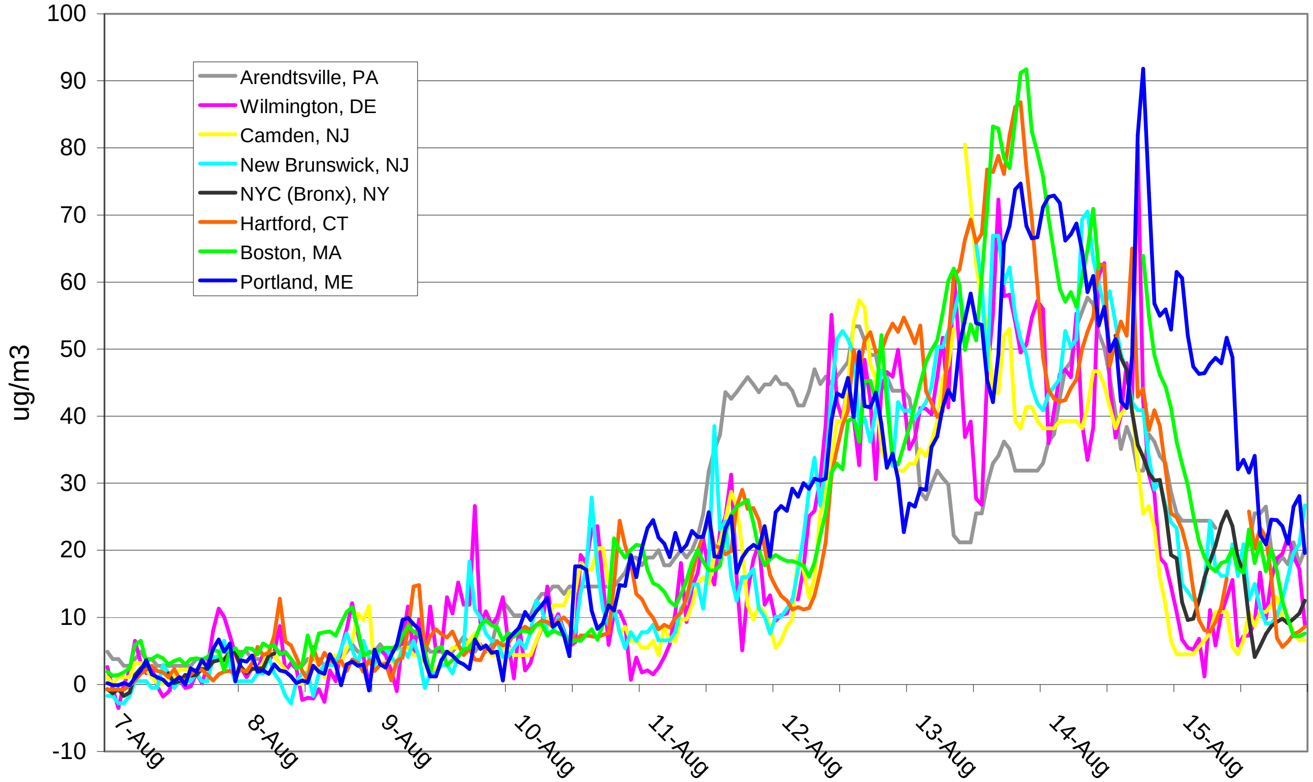
Aug 16, 2002 8 am EDT



4.2. Temporally and spatially resolved $PM_{2.5}$ measurements

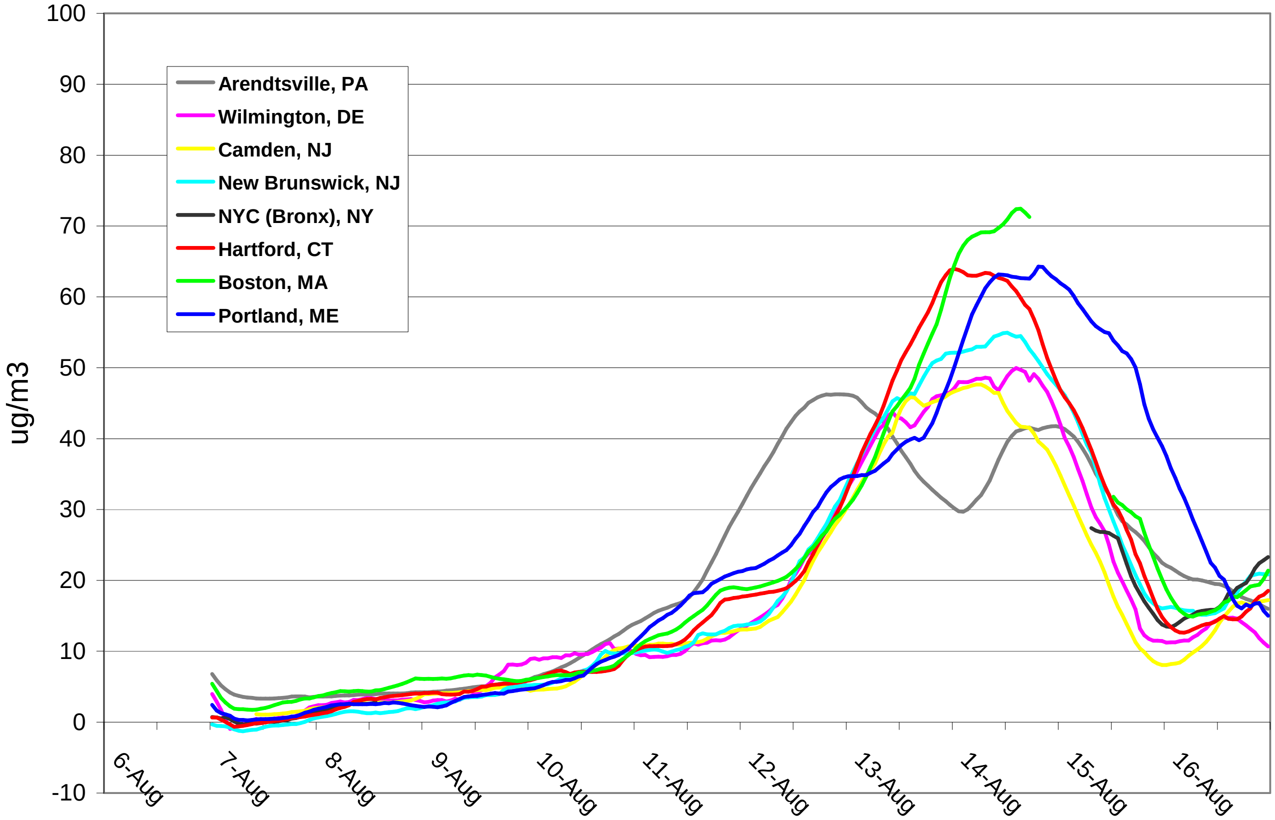
Higher temporal resolution data provide insight into how the events played out in much more detail than can be captured by eight frames on a page; however the most complete picture is obtained when these high *temporal* resolution data can be presented in the context of the relatively greater *spatial* detail provided by maps such as we have seen in Figure 4-1 through Figure 4-3. In Figure 4-4 and Figure 4-5, we present continuous $PM_{2.5}$ data (hourly average and 24-hour rolling average filtered, respectively) for the August 8-16, 2002 time period.

Figure 4-4. Hourly average fine aerosol at 8 sites during the August 2002 episode



Looking at Figure 4-4 in the context of the maps presented in the earlier figures, it is interesting to note the rapid increase, first, in Arendtsville, PA at noon on the 11th, followed by a rise in concentrations along the East Coast around noon on the 12th. This is consistent with Figure 4-1, which shows high $PM_{2.5}$ levels covering western Pennsylvania by 3 p.m. on the 11th and that high $PM_{2.5}$ area has moved over to cover the East Coast by 3 p.m. the next day. This also makes sense with respect to Figure 4-2 and Figure 4-3, which show the high pressure system established on the East Coast by the 11th with surface level back trajectories having shifted from northerly flow to slow southwesterly flow in the western portion of the domain by the morning of the 11th and the coastal sites having switched by the morning of the 12th.

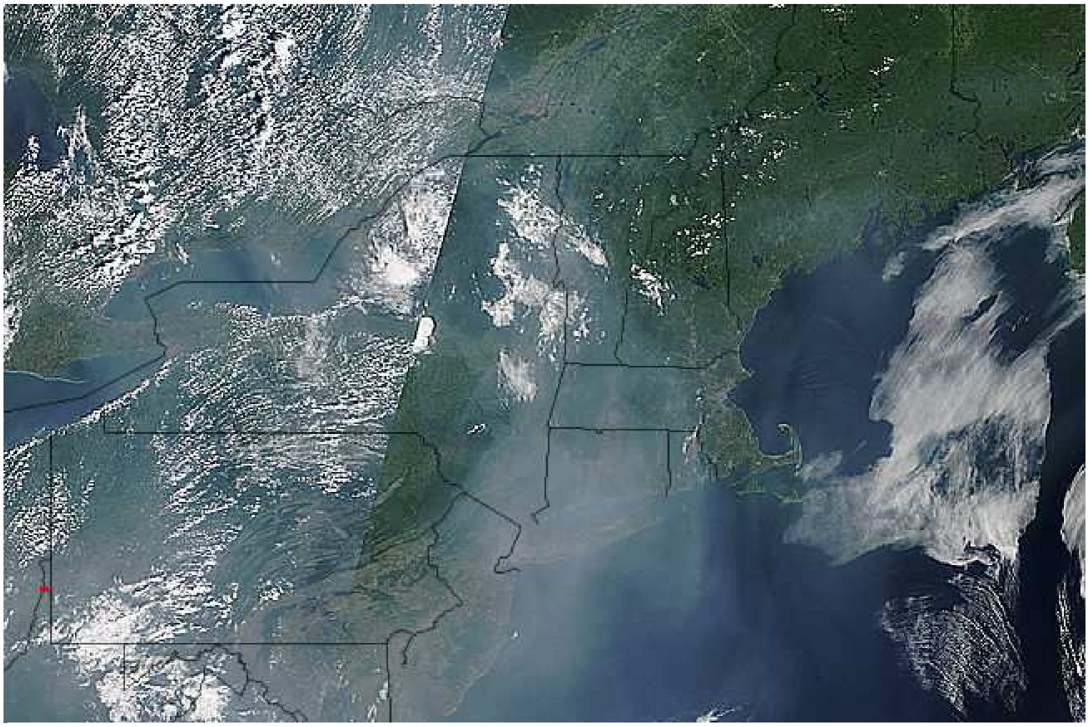
Figure 4-5. 24-hour rolling average fine aerosol at 8 MANE-VU sites during the August 2002 episode



Also note the very high levels observed close to mid-day on the 13th at sites between New York City and Portland, Maine. This is consistent with the strong gradients shown for 3 p.m. on the 13th in Figure 4-1. These rapid increases in concentration are easily explained by the back trajectories of Figure 4-3 that show the advancing front (at this point over Lake Michigan) beginning to push, at upper levels of the atmosphere, an air mass from the upper Midwest due east across the northern half of MANE-VU. At lower levels (see 200 meter trajectories), it can be seen that closer to the surface, this air mass had spent the previous three to four days winding around the Tennessee and Ohio River Valleys before it was driven into the northern reaches of MANE-VU at the peak of the pollution event.

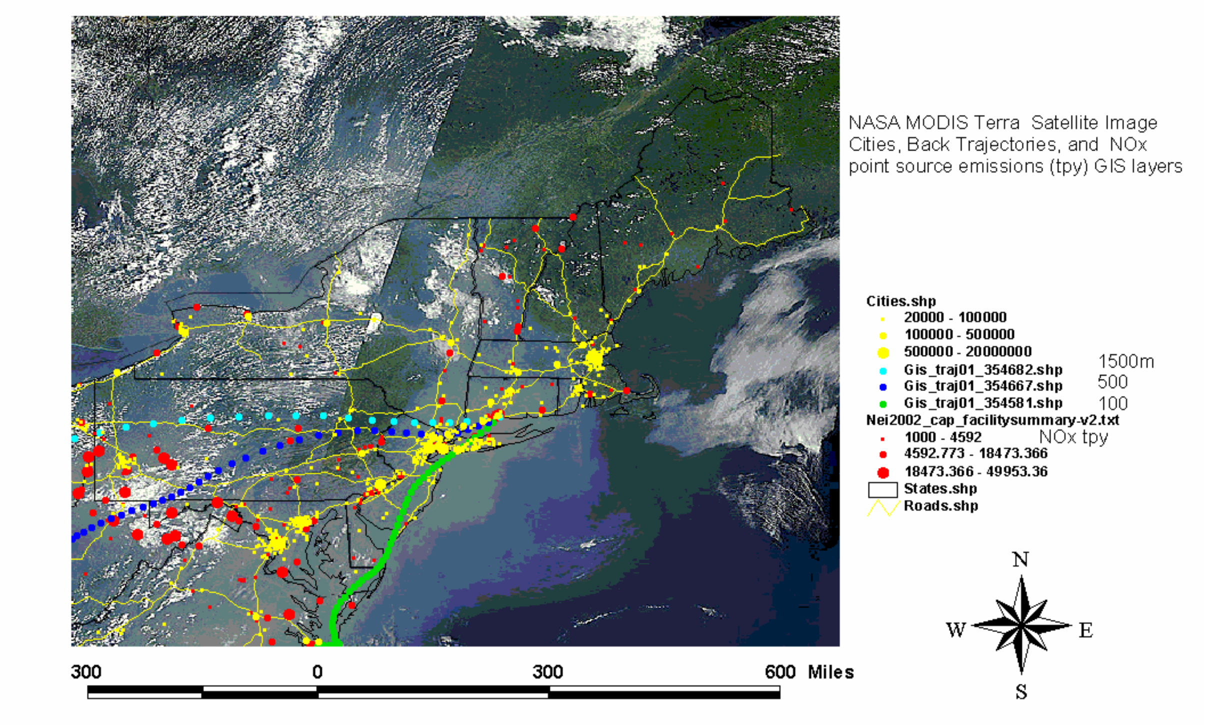
The following figures bring much of this information together in a single image. Figure 4-6 contains satellite photos from MODIS, a mosaic of two consecutive satellite passages on August 13, 2002 from NASA’s TERRA satellite. Figure 4-7 shows the same image with geo-referenced activity data and inventory information layered on top to allow for simultaneous depiction of cities, roads, point source emissions, and back trajectories that play a role in the air pollution/haze that affected a large part of the Northeast during this episode.

Figure 4-6. Composite images from NASA's TERRA Satellite on August 13, 2002 showing fine particle pollution/haze.



Note the milky/gray haze due to particle pollution as distinct from the puffy white clouds over broad regions of southern New England and the eastern Mid-Atlantic region.

Figure 4-7. NASA MODIS Terra Satellite Image, Back Trajectories and NO_X Inventory



Geo-referenced activity and inventory data (on top of the satellite images presented above) demonstrating the relationship between observed pollution and upper level winds (driving weather patterns from West to East), mid-level winds (tracking back to major point sources), and lower level winds (tracking back to major population centers along the East Coast).

4.3. Implications for control strategies

A 2003 assessment of fine particulate matter by NARSTO[15] states, "[c]urrent air-quality management approaches focusing on reductions of emissions of SO_2, NO_X, and VOCs are anticipated to be effective first steps towards reducing $PM_{2.5}$ across North America, noting that in parts of California and some eastern urban areas VOC (volatile organic compounds) emissions could be important to nitrate formation."

This conclusion seems to be well supported by the historical record which documents a pronounced decline in particulate sulfate concentrations across the eastern United States during the 1990s. The timing of this observed decline suggests that this is linked to reductions in SO_2 emissions resulting from controls implemented under the federal Acid Rain program beginning in the early to mid-1990s. From 1989 to 1998, SO_2 emissions in the eastern half of the country — that is, including all states within a region defined by the western borders of Minnesota and Louisiana — declined by about 25 percent. This decline in SO_2 emissions correlated with a decline of about 40 percent in average SO_2 and sulfate concentrations, as measured at Clean Air States and Trend Networks (CASTNet) monitoring sites in the same region over the same time period. In fact, at prevailing levels of atmospheric SO_2 loading, the magnitudes of the emissions and concentration changes were not statistically different. This finding suggests that regional reductions in SO_2 emissions have produced near-proportional reductions of particulate sulfate in the eastern United States (NARSTO, 2003). Reductions since 1990 in precursor SO_2 emissions are likely also responsible for a continued decline in median sulfate concentrations in the northeastern United States. Nevertheless, episodes of high ambient sulfate concentrations (with peak levels well above the regional median or average) continue to occur, especially during the summertime when regional transport from the Ohio River Valley is also at its peak. This suggests that further reductions in regional and local SO_2 emissions would provide significant further air quality and visibility benefits (NARSTO, 2003).

For urban areas of the eastern United States, an effective emissions management approach may be to combine regional SO_2 control efforts aimed at reducing summertime $PM_{2.5}$ concentrations with local SO_2 and OC control efforts. Local SO_2 reductions would help reduce wintertime $PM_{2.5}$ concentrations, while OC reductions can help reduce overall $PM_{2.5}$ concentrations year-round. For areas with high wintertime $PM_{2.5}$ levels, strategies that involve NO_X reductions may also be effective (NARSTO, 2003).

Further support for this general approach may be found in a review of several studies by Watson (2002) which concluded that SO_2 emission reductions have in most cases been accompanied by statistically significant reductions in ambient sulfate concentrations. One study (Husar and Wilson, 1993) shows that regionally averaged light extinction closely tracks regionally averaged SO_2 emissions for the eastern United States from 1940 through the mid-1980s. Another study by Malm *et al.* (2002) shows that

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[15] NARSTO was formerly an acronym for the "North American Research Strategy for Tropospheric Ozone." More recently, the term NARSTO became simply a wordmark signifying a tri-national, public-private partnership for dealing with multiple features of tropospheric pollution, including ozone and suspended particulate matter. For more information on NARSTO see http://www.cgenv.com/Narsto/.

regionally averaged emissions and ambient concentrations decreased together from 1988 through 1999 over a broad region encompassing the states of Connecticut, Delaware, Illinois, Indiana, Kentucky, Maine, Massachusetts, Maryland, Michigan, New Hampshire, New Jersey, New York, Ohio, Pennsylvania, Rhode Island, Vermont, Virginia, Wisconsin, and West Virginia (Watson, 2002).

These studies and available data from the IMPROVE (Interagency Monitoring of Protected Visual Environment) monitoring network provide strong evidence that regional SO_2 reductions have yielded, and will continue to yield, reductions in ambient secondary sulfate levels with subsequent reductions in regional haze and associated light extinction. They indicate that reductions in anthropogenic primary particle emissions will also result in visibility improvements, but that these will not have a zone of influence as large as those of the secondary aerosols (Watson, 2002).

Watson (2002) notes that during the 65 years in which the regional haze program aims to reach its final visibility goals, several opportunities to revise this basic control approach will arise through the decadal SIP cycle. This enables new scientific results to continue to exert a positive influence as states implement new regulatory control programs for SO_2, NO_X and VOCs, and as ambient concentrations of these pollutants change relative to each other and relative to ambient ammonia levels. As these relationships between species change, atmospheric chemistry may dictate a revised control approach to those previously described. Further research on these issues should be a priority for supporting 2018 SIP submissions. They include the possibility that:

- Reduction of sulfate in a fully neutralized atmosphere (excess ammonia) could encourage ammonium nitrate formation.
- Ever-greater emissions reductions could be required to produce a given level of improvement in ambient pollutant concentrations because of non-linearities in the atmospheric formation of sulfate.
- Changes in ambient conditions favoring the aqueous oxidation of sulfate (this pathway largely accounts for the non-linearity noted above) may have implications for future emissions control programs. Causes of changing ambient conditions could include, for example, climate change.

West *et al.* (1999) examine a scenario for the eastern United States where $PM_{2.5}$ mass decreases linearly with ammonium sulfate until the latter is fully neutralized by ammonia. Further reductions would free ammonia for combination with gaseous nitric acid that, in turn, would slightly increase $PM_{2.5}$ until all of the nitric acid is neutralized and further sulfate reductions are reflected in lower $PM_{2.5}$ mass. This is an extreme case that is more relevant to source areas (e.g., Ohio) where nitric acid (HNO_3) is more abundant than in areas with lower emissions (e.g., Vermont) (Watson, 2002).

In most situations with non-neutralized sulfate (typical of the eastern United States), ammonia is a limiting agent for the formation of nitrate but will not make any difference until sulfate is reduced to the point where it is completely neutralized. At that point, identifying large sources of ammonia emissions will be important. This point is likely to be many years in the future, however (Watson, 2002).

Based on analyses using the Community Multi-Scale Air Quality (CMAQ) model, the aqueous phase production of sulfate in the Northeast appears to be very oxidant limited and hence non-linear. Thus, conditions that are conducive to a dominance of the gas-phase production pathway drive the summer peaks in ambient sulfate levels. Nonetheless, the expected reduction in ambient sulfate levels resulting from a given reduction in SO_2 emissions is less than proportional overall due to the non-linearity introduced by the aqueous pathway for sulfate formation (NARSTO, 2003). These non-linearity effects are more pronounced for haze than for sulfate deposition, especially at higher sulfate air concentrations (USNPS, 2003).

Finally, we note that because visibility in the clearest areas is sensitive to even minute increases in particle concentrations, strategies to preserve visibility on the clearest days may require stringent limits on emissions growth. In this context, even the dilute emissions from distant sources can be important (NARSTO, 2003)

4.4. Conclusion: Simplifying a complex problem

A conceptual understanding of fine particles from a regional perspective across MANE-VU and throughout the eastern U.S. is well understood, yet remains complex due to the multiplicity of source regions (both regional and local), pollutants (SO_2, NO_X, organic carbon, and primary $PM_{2.5}$), and seasons (summer and winter) that are involved in fine particle formation.

Regional approaches to the control of precursor SO_2 and NO_X emissions have been started through Title IV of the Clean Air Act, the NO_X SIP Call, the CAIR, and the establishment and support of Regional Planning Organizations to assist with Regional Haze Rule compliance. With the modeling foundation developed for the CAIR program, the USEPA has presented a compelling technical case on the need for additional regional SO_2 and NO_X reductions in the eastern U.S. to reduce particulate levels and protect public health. While states in the Northeast disagree with the extent of SO_2 and NO_X reductions and the timeline for those reductions to occur, the program is an excellent next step toward reducing fine particles in MANE-VU. It is tempting to suggest that the regional control of SO_2 and NO_X are the extent of the problem facing MANE-VU, but as the conceptual description contained in this report demonstrates, the reduction of fine particles in the eastern U.S. requires a careful balance of regional and local controls for SO_2, NO_X, sources of organic carbon and primary $PM_{2.5}$ during both summer and winter.

The (relatively) higher emissions of SO_2 and NO_X from regions upwind of MANE-VU as well as the long “reach” of sulfate pollution requires continued regional control of these fine particle precursors. However, local accumulation of SO_2-derived sulfate, NO_X-derived nitrate, and primary PM (mostly in the form of black carbon/diesel exhaust) can significantly boost urban $PM_{2.5}$ levels. Residential wood combustion in rural river valleys can significantly raise PM levels as well and affect rural visibility in areas near to Class I areas.

The balance between regional and local controls parallels the balance that needs to be achieved between pollutants. The regional contribution to fine particle pollution is driven by sulfates and organic carbon, whereas the local contribution to $PM_{2.5}$ is derived from SO_2, NO_X, organic carbon, and primary $PM_{2.5}$ (including black carbon/diesel exhaust).

Finally, control strategies which focus on regional SO_2 emissions reductions are needed throughout the summer and winter months, suggesting that a year-round approach to control is needed. Urban nonattainment counties with local emissions of NO_X and VOC will be driven to reduce these emissions during the summer for ozone benefits, but these same pollutants – as well as primary particulate emissions – contribute to high $PM_{2.5}$ levels in winter, suggesting that annual controls for all of these pollutants make sense in a multi-pollutant context. Finally, residential wood smoke near Class I areas is clearly a winter-only issue, and further controls may be desirable near specific Class I sites where organic carbon is a contributor on the 20 percent worst visibility days that occur in winter months.

To bring attainment to the current fine particle nonattainment counties and meet reasonable progress goals toward national visibility goals, there continues to be a need for more regional SO_2 and NO_X reductions coupled with appropriate local SO_2, NO_X, VOC, and primary $PM_{2.5}$ (including diesel exhaust) controls where local accumulation is shown to add to the regional burden of sulfate and nitrate $PM_{2.5}$ (primarily in winter). These local controls will vary by location and by season, but the regional control of SO_2 and NO_X should be maintained on an annual basis given the contribution of regional sulfate and nitrate to fine particle peaks during both summer and winter months.

Appendix A: Excerpts from EPA Guidance Document, Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, $PM_{2.5}$, and Regional Haze

APPENDIX A: EPA GUIDANCE DOCUMENT EXERPT

11.0 How Do I Get Started? - A “Conceptual Description”

A State/Tribe should start developing information to support a modeled attainment demonstration by assembling and reviewing available air quality, emissions and meteorological data. Baseline design values should be calculated at each monitoring site, as described in Section 3. For PM applications, speciated data should be reviewed to get a sense of what component(s) might be contributing most significantly to nonattainment or light extinction. If past modeling has been performed, the emission scenarios examined and air quality predictions may also be useful. Readily available information should be used by a State/Tribe to develop an initial conceptual description of the nonattainment or reasonable haze problem in the area which is the focus of a modeled demonstration. A conceptual description is instrumental for identifying potential stakeholders and for developing a modeling/analysis protocol. It may also influence a State’s choice of air quality model, modeling domain, grid cell size, priorities for quality assuring and refining emissions estimates, and the choice of initial diagnostic tests to identify potentially effective control strategies. In general, a conceptual description is useful for helping a State/Tribe identify priorities and allocate resources in performing a modeled demonstration.

In this Section, we identify key parts of a conceptual description. We then present examples of analyses which could be used to describe each of these parts. We note that initial analyses may be complemented later by additional efforts performed by those implementing the protocol.

11.1 What Is A “Conceptual Description”?

A “conceptual description” is a qualitative way of characterizing the nature of an area’s nonattainment or regional haze problem. It is best described by identifying key components of a description. Examples are listed below. There are 3 different examples. One each for ozone, annual $PM_{2.5}$, and regional haze. The examples are not necessarily comprehensive. There could be other features of an area’s problem which are important in particular cases. For purposes of illustration later in the discussion, we have answered each of the questions posed below. Our responses appear in parentheses.

11.1.1 8-Hour Ozone NAAQS

1. Is the nonattainment problem primarily a local one, or are regional factors important?
(Surface measurements suggest transport of ozone close to 84 ppb is likely. There are some other nonattainment areas not too far distant.)

2. Are ozone and/or precursor concentrations aloft also high?
(There are no such measurements.)

3. Do violations of the NAAQS occur at several monitoring sites throughout the nonattainment area, or are they confined to one or a small number of sites in proximity to one another?
(Violations occur at a limited number of sites, located throughout the area.)

4. Do observed 8-hour daily maximum ozone concentrations exceed 84 ppb frequently or just on a few occasions?
(This varies among the monitors from 4 times up to 12 times per year.)

5. When 8-hour daily maxima in excess of 84 ppb occur, is there an accompanying characteristic spatial pattern, or is there a variety of spatial patterns?
(A variety of patterns is seen.)

6. Do monitored violations occur at locations subject to mesoscale wind patterns (e.g., at a coastline) which may differ from the general wind flow?
(No.)

7. Have there been any recent major changes in emissions of VOC or NO_X in or near the nonattainment area? If so, what changes have occurred?
(Yes, several local measures [include a list] believed to result in major reductions in VOC [quantify in tons per summer day] have been implemented in the last five years. Additionally, the area has seen large regional NO_X reductions from the NO_X SIP call.)

8. Are there discernible trends in design values or other air quality indicators which have accompanied a change in emissions?
(Yes, design values have decreased by about 10% at four sites over the past [x] years. Smaller or no reductions are seen at three other sites.)

9. Is there any apparent spatial pattern to the trends in design values?
(No.)

10. Have ambient precursor concentrations or measured VOC species profiles changed?
(There are no measurements.)

11. What past modeling has been performed and what do the results suggest?
(A regional modeling analysis has been performed. Two emission scenarios were modeled: current emissions and a substantial reduction in NO_X emissions throughout the regional domain. Reduced NO_X emissions led to substantial predicted reductions in 8-hour daily maximum ozone in most locations, but changes near the most populated area in the nonattainment area in question were small or nonexistent.)

12. Are there any distinctive meteorological measurements at the surface or aloft which appear to coincide with occasions with 8-hour daily maxima greater than 84 ppb?
(Other than routine soundings taken twice per day, there are no measurements aloft. There is no obvious correspondence with meteorological measurements other than daily maximum temperatures are always > 85 F on these days.)

Using responses to the preceding questions in this example, it is possible to construct an initial conceptual description of the nonattainment area's ozone problem. First, responses to questions 1 and 11 suggest there is a significant regional component to the area's nonattainment problem. Second, responses to questions 3, 4, 7, 8, and 11 indicate there is an important local component to the area's nonattainment problem. The responses to questions 4, 5 and 12 indicate that high ozone concentrations may be observed under several sets of meteorological conditions. The responses to questions 7, 8, and 11 suggest that ozone in and near the nonattainment area may be responsive to both VOC and NO_X controls and that the extent of this response may vary spatially. The response to question 6 suggests that it may be appropriate to develop a strategy using a model with 12 km grid cells.

The preceding conceptual description implies that the State/Tribe containing the nonattainment area in this example will need to involve stakeholders from other, nearby States/Tribes to develop and implement a modeling/analysis protocol. It also suggests that a nested regional modeling analysis will be needed to address the problem. Further, it may be necessary to model at least several distinctive types of episodes and additional analyses will be needed to select episodes. Finally, sensitivity (i.e., diagnostic) tests, or other modeling probing tools, will be needed to assess the effects of reducing VOC and NO_X emissions separately and at the same time.

11.1.2 Annual $PM_{2.5}$ NAAQS

1. Is the nonattainment problem primarily a local one, or are regional factors important?
(Surface measurements suggest that only design values in or immediately downwind of the city violate the NAAQS. However, other nearby design values come close to the concentration specified in the NAAQS)

2. What is the relative importance of measured primary and secondary components of $PM_{2.5}$ measured at sites violating the NAAQS?
(Secondary components (i.e., SO_4, NO_3, OC) constitute about 80% of the measured mass of $PM_{2.5}$. There are higher concentrations of primary $PM_{2.5}$ in the core urban area compared to the suburbs and more rural areas.)

3. What are the most prevalent components of measured $PM_{2.5}$?
(The most important components in ranked order are mass associated with SO_4, OC and inorganic primary particulate matter (IP)).

4. Does the measured mix of PM components appear to roughly agree with mix of emission categories surrounding the monitoring sites?
(No. Relative importance of measured crustal material (IP) appears less than what might be inferred from the inventory).

5. Do there appear to be any areas with large gradients of primary $PM_{2.5}$ in monitored or unmonitored areas?
(Cannot really tell for sources of crustal material until we resolve the preceding

inventory/monitoring discrepancy. There are no other obvious major sources of primary particulate matter).

6. Is there any indication of what precursor might be limiting formation of secondary particulate matter?
(No indicator species analyses have been performed. Past analyses performed for ozone-related SIP revisions suggest that ozone in this area may be limited by availability of VOC).

7. Do monitored violations occur at locations subject to mesoscale wind patterns (e.g., at a coastline) which may differ from the general wind flow?
(No.)

8. Have there been any recent major changes in emissions of PM or its precursors in or near the nonattainment area? What?
(Yes, measures believed to result in major reductions in VOC and NO_X have been implemented in the last 5 years. Reductions in power plant NO_X have resulted from the NO_X SIP call and SO_2 emissions reductions have resulted from the national program to reduce acid deposition.)

9. Are there discernible trends in design values or other air quality indicators which have accompanied a change in emissions?
(The trend appears to be downward, but the most recent air quality data has been higher. Overall, the period of record is insufficiently long to tell).

10. Is there any apparent spatial pattern to the trends in design values?
(No.)

11. What past modeling has been performed and what do the results suggest?
(A regional modeling analysis has been performed for ozone and $PM_{2.5}$. Two emission scenarios were modeled: current emissions and a substantial reduction in NO_X and SO_2 emissions throughout a regional domain. Reduced NO_X emissions led to substantial predicted reductions in 8-hour daily maximum ozone in most locations. Modeled SO_2 reductions from the CAIR rule had a strong impact on sulfate concentrations)

12. Are there any distinctive meteorological measurements at the surface or aloft which appear to coincide with occasions with $PM_{2.5}$ concentrations in excess of 15.0 :g/m^3?
(Other than routine soundings taken twice per day, there are no measurements aloft. There is no obvious correspondence with meteorological measurements other than daily maximum temperatures are often > 85F on days with the highest $PM_{2.5}$ observations.)

13. Do periods with high measured particulate matter or components of particulate matter appear to track each other or any other measured pollutant?
(There appears to be some correspondence between measured high concentrations of SO_4 and ozone).

Using responses to the preceding questions in this example, it is possible to construct an initial conceptual description of the nonattainment area's ozone problem. First, responses to questions 1, 2 and 3 suggest there is a significant regional component to the area's nonattainment problem. Second, responses to questions 1 and 3 indicate there is a local component to the problem. The responses to questions 11,12 and 13 suggest that there may be a link between reducing ozone and reducing particulate matter. Thus, it may be appropriate to assess effects of previously committed to strategies to reduce ozone and national PM control measures before simulating additional control measures. The responses to questions 4 and 5 suggest that it is premature to determine whether a "local area analysis" will be needed. The response to question 7 suggests that it may not be necessary to model with very small grid cells, at least for the secondary components of $PM_{2.5}$.

The preceding conceptual description implies that the State containing the nonattainment area in this example will need to involve stakeholders from other, nearby States to develop and implement a modeling/analysis protocol. It also suggests that a nested regional modeling analysis will be needed to address the problem.

11.1.3 Example reasonable progress application

1. What components of particulate matter appear to have high concentrations on days with poor visibility?
(Mass associated with SO_4 and coarse particulate matter (CM) seem to have the highest concentrations on most such days).

2. What are typical values for the humidity adjustment factor during the times of year when most of the days with poor visibility occur?
(Typical values appear to be about "4.0").

3. Does visibility appear to track well among nearby Class I areas?
(Yes, but not always).

4. Does poor visibility seem to occur under any specific meteorological conditions?
(This information is not readily available).

5. Does poor visibility seem to coincide with high observed concentrations of any particular other pollutant?
(There seems to be some correspondence with high regional ozone concentrations)

6. What components of particulate matter appear to have relatively high concentrations on days with good visibility?
(Coarse particulate matter and OC)

7. What are typical values for the humidity adjustment factor during times of year when most of the days with good visibility occur?
(About "2.3")

8. Does good visibility appear to occur under any specific meteorological conditions? (Don’t know.)

Answers to the preceding questions suggest that strategies to reduce sulfate concentrations and, perhaps, regional ozone concentrations might be effective in reducing light extinction on days when visibility is currently poor. The responses suggest that a strategy which focuses on this alone should first be tried for the days with good visibility as well. Even though sulfate concentrations appear low on such days, the fact that sulfates scatter light efficiently (see Equation (6.1)) and relative humidity is still high enough to enhance this effect is worth considering. Responses suggest that further meteorological analyses would be worthwhile prior to selecting strategies to simulate with a resource intensive regional model.

It should be clear from the preceding examples that the initial conceptual description of an area’s nonattainment problem draws on readily available information and need not be detailed. It is intended to help launch development and implementation of a modeling/analysis protocol in a productive direction. It will likely be supplemented by subsequent, more extensive modeling and ambient analyses performed by or for those implementing the modeling/analysis protocol discussed in Section 12.0.

Questions like those posed in Section 11.1 can be addressed using a variety of analyses ranging in complexity from an inspection of air quality data to sophisticated mathematical analyses. We anticipate the simpler analyses will often be used to develop the initial conceptual description. These will be followed by more complex approaches or by approaches requiring more extensive data bases as the need later becomes apparent. These analyses are intended to channel resources available to support modeled attainment demonstrations onto the most productive paths possible. They will also provide other pieces of information which can be used to reinforce conclusions reached with an air quality model, or cause a reassessment of assumptions made previously in applying the model. As noted in Section 7, corroboratory analyses should be used to help assess whether a simulated control strategy is sufficient to meet the NAAQS.

Appendix B: Monitoring Data from Class I sites in MANE-VU

Below are figures that were developed by Tom Downs of the Maine Department of Environmental Protection. These figures represent baseline monitoring data for the Class I sites (and Washington DC) based on IMPROVE monitoring network data using the EPA approved “default” algorithm for calculating reconstructed extinction and estimating natural background conditions. These statistics may need to be recreated using the alternative methodology approved by the IMPROVE steering committee and adopted by the MANE-VU states. Glide path graphs were created on the VIEWS website (http://vista.cira.colostate.edu/views/) using the Annual Summary Trends tool. Seasonal graphs were created from data downloaded from the VIEWS website using the Annual Summary Composition tool and should be updated to include 2004 data for a complete description of regional haze baseline data.

APPENDIX B: MONITORING DATA FROM CLASS I SITES IN MANE-VU

Figure B-1. Monitoring Data from Acadia NP, ME

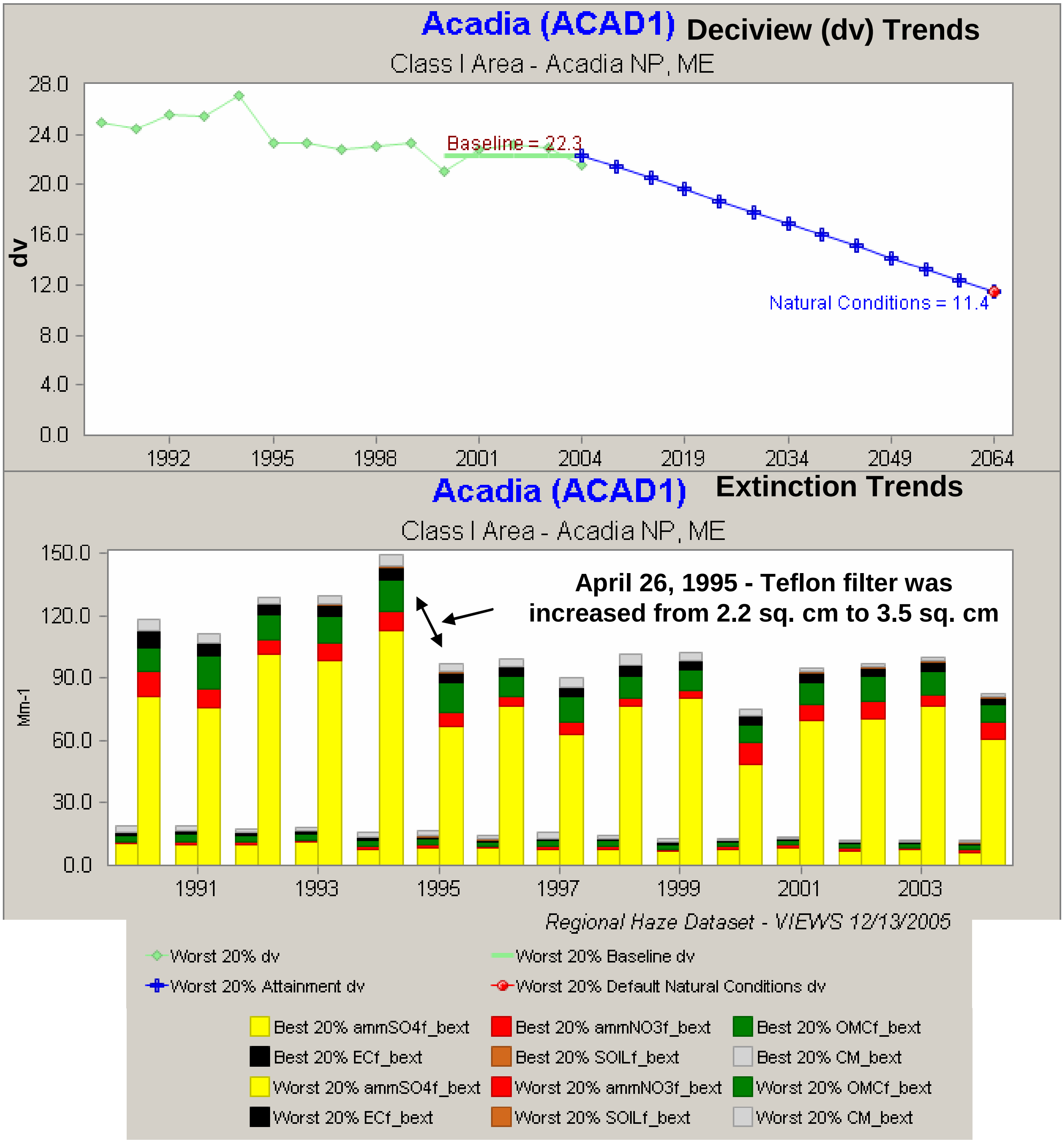


Figure B-2. Monitoring Data from Brigantine, ME

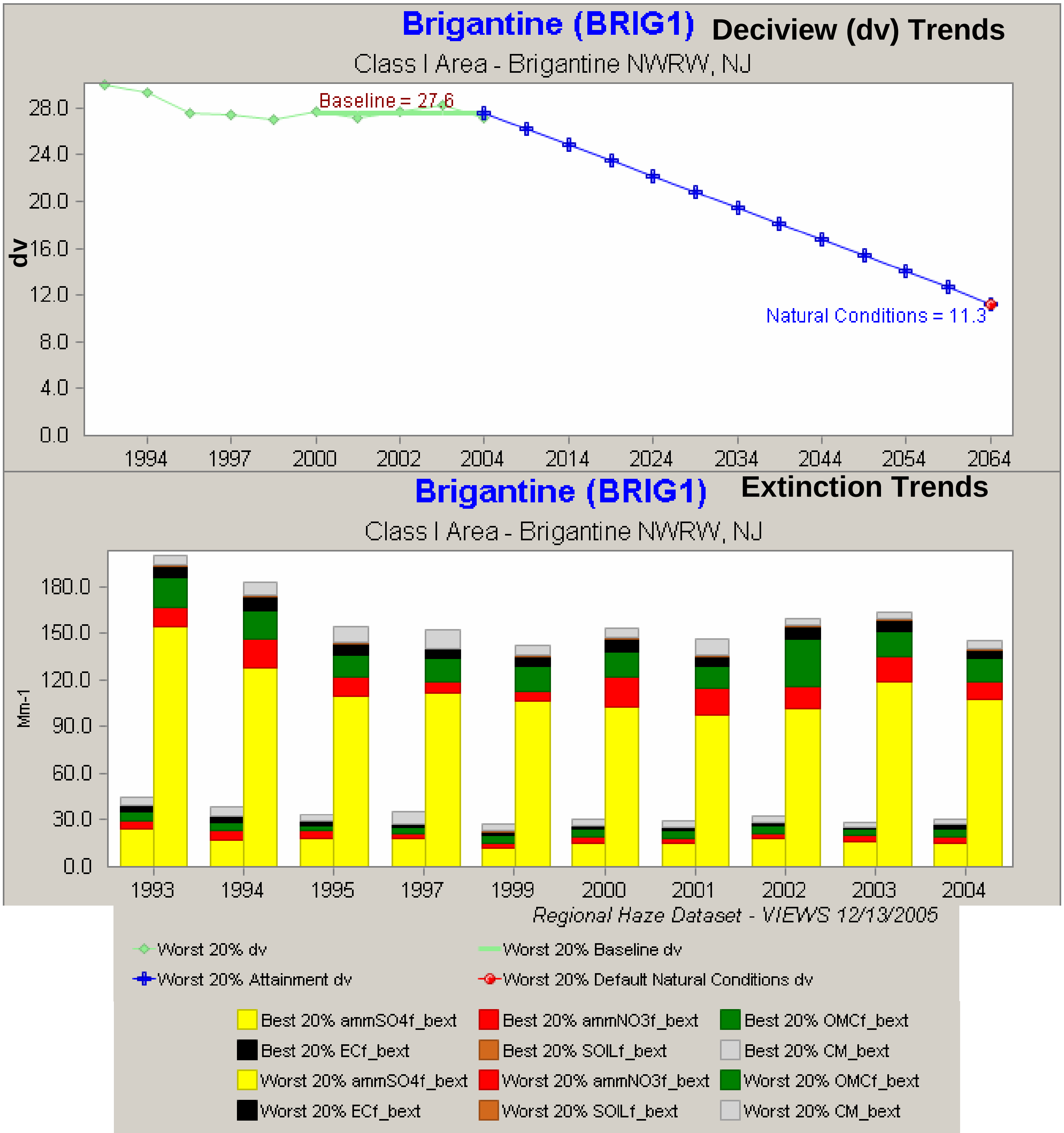
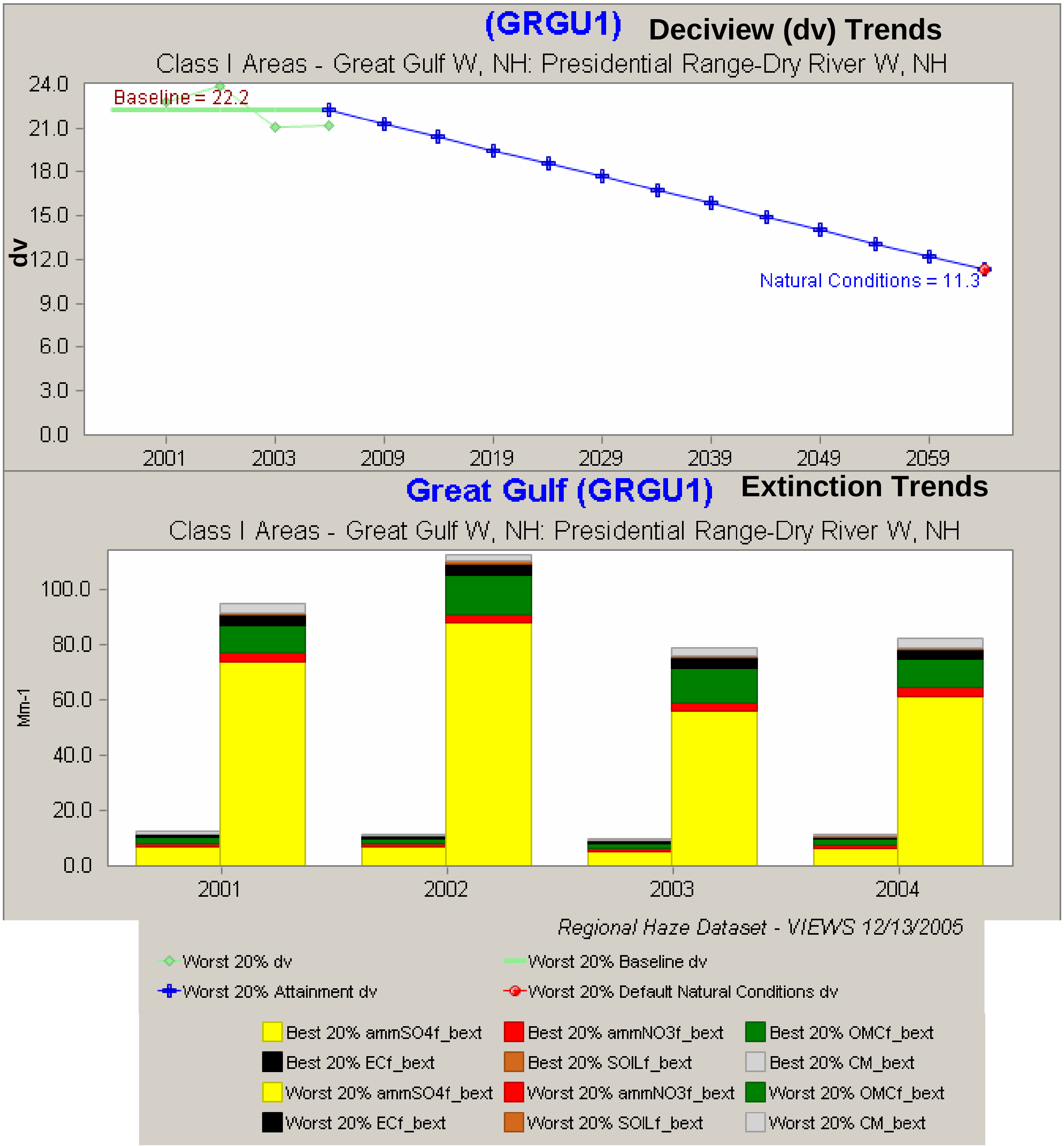


Figure B-3. Monitoring Data from Great Gulf, NH



Regional Haze Dataset - VIEWS 12/13/2005

Figure B-4. Monitoring Data from Lye Brook, VT

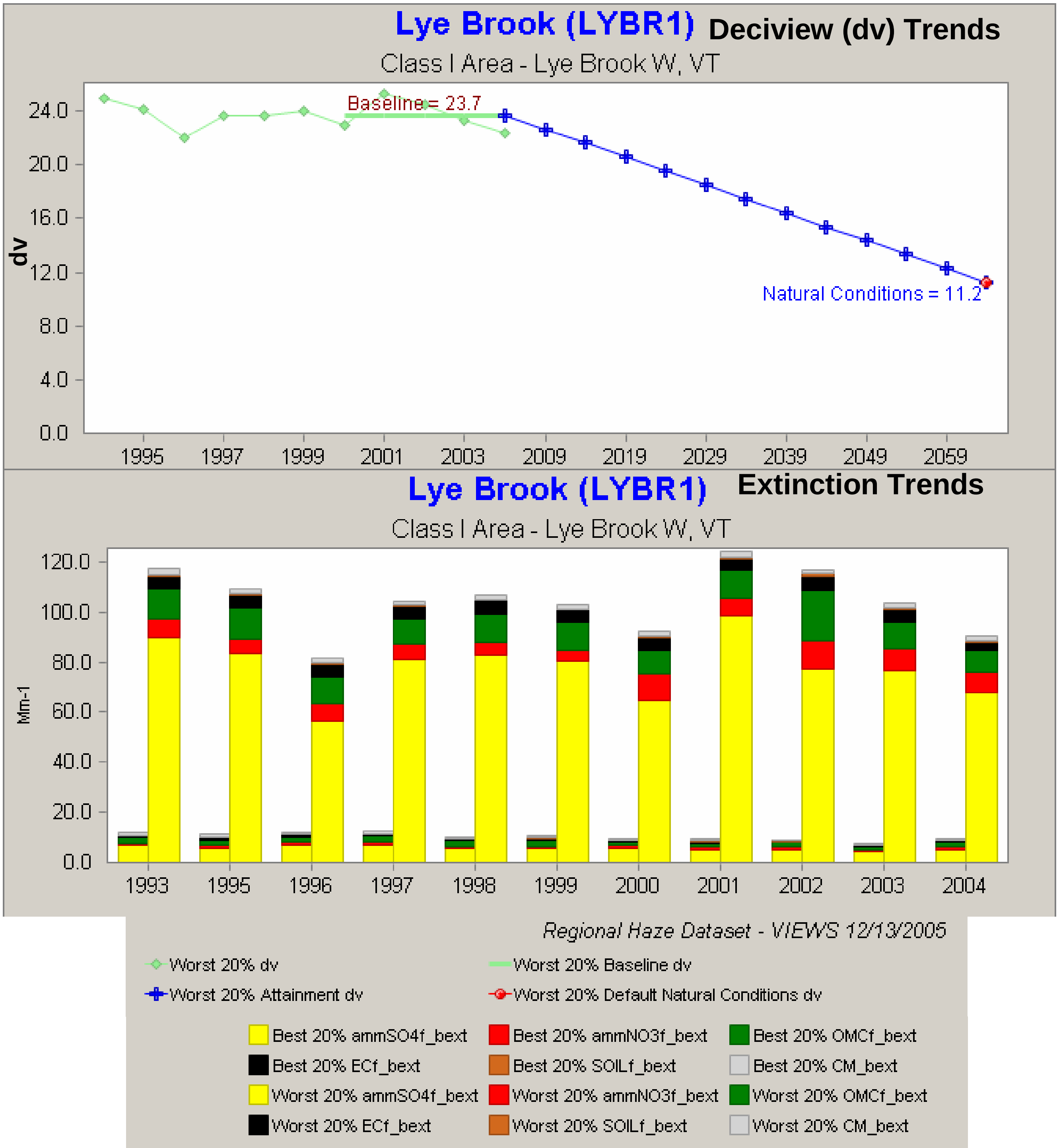


Figure B-5. Monitoring Data from Moosehorn, ME

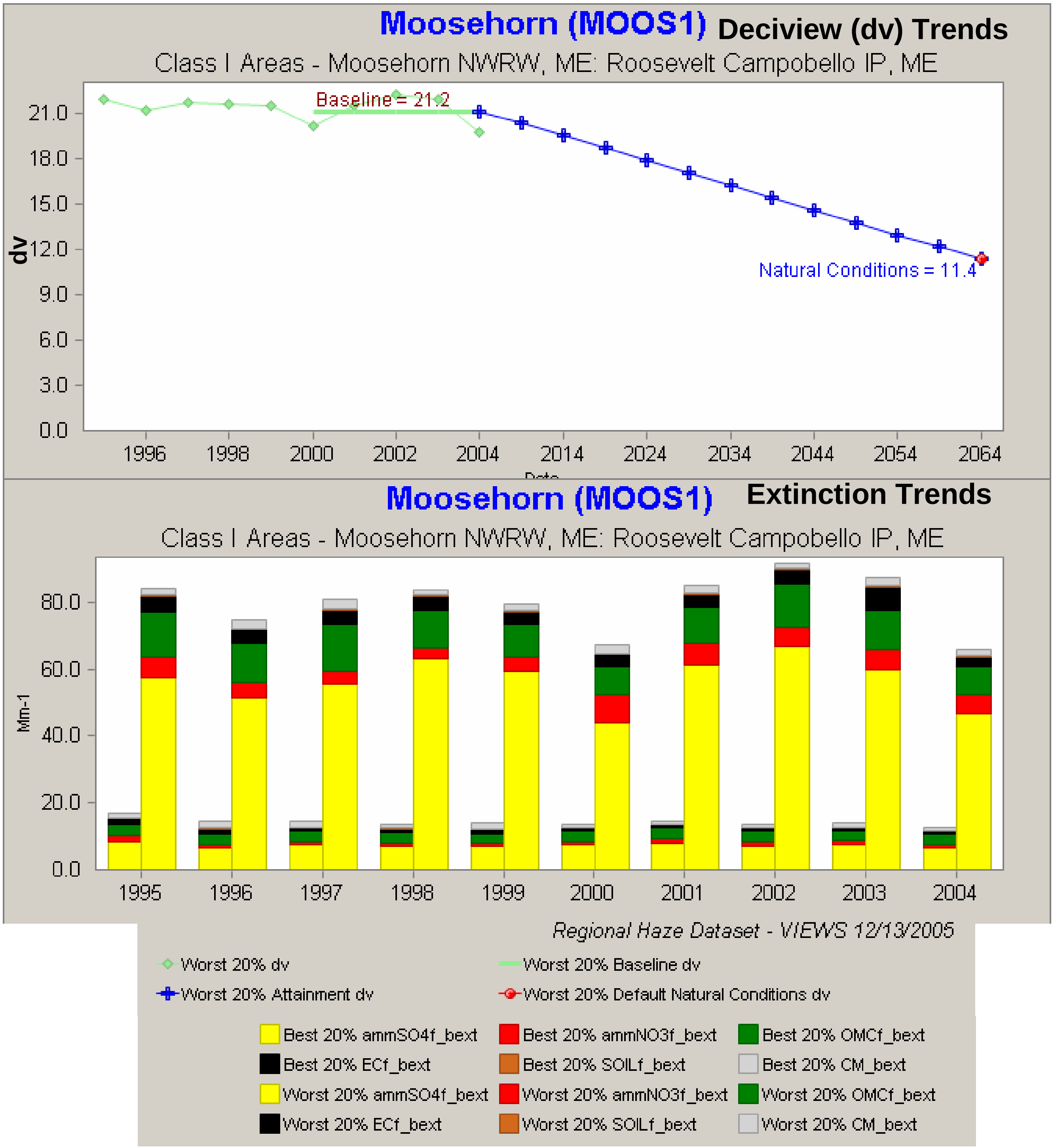


Figure B-6. Monitoring Data from Washington, DC

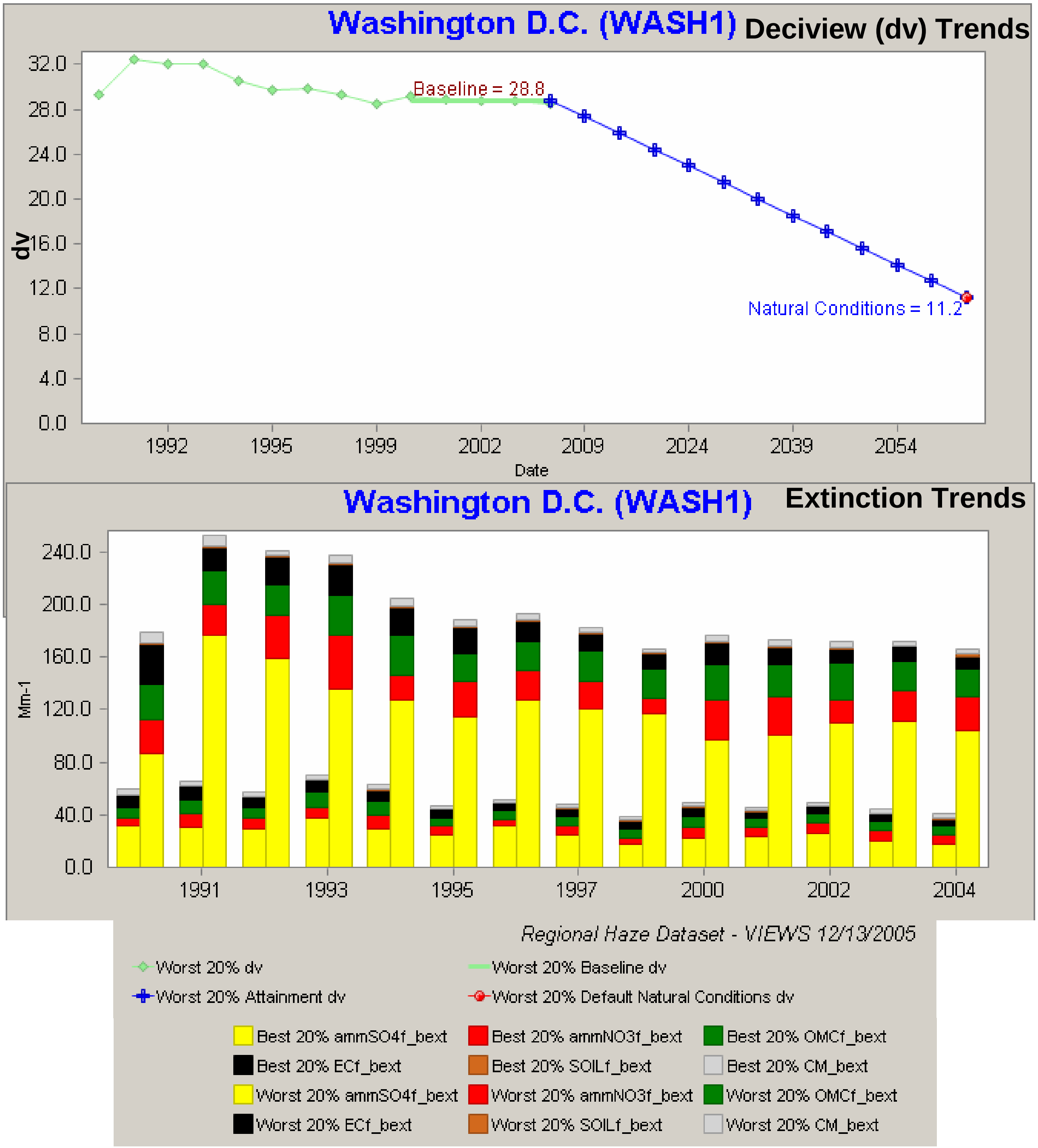
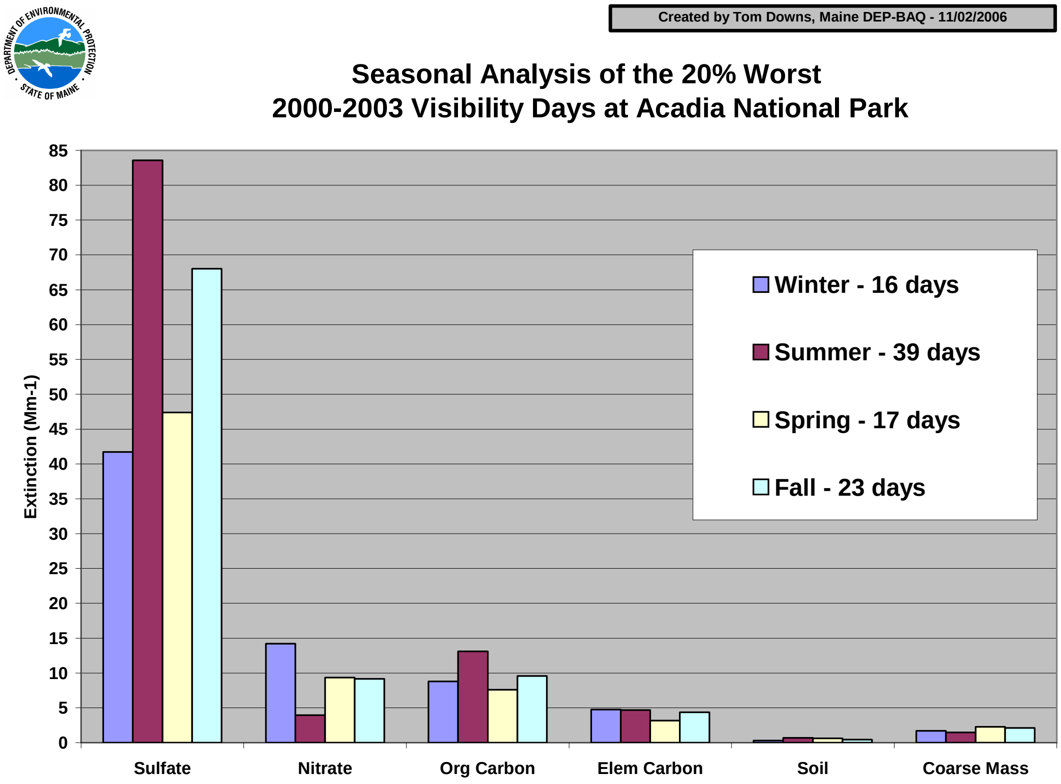


Figure B-7. 20% Worst and Best 2000-2003 Visibility Days at Acadia NP, ME



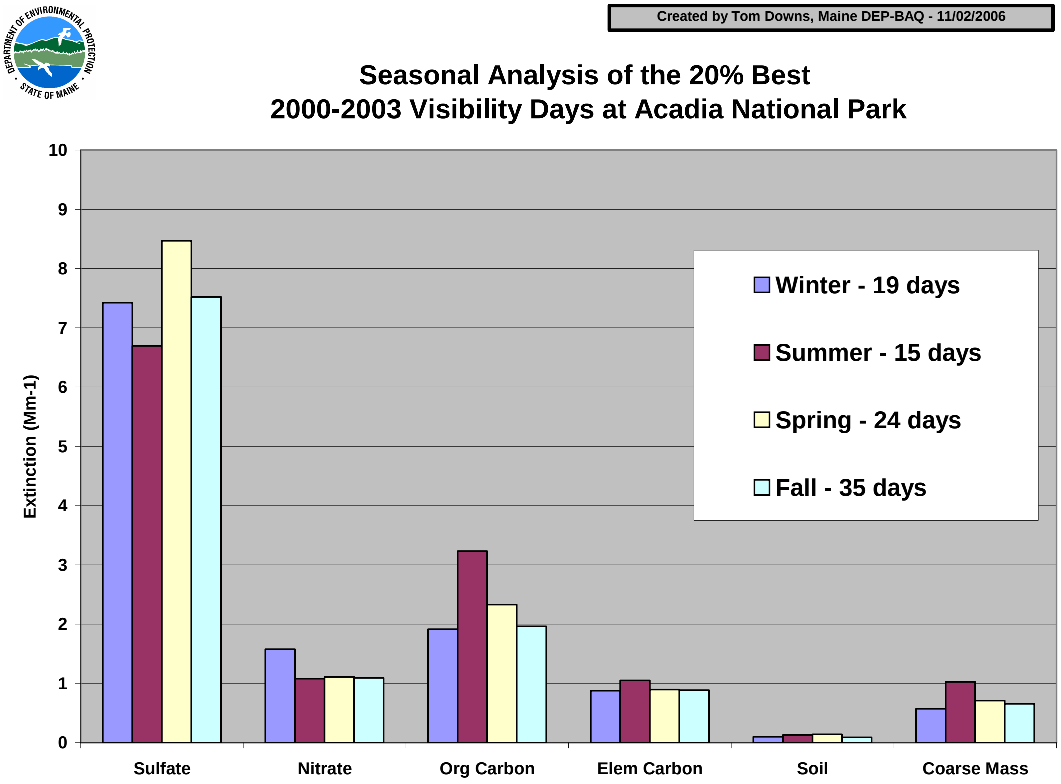
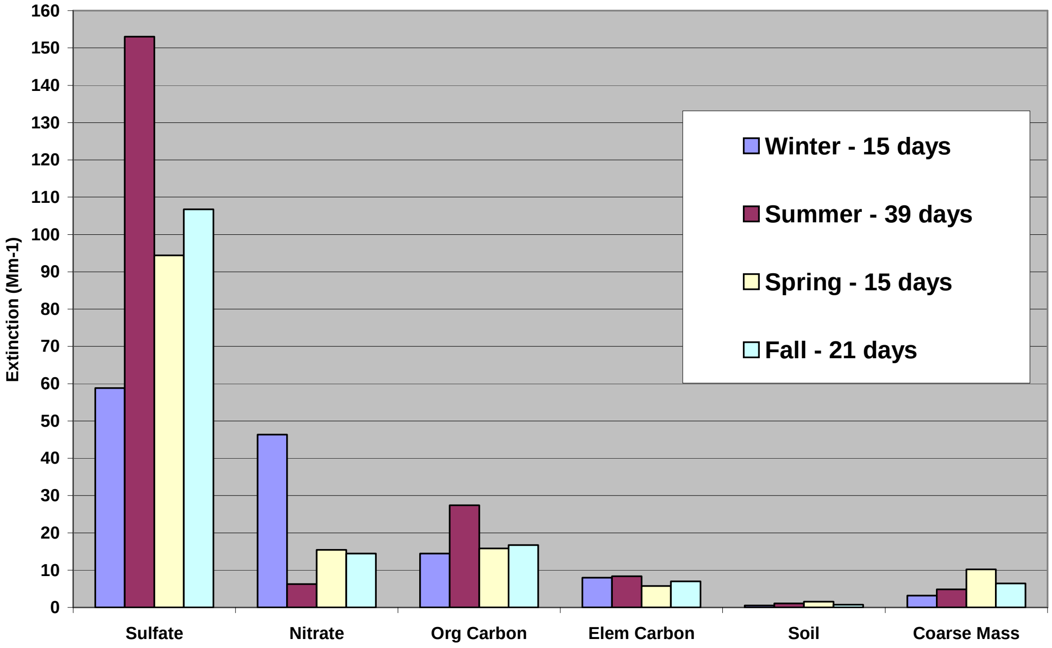


Figure B-8. 20% Worst and Best 2000-2003 Visibility Days at Brigantine, NJ

Created by Tom Downs, Maine DEP-BAQ - 11/02/2006

Seasonal Analysis of the 20% Worst
2000-2003 Visibility Days at Brigantine, NJ



Created by Tom Downs, Maine DEP-BAQ - 11/02/2006

Seasonal Analysis of the 20% Best
2000-2003 Visibility Days at Brigantine, NJ

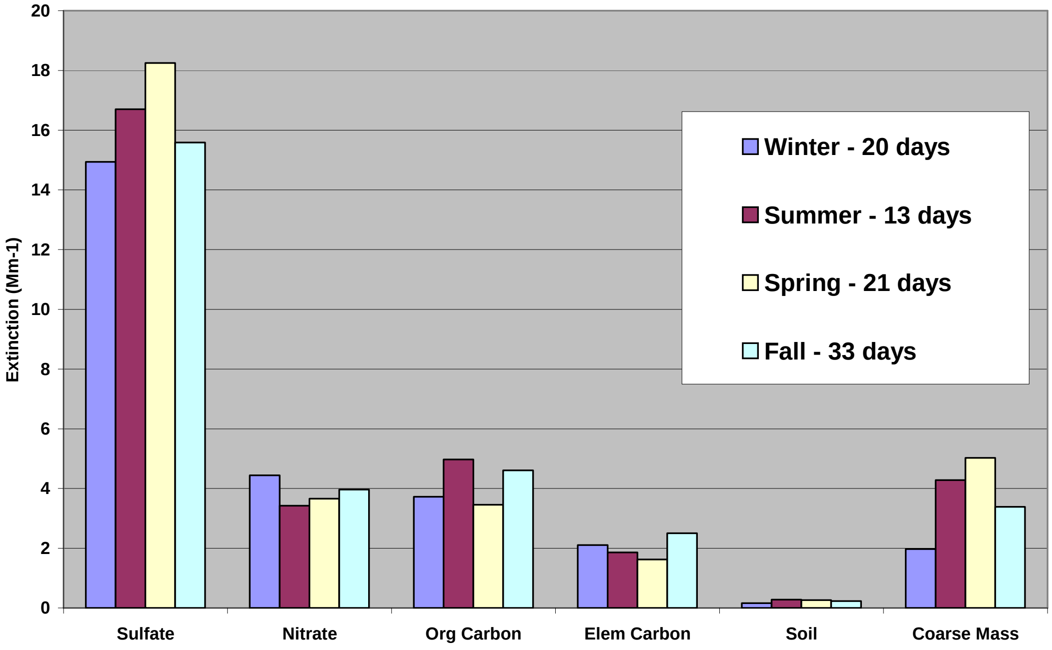
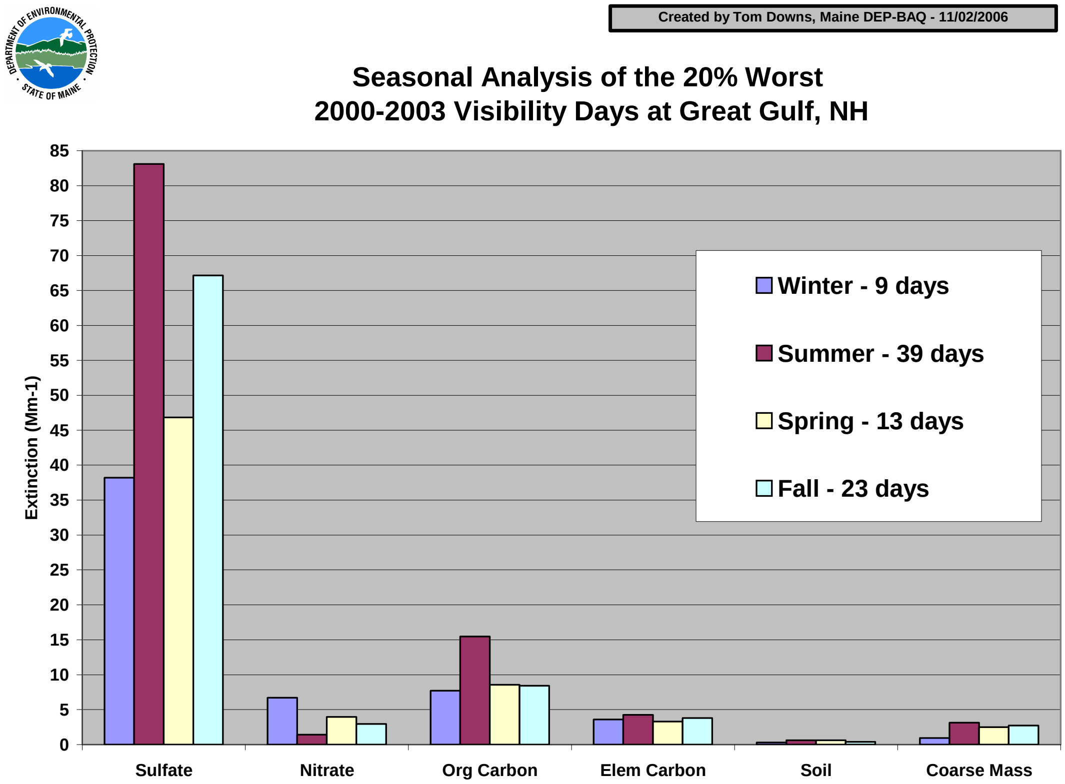
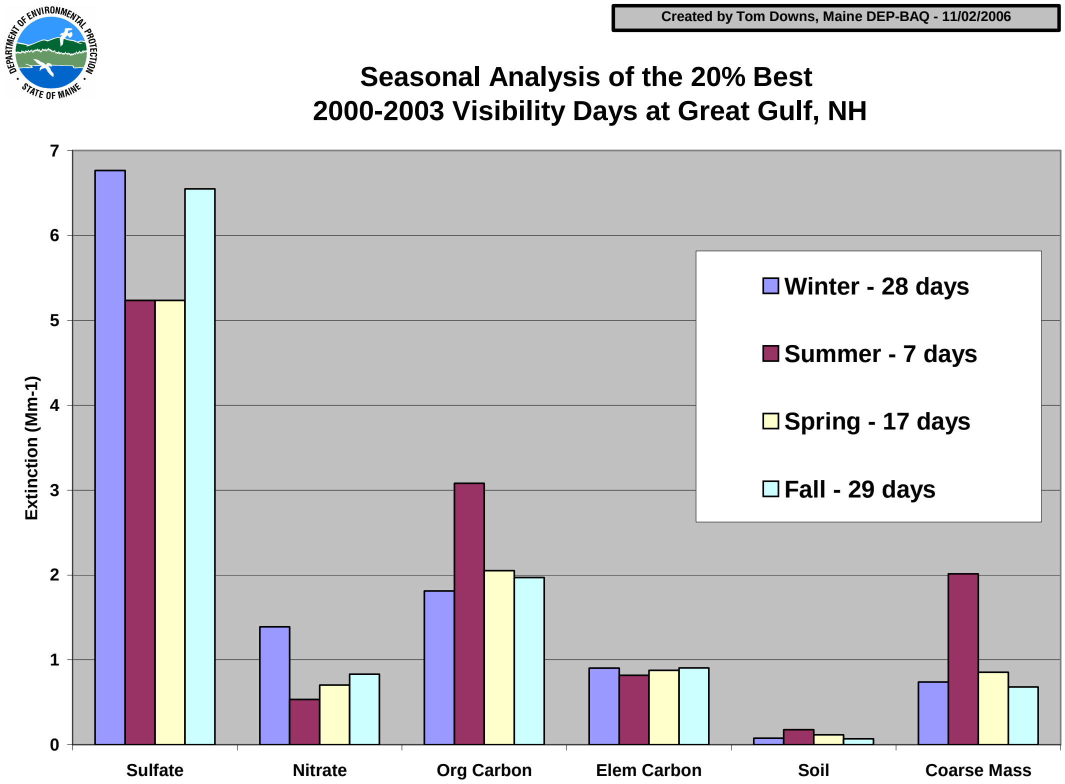


Figure B-9. 20% Worst and Best 2000-2003 Visibility Days at Great Gulf, NH

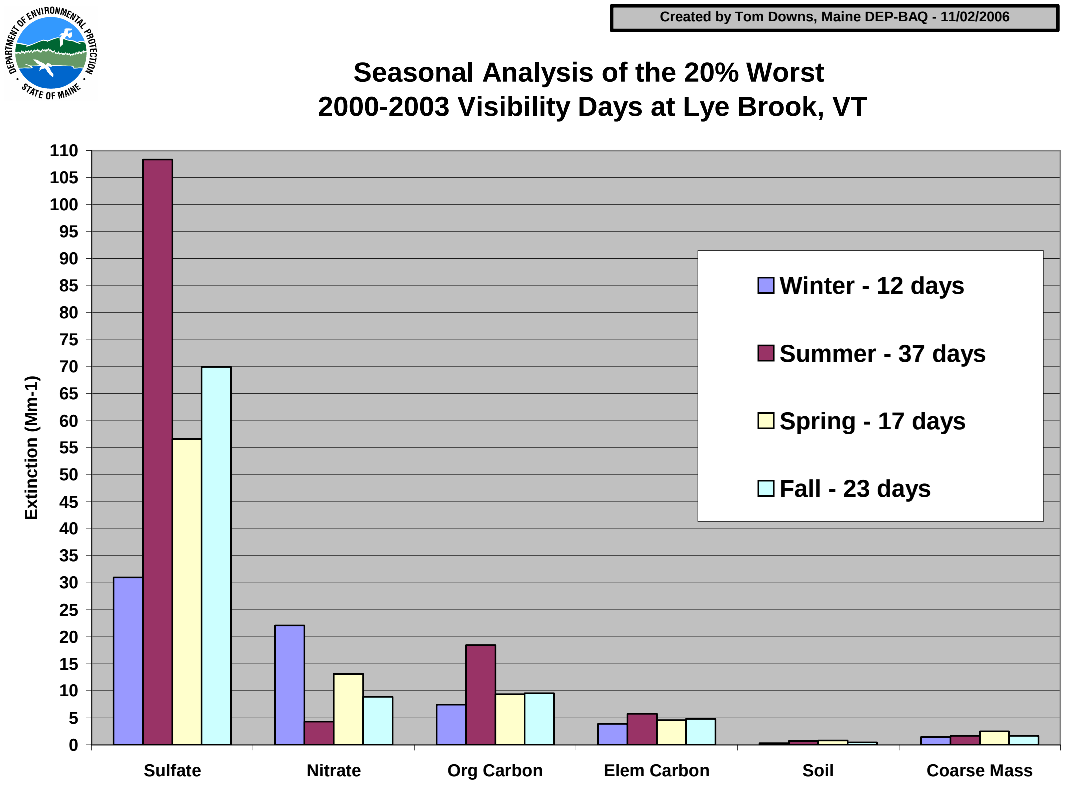

Created by Tom Downs, Maine DEP-BAQ - 11/02/2006

Seasonal Analysis of the 20% Worst 2000-2003 Visibility Days at Great Gulf, NH

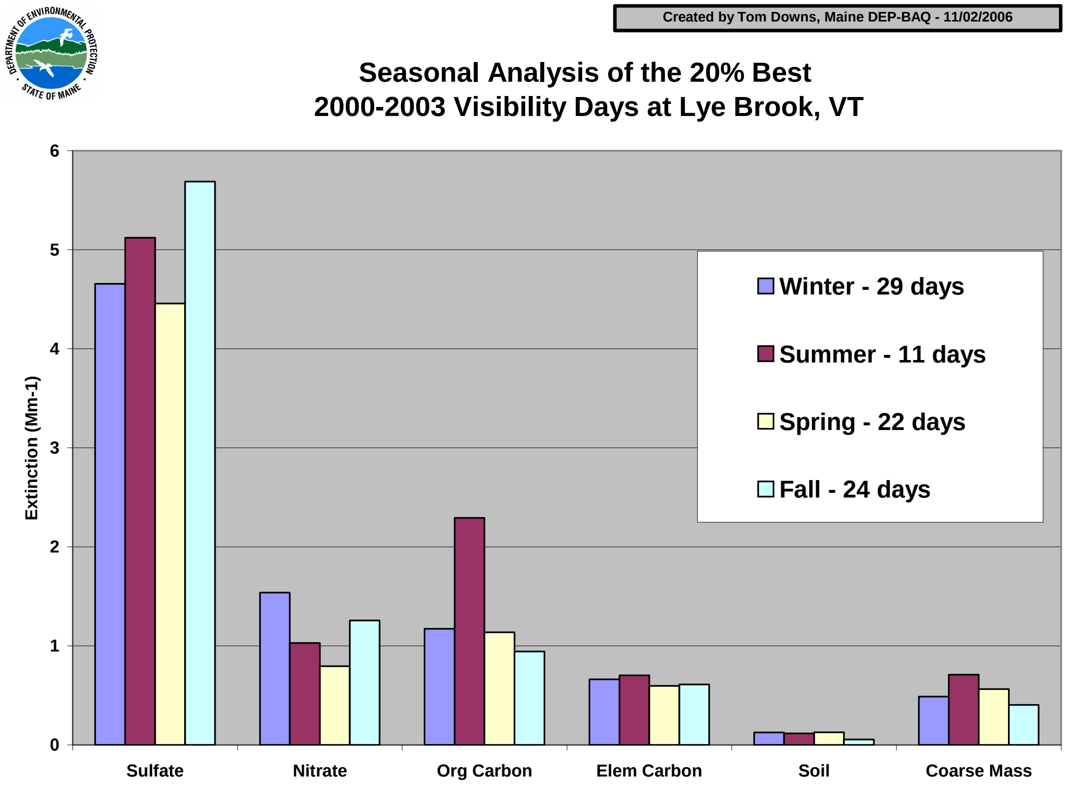

Created by Tom Downs, Maine DEP-BAQ - 11/02/2006

Seasonal Analysis of the 20% Best 2000-2003 Visibility Days at Great Gulf, NH

Figure B-10. 20% Worst and Best 2000-2003 Visibility Days at Lye Brook, VT

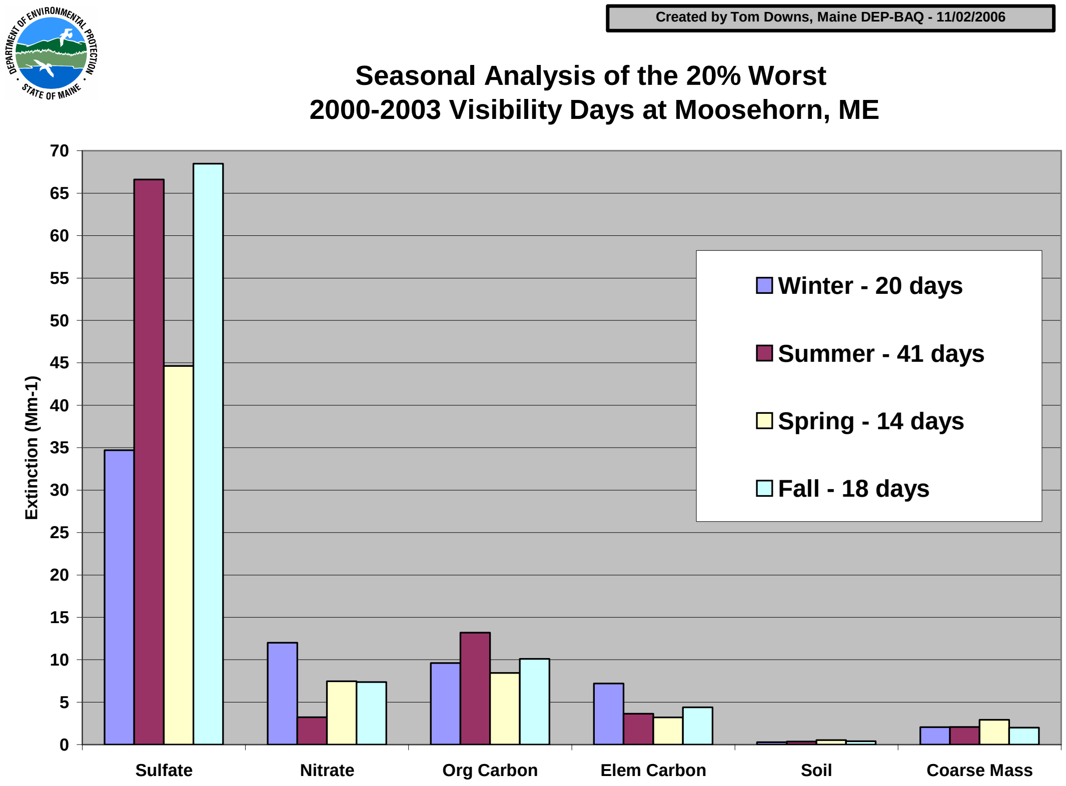

Created by Tom Downs, Maine DEP-BAQ - 11/02/2006

Seasonal Analysis of the 20% Worst
2000-2003 Visibility Days at Lye Brook, VT


Created by Tom Downs, Maine DEP-BAQ - 11/02/2006

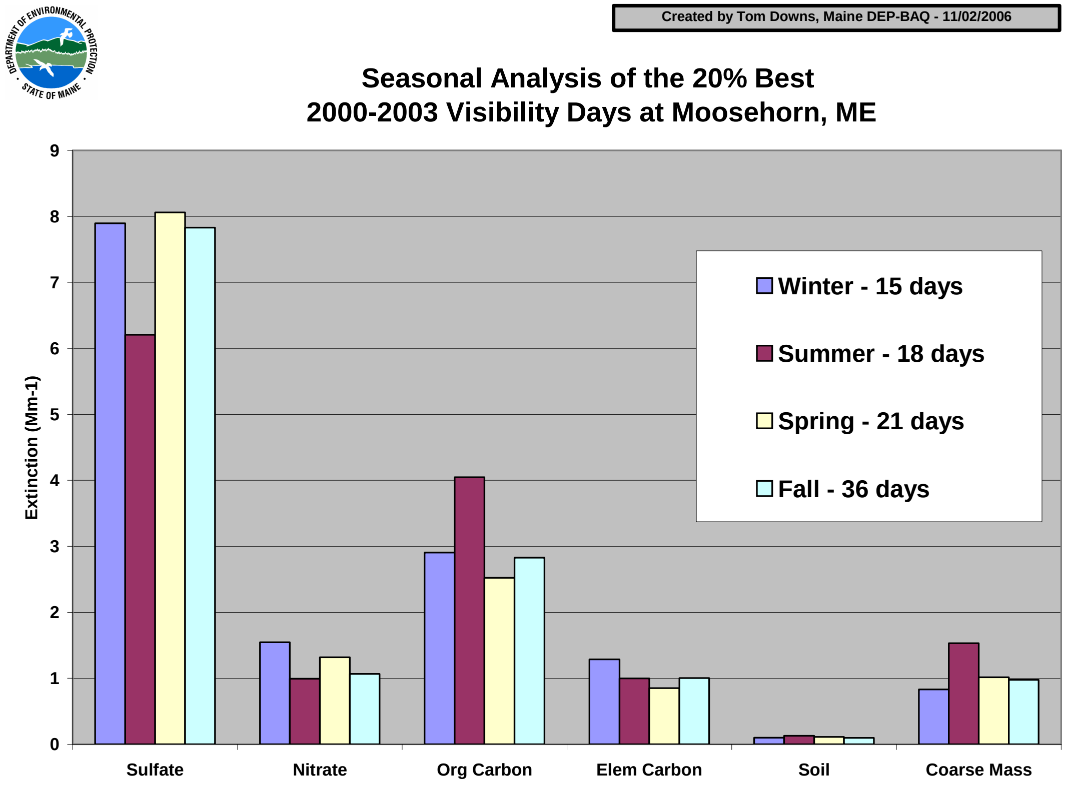
Seasonal Analysis of the 20% Best
2000-2003 Visibility Days at Lye Brook, VT

Figure B-11. 20% Worst and Best 2000-2003 Visibility Days at Moosehorn, ME



Created by Tom Downs, Maine DEP-BAQ - 11/02/2006

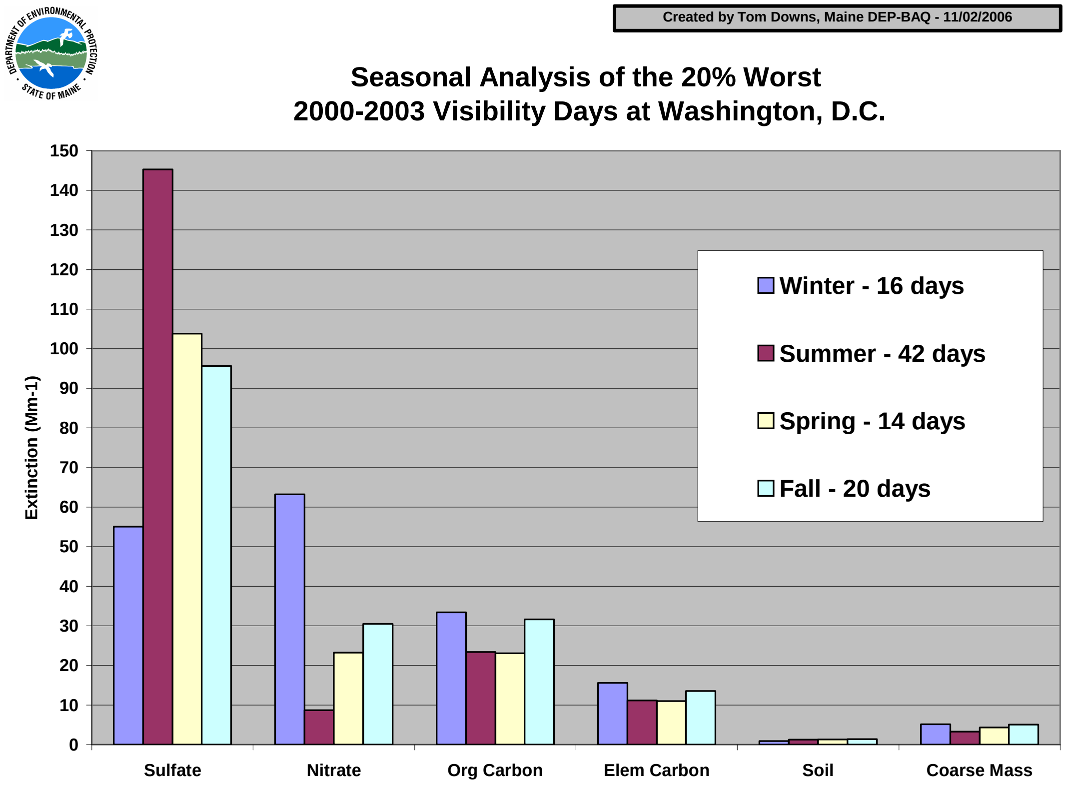
Seasonal Analysis of the 20% Worst 2000-2003 Visibility Days at Moosehorn, ME



Created by Tom Downs, Maine DEP-BAQ - 11/02/2006

Seasonal Analysis of the 20% Best 2000-2003 Visibility Days at Moosehorn, ME

Figure B-12. 20% Worst and Best 2000-2003 Visibility Days at Washington, D.C.



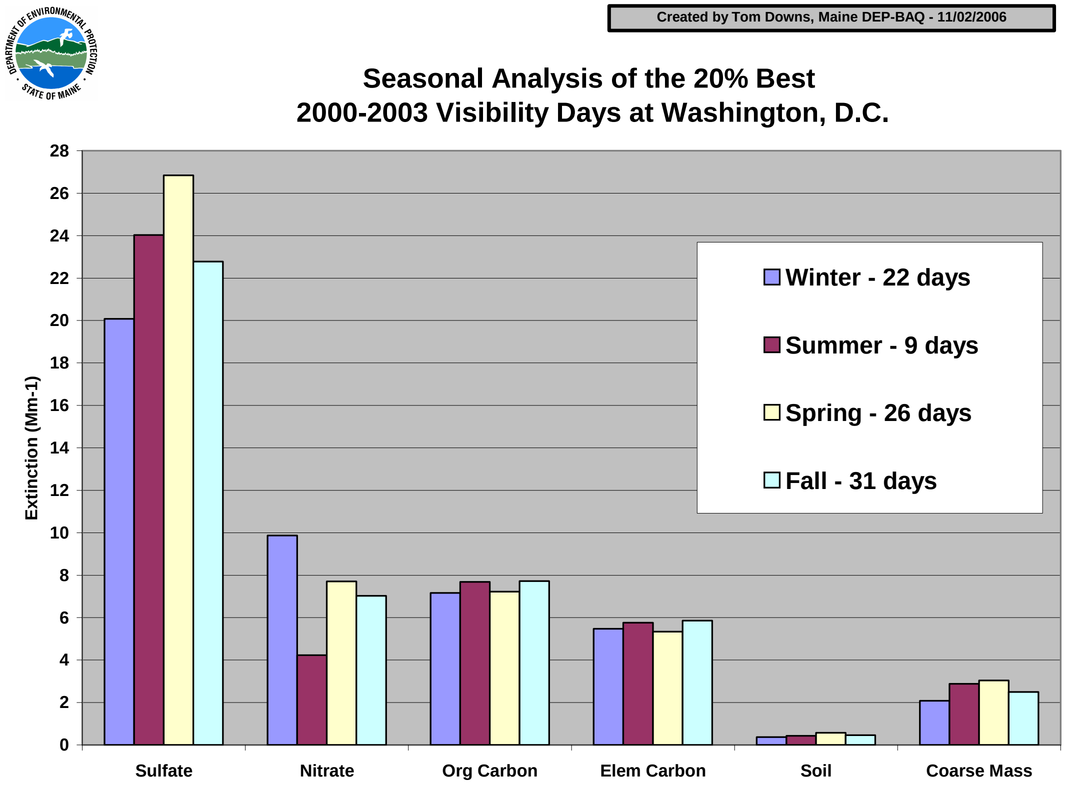
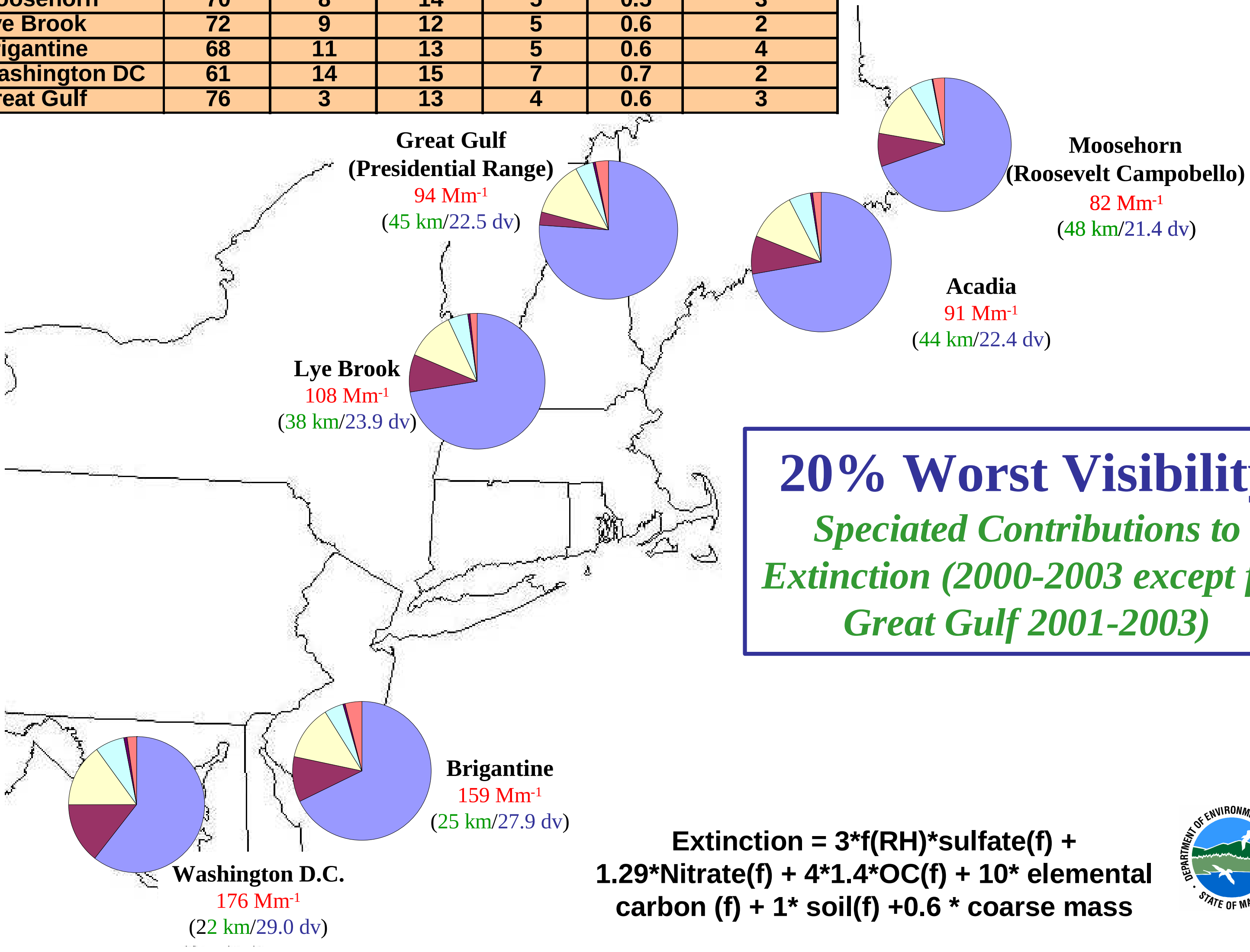


Figure B-13. 20% Best 2000-2003 Visibility Days Speciated Contributions to Extinction

	percent contributon to particle extinction					
Site	Sulfate	Nitrate	Org C	Elem C	Soil	Coarse Mass
Acadia	72	9	11	5	0.6	2
Moosehorn	70	8	14	5	0.5	3
Lye Brook	72	9	12	5	0.6	2
Brigantine	68	11	13	5	0.6	4
Washington DC	61	14	15	7	0.7	2
Great Gulf	76	3	13	4	0.6	3

Created by Tom Downs,
Maine DEP-BAQ 12/13/2005



20% Worst Visibility

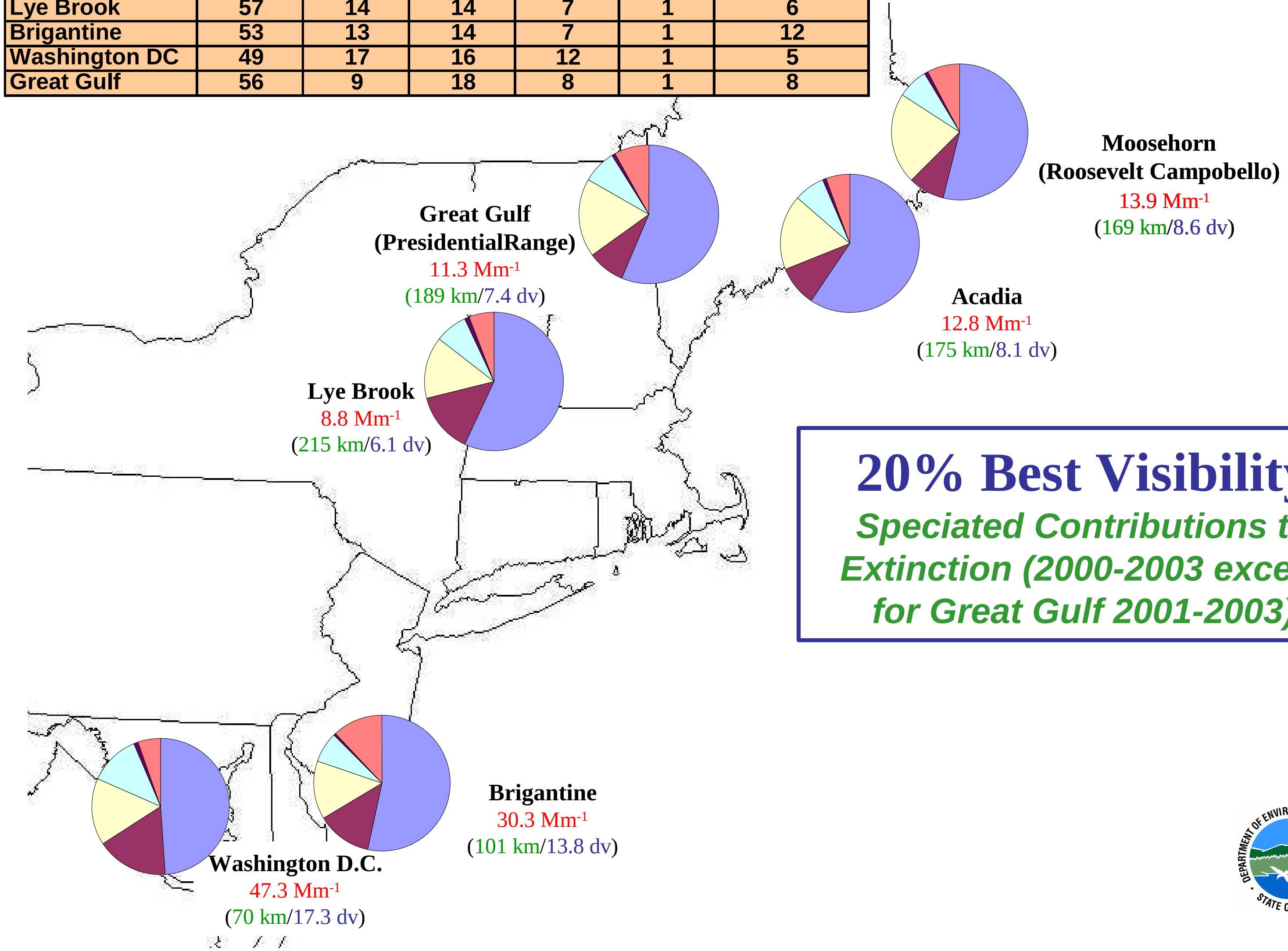
Speciated Contributions to Extinction (2000-2003 except for Great Gulf 2001-2003)

Extinction = 3*f(RH)*sulfate(f) + 1.29*Nitrate(f) + 4*1.4*OC(f) + 10* elemental carbon (f) + 1* soil(f) +0.6 * coarse mass

Figure B-14. 20% Best 2000-2003 Visibility Days Speciated Contributions to Extinction

Site	percent contributon to particle extinction					
	Sulfate	Nitrate	Org C	Elem C	Soil	Coarse Mass
Acadia	60	9	18	7	1	6
Moosehorn	54	9	22	7	1	8
Lye Brook	57	14	14	7	1	6
Brigantine	53	13	14	7	1	12
Washington DC	49	17	16	12	1	5
Great Gulf	56	9	18	8	1	8

Created by Tom Downs,
Maine DEP-BAQ 12/13/2005



20% Best Visibility

Speciated Contributions to Extinction (2000-2003 except for Great Gulf 2001-2003)

Appendix C: Additional Considerations for PM$_{2.5}$ Air Quality Management

APPENDIX C: ADDITIONAL CONSIDERATIONS FOR PM$_{2.5}$ AIR QUALITY MANAGEMENT

C.1. Averaging times and data interpretation

In analyzing the chemical data available for interpreting the air quality event of August 2002, it is important to point out that the use of different averaging times can have a profound effect on our understanding of the progression of any specific episode. Many subtleties of synoptic-scale meteorology and atmospheric chemistry are "aliased out" of data sets with temporal resolution greater than 3-6 hours. These effects are demonstrated in Figure C-1 which show fine aerosol TEOM data from New Haven for the "episode" period August 10-16, 2002. In these figures, the hourly TEOM values have been aggregated into 3-, 6- and 24-hour mean values. Average concentrations are inversely proportional to the length of the averaging period and the ratio of peak hourly concentration within a daily average ranges from about 1.5 to 1.75 for this episode.

Figure C-1. Effects of averaging times (or temporal resolution) on time series information

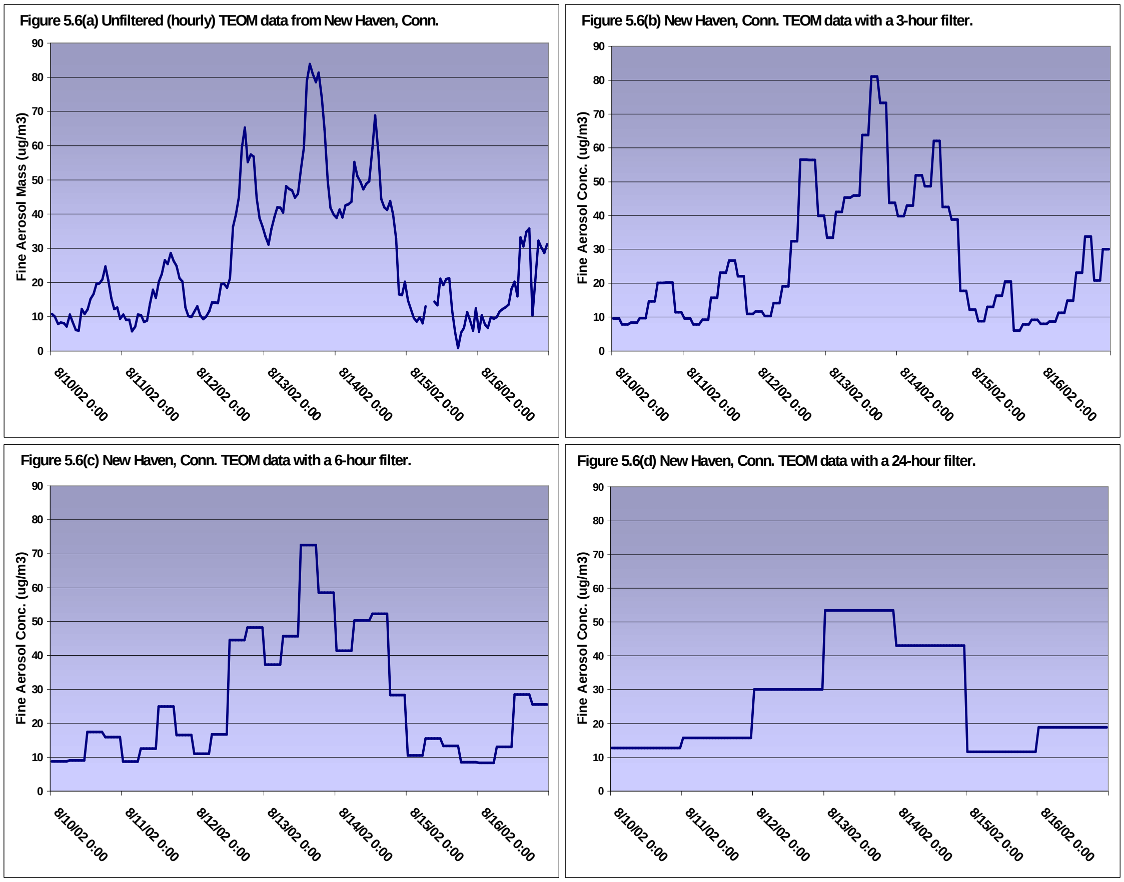


Figure 5.6(a) Unfiltered (hourly) TEOM data from New Haven, Conn.

Figure 5.6(b) New Haven, Conn. TEOM data with a 3-hour filter.

Figure 5.6(c) New Haven, Conn. TEOM data with a 6-hour filter.

Figure 5.6(d) New Haven, Conn. TEOM data with a 24-hour filter.

C.2. Rural versus urban $PM_{2.5}$ mass

Comparison of $PM_{2.5}$ concentrations from rural areas with those from urban/suburban areas can add significantly to our understanding of the impact on air quality of both urban sources and of medium to long-range fine aerosol transport. To assist with this approach, data from 10 pairs of rural and urban/suburban FRM sites throughout the MANE-VU region were selected and analyzed.

Table C-1 shows basic site description information including the approximate, straight-line distance between the site pairs.

Due to the difficulty in finding a significant number of urban-rural site pairs that operated on the same sampling schedule, sites with a mixture of schedules were used to insure samples representative of the entire MANE-VU region. As a result, three of the 20 sites employed an everyday schedule while two sites sampled every sixth day (the remainder sampled every third day). Data from the three everyday sites were edited so as to include data from the 1-in-3 schedule only. In all, a total of 1098 data points were possible from the 10 site pairs for 2002. Of the 1098 possible point-pairs, 951 (87%) were valid and were used in this analysis.

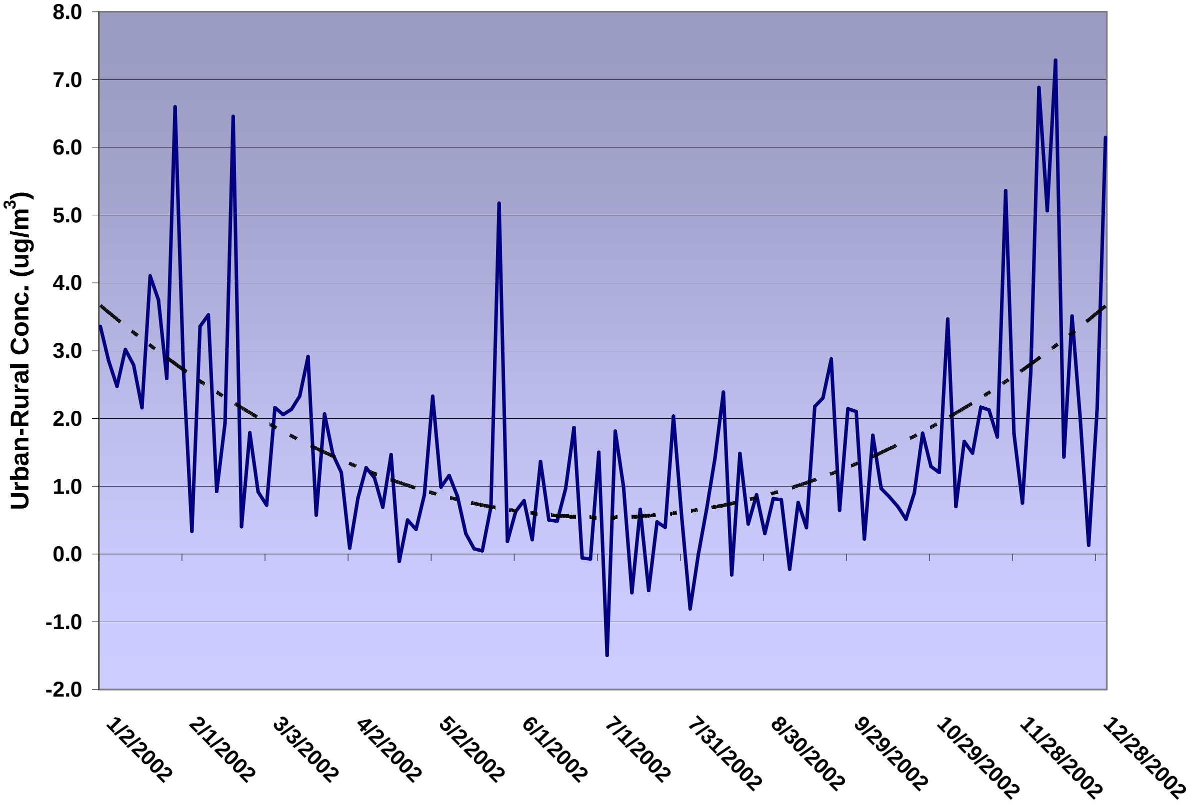
Table C-1. MANE-VU urban-rural site pair information

State	Site No	City	Land use	Location type	Longitude	Latitude	Inter-site Distance (mi)
DE	100051002		Agricultural	Rural	-75.55560	38.98470	
DE	100010002	Seaford	Residential	Suburban	-75.61310	38.64440	24.0
MA	250154002	Ware	Forest	Rural	-72.33472	42.29833	
MA	250130016	Springfield	Commercial	Urban & Center City	-72.59140	42.10890	17.6
MD	240030014		Agricultural	Rural	-76.65310	38.90250	
MD	245100049	Baltimore	Residential	Urban & Center City	-76.63750	39.26170	25.2
ME	230052003	Cape Elizabeth	Residential	Rural	-70.20778	43.56083	
ME	230010011	Lewiston	Commercial	Urban & Center City	-70.21500	44.08940	37.0
NJ	340218001		Agricultural	Rural	-74.85470	40.31500	
NJ	340210008	Trenton	Residential	Urban & Center City	-74.76360	40.22220	7.7
NY	360010012	Albany	Agricultural	Rural	-73.75690	42.68070	
NY	360930003	Schenectady	Residential	Suburban	-73.94020	42.79960	11.7
NY	361030001	Babylon	Commercial	Rural	-73.42030	40.74580	
NY	360590013	Bethpage	Residential	Suburban	-73.49060	40.76080	3.3
NY	360130011	Westfield	Agricultural	Rural	-79.60250	42.29080	
PA	420490003	Erie	Commercial	Suburban	-80.03860	42.14180	22.2
PA	420030093		Residential	Rural	-80.02080	40.60720	
PA	420030021	Pittsburgh	Residential	Suburban	-79.94140	40.41360	14.0
PA	420290100		Commercial	Rural	-75.76860	39.83440	
DE	100031012	Newark	Residential	Suburban	-75.76170	39.69190	10.0

As expected, urban/suburban areas, with their rich supply of emission sources, almost always reported higher concentrations than their nearby sister sites in rural areas. Of the 951 valid data pairs, 660 showed higher urban/suburban levels while 291 cases showed higher rural levels.

One interesting aspect of the 2002 urban-rural data concerns the pattern in seasonal differences between such site pairs. Figure C-2 shows the difference (urban-rural) between the 10 site pairs as a time series.

Figure C-2. Difference in FRM data between 10 urban-rural site pairs for 2002



Although some rural-to-urban seasonal differences are to be expected, the variation in the magnitude of this difference is surprising. In the warm/hot months, the mean rural/urban difference amounts to no more than ~0.7 μg/m^3 (based on a best-fit 2nd order polynomial curve), which is a relatively small differential. However, during the cool/cold months that difference climbs to almost 4 μg/m^3, demonstrating a total annual seasonal variation of at least 3 μg/m^3. Because the mean annual concentration of all sites is 12.6 μg/m^3, an annual variation of 3 μg/m^3 becomes significant.

One explanation for the observed seasonal variation concerns the temporal distribution of local and transported emissions. In the summertime, MANE-VU sites repeatedly experience sulfate events due to transport from regions to the south and west. During such events, rural and urban sites throughout MANE-VU record high (i.e., >15 μg/m^3) daily average $PM_{2.5}$ concentrations. During summer stagnation events, atmospheric ventilation is poor and local emissions are added to the transported burden with the result that concentrations throughout the region (rural and urban) are relatively uniform. There are enough of these events to drive the urban-rural difference down to less than 1 µg/m^3 during warm/hot months.

During the wintertime, strong local inversions frequently trap local emissions during the overnight and early morning periods, resulting in elevated urban concentrations. Rural areas experience those same inversions but have relatively fewer local sources so that wintertime concentrations in rural locations tend to be lower than those in nearby urban areas. Medium and long-range fine aerosol transport events do occur during the winter but at a much reduced rate compared to summertime. So, it is the interplay between local and distant sources as well as meteorological conditions that drive the observed seasonal urban-rural difference in FRM concentrations.

C.3. Seasonal relationship between $PM_{2.5}$ and NO_X

Because nitrogen oxides (NO_X) can be a good indicator of regional as well as local emissions, NO_X data for the MANE-VU region was downloaded from USEPA's AQS. Ultimately, data from six widely separated MANE-VU NO_X sites were selected (one site each in CT, DC, MA, NH, PA and VT). Sites were selected both for high data capture rates and geographic location. The NO_X data were then aggregated into regional averages on a daily basis and compared to $PM_{2.5}$ FRM data from 34 "everyday" sampling sites (which were also averaged on a regional basis).

During 2002, there were virtually no periods when regional mean $PM_{2.5}$ concentrations rose above 20 µg/m^3 and were not accompanied by rising (or already high) NO_X concentrations. However, as seen in Figure C-3, NO_X concentrations vary widely on an annual basis and tend to occur out-of-sync with fine particle concentrations.

Although the min/max extremes of these two pollutants are offset in time, they are highly correlated during some parts of the year. For example, Figure C-4 shows the regional $PM_{2.5}$ and NO_X data for the coldest (Jan., Feb., Nov., and Dec.) and hottest (May, June, July and Aug.) seasons of 2002. Wintertime NO_X and $PM_{2.5}$ concentrations are rather well correlated (r^2=0.67) while summertime concentrations are not at all linked. This dichotomy can be explained by several coincident effects including: 1) reduced UV radiation during cold months (which prevents photolysis of NO_2 to O_3); 2) the increase in space heating requirements from stationary sources (which preferentially increases morning NO_X emissions; increased NO_X emissions due to "cold-start" mobile source engines and 3) decreased mixing height depths due to reduced solar input (which allows morning concentrations to build quickly). Note that the Spring/Fall $PM_{2.5}$ vs. NO_X correlation (not shown) lies about mid-way between the winter/summer values shown in Figure C-4.

Figure C-3. Regional PM$_{2.5}$ and NO$_X$ in 2002

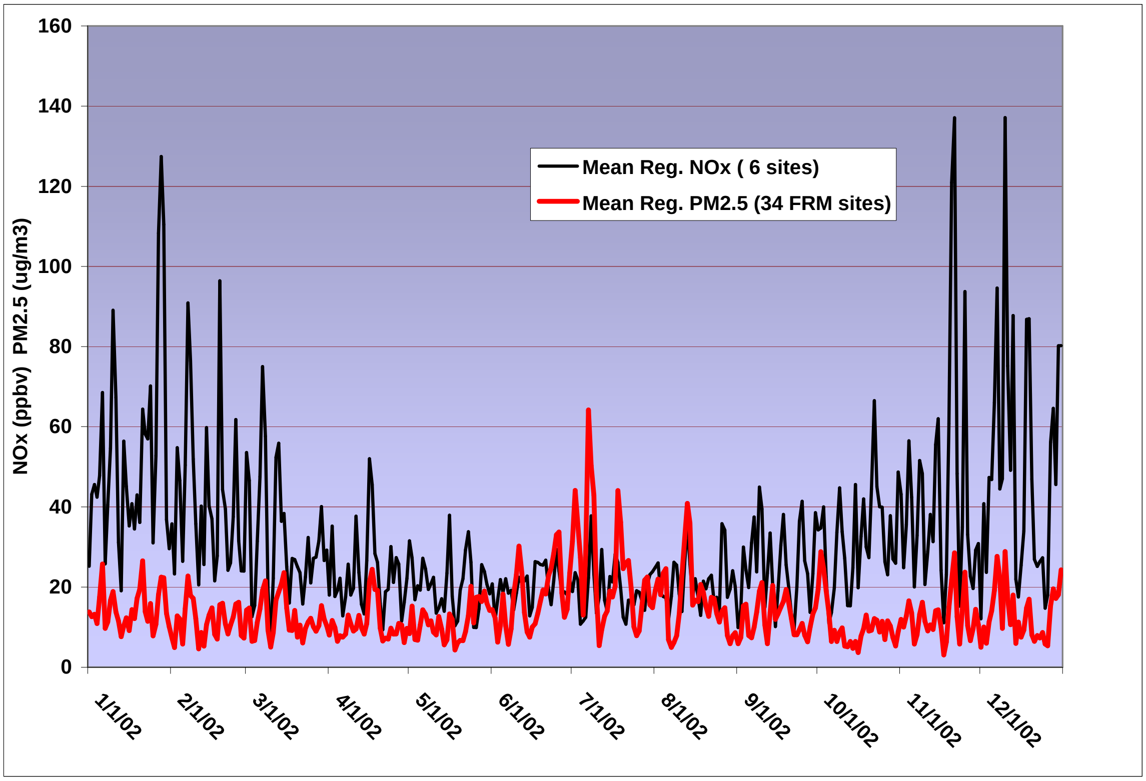
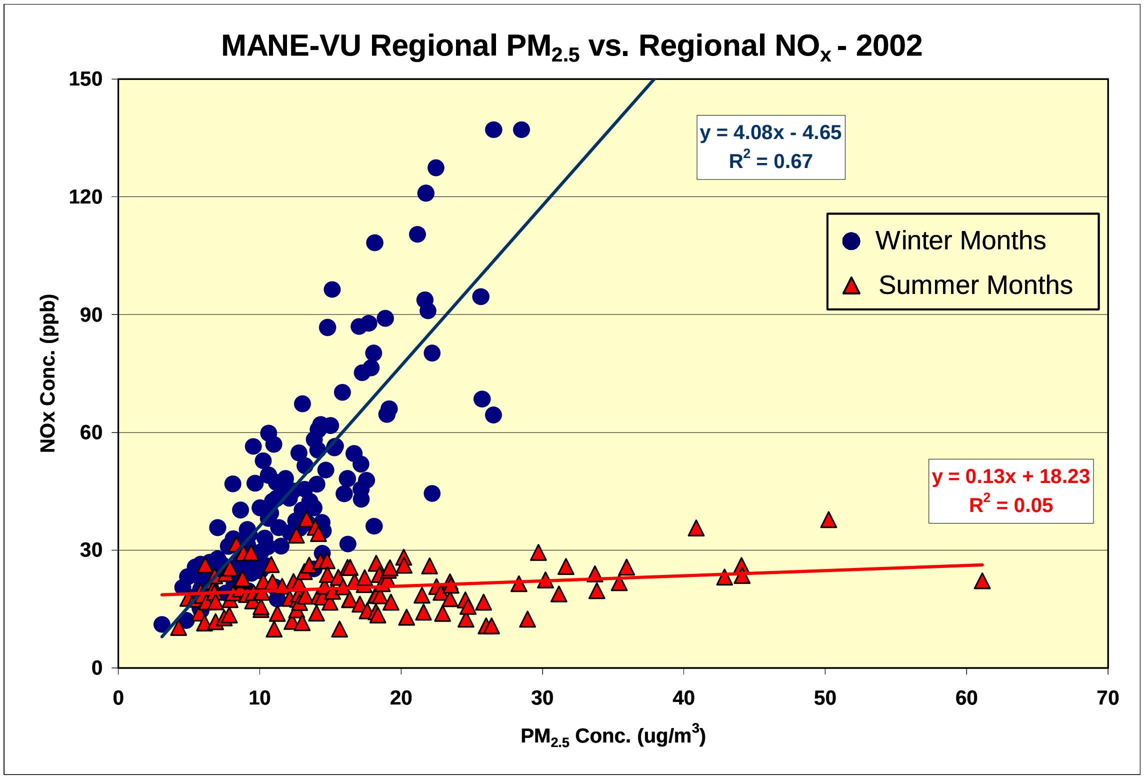


Figure C-4. PM$_{2.5}$ vs. NO$_X$ correlation by season



Conceptual Model of $PM_{2.5}$ Concentrations in Maryland

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Abstract

Concentrations of $PM_{2.5}$ in the State of Maryland, while highest at urban monitors, are remarkably homogeneous across the state – particularly during the summer months. Maximum concentrations occur in the summer although urban monitors also observe a secondary, winter season peak. At all locations, annual mean concentrations are in excess of median concentrations due to a small number (~5-10%) of extremely polluted days. This subset of "dirty" days occurs primarily during the warm season (May-September) and is associated with light winds, strong low level inversions, regional scale transport of pollutants from west to east – similar to high O_3 episodes – and enhanced concentrations of sulfate particles. A similar transport pattern occurs in winter season cases also there is a higher frequency of stagnation in these cases as well as stronger near-surface inversions. Winter episodes thus feature a stronger influence of local emissions – especially carbon and nitrogen particles. Recently implemented regional control strategies, to the extent that they reduce sulfur and nitrogen emissions, may be effective at reducing $PM_{2.5}$ concentrations on the worst days although there remains significant local emission inputs to $PM_{2.5}$ in Maryland.

Executive Summary

1. This report summarizes observations of fine particulate matter with an aerodynamic radius of ≤ 2.5 µm, also known as $PM_{2.5}$, in the State of Maryland during the period 2000-2005.
2. Average $PM_{2.5}$ concentrations for this period at monitors across Maryland range from 12-17 μgm^{-3} with the highest concentrations observed at urban scale sites.
3. Although urban monitors observe the highest concentrations, all Maryland $PM_{2.5}$ monitors are strongly correlated and the correlation between monitors is highest during the summer season. This indicates that $PM_{2.5}$ is ubiquitous in Maryland, is not an overwhelmingly urban pollutant, and that all locations share in a common, regional scale "load" of $PM_{2.5}$.
4. Although there is no fool-proof method to quantify the regional scale "load" of $PM_{2.5}$, comparisons of urban, suburban and remote rural monitors suggest that the regional component of $PM_{2.5}$ accounts for roughly 60-75% of the total observed $PM_{2.5}$. This fraction increases to 80-90% during the summer season.
5. $PM_{2.5}$ concentrations peak during the summer season (June-August) in Maryland although urban scale sites also have a secondary maximum during the winter (December-February) months. The summer maximum are driven primarily by increases in the amount of sulfate while winter season peaks are driven more by increases in nitrogen and carbon compounds.
6. $PM_{2.5}$ concentrations vary by the day of the week, on the order of 2-3 μgm^{-3}, with highest concentrations occurring near the end of the work week and lowest concentrations on Sunday. This reflects day of week differences in motor vehicle and industrial emissions. While average concentrations do not vary significantly by the day of the week, the frequency of high $PM_{2.5}$ concentrations days (90th percentile) is much greater during the work week.
7. $PM_{2.5}$ concentrations have a daily (diurnal) cycle with highest concentrations during the morning and afternoon rush hours, when emissions are highest and vertical mixing is weakest, and lowest concentrations during the well-mixed (diluted) afternoon hours.
8. The diurnal cycle is markedly different for the most severe (90th percentile) cases. In those cases, the mid-day dilution effects are less evident so that concentrations remain nearly unchanged through the daylight hours. This effect is more pronounced in the summer months and suggests that the air aloft, which mixes downward in the afternoon, is heavily laden with transported $PM_{2.5}$.
9. The highest $PM_{2.5}$ cases are characterized overwhelming by westerly transport of air parcels although, in winter, there is a secondary maximum of cases where re-circulation, or stagnation, occurs. Observation at rural monitors west of Maryland show that, on the worst $PM_{2.5}$ days, this air mass is primarily made up of sulfate particles.

Introduction

This report summarizes observations of fine particulate matter with an aerodynamic radius of ≤ 2.5 µm, also known as $PM_{2.5}$, in the State of Maryland. $PM_{2.5}$ is regulated as a criteria pollutant by the US EPA with revised health and safety standards promulgated in 2006. The purpose of this report is to place the observations of $PM_{2.5}$ in the context of climate and weather conditions in order to aid policy makers in determining the best implementation plan to reach attainment with the $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS).

Data

$PM_{2.5}$ has been measured routinely by a statewide network of monitors operated by the Maryland Department of the Environment (MDE) beginning in 1999. Due to data collection and quality issues associated with bringing a number of new monitors online during 1999, this study looks only at data collected during the period 2000-2005.

The majority of the data discussed in this report are from the network of Federal Reference Monitors (FRM) deployed across Maryland. The FRM $PM_{2.5}$ monitors are gravimetric, or passive, monitors that measure the integrated amount of $PM_{2.5}$ collected during a 24-hour period. Most monitors in Maryland collect data every third day and a subset collect daily. Statistical issues related to the uneven collection schedule were discussed in a previous report to MDE-ARMA. This report is included as ***Appendix A***. For the purposes of this report, daily monitor data are used whenever possible.

In addition to FRM monitors, MDE also operates continuous monitors that use a tapered element oscillating microbalance (TEOM) to measure $PM_{2.5}$ on short time scales – typically a one hour average. Continuous monitors are not currently designated as a FRM but, due to their good time resolution, provide useful information relevant to this study. Observations from the Old Town TEOM in Baltimore City are used at various places in this report.

Finally, because fine particles are made up of a mix of pollutants, MDE operates speciation monitors as part of the EPA Speciated Trends Network (STN). These monitors measure the individual components of $PM_{2.5}$, particularly sulfates, nitrates and carbon species. Observations from the Essex monitor, northeast of Baltimore City, are used in this report. In addition, a consortium of governmental organizations operates a network of speciation monitors as part of the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. Monitors located in rural WV and Washington DC are germane to this report and data from these monitors are also used.

The location of the Maryland $PM_{2.5}$ network is shown in *Figure 1*. The Maryland monitor network includes sites that can be characterized as urban, suburban and rural. Some statistical measures within this report will analyze similarities and differences between observations at urban, suburban and rural sites and ***Appendix B*** provides a list characterizing the location of the various Maryland $PM_{2.5}$ monitors. A related document (Power Point) provides location information and aerial views of many of the Maryland monitors (***Appendix C***).

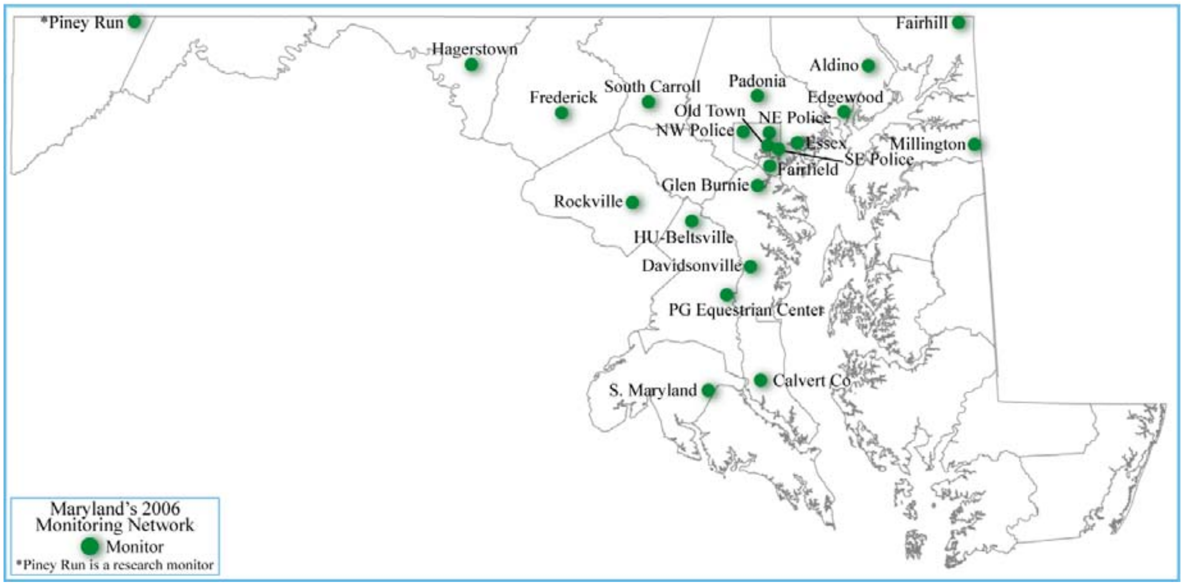


Figure 1. Maryland $PM_{2.5}$ FRM monitor locations.

In addition to the Maryland monitors, data from regional scale FRM $PM_{2.5}$ monitors are also referred to in this report. These monitors, located in PA, WV and VA, are designated as regional scale because they are typically located at high elevation in non-urban locations. The high elevation and non-urban locations of these monitors places them at a distance from concentrated emissions sources and provides a measure of $PM_{2.5}$ concentrations that are consistent with observations over a larger scale than an urban scale monitor can provide. Details on these monitors are provided in ***Appendix B***.

$PM_{2.5}$ Concentrations in Maryland (2000-2005 Average)

Mean $PM_{2.5}$ concentrations at the Maryland monitors for the period 2000-2005 are given in *Figure 2*. Monitors that re-located during the period, and do not have a complete, uninterrupted set of data, are not included. Average concentrations range from 12-17 μgm^{-3}. These concentrations are similar in magnitude to many eastern U.S. metropolitan areas and straddle the current yearly NAAQS for $PM_{2.5}$ (15.5 μgm^{-3}). As expected, the highest concentrations are found at the urban and near-urban monitors. As noted in ***Appendix A***, most monitors report data on every third day. The exceptions are three Baltimore urban monitors - Old Town, FMC and Essex - that report daily. The lowest concentrations are found in south suburban Maryland (Rockville and Davidsonville).

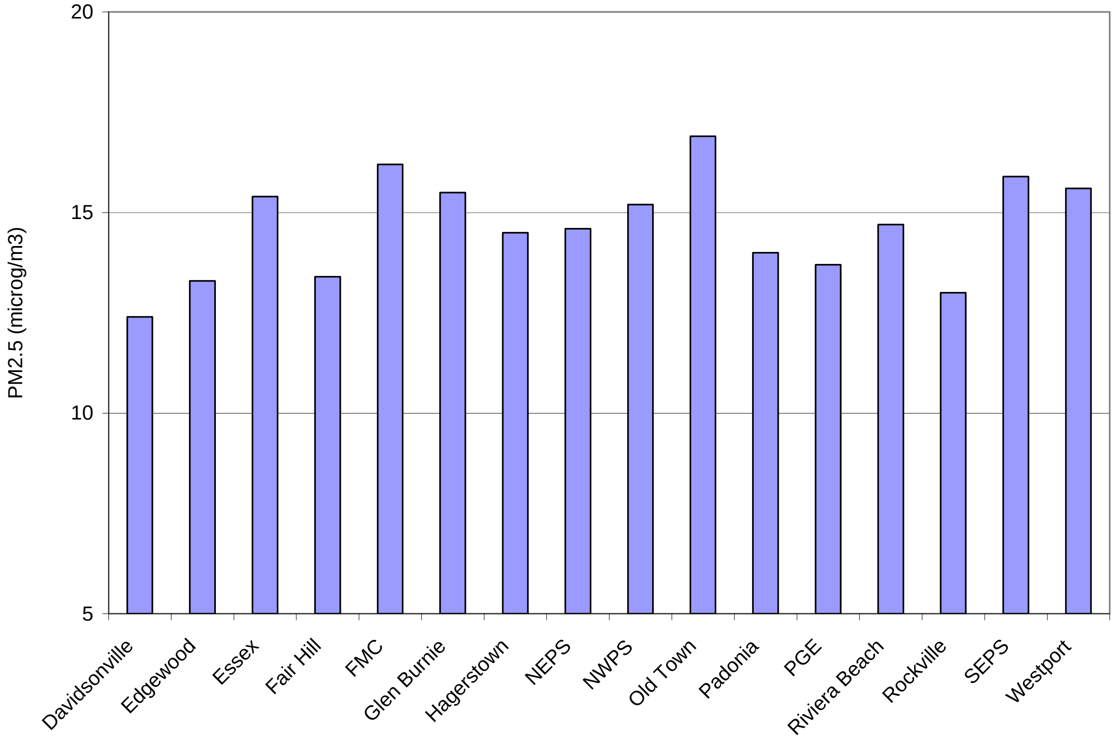


Figure 2. Mean $PM_{2.5}$ concentrations for the period 2000-2005 for Maryland FRM monitors. Certain monitors that are currently operational were re-located during this period and are not represented in this figure.

The urban sites, as defined in ***Appendix B***, have an average concentration of 15.7 μgm^{-3}, or slightly above the NAAQS. The suburban sites observed lower concentrations (13.6 μgm^{-3}). Hagerstown, a mid-size city in western Maryland, reports an average of 14.5 μgm^{-3} and the regional scale sites (not shown) report an average of 12.4 μgm^{-3}.

The most outstanding feature of the average $PM_{2.5}$ concentration in Maryland is the high degree of correlation between monitors across the state. *Figure 3* shows the correlation between all Maryland monitors and concentrations measured at the site with the highest average concentrations, Old Town – located near center city Baltimore. Even the far distant Hagerstown monitor shows a correlation coefficient of 0.78, and the remainder of the coefficients varies from 0.83-0.98. As an example, a scatter plot of $PM_{2.5}$ concentrations at Old Town and Fair Hill, Maryland – Fair Hill is located just south of the Pennsylvania border in extreme northeastern Maryland – is shown in *Figure 4*. For concentrations $\leq 25\ \mu gm^{-3}$, the agreement is extremely close but becomes less so at the higher end of the distribution.

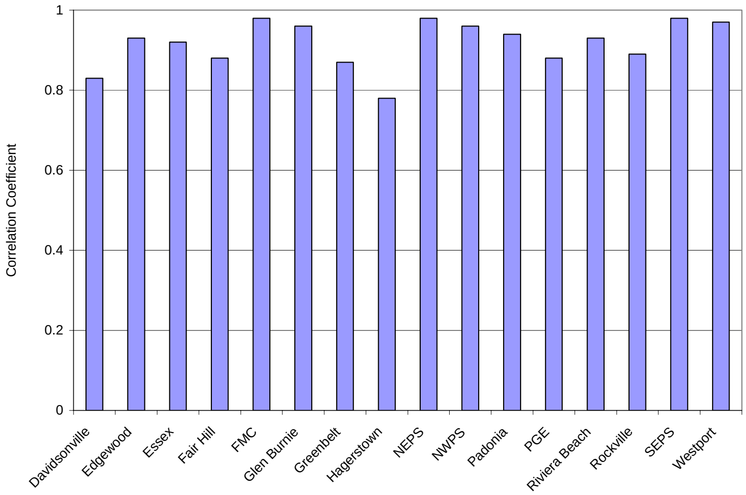


Figure 3. Correlation coefficients between 24-hour average $PM_{2.5}$ concentrations at Old Town, Maryland and the remainder of the Maryland FRM monitors.

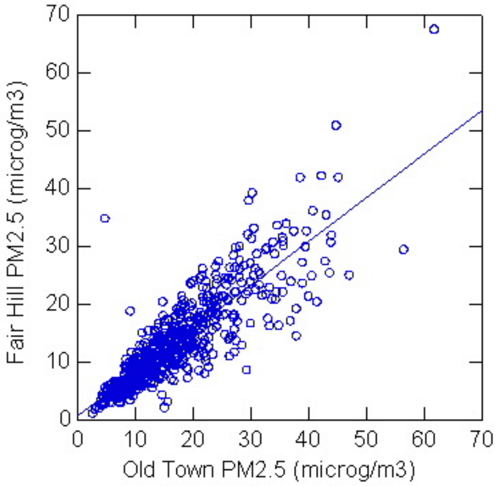
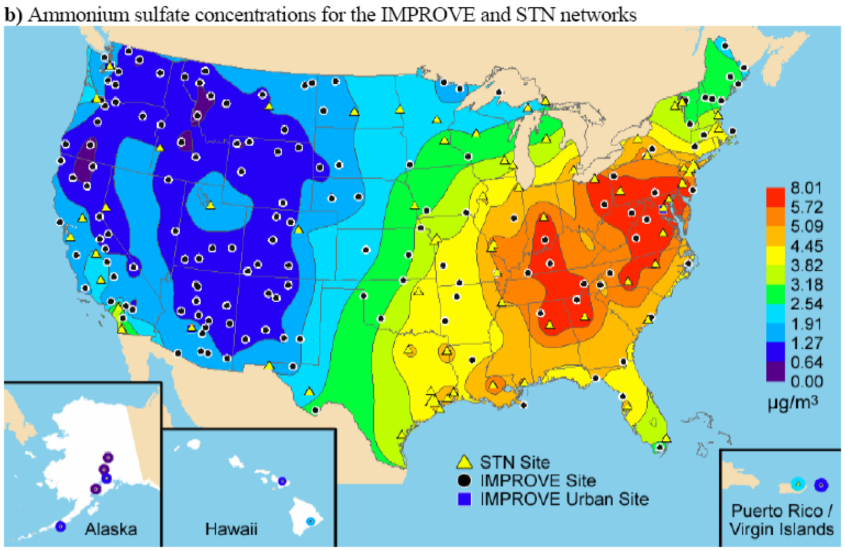


Figure 4. Scatter plot of 24-hour average $PM_{2.5}$ concentrations at Old Town, Maryland and Fair Hill, Maryland for the period 2000-2005. The best linear fit line is given as: $[PM_{2.5}]_{Fair\ Hill} = 0.78 + 0.75*[PM_{2.5}]_{Old\ Town}$.

The high correlation between all monitors suggests that there is some shared, regional scale "load" of $PM_{2.5}$. That is, a common source(s) of $PM_{2.5}$, either through primary emissions or secondary formation, that is ubiquitous and distributed evenly throughout the state. Primary emissions of $PM_{2.5}$, such as motor vehicle exhaust, tend to be short-lived with primarily local impacts and most strongly affect only nearby monitors. Secondary formation processes, such as the conversion of $SO_{2(g)}$ to particulate sulfate, occur on longer time scales and can affect larger areas downstream.

The primary component of $PM_{2.5}$ that accounts for the shared, regional load is sulfate. In *Figure 5*, the distribution of ammonium sulfate across the US is shown. Sulfate concentrations are highest, and similar in magnitude, across most of the eastern US and, as fraction of total $PM_{2.5}$, shown in *Figure 6*, account for approximately half of total $PM_{2.5}$ concentrations. The primary source of sulfates is coal combustion and these sources, typically electrical generation units, are spread throughout the region, not always in association with large cities. The distribution of SO_2 emissions, the precursors of sulfate, in the eastern US during the summer season are shown in *Figure 7*. The process of conversion from SO_2 as it leaves the stacks to sulfate particles occurs over many hours and the lifetime of sulfate is several days. Accordingly, sulfate can be transported long distances and attain homogeneous region-wide concentrations.



b) Ammonium sulfate concentrations for the IMPROVE and STN networks

Figure 5. Ammonium sulfate concentrations measured at $PM_{2.5}$ speciation monitor sites ombining the rural IMPROVE monitors and the more urban scale STN monitors. http://vista.cira.colostate.edu/improve/Publications/Reports/2006/PDF/Chapter2.SpatialTrendsConcentration&Extinction.pdf

d) Ammonium sulfate fractional contribution to reconstructed fine mass for the IMPROVE and STN networks

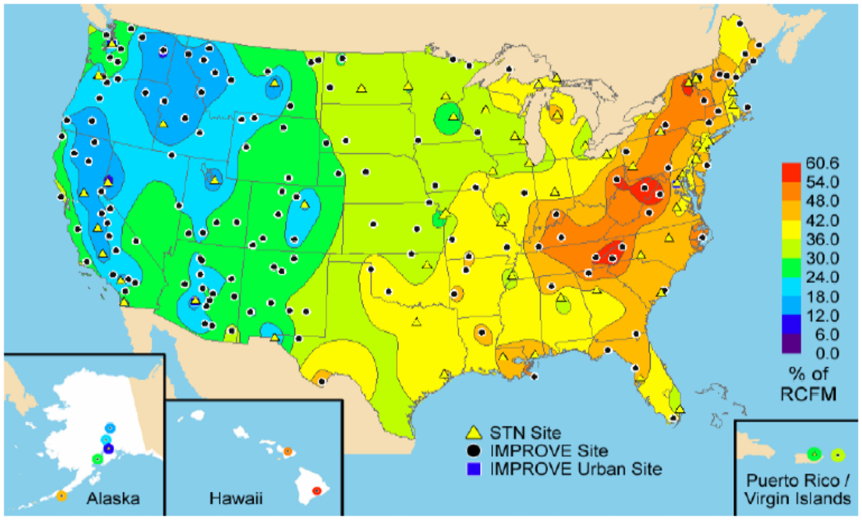


Figure 2.2. Isopleth maps of annual ammonium sulfate concentrations in panels a and b and percent contributions to reconstructed fine mass in panels c and d. Panels a–d include all sites from the IMPROVE network that met the prescribed completeness criteria including the urban sites from 2000–2004. Panels b and d also include all sites from the STN network that met the prescribed completeness criteria.

Figure 6. As in Figure 5 but showing ammonium sulfate concentrations as a fraction of total concentrations as measured at $PM_{2.5}$ speciation monitor networks (IMPROVE and STN).

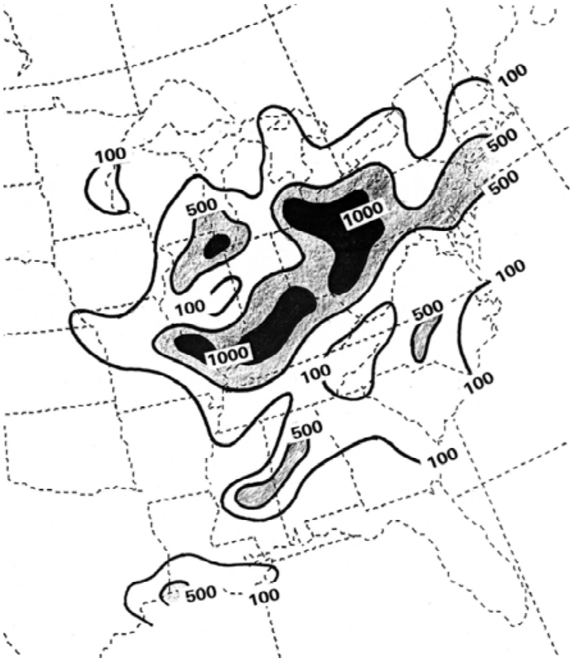


Figure 7. Distribution of SO_2 emissions during the summer over the eastern United States in metric tons per day (After Brueske, 1990). Source: http://www.spc.noaa.gov/publications/corfidi/fig3jpgmed.jpg

One way to quantify the magnitude of regional, or "background", $PM_{2.5}$, relative to local concentrations, is to determine the so-called "urban excess". That is, the amount of $PM_{2.5}$ that the urban environment adds to the regional load. The urban excess is often expressed as a simple paired comparison of remote and urban mean concentrations. An example from a recent EPA trends analysis is shown in *Figure 8*. Several eastern cities, including Baltimore, are shown on the right side of the figure. For this report, we pair concentrations at the remote Keeney Knob site in central WV with several local monitors (*Figure 9*). Compared to Old Town, the remote, regional scale concentrations represent 62% of the urban mean. At the suburban site at Padonia, north of Baltimore, the fraction increases to 75% and is 72% at Hagerstown.

In summary, average $PM_{2.5}$ concentrations in Maryland range from 12-17 μgm^{-3} with highest concentrations found in urban areas. $PM_{2.5}$ concentrations across the state are highly correlated, however, with a "regional scale load" of $PM_{2.5}$ that accounts for roughly 62-75% of the total observed $PM_{2.5}$ in urban areas.

Figure 12. Urban excess for total $PM_{2.5}$ gravimetric mass.

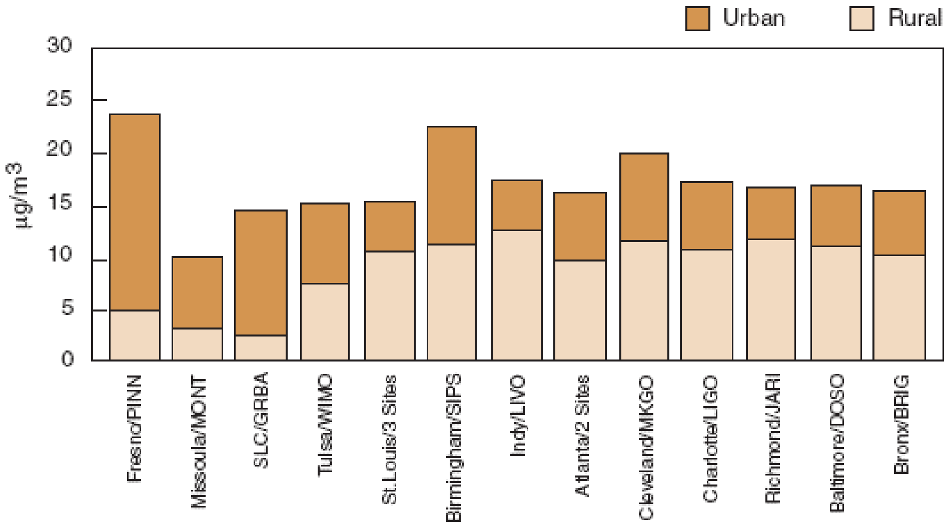


Figure 8. A comparison of urban and rural $PM_{2.5}$ concentrations as a meausure of "urban excess" $PM_{2.5}$. The second from the right column is Baltimore paired to Dolly Sods National Forest in remote WV. This figure and discussion is contained in http://www.epa.gov/air/airtrends/aqtrnd03/pdfs/2_chemspecofpm25.pdf.

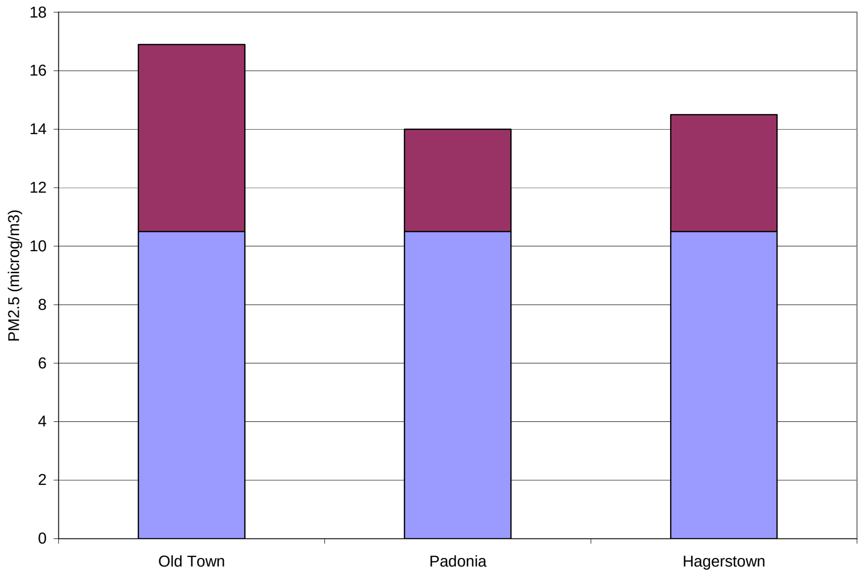


Figure 9. Mean concentrations at the remote, rural site located at Keeney Knob, WV (blue column) superimposed on mean concentrations at selected Maryland monitors. The difference, maroon column, is a rough measure of the "urban excess" or additional $PM_{2.5}$ added by local sources.

$PM_{2.5}$ Concentrations in Maryland (Seasonal Variations)

$PM_{2.5}$ concentrations in Maryland vary from urban to rural locations and also vary seasonally with highest concentrations occurring in the summer (June-August, JJA) months (*Figure 10*). Urban, suburban and central Maryland monitors, as well as more remote, rural sites in the region, all show peaks in the summer months. In addition, the Old Town (urban scale) monitor shows a secondary peak during the winter months (December-February, DJF). This seasonal pattern, and the differences between urban and rural concentrations, is consistent with prior measurements in the eastern US (*Figure 11*). At rural sites, like Shenandoah National Park and Dolly Sods National Forest, WV, the summer season maximum is pronounced with much lower concentrations observed for the remainder of the year. Urban monitors, such as Washington DC (*Figure 11*), and Old Town (*Figure 10*), have an additional, though smaller, winter season peak.

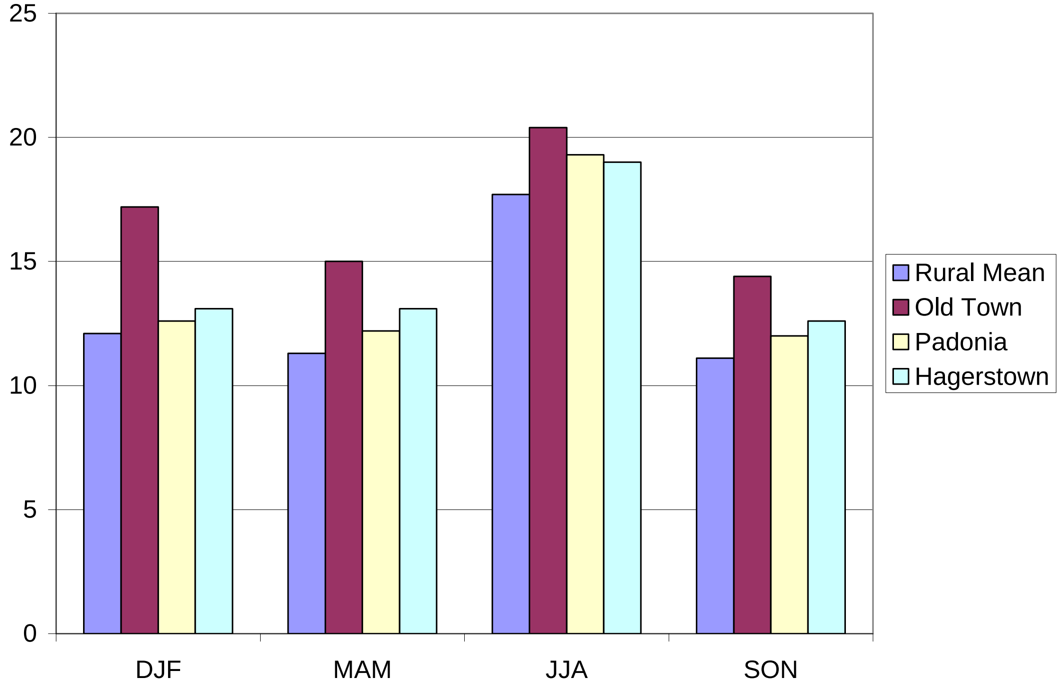


Figure 10. Seasonal average $PM_{2.5}$ concentrations at selected sites in Maryland (Old Town Baltimore, Padonia (suburban Baltimore) and Hagerstown (western MD)) for the period 2000-2005. In addition, seasonal average concentrations for a set of four monitors in VA, PA and WV (“Rural Mean”) are given.

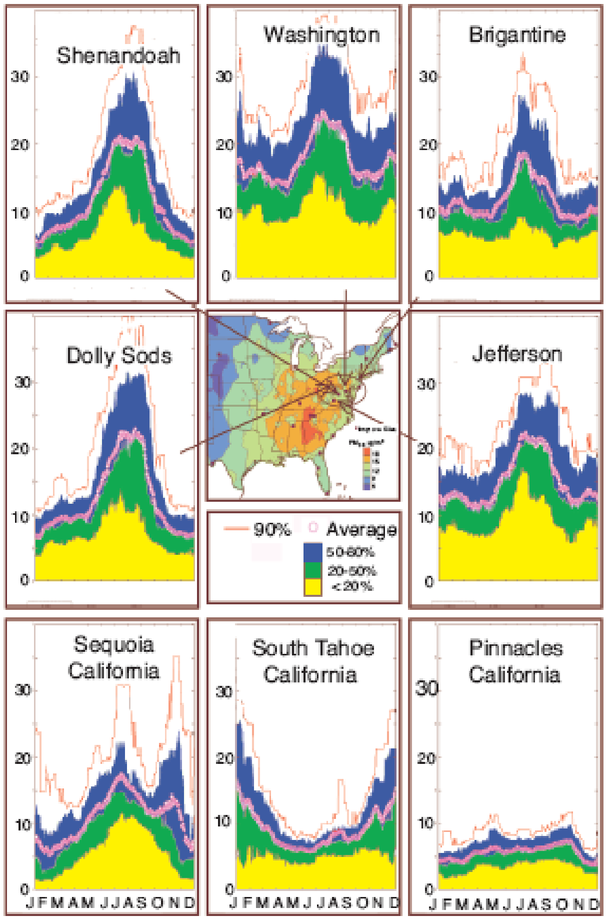


Figure 6.11. Seasonal variations of $PM_{2.5}$ mass concentrations at selected IMPROVE monitoring locations (1992-1999) for the cleanest (20 percent), moderate (20-50 percent), and highest PM (50-80 percent and 90 percent) days. The units of measurement are µg/m³. (R. Husar, pers. comm.).

Figure 11. Seasonal concentrations of $PM_{2.5}$ at selected IMPROVE monitors for the period 1992-1999. Reprinted in:NARSTO (2004) Particulate Matter Assessment for Policy Makers: A NARSTO Assessment. P. McMurry, M. Shepherd, and J. Vickery, eds. Cambridge University Press, Cambridge, England.

At rural monitors, the summer season maximum in $PM_{2.5}$ is primarily driven by increases in ammonium sulfate ($[NH_4]_2SO_4$) concentrations. The efficiency of ammonium sulfate formation is maximized in a moist and highly oxidizing atmosphere, and so is more efficient in the summer months when humidity is high and sunshine plentiful. In *Figure 12*, speciated $PM_{2.5}$ concentrations are given for Dolly Sods Wilderness Area for 2004 (other years show similar patterns). The worst $PM_{2.5}$ days, labeled "W", all occur in the warm season and are all dominated by sulfate. In an urban environment (Washington, DC, *Figure 13*), summer season $PM_{2.5}$ is also dominated by sulfate but the winter season secondary maxima contain a significant fraction of nitrate and organic carbon. The larger concentrations of nitrate and organic carbon are not observed in rural environments due to much lower motor vehicle emissions.

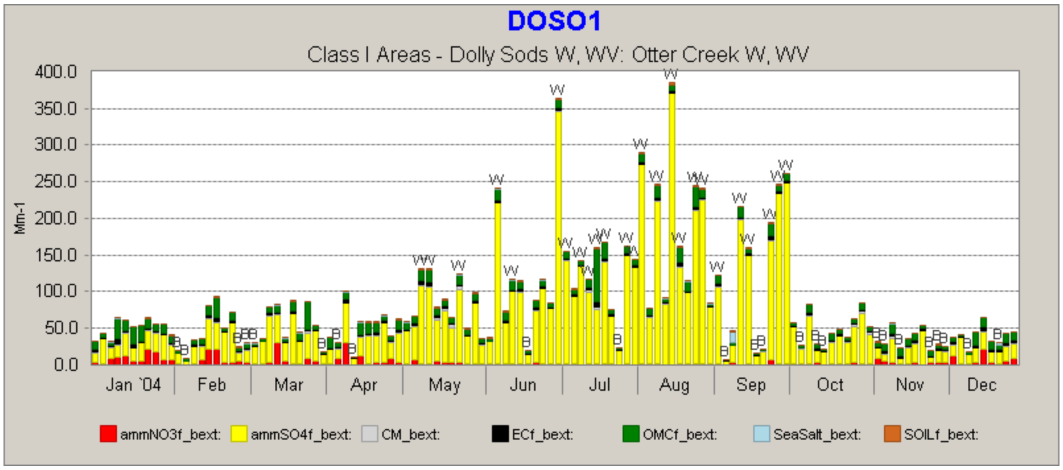


Figure 12. Speciated PM$_{2.5}$ concentrations for Dolly Sods Wilderness Area (WV) for 2004. Ammonium sulfate concentrations are in yellow. Data and plot courtesy of the Interagency Monitoring of Protected Visual Environments Program (IMPROVE) (http://vista.cira.colostate.edu/improve).

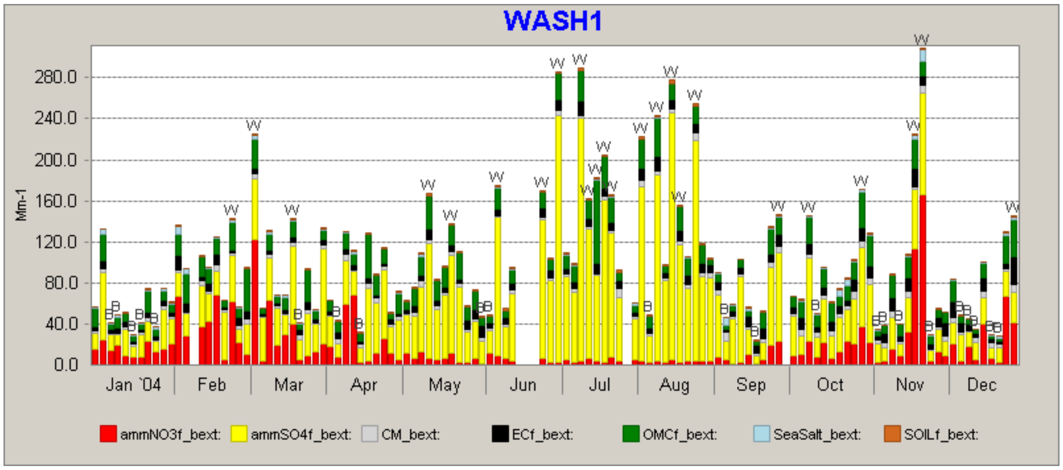


Figure 13. As in Figure 12, but for Washington, DC. Nitrate concentrations are given in red and organic carbon in green.

In Maryland, the effect of the summer season dominance of ammonium sulfate, as a fraction of total PM$_{2.5}$, is to make concentrations more homogeneous across the state. As noted above, sulfur emissions are primarily due to coal combustion from sources spread across the region with the strongest density to the west of Maryland and in the

Ohio River Valley (*Figure 7*). Because of the long lifetime of sulfate particles, they can travel long distances from their sources and become evenly spread across the region. As a result, correlation coefficients between urban, suburban and rural $PM_{2.5}$ in Maryland during the summer months, when sulfate is dominant, becomes greater (*Figure 14*, and compare to *Figure 3*). The "urban excess" of $PM_{2.5}$ in the summer months is correspondingly smaller. Comparing summer observations (*Figure 15*) with full year observations (*Figure 8*) we find that the regional load, which is roughly 62-75% overall, increases to 83-90% in the summer months. Returning to our example of Old Town and the distant exurban site at Fair Hill, we see a much tighter correspondence (compare *Figure 16* with *Figure 4*). The best fit line in summer has a slope of 0.91 compared to 0.75 for all days.

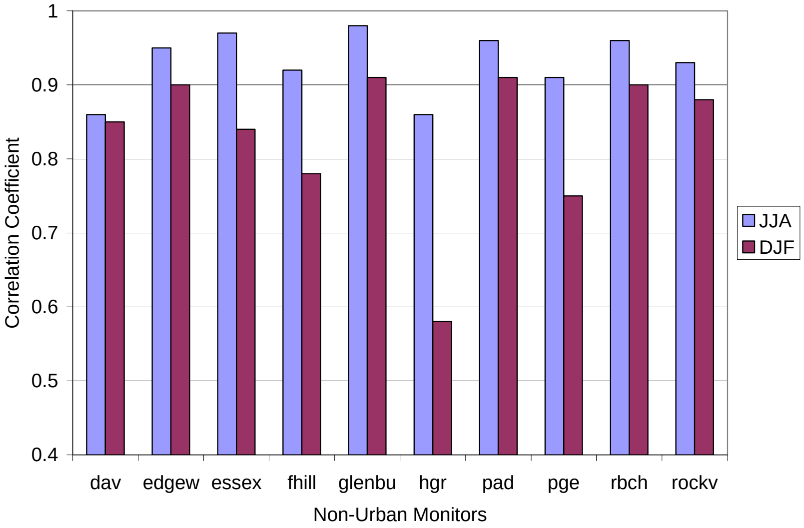


Figure 14. Correlations between $PM_{2.5}$ concentrations measured at Old Town (Baltimore) and non-urban locations in Maryland, as in *Figure 3*, but for only the summer (JJA) and winter (DJF) seasons.

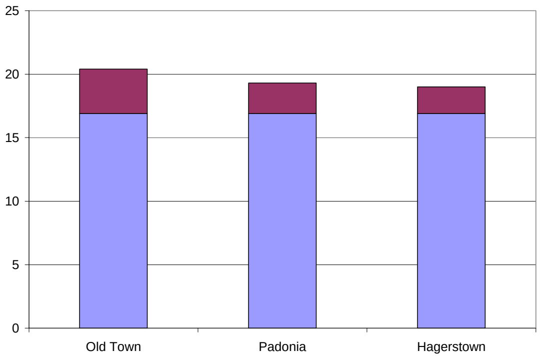


Figure 15. As in *Figure 8* but for only the summer season months (JJA). The ratio of Maryland monitors PM to Keeney Knob, WV increases by 34% for Old Town, 17% for Padonia and 24% for Hagerstown compared to the full year average.

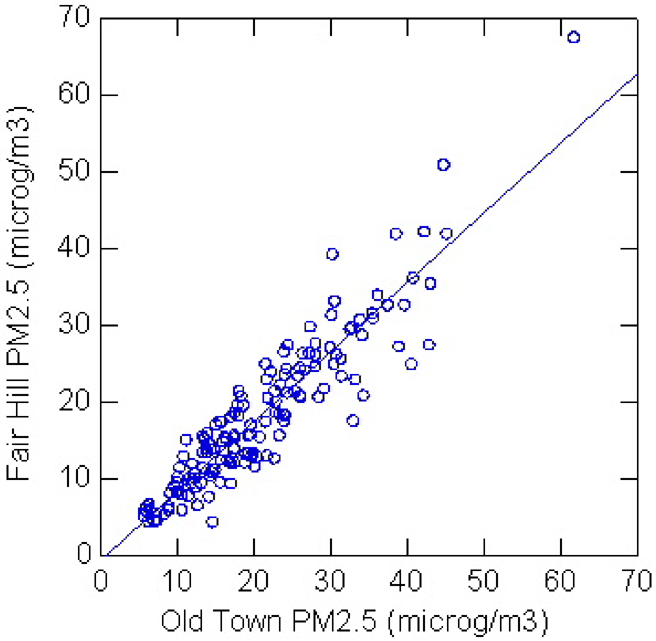


Figure 16. As in *Figure 4* but only for the summer season months (JJA). The best fit line is given by $[PM_{2.5}]_{\text{Fair Hill}} = [PM_{2.5}]_{\text{Old Town}}*0.91 - 0.59$.

In summary, $PM_{2.5}$ concentrations are highest during the summer season across Maryland. This summer maximum is characterized by a large, regional scale sulfate load with rural locations observing 83-90% of the urban scale concentrations. Urban scale monitors also observe a secondary winter season maximum that is not observed at rural locations. The winter season $PM_{2.5}$ is associated with significant concentrations of nitrate and carbon compounds.

$PM_{2.5}$ Concentrations in Maryland (Daily Variations)

$PM_{2.5}$ concentrations in Maryland vary seasonally and also by day of the week. The highest concentrations are typically observed on weekdays and peak in the Thursday-Friday period (*Figure 17*). This day of week difference is consistent with motor vehicle usage. As an example, in *Figure 18*, vehicle miles traveled (VMT) for a six week period in the Detroit area is shown. VMT is calculated as the number of vehicles using the system times the distance they travel. For the time period displayed in *Figure 18*, Sundays are the low points on the graph. On weekdays, the trend toward highway travel later in the week (Thursdays and Fridays) is common in most urban areas. While commuting trips are relatively stable throughout the week, discretionary trips are higher as the weekend approaches. The day of week plot for Maryland (*Figure 17*) suggests that day of week emissions variations can account for ~ 2 μgm^{-3} difference in $PM_{2.5}$ concentrations in Maryland. This difference is consistent across seasons.

Although higher weekday emissions lead to only slightly higher mean concentrations, day of the week differences appear to be important during the most severe $PM_{2.5}$ cases. In *Figure 19*, the day of week breakdown for the highest 90th percentile ($PM_{2.5} > 30.75\ \mu gm^{-3}$) of $PM_{2.5}$ days statewide is given. The weekday average number of days in the 90th percentile is 47 while the weekend days are lower – Saturday is 34 and Sunday 22. This suggests that while weekday emissions differences have a small overall impact on $PM_{2.5}$ concentrations, they can be a significant influence during $PM_{2.5}$-conducive weather conditions.

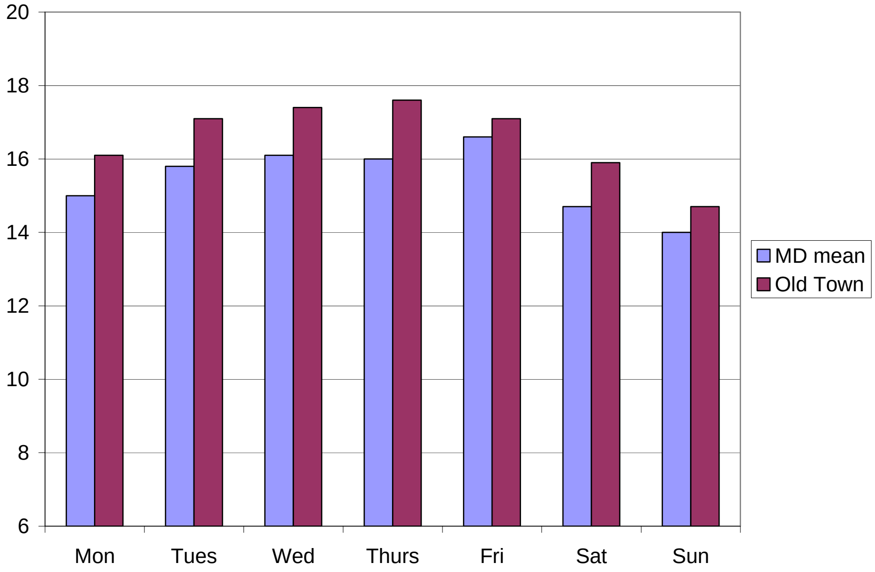


Figure 17. Day of week average $PM_{2.5}$ concentrations for statewide Maryland monitors and for Old Town.

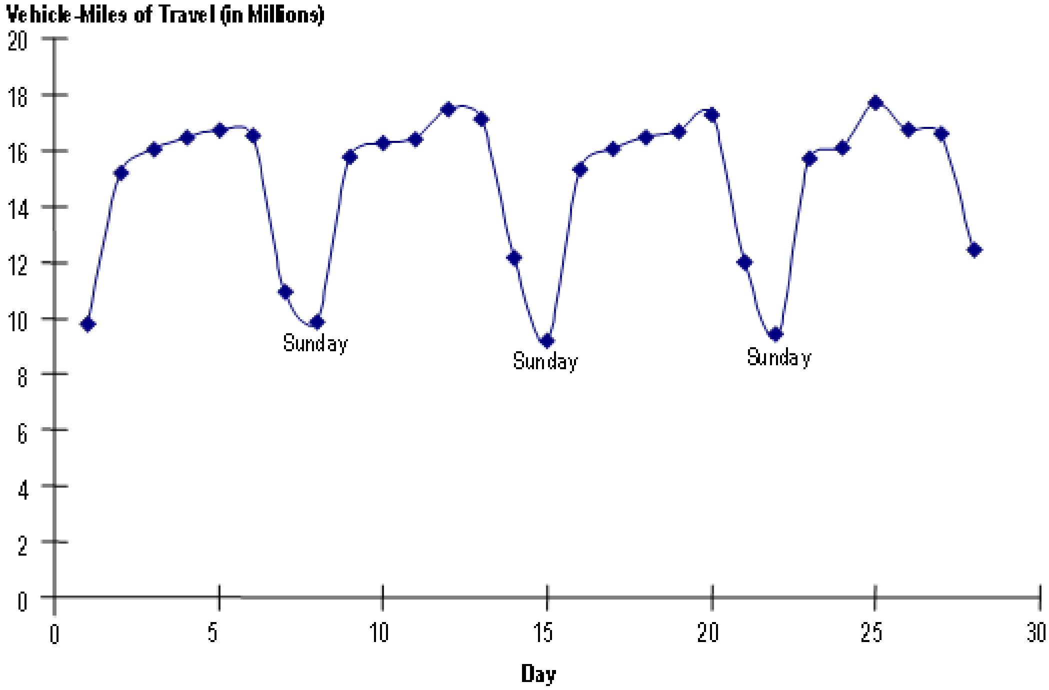


Figure 18. Graph of vehicle-miles of travel (VMT) for the Detroit metropolitan freeways for the period March 11-April 7, 2001. VMT is a common measure of highway usage (http://ops.fhwa.dot.gov/congestion_report/chapter2.htm).

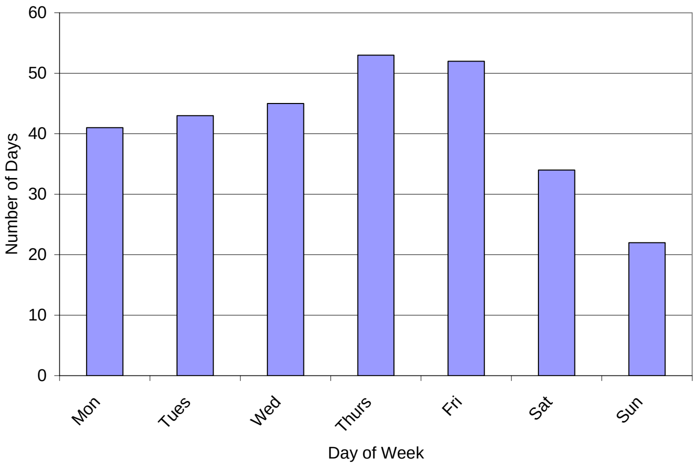


Figure 19. 90th percentile $PM_{2.5}$ days in Maryland by day of week.

$PM_{2.5}$ concentrations in Maryland (Intra-Day Variations)

Daily cycles of $PM_{2.5}$ concentrations in urban areas show the influence of local sources as well as the effects of transported pollutants. The diurnal pattern shows a two peak pattern that reflects emissions and mixing effects (*Figure 20*). The morning rush hour, when motor vehicle emissions are maximized, is shown as a sharp peak in concentrations during the early morning hours. In addition to increasing in strength as more cars are on the road, the emissions are also trapped within a shallow boundary layer. The boundary layer, or mixing depth of the atmosphere, is typically at a minimum during the early morning hours. This follows from surface-atmosphere differences in heat conduction. The ground is a good conductor of heat while the atmosphere is not. As a result, the ground cools quickly overnight while the atmosphere near the ground cools slowly. A surface-based inversion develops as a result of this gradient in temperature, with warm air over cool land surfaces, and traps pollutants within a layer just several hundred meters deep. By mid-day, heating of the earth's surface breaks the inversion and deep vertical mixing follows. This mixing tends to dilute the polluted air parcels with cleaner air from aloft and concentrations fall. This trend to lower $PM_{2.5}$ during the well-mixed afternoon hours is seen in *Figure 20*. Concentrations rise again toward evening through a combination of increased emissions during the afternoon rush hour and decreased mixing as the sun sets and the ground cools. As particles dry deposit to the surface during the nighttime hours, and emissions are low, concentrations fall again to a minimum just before the morning rush hour.

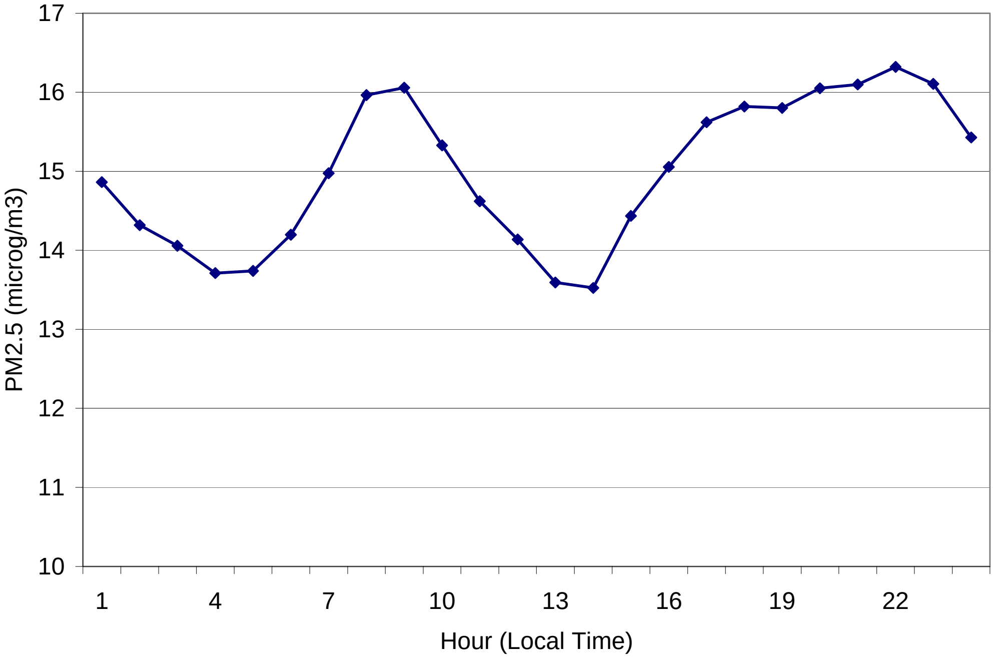


Figure 20. Time series of hourly $PM_{2.5}$ concentrations measured by a continuous monitor at Old Town, Maryland.

The diurnal cycle shown in *Figure 20* is changed subtly in high $PM_{2.5}$ cases. In *Figure 21*, hourly $PM_{2.5}$ concentrations during the 90th percentile cases are shown. The 90th percentile cases show a similar two-peak pattern but with important differences. First, the morning maximum extends until mid-day. This could result from either a stronger low level inversion, trapping pollutants in a narrow layer for more hours, or a dirty residual layer – the air resident above the nighttime boundary layer - mixing downward. The period of lower mid-day $PM_{2.5}$ during the well-mixed afternoon hours in the 90th percentile cases lasts only for 3 hours before concentrations return to near the morning levels while, for the 0-90th percentile cases, lower concentrations last for 8 hours from ~ 1000 to ~ 1800 local time. Another way of looking at the difference is given in *Figure 22*. In *Figure 22*, the ratio of hourly concentrations to the daily maximum is given. For the 0-90th percentile cases, the two rush hours, where motor vehicle emissions dominate, are clearly demarcated. In the high $PM_{2.5}$ cases, concentrations rise through the usually well-mixed afternoon hours.

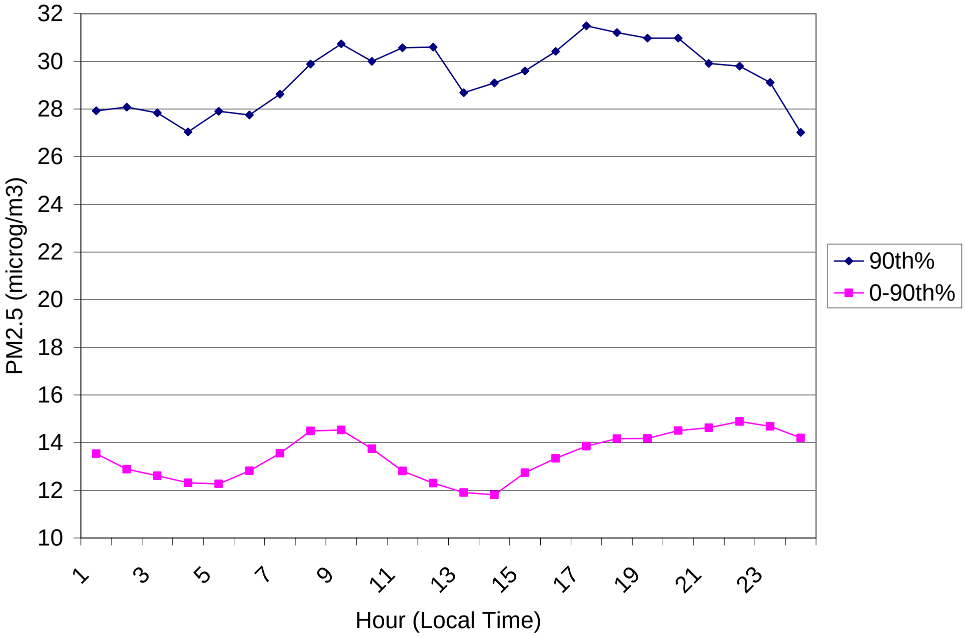


Figure 21. Hourly $PM_{2.5}$ concentrations at Old Town, Maryland for the 90th percentile and above cases (dark blue, diamonds) and the 0-90th percentile cases (magenta, square).

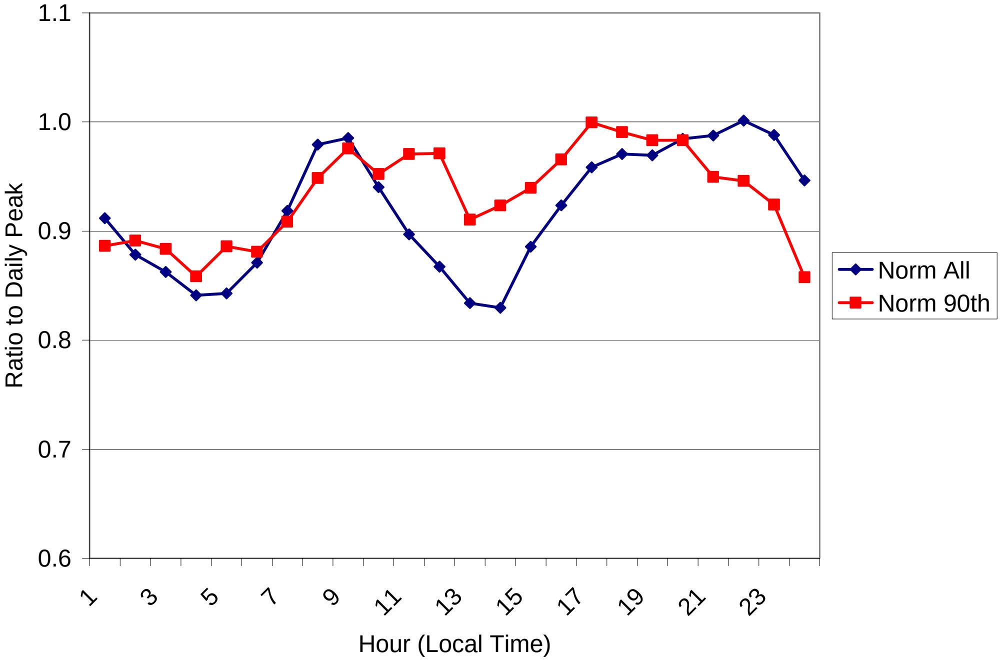


Figure 22. As in *Figure 21*, but with hourly concentrations normalized by ratio to the daily peak concentrations.

Disaggregating the data further provides more insight into the nature of high $PM_{2.5}$ cases in Maryland. In *Figure 23*, the 90th percentile cases are further divided into summer and winter season cases. In summer, the overall concentrations tend to be higher but, more importantly, the diurnal pattern is quite different. In the winter cases, the influence of the low level inversion is stronger. Note that concentrations remain high until mid-day. At that point, mixing reduces $PM_{2.5}$ levels with a modest rise during the evening rush hour. In summer, however, concentrations dip slight immediately after rush hour, but, as mixing proceeds in the afternoon hours, concentrations actually rise. This indicates that significant $PM_{2.5}$ concentrations are present aloft and are mixing downward. If that were not the case, dilution due to deeper mixing would reduce concentrations.

In summary, hourly observations at urban scale Maryland monitors show two daily peaks coincident with the morning and afternoon rush hours. As vertical mixing maximizes during the warmer mid-day hours, concentrations fall to a value consistent with average regional scale concentrations. During high $PM_{2.5}$ days, the daily pattern is significantly different and varies by season. During summer high $PM_{2.5}$ events, regional scale concentrations are very high – that is, there is little “urban excess” – so that $PM_{2.5}$ concentrations fall only slight, if at all, during the well-mixed afternoon hours. In winter, the regional loading is weaker but a stronger morning inversion leads to an extension of the morning rush hour effect.

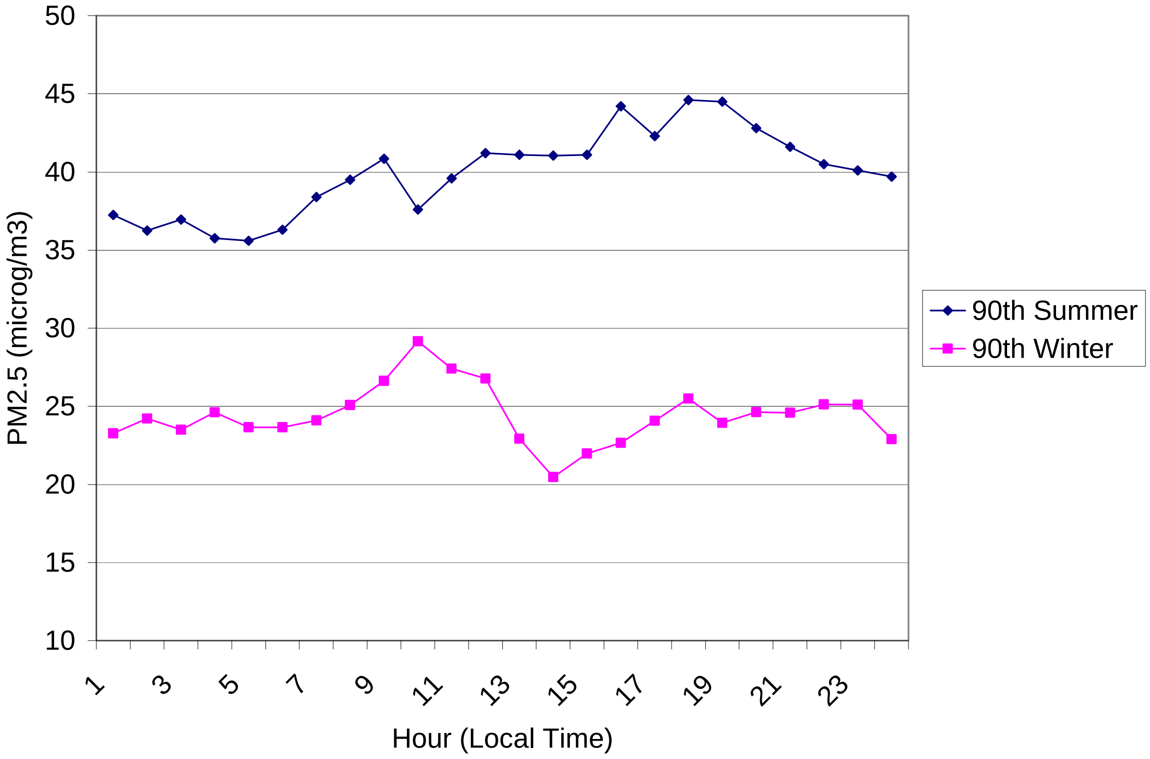


Figure 23. Hourly average PM$_{2.5}$ concentrations at Old Town for the 90th percentile summer and winter cases in Maryland.

$PM_{2.5}$ in Maryland: High $PM_{2.5}$ Cases

As noted above, $PM_{2.5}$ concentrations follow a different daily pattern in the highest (dirtiest) cases and, in particular, during the summer months. Are these cases somehow unique? One of the common attributes of $PM_{2.5}$ at all locations is that the distribution of concentrations is not normal.[1] An example for Old Town is given in *Figure 24*. The skewed nature of the distribution at Old Town is common to all Maryland $PM_{2.5}$ monitors. A distribution with a strong right-tail, as is the case here, results in the mean of the distribution being well in excess of the median. As *Figure 25* shows, this is the case for all Maryland monitors.

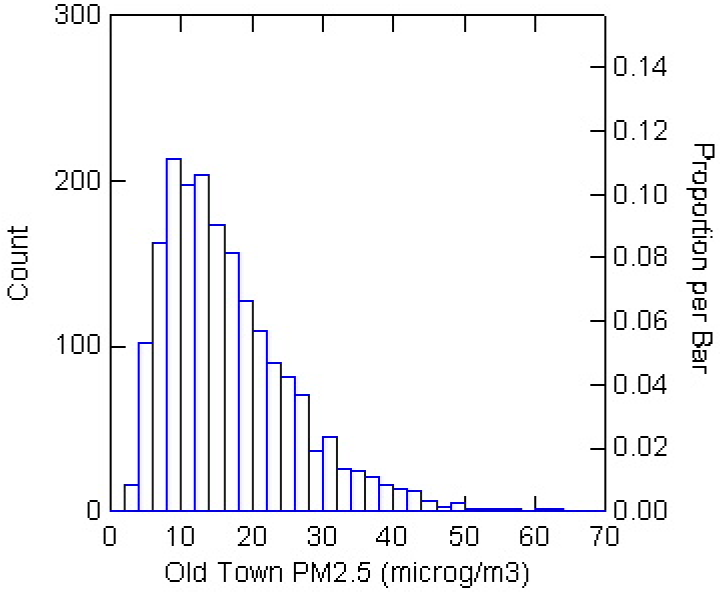


Figure 24. Daily average $PM_{2.5}$ concentrations at Old Town, Maryland.

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[1] The distribution of $PM_{2.5}$ concentrations for Old Town, as well as for all monitors in Maryland, are significantly different from normal with longer than expected right tails (asymmetric). For Old Town, the skewness measure, a measure of the symmetry of a distribution about its mean, is significantly positive and nonzero (skewness = 1.19). A skewness coefficient is considered significant if the absolute value of skewness divided by the standard error of skewness (SQR(6/n)) is greater than 2 – for Old Town, this value is 19.8. In the same manner, Old Town, as well as all Maryland monitors have much larger extremes (tails) than a normal distribution. The measure of the length of the tails of the distribution is kurtosis. For Old Town, the measure of kurtosis is 1.67 with a standard error of kurtosis of 0.11. The absolute value of kurtosis divided by the standard error of kurtosis is 15.2 and as such is significantly greater than 2.

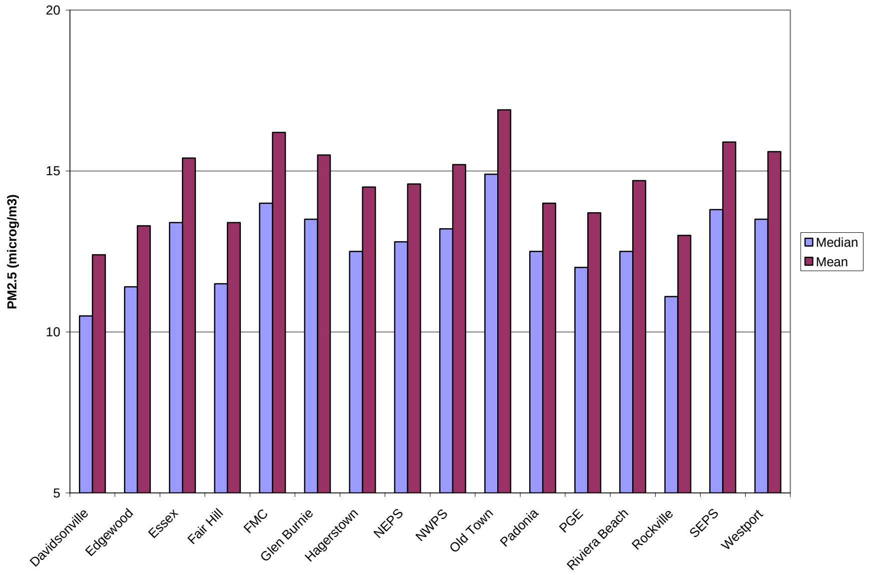


Figure 25. Median and mean $PM_{2.5}$ concentrations for Maryland monitors. The higher mean concentrations indicates that the overall distribution is right-skewed with a larger than normal subset of high $PM_{2.5}$ cases.

The implications of a highly skewed distribution are several. First, it suggests that there may be more than one physical process contributing significantly to the $PM_{2.5}$ distribution. That is, the high $PM_{2.5}$ cases may result from factors that are not as strongly present in the "normal" cases. This is to be expected in the eastern US where there can be large influences on any given day from any of the major constituents of $PM_{2.5}$. Sulfate can dominate, particularly in summer, while nitrogen and carbon, which reflect motor vehicle emissions, tend to dominate in the urban environment. Second, compliance with the NAAQS, based on annual mean concentrations, may depend on the presence or absence of the extreme cases. For example, mean concentrations at Old Town, as well as the other two daily reporting sites in Baltimore, are above the yearly standard of 15 μgm^{-3}. Removing the highest 10th percentile of $PM_{2.5}$ days ($\geq$ 29.4 μgm^{-3}) reduces the yearly mean to 14.3 μgm^{-3}. There are also implications for daily $PM_{2.5}$ forecasting. The 95th percentile of the 2000-2005 $PM_{2.5}$ distribution at Old Town is 35.2 μgm^{-3}. The other daily reporting sites in Maryland, Essex and FMC are similar (32.1 μgm^{-3} and 34.4 μgm^{-3} respectively). These concentrations are close to the newly proposed daily NAAQS for $PM_{2.5}$.

In the following section, we will look in detail at seasonal high $PM_{2.5}$ episodes but we can here make some general observations. In particular, the transport pattern associated with the worst $PM_{2.5}$ days is consistent. In *Figure 26*, back trajectories for Baltimore for the 95th percentile of $PM_{2.5}$ days are shown. The back trajectories estimate the path of air parcels arriving in the Baltimore area. Overall, slow westerly transport is the rule. There are a handful (9) of cases with winds from the east and a slightly larger number of re-circulation cases, but the vast majority of cases involve westerly transport. As noted in *Figure 7*, significant sources of SO_2 emissions are located west of Baltimore along with major large industrial centers.

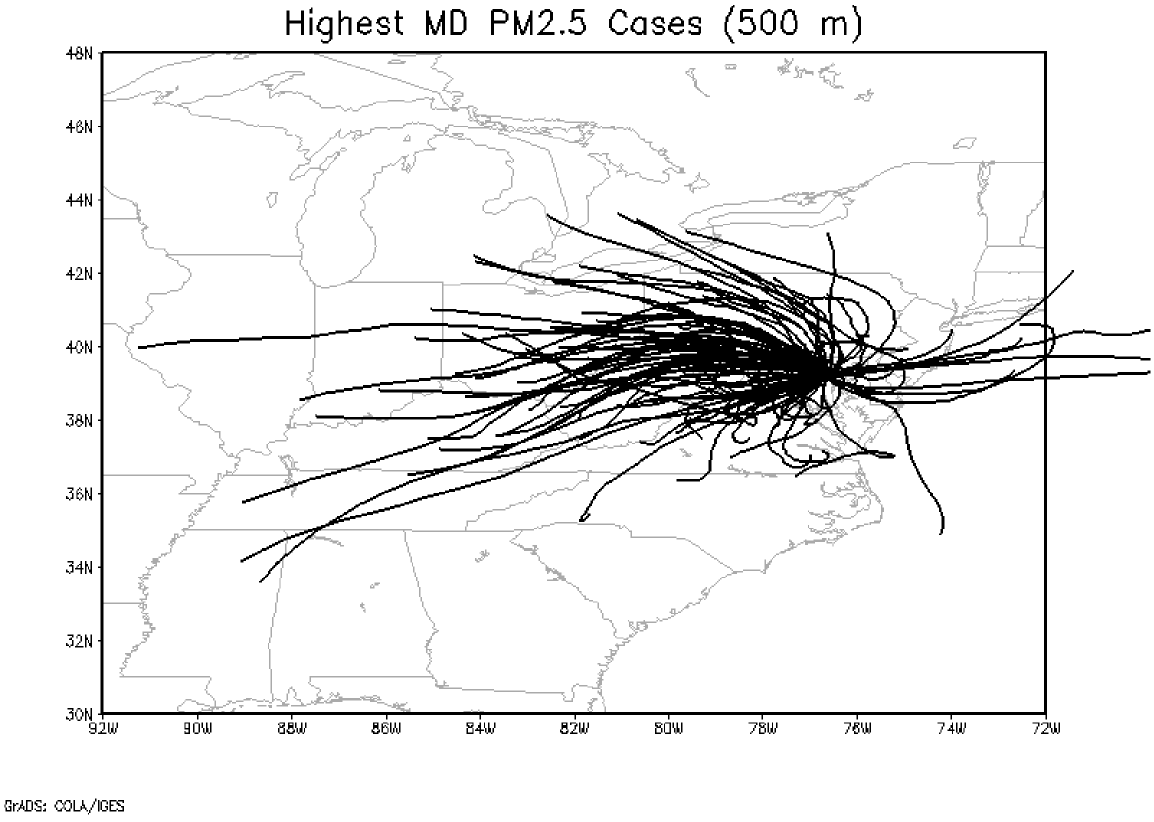
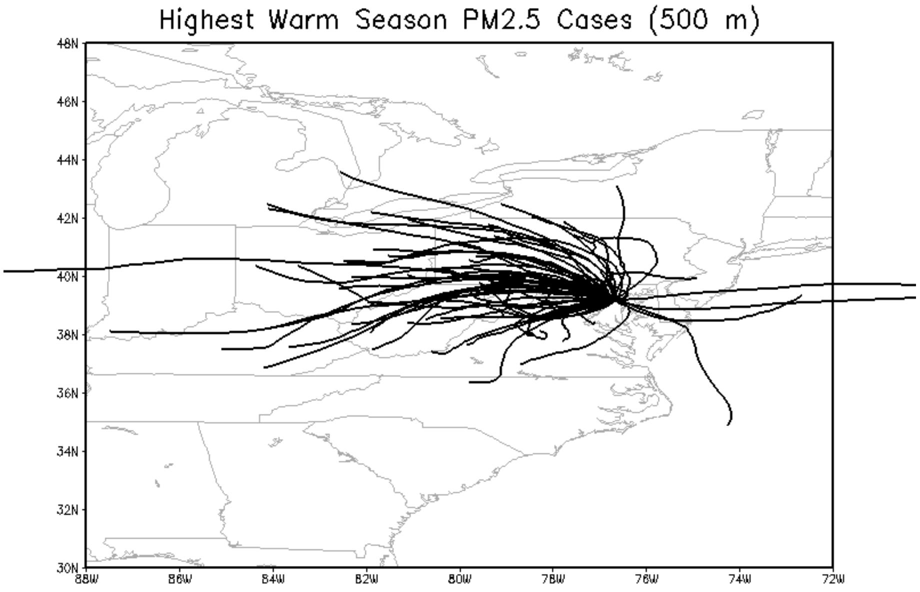


Figure 26. Back trajectories for the 95th percentile of pm cases in Maryland. The back trajectories are determined using the NOAA HYSPLIT model (http://www.arl.noaa.gov/ready/hysplit4.html) . The back trajectories shown here, and in succeeding figures terminate at BWI at 500 m above ground level (agl) at 1200 UTC (0700 EST) and are for 24 hours of travel time.

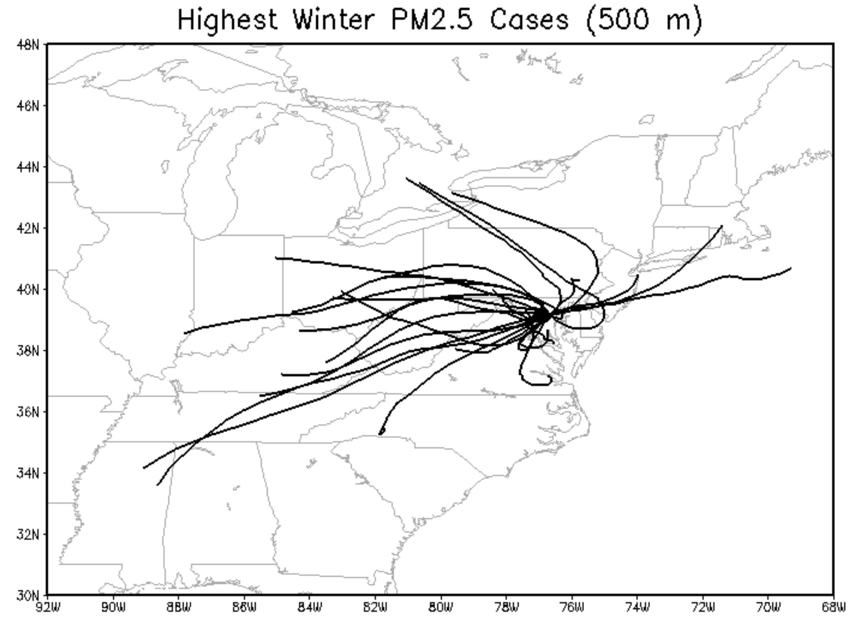
There are seasonal differences in transport patterns. In *Figure 27*, back trajectories for only warm season (May-September) high $PM_{2.5}$ cases are shown with winter cases shown in *Figure 28*. As a fraction of the total, the winter cases are less dominated by westerly transport with approximately one-third of the winter cases exhibiting some degree of re-circulation or stagnation of air masses. During the summer season, recirculation accounts for only ~ 15%. During the worst $PM_{2.5}$ cases, therefore, the transport pattern is overwhelming westerly. The make up of air parcels arriving from the west is primarily sulfate. As shown in *Figure 29*, concentrations at Dolly Sods, upwind of Maryland in westerly transport that characterizes poor $PM_{2.5}$ days, is primarily composed of sulfur compounds.



Highest Warm Season PM2.5 Cases (500 m)

GrADS: COLA/IGES

Figure 27. As in *Figure 26* but for warm season (May-September) cases.



Highest Winter PM2.5 Cases (500 m)

GrADS: COLA/IGES

Figure 28. As in *Figure 27* but for winter (December-February) cases.

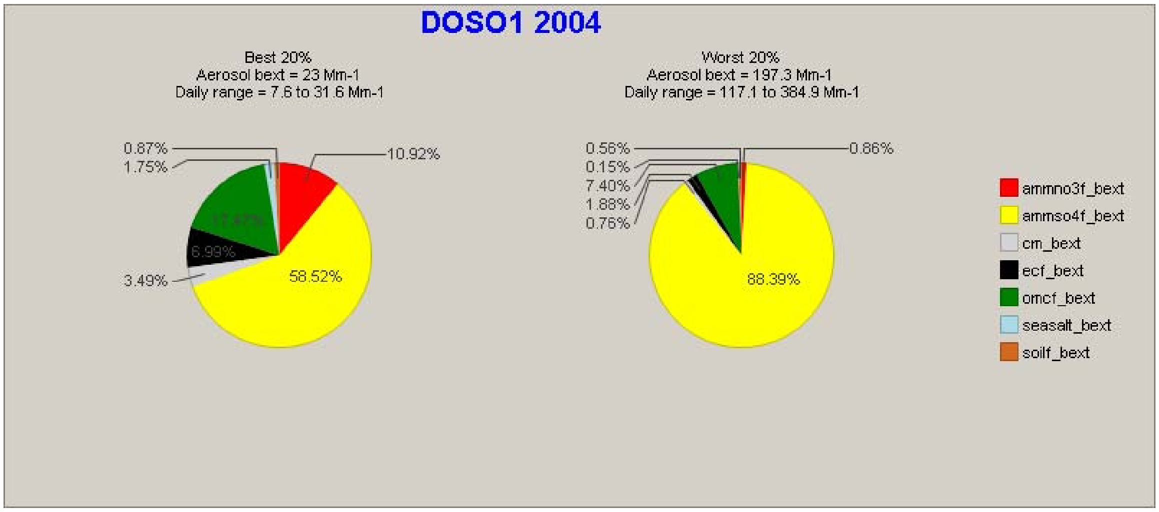


Figure 29. Speciated $PM_{2.5}$ measurements from the IMPROVE monitor at Dolly Sods, WV, for 2004 during the best (cleanest) days (left) and the worst (dirtiest) days (right).

In summary, the distribution of $PM_{2.5}$ concentrations in Maryland is right-skewed with mean concentrations strongly affected by a small fraction of very high $PM_{2.5}$ days. These days are predominantly characterized by westerly transport aloft, particularly during the summer season. Winter season high $PM_{2.5}$ cases show a higher incidence of stagnation along with westerly transport.

$PM_{2.5}$ Episodes: Meteorological Influences

Summer Season

$PM_{2.5}$ and O_3 concentrations in the summer season are highly correlated (*Figure 30*) and meteorological conditions associated with summer season multi-day $PM_{2.5}$ episodes are similar in nature to severe O_3 episodes. This coincidence follows for several reasons. First, $PM_{2.5}$ and O_3 share sources and precursors. For example, volatile organic compounds (VOCs) form a significant fraction of $PM_{2.5}$ mass and are also a critical O_3 precursor. NO_x, while a small fraction of $PM_{2.5}$ in summer, is generally the limiting factor for O_3 and a large percentage of regional scale NO_x concentrations have their source in coal-burning power generation units that also produce sulfur compounds - the main fraction of summer season $PM_{2.5}$. Second, weather conditions conducive to O_3 formation are also conducive to $PM_{2.5}$ accumulation. In particular, any weather processes that limit horizontal or vertical mixing will increase concentrations of both pollutants. Local (limited mixing) and regional (westerly transport) scale processes that increase $PM_{2.5}$ can both be maximized by weather patterns that feature light surface winds, strong, or multiple inversions, and westerly transport aloft.

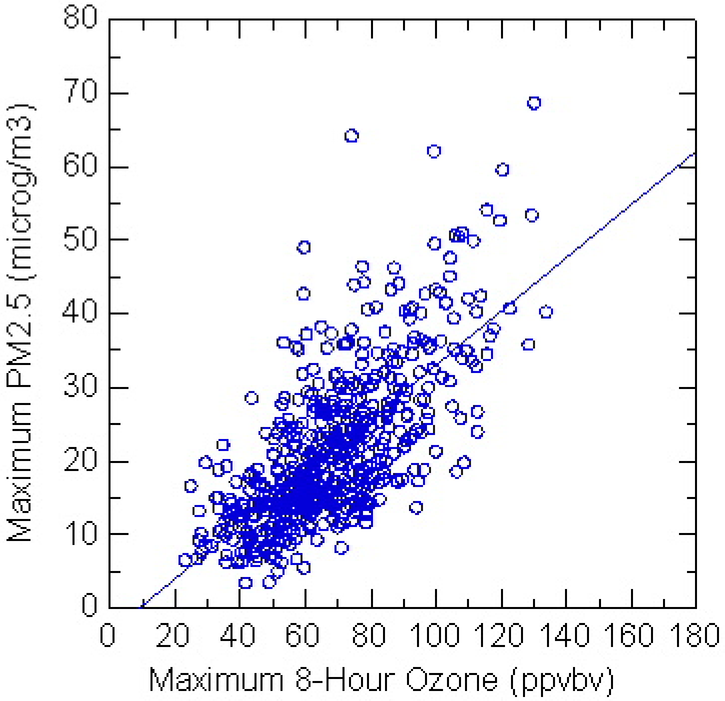


Figure 30. Peak daily 8-hour O_3 and 24-hour $PM_{2.5}$ concentrations in the Baltimore metropolitan area (Summer, 2000-2005).

O_3 and $PM_{2.5}$ conducive weather patterns do diverge in some important respects. O_3 formation is strongly dependent on incoming UV radiations to drive the photo-chemical reactions that produce O_3. Sunny skies mean more O_3. While sunlight is helpful for the oxidation of some $PM_{2.5}$ precursors, primarily SO_2 and organic carbon particles, it is a less important factor in relative terms. As a result, Maryland can observe high $PM_{2.5}$ concentrations, with low O_3, in the presence of significant cloud cover. In addition, while O_3 is not strongly correlated with relative humidity – high relative humidity typically means a better chance for cloud formation, $PM_{2.5}$ is associated with high humidity regimes. The conversion of $PM_{2.5}$ precursor gases, especially SO_2, to particles is enhanced in high moisture environments, and this process is enhanced further by cloud droplet processing.

Taken together, the large scale weather conditions conducive to summer season $PM_{2.5}$ formation are often associated with weather patterns also conducive to O_3, while smaller (meso) scale effects can vary the relative strength of O_3 and $PM_{2.5}$ on any given day. The large scale factors include: (1) An upper air ridge with its major axis west of Maryland. Subsidence, or downward motion, occurs downwind (east) of the ridge axis leading to decreased cloud formation and less vertical mixing; (2) With a ridge west of Maryland, winds aloft are westerly and tend to advect air masses high in $PM_{2.5}$ precursors from the Ohio River Valley and Midwest; (3) Surface high pressure typically leads the upper air ridge axis by a quarter of a wavelength so that the center of surface high pressure is overhead when the upper air ridge is west of Maryland. With high pressure overhead, temperatures increase, pressure gradients are weak and surface winds are light. This allows local pollutants to accumulate and mix with pollutants transported into the area aloft.

Summer $PM_{2.5}$ Episode: July 15-22, 2002

The interaction of weather with $PM_{2.5}$ in the summer season will be shown with reference to a strong $PM_{2.5}$ episode during July 2002. This episode is chosen because it met the criteria for severe $PM_{2.5}$ events (***Appendix D***) and enhanced $PM_{2.5}$ monitoring was carried out in Maryland during that month with the Essex site obtaining daily $PM_{2.5}$ speciation data. Each high $PM_{2.5}$ event is, of course, slightly different, but this event featured most of the key factors. Enhanced $PM_{2.5}$ levels were observed from July 15-22 (*Figure 31*). Peak concentrations exceed 50 μgm^{-3} on July 17-18 and, while enhanced on the other days of the episode, are in the 20-30 μgm^{-3} range. In addition, mean statewide and peak concentrations are quite close in magnitude, an indication of the regional scale of this event.

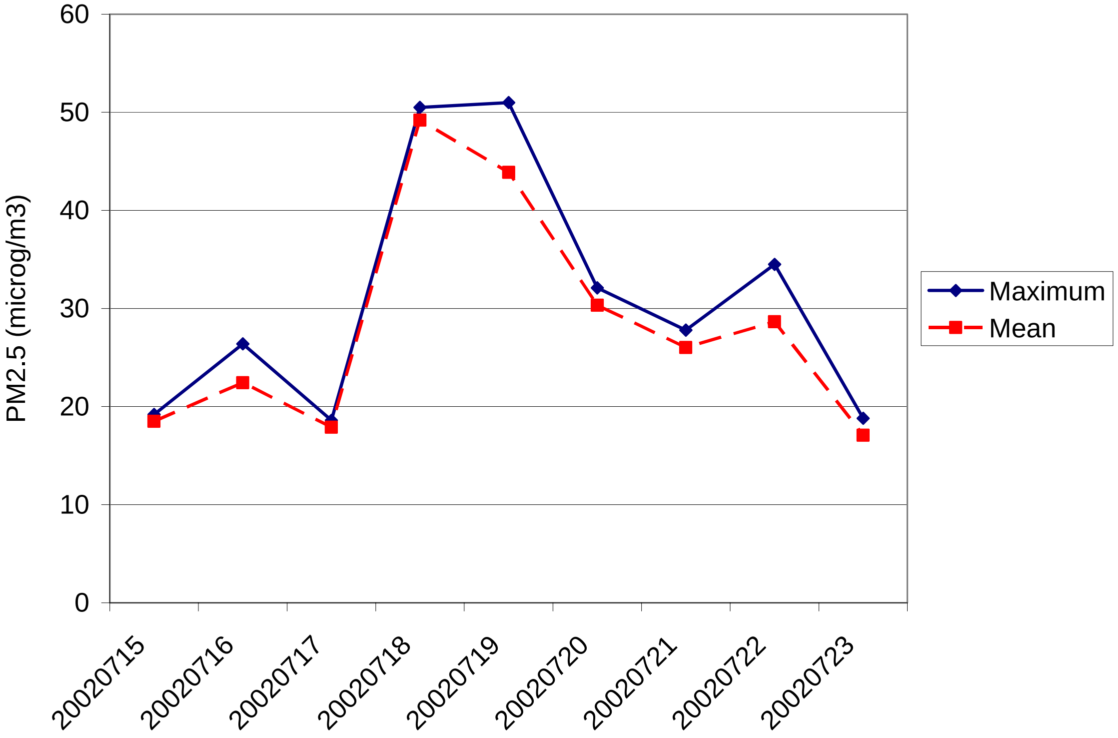


Figure 31. Daily $PM_{2.5}$ concentrations in Maryland during the high $PM_{2.5}$ episode of July, 2002. Concentrations from the monitors with the maximum $PM_{2.5}$ is given in blue and the average of all Maryland monitors in red.

The weather conditions associated with this episode are similar to the standard form with an upper air ridge of high pressure to the west (*Figure 32*), surface high pressure overhead (*Figure 33*) and generally west to northwest transport of pollutants (*Figure 34*). Ozone is enhanced throughout the period (*Figure 35*) as expected for this weather pattern. Note, however, that O_3 concentrations show little day-to-day variability when compared to $PM_{2.5}$.

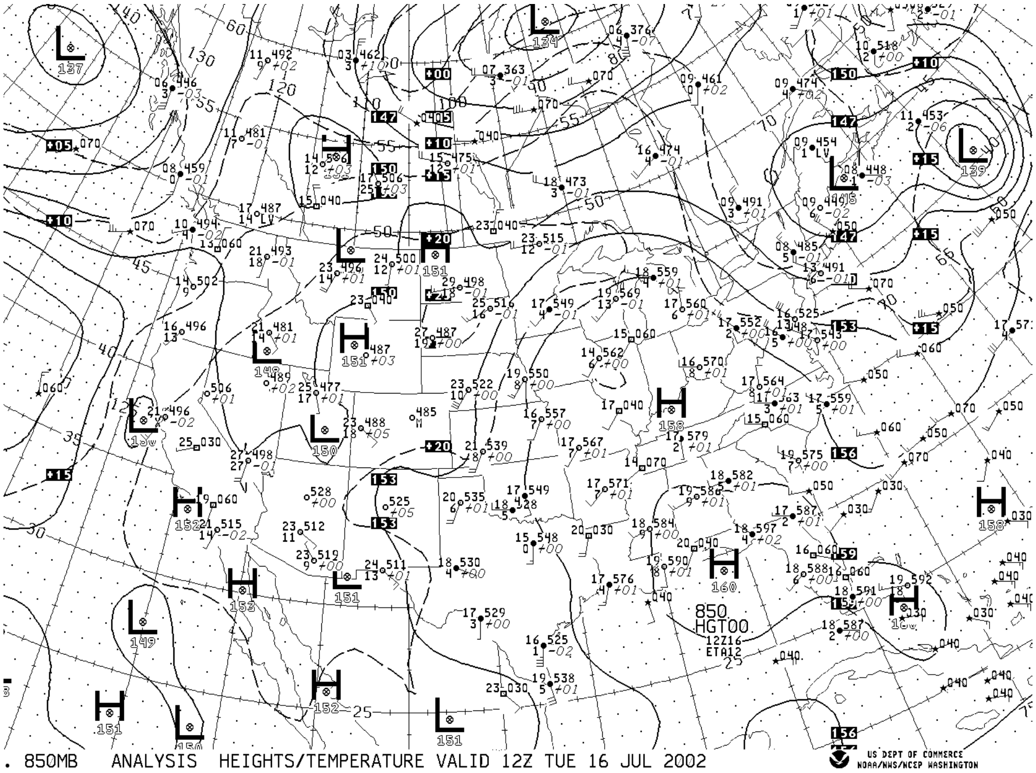


Figure 32. NCEP analysis of 850 mb weather variables for 1200 UTC on July 16, 2002. Contours are geopotential height, with station data showing height, temperature, dew point depression, height tendency and wind speed and direction.

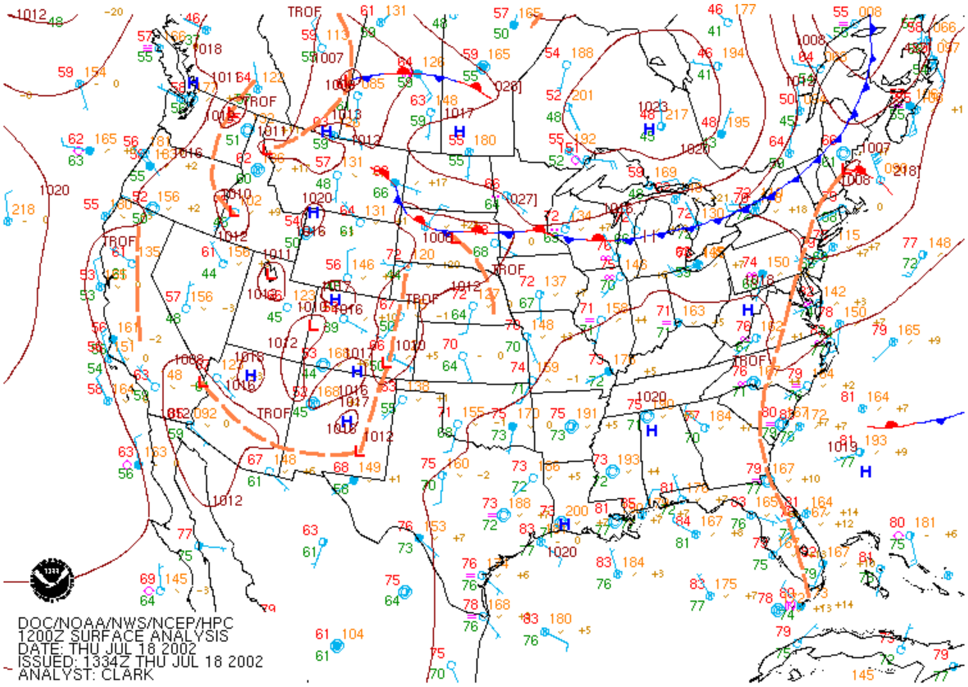


Figure 33. NCEP surface analysis for 1200 UTC on July 18. 2002.

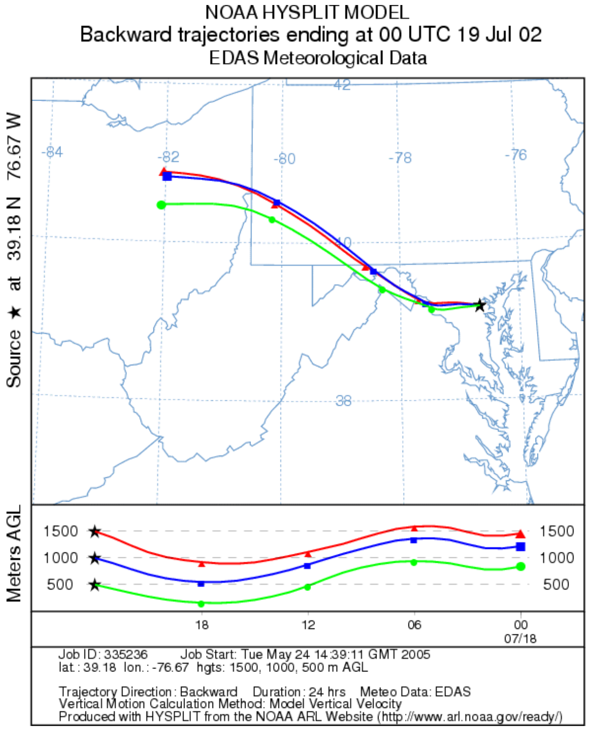


Figure 34. HYSPLIT back trajectories terminating at BWI for 0000 UTC on July 19, 2002. Trajectories are for 24-hours of travel and terminate at 500 (green line), 1000 (blue line) and 1500 (red line) meters agl.

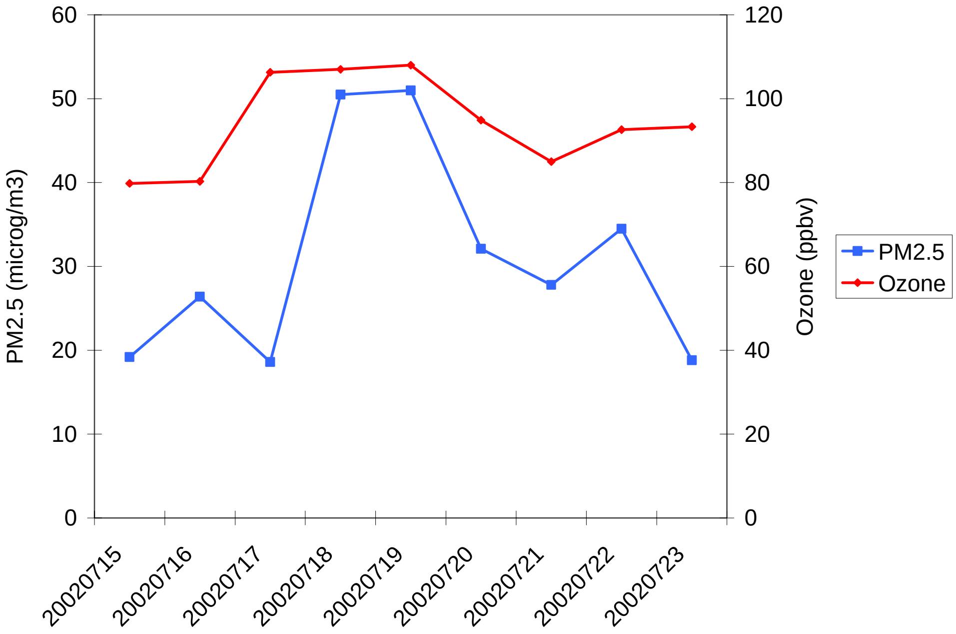


Figure 35. Peak O_3 (8-hour average) in Baltimore and $PM_{2.5}$ (24-hour average) in Maryland for July 15-23, 2002.

What accounts for the strong peak in $PM_{2.5}$ concentrations? From the Essex data, it is apparent that the peak in $PM_{2.5}$ concentrations is associated with increased sulfate levels. The key source of sulfate is coal combustion and it appears that the westerly transport during that period introduced significant sulfate levels to Maryland. Hourly observations on July 18-19 show that $PM_{2.5}$ concentrations tended to rise (*Figure 36*) during the well mixed afternoon hours indicative of high pm concentrations in the residual layer aloft. Daily speciated $PM_{2.5}$ observed at Essex, Maryland (*Figure 37*) show that nearly all of the observed increase in $PM_{2.5}$ during July 18-19 is due to increases in ammonium sulfate. Hourly observations on July 18-19 show that $PM_{2.5}$ concentrations rose during the well mixed afternoon hours (*Figure 36*) indicative of significant $PM_{2.5}$ within the residual layer aloft. Daily speciated $PM_{2.5}$ observed at Essex (*Figure 37*) shows that nearly all of the increase in pm on July 18-19 is due to increases in ammonium sulfate.

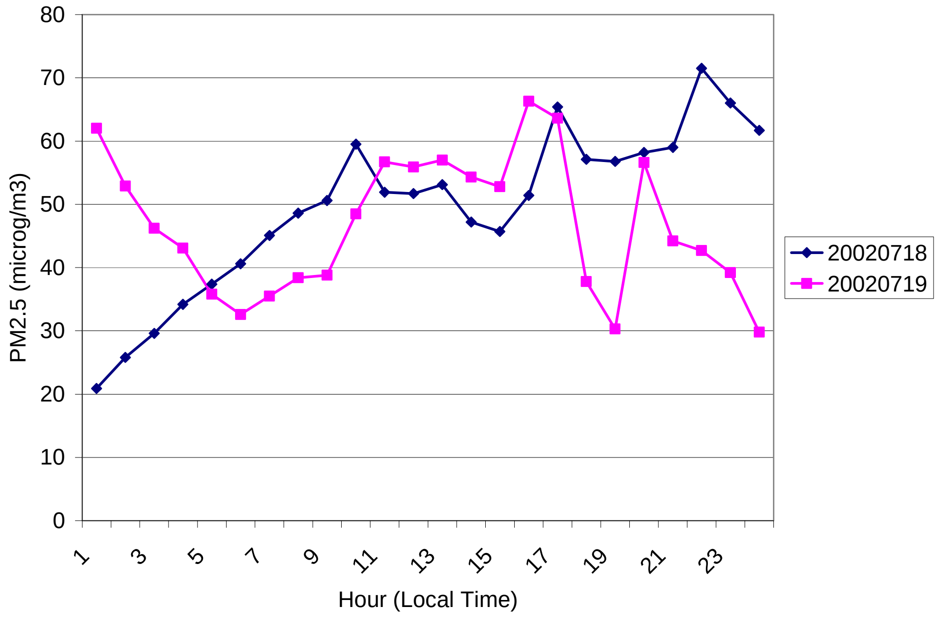


Figure 36. Hourly $PM_{2.5}$ concentrations at Old Town, Maryland for July 18-19,2002.

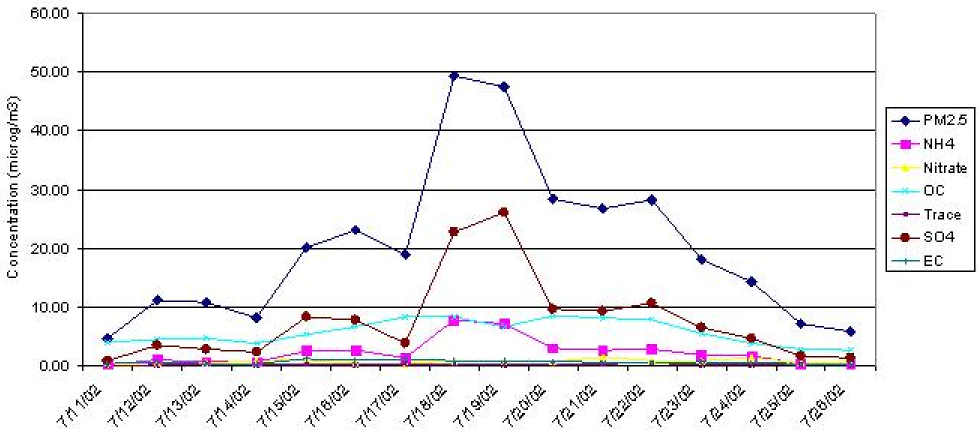


Figure 37. Daily average concentrations of speciated $PM_{2.5}$ observed at Essex, Maryland for July 11-28, 2002.

In summary, summer season $PM_{2.5}$ episodes feature weather patterns quite similar to high O_3 events. Westerly transport aloft provides a rich source of regional scale $PM_{2.5}$ and its precursors and light near surface winds allow local emission to accumulate as well. On the most extreme $PM_{2.5}$ days, evidence suggests that the bulk of the excess $PM_{2.5}$ is composed of sulfate compounds.

Winter Season PM$_{2.5}$ Episodes

High PM$_{2.5}$ days are less frequent in winter than summer (*Table 2*) and, while having many similar characteristics with respect to weather patterns, are also more complex with respect to PM$_{2.5}$ constituents. This difference may have implications for the efficacy of control strategies.

Frequency of Days with Maximum PM$_{2.5}$ $\geq$ 35 μgm^{-3}		
Season	Number of Days	Percentage
DJF	42	29%
MAM	14	10%
JJA	66	46%
SON	22	15%
Total	144	100%

Table 2. Breakdown of high PM$_{2.5}$ days in Maryland by season for the period 2000-2005.

The most important difference in winter season cases is the greater likelihood of stagnation occurring during the pollution episode. In *Figure 38 and Figure 39*, composite plots of average weather conditions during winter season high PM$_{2.5}$ cases during 2000-2003 are shown. The average sea level pressure field (*Figure 38*) shows a lobe of high pressure centered over the Atlantic coastal region. Weak pressure gradients are associated with high pressure overhead and this leads to light and variable near-surface winds. In *Figure 39*, very light winds near the surface (1000 mb) winds are associated with locations near the high pressure center. For the 90th percentile PM$_{2.5}$ winter season cases (2000-2005), average surface wind speeds at BWI are 55% less than those observed for the remaining winter season cases. The greater frequency of stagnation in winds aloft during winter season high PM$_{2.5}$ cases was previously remarked upon in the discussion of back trajectories (*Figure 26 and Figure 28*).

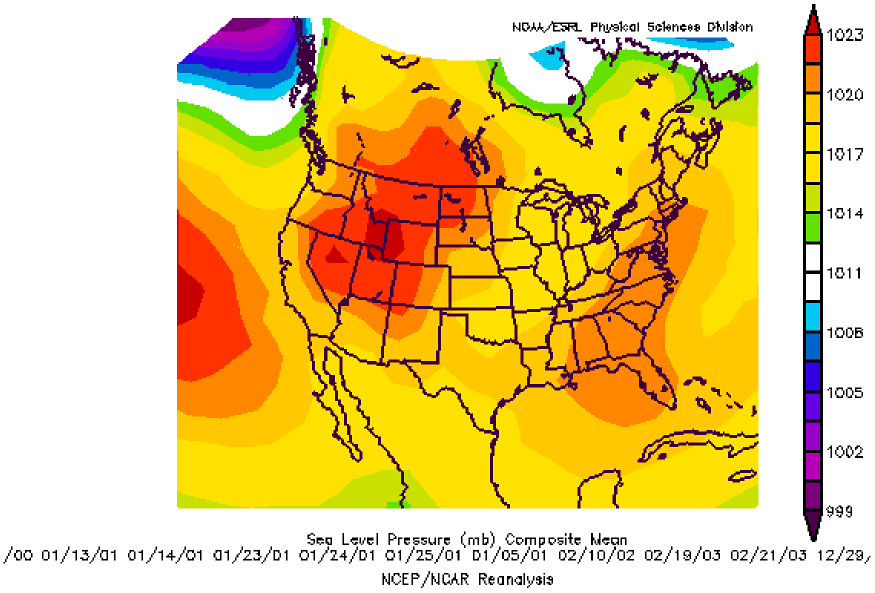


Figure 38. Composite sea level pressure map for all winter season days in Maryland with observed pm ≥ 40 µgm^{-3} for the period 2000-2005. Figure courtesy of NOAA/ERSL (http://www.cdc.noaa.gov/cgi-bin/PublicData/getpage.pl).

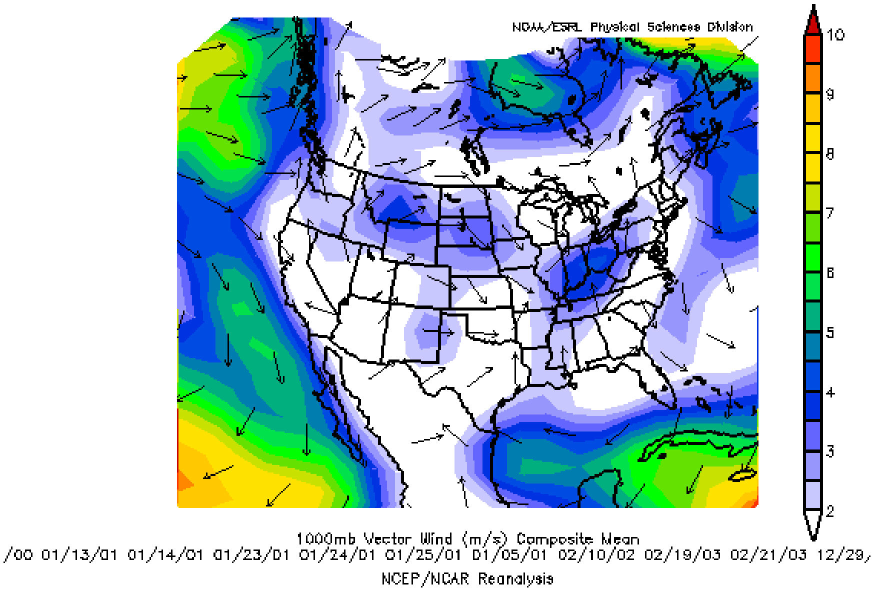


Figure 39. As in Figure 39 but for 1000 mb mean wind speed.

Another important feature of winter season high $PM_{2.5}$ cases is the presence of a very strong near surface inversion. In the summer months, full sun and attendant strong heating of the earth's surface allows deep vertical mixing beginning during the late morning hours. The air mass mixed downward, as discussed above, is not always clean and, in fact, may be laden with sulfate in the "right" (westerly transport, high humidity) conditions. *Figure 23* showed that, on average, in high summer $PM_{2.5}$ cases, mixing tends *not* to lower $PM_{2.5}$ concentrations. In winter, however, while the air mass aloft is typically cleaner than near-surface air parcels, vertical mixing is often quite limited. As a result, although cleaner is mixed downward during the day, it occurs later and often for a very short period. Vertical mixing in winter is limited by weaker solar isolation and can be further reduced in the presence of snow cover. Snow cover, highly reflective, keeps the surface cool and, if warm air advection is occurring above the surface, leads to strong and long lasting morning inversions. This winter season effect is also shown in *Figure 23*. In winter, $PM_{2.5}$ tends to peak in the late morning and early afternoon hours, indicative of limited mixing. Concentrations fall off as mixing finally occurs but only for a few hours until the sun sets and mixing ceases.

Overall, the combination of light winds and limited vertical mixing during winter season events can lead to a more local scale "signature" of pollutants. During summer episodes, sulfate is typically the dominant pollutant, but in winter, organic carbon and nitrates, characteristic of motor vehicle emissions and home heating, become more important. The mix of local and regional effects can vary from episode to episode. These differences are highlighted in the discussion of two winter season episodes that follow.

February 19-21, 2003

This episode followed a coastal storm and heavy snow event on February 16-17. Highest $PM_{2.5}$ concentrations occurred during the period February 19-21 (*Figure 40*). This episode is characterized by a stable air mass, extended periods of near surface stagnation, and transport from the west to southwest. The stability of the boundary layer is, in part, due to a significant snow pack that followed the coastal storm and heavy snow event.

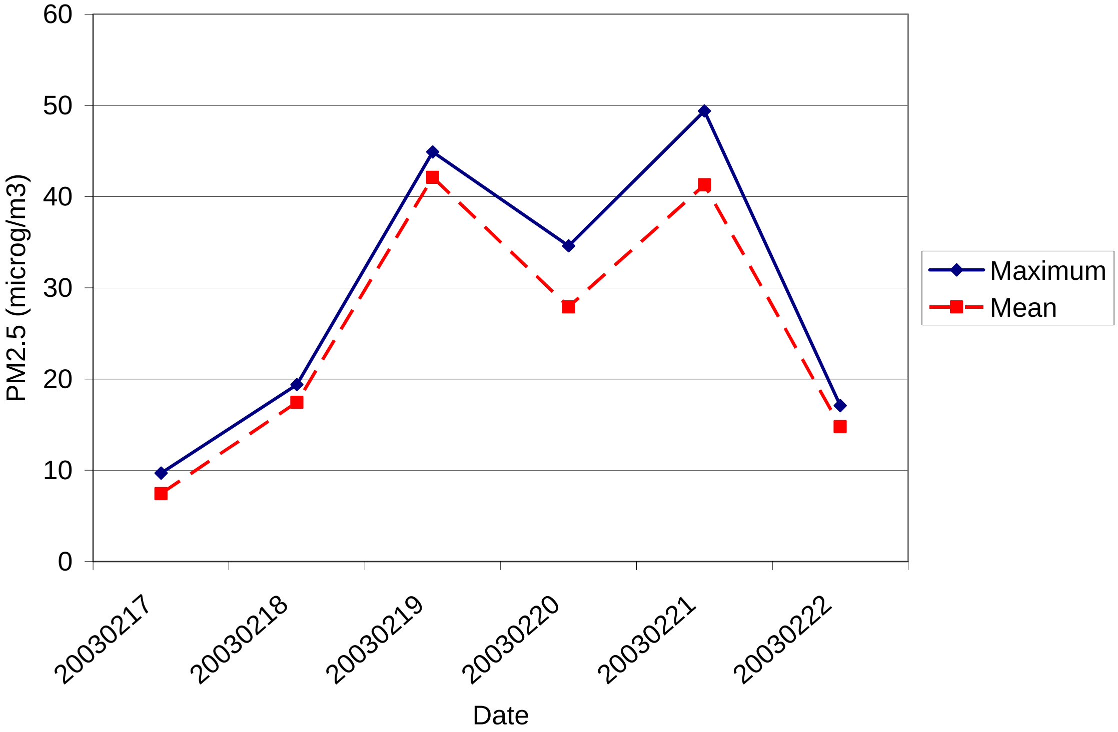


Figure 40. Daily maximum (solid blue line) and mean (dashed red line) $PM_{2.5}$ concentrations for the State of Maryland for the period February 17-22, 2003.

As is common in most winter season $PM_{2.5}$ cases (*Figure 38*), surface high pressure is overhead (*Figure 41*). The snow cover, noted above, results in a very strong surface-based inversion (*Figure 42*). A strong inversion and light winds leads to a typical winter season $PM_{2.5}$ diurnal profile (*Figure 43)* with enhanced morning rush hour concentrations lasting until noon.

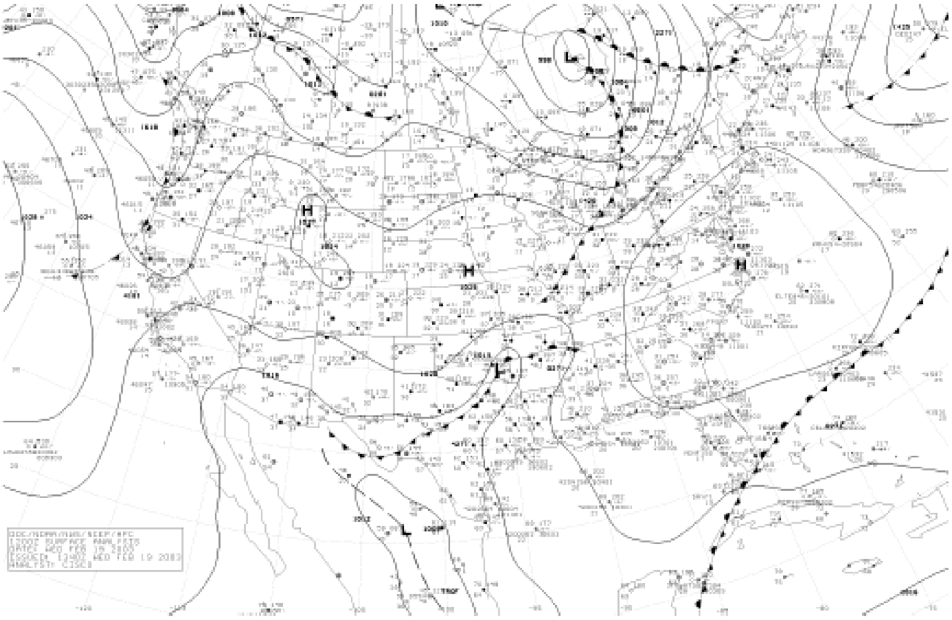


Figure 41. NCEP surface analysis for 1200 UTC on February 19. 2003.

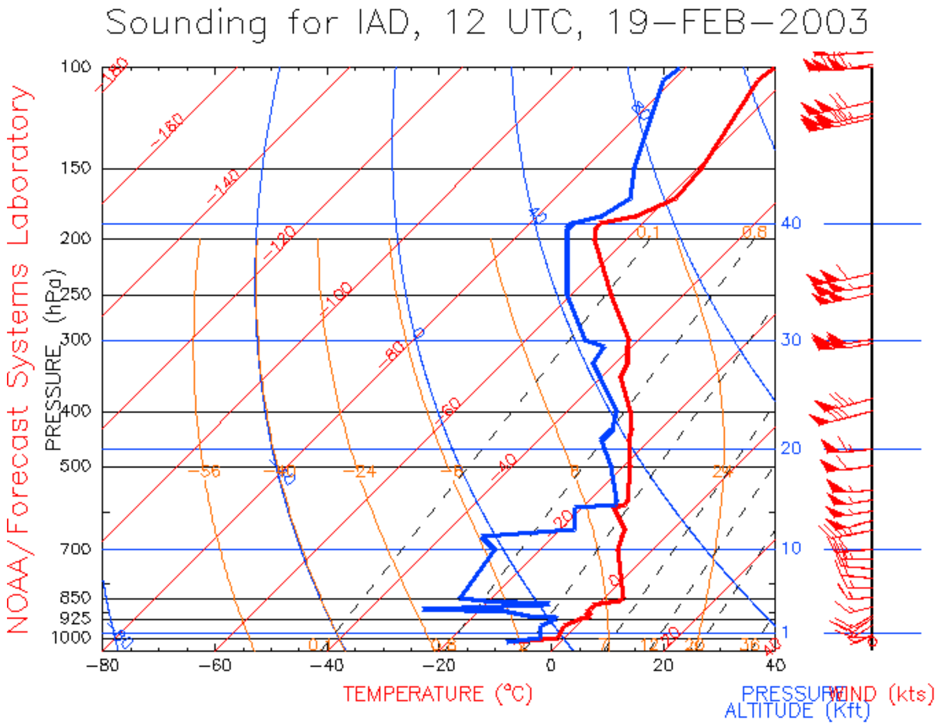


Figure 42. Skew-T diagram giving vertical temperature (red line) and dew point temperature (blue line) observations from the 1200 UTC balloon ascent at Dulles International Airport (IAD) on February 19, 2003. Winds are given in the right margin. Each half-barb is 5 knots, solid pennants are 50 knots.

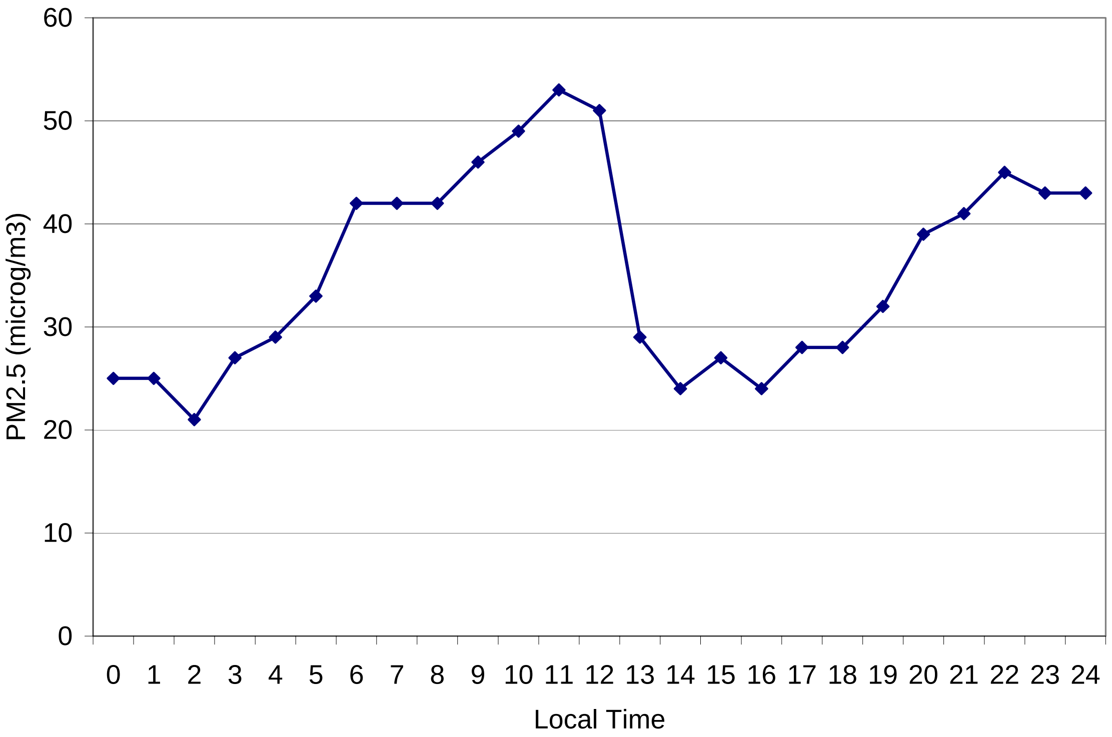


Figure 43. Hourly $PM_{2.5}$ concentrations at Old Town, Maryland for February 19, 2003.

High pressure overhead results in very light winds at BWI with average daily wind speeds only 34% of the winter average. Light surface winds tends to allow local pollutants to accumulate. In addition, relative humidity averaged 85% during the heart of the episode (45% higher than average winter conditions). High relative humidity and cool weather makes for very efficient conversion of NO_x to particulate nitrate. With significant local motor vehicle and home heating sources near Baltimore, additional increases in $PM_{2.5}$ from nitrate is expected. In addition, westerly to southwesterly transport was a factor throughout the episode (*Figure 44*). Westerly transport is characterized by a strong sulfate component. As a result, this episode is a combination of both local and regional impacts. Speciated $PM_{2.5}$ measurements are available at Essex and Washington DC only for February 20th. All $PM_{2.5}$ constituent are enhanced during this event in the range of 2-7 μgm^{-3} above their winter season averages. Relative to winter average concentrations, SO_4 shows the biggest relative increase – three times normal – although absolute concentrations are only 9.7 μgm^{-3}. Organic carbon (OC) is the largest absolute contributor to $PM_{2.5}$ on this day with concentrations (depending on the k factor applied) of 13-17 μgm^{-3}. NO_3 is also enhanced and reaches 4.8 μgm^{-3}. Observations in Philadelphia show similar concentrations but with a stronger NO_3 component (8.6 μgm^{-3}) with OC again forming the largest part of the observed $PM_{2.5}$. Concentrations from the IMPROVE monitor in Washington DC for the entire year are shown in *Figure 45*. During this period, and through the winter months, the highest $PM_{2.5}$ cases, marked "W" for the worst air quality days, is a combination of enhanced sulfate and nitrate.

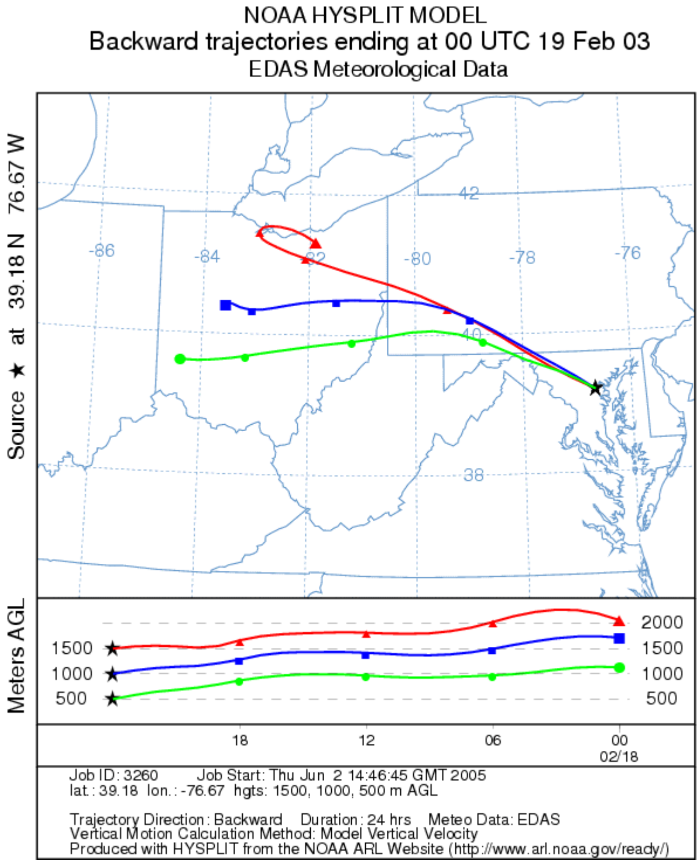


Figure 44. HYSPLIT back trajectories terminating at BWI for 0000 UTC on February 19, 2003. Trajectories are for 24-hours of travel and terminate at 500 (green line), 1000 (blue line) and 1500 (red line) meters agl.

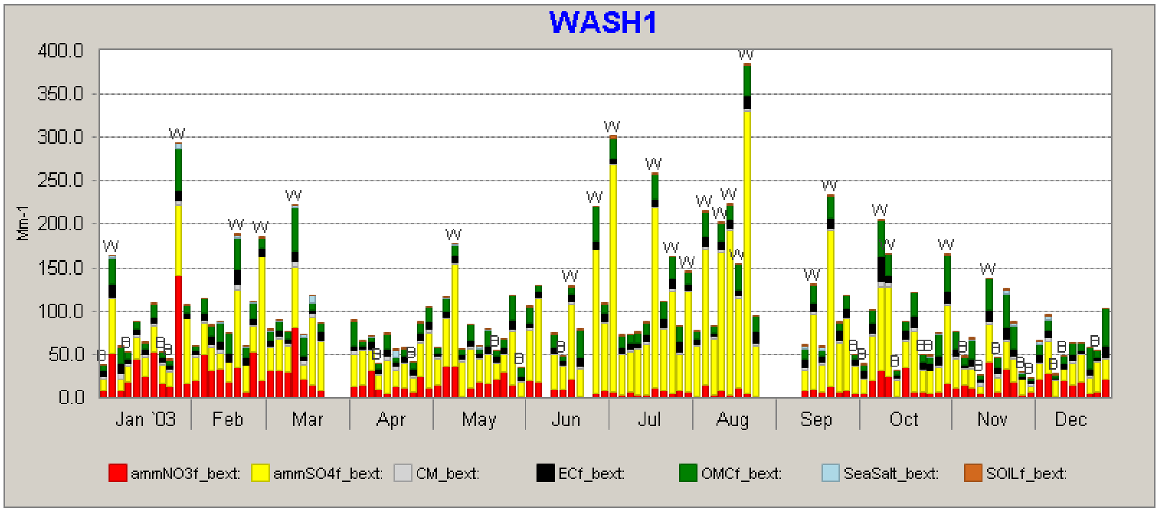


Figure 45. Daily speciated $PM_{2.5}$ concentrations from the Washington, DC IMPROVE monitor for 2003. Labels "W" and "B" represent the worst and best air quality days during the year.

January 12-15, 2001

The highest $PM_{2.5}$ concentrations during this episode were observed in Maryland from January 12-15 while, region-wide, the peak of the episode occurs on January 14 (*Figure 46*). In the synoptic scale, the episode is characterized by surface high pressure over the region consistent with the winter average conditions (cf. *Figure 38* and *Figure 47*). The keys to the episode are westerly transport in the onset stage, followed by re-circulation and moistening of the air mass in the mature stage.

The onset of the episode was characterized again by westerly transport (*Figure 48*). By the morning of the 13th, $PM_{2.5}$ is strongly enhanced regionwide (*Figure 49*) and a strong morning inversion keeps concentrations high until noon. By January 14th, stagnation becomes pronounced. The 48-hour back trajectory in *Figure 50* suggests that the air mass advected from the west on January 12th lingers over Maryland through the 14th. Surface weather observations at BWI show the extent of the stagnation. While average winds during the afternoon hours on January 12th are ~ 6 kts, they fall off to 2 kts or less from the 13th through the 15th – the period of high $PM_{2.5}$ concentrations. In addition, relative humidity, which favors nitrate and sulfate formation processes, increases through the period as well (*Figure 51*). A strong surface based inversion is again present (*Figure 52*). While no STN data is available for this period, IMPROVE monitor in Washington DC does provide data for January 13 (*Figure 53*). $PM_{2.5}$ on January 13 is the highest concentrations during the winter monthis in Figure 54 and the large nitrate contribution is consistent with high humidity, stagnation, local scale event driven by motor vehicle and home heating emissions.

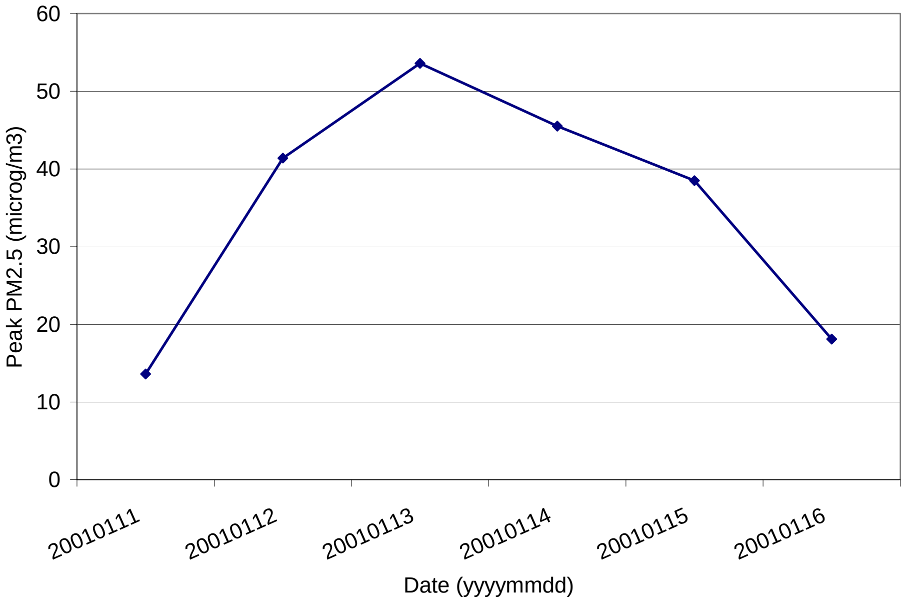


Figure 46. Daily maximum $PM_{2.5}$ concentrations for the State of Maryland for the period January 11-16, 2001.

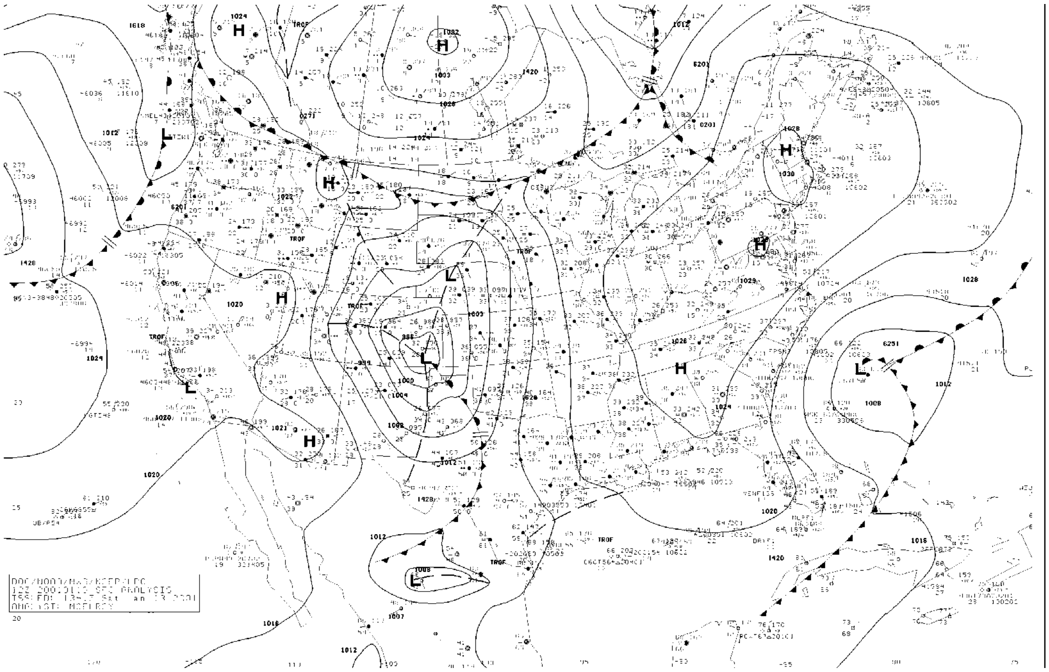


*Figure 47***.** NCEP surface analysis for 1200 UTC on January 13. 2001.

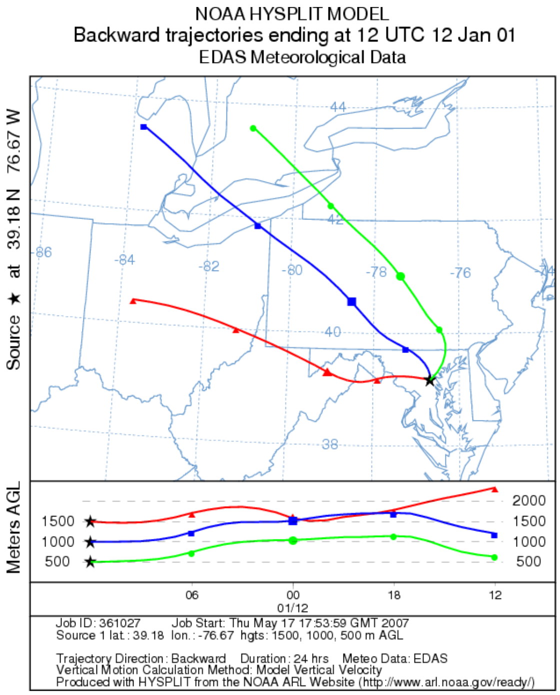


Figure 48. HYSPLIT back trajectories terminating at BWI for 1200 UTC on January 12, 2001. Trajectories are for 24 hours of travel and terminate at 500 (green line), 1000 (blue line) and 1500 (red line) meters agl.

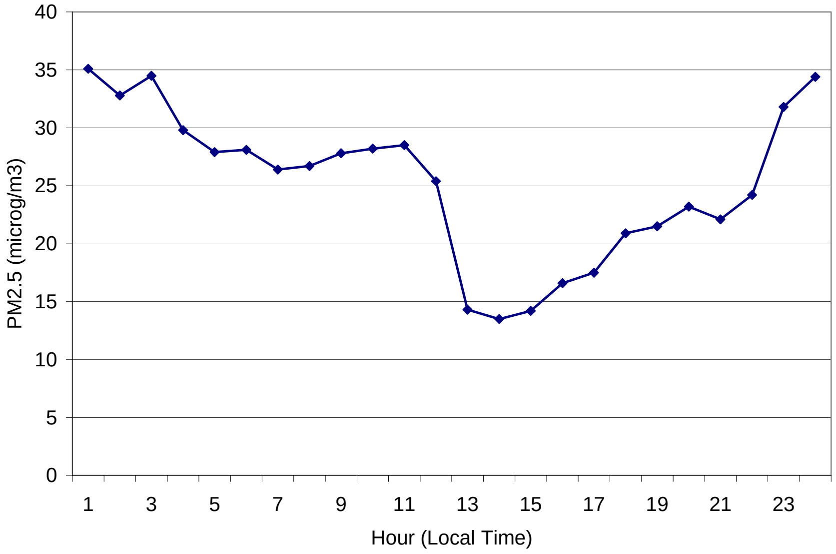
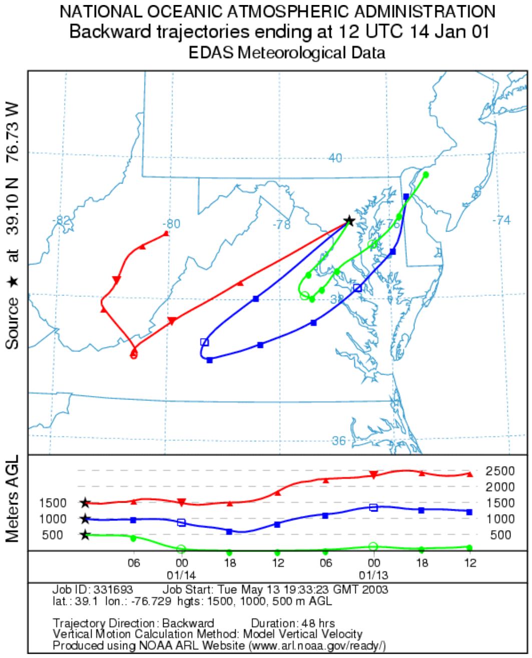


Figure 49. Hourly $PM_{2.5}$ concentrations at Old Town, Maryland for January 13, 2001.



Job ID: 331693 Job Start: Tue May 13 19:33:23 GMT 2003
lat.: 39.1 lon.: -76.729 hgts: 1500, 1000, 500 m AGL

Trajectory Direction: Backward Duration: 48 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Produced using NOAA ARL Website (www.arl.noaa.gov/ready/)

Figure 50. HYSPLIT back trajectories terminating at BWO for 0000 UTC on January 14, 2001. Trajectories are for 48 hours of travel and terminate at 500 (green line), 1000 (blue line) and 1500 (red line) meters agl.

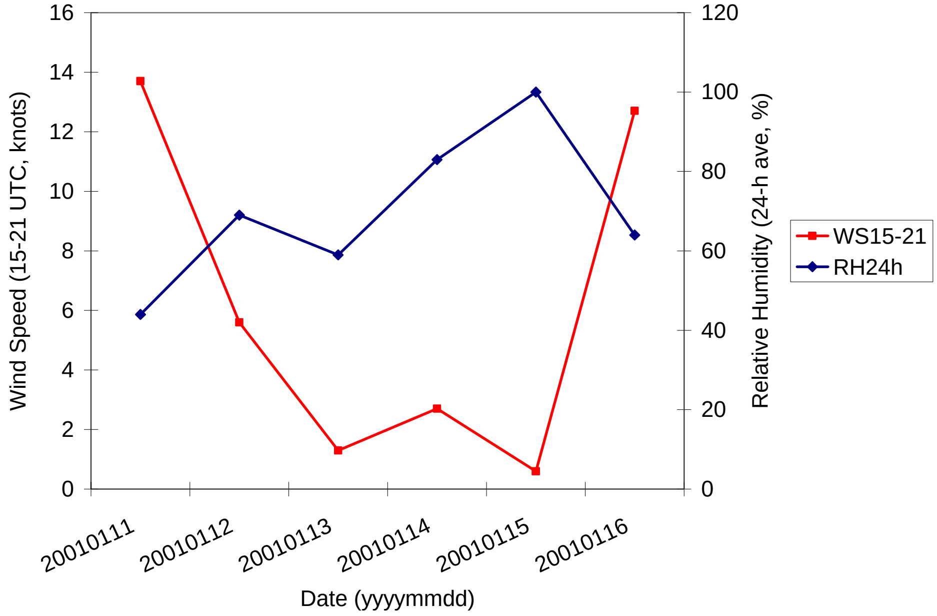


Figure 51. Daily average relative humidity (%) at BWI (red line, right axis) and mid-day (1500-2100 UTC) average wind speed for January 11-16, 2001.

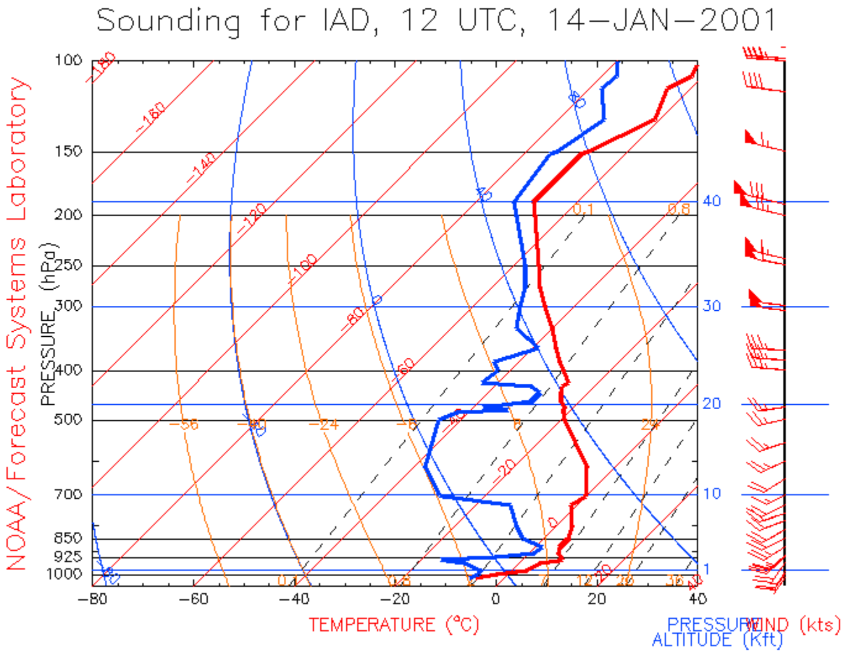


Figure 52. Skew-T diagram giving vertical temperature (red line) and dew point temperature (blue line) observations from the 1200 UTC balloon ascent at Dulles International Airport (IAD) on January 14, 2001. Winds are given in the right margin. Each half-barb is 5 knots, solid pennants are 50 knots.

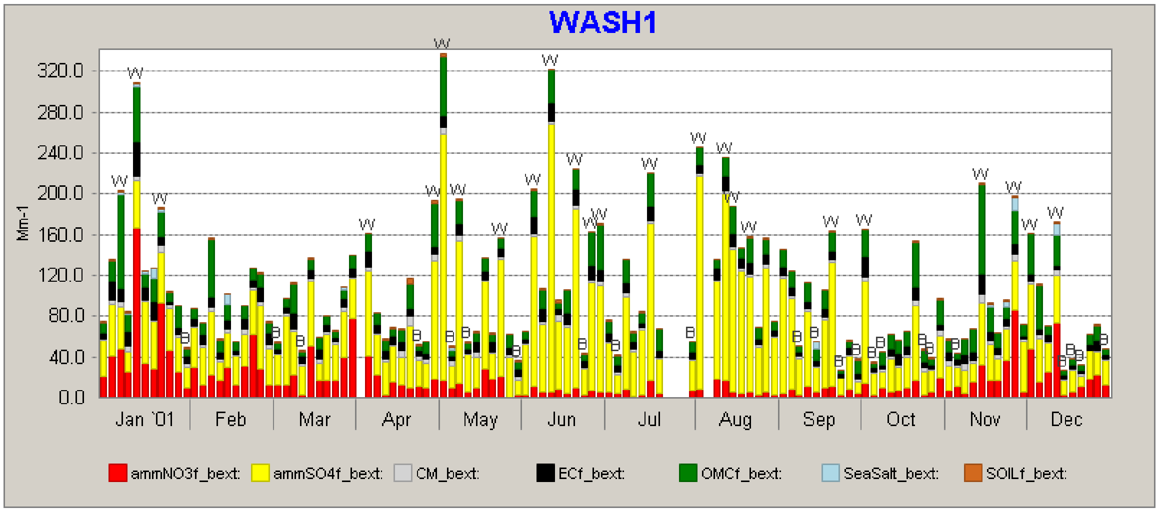


Figure 53. Daily speciated PM$_{2.5}$ concentrations from the Washington, DC IMPROVE monitor for 2001. Labels "W" and "B" represent the worst and best air quality days during the year.

Conclusions

This report summarizes observations of fine particulate matter with an aerodynamic radius of ≤ 2.5 µm, also known as $PM_{2.5}$, in the State of Maryland during the period 2000-2005. Average $PM_{2.5}$ concentrations for this period at monitors across Maryland range from 12-17 µgm^{-3} with the highest concentrations observed at urban scale sites. Although urban monitors observe the highest concentrations, all Maryland $PM_{2.5}$ monitors are strongly correlated and the correlation between monitors is highest during the summer season.

The data summary indicates that $PM_{2.5}$ is ubiquitous in Maryland, is not an overwhelmingly urban pollutant, and that all locations share in a common, regional scale "load" of $PM_{2.5}$. Although there is no fool-proof method to quantify the regional scale "load" of $PM_{2.5}$, comparisons of urban, suburban and remote rural monitors suggest that the regional component of $PM_{2.5}$ accounts for roughly 60-75% of the total observed $PM_{2.5}$. This fraction increases to 80-90% during the summer season.

$PM_{2.5}$ concentrations peak during the summer season (June-August) in Maryland although urban scale sites also have a secondary maximum during the winter (December-February) months. The summer maximum are driven primarily by increases in the amount of sulfate while winter season peaks are driven more by increases in nitrogen and carbon compounds. $PM_{2.5}$ concentrations also vary by the day of the week, on the order of 2-3 µgm^{-3}, with highest concentrations occurring near the end of the work week and lowest concentrations on Sunday. This reflects day of week differences in motor vehicle and industrial emissions. While average concentrations do not vary significantly by the day of the week, the frequency of high $PM_{2.5}$ concentrations days (90th percentile) is much greater during the work week.

$PM_{2.5}$ concentrations have a daily (diurnal) cycle with highest concentrations during the morning and afternoon rush hours, when emissions are highest and vertical mixing is weakest, and lowest concentrations during the well-mixed (diluted) afternoon hours. The diurnal cycle is markedly different for the most severe (90th percentile) cases. In those cases, the mid-day dilution effects are less evident so that concentrations remain nearly unchanged through the daylight hours. This effect is more pronounced in the summer months and suggests that the air aloft, which mixes downward in the afternoon, is heavily laden with transported $PM_{2.5}$. The highest $PM_{2.5}$ cases are characterized overwhelming by westerly transport of air parcels although, in winter, there is a secondary maximum of cases where re-circulation, or stagnation, occurs. Observations at rural monitors west of Maryland show that, on the worst $PM_{2.5}$ days, this air mass is primarily made up of sulfate particles.

Appendix A: Assessment of FRM Data

Compliance with the $PM_{2.5}$ NAAQS is based on observations made by gravimetric filters using the Federal Reference Method (FRM). Due to cost constraints, only a fraction (~ 20%) of all FRM monitors report daily with the remainder reporting every third day. For Maryland, typically 10-17 FRM monitors report every third day with only 3 monitors (all near Baltimore) reporting daily. This discontinuity in sampling frequency may introduce problems in statistical analyses – particularly in the analysis of statewide concentrations and the analysis of episodic high $PM_{2.5}$ episodes. Overall, the high sampling frequency cases tend to observe higher $PM_{2.5}$ concentrations (Table A1) suggesting that the data collected on these days are qualitatively different from the low sampling days. This task will assess whether there are statistically significant differences between the high sampling frequency (3rd day) and low sampling frequency (days 1 and 2) cases.

Complicating any analysis of $PM_{2.5}$ data, particularly daily peak concentrations, is the non-normal distribution of the observed data. As shown in Figure A1, the distribution of daily peak 24-hour average $PM_{2.5}$ concentrations in Maryland, as well as 24-hour concentrations at any single monitor within the state, is highly skewed. Basic statistical measures for statewide maximum $PM_{2.5}$ and a Baltimore monitor (Old Town) are given in Table A1. The large difference between mean (17.7 μgm^{-3}) and median (15.5 μgm^{-3}) concentrations for the statewide maximum concentrations is an initial clue that the distribution is not normal. Skewness and kurtosis measures are generally used to diagnose differences from normal in any given distribution. *Skewness* is a measure of the symmetry of the distribution about its mean. If skewness is significantly non-zero, the distribution is asymmetric. A standard threshold above which the skewness coefficient is considered significant is if the absolute value of the skewness coefficient divided by the standard error of skewness (SES) is > 2. The SES is typically defined as $(6/n)^{½}$, where *n* is the number of cases in the sample. For both statewide monitors and Old Town, and all other monitors as well, the absolute values of skewness/SES are well in excess of 2 and thus the distribution is asymmetric. The positive value for skewness means that the distribution is dominated by a strong "right tail" of high $PM_{2.5}$ concentrations.[1] *Kurtosis* is a measure of whether the center of the distribution is strongly "peaked". Positive kurtosis means that the distribution is more peaked, that is, less smooth and bell shaped, than the normal distribution. The kurtosis coefficient is considered significant, and the sample distribution significantly different from normal, if the measure of kurtosis divided by the standard error of kurtosis (SEK) is > 2. The SES is defined as $(24/n)^{½}$. In this case, the kurtosis measure is significantly positive meaning the sample distribution is more centrally peaked than normal. In summary, the statewide maximum $PM_{2.5}$ distribution, and individual monitors as well, are significantly different from normal. The distribution is asymmetric, with a strong right tail, and strongly peaked.

As an aside, Figure A2 shows that a natural log-transform of the $PM_{2.5}$ data is sufficient to approximate a normal distribution. To the extent that this dataset is used for $PM_{2.5}$ forecast algorithm development using linear regression techniques, a log transform of the predicand is necessary for best results.

The results above raise a number of issues. First, they call into question the usefulness of mean concentrations as the NAAQS for $PM_{2.5}$. The NAAQS is based on yearly mean measures yet, in a highly skewed distribution, mean concentrations tell little about the nature of the observed distribution. In this case, the mean value is strongly affected by the high $PM_{2.5}$ outliers and does not accurately reflect the "usual" $PM_{2.5}$ exposure of the population. For example, if the highest 5th percentile ($> 37.2\ \mu gm^{-3}$) is excluded from the Old Town monitor, mean concentrations fall from $16.7\ \mu gm^{-3}$ (above the NAAQS of $15.5\ \mu gm^{-3}$) to only $14.5\ \mu gm^{-3}$. Second, and of more importance for the present task, the usual statistical measures of whether two samples are drawn from the same population are not applicable when the distributions are not normal.

In this case, therefore, the appropriate statistical test must be non-parametric. That is, the test must be applicable without assumptions as to the shape of the distribution. The most common non-parametric test to determine if two samples are from the same distribution is the Komolgorov-Smirnov (K-S) test. The K-S test statistic (D_s) looks for the largest difference, in absolute value, between the distributions of two samples of data. In specific, D_s is the largest difference between the empirical cumulative distribution functions of the two samples. If D_s is sufficiently large, the null hypothesis, that the two samples come from the same distribution, can be rejected. The critical level of D_s depends on sample size (Wilks, 2006). In Figure A3, a rough illustration of the D_s statistic is shown. The largest difference in our data appears to occur in the extreme of the distribution – the highest $PM_{2.5}$ cases.

The D_s statistic is given below for two samples of *n* and *m* observations. The null hypothesis that two samples come from the same distribution is rejected at α * 100% if:

$$D_s > \left[-\frac{1}{2}\left(\frac{1}{n}+\frac{1}{m}\right)\ln\left(\frac{\alpha}{2}\right)\right]^{1/2}$$

In this case, the small frequency cases (1 and 2 day observations) have 1381 members (*n*) and the large frequency cases (3rd day observations) have 727 members (*m*). Using results from the SYSTAT statistical software package two-sample K-S test, $D_s = 0.1018$ for these samples and the null hypothesis is accepted at $p = 0.0001$. As a result, the null hypothesis is accepted at a 99.9% likelihood and the high and low frequency samples can be considered to derive from the same distribution.

Given this result, we are able to make use of the entire statewide dataset of low and high frequency sampling cases in the succeeding analyses. It also gives forecasters a much larger (3x) database from which to train statistical forecast algorithms. In the analyses of statewide $PM_{2.5}$ that follows in Tasks 3 and 4 of this report, the entire daily database will be used except where otherwise noted.

Maryland Statewide Daily Maximum PM$_{2.5}$ 2000-2005		
	High Sampling Frequency (Every 3rd Day)	Low Sampling Frequency (Days 1 and 2)
Median	17.0	14.8
Mean	19.0	17.0
90th %ile	33.3	29.5
95th %ile	39.2	36

Table A1. Basic statistical measures for statewide maximum PM$_{2.5}$ for every third day when all FRM monitors report and other days when only daily FRM monitors report.

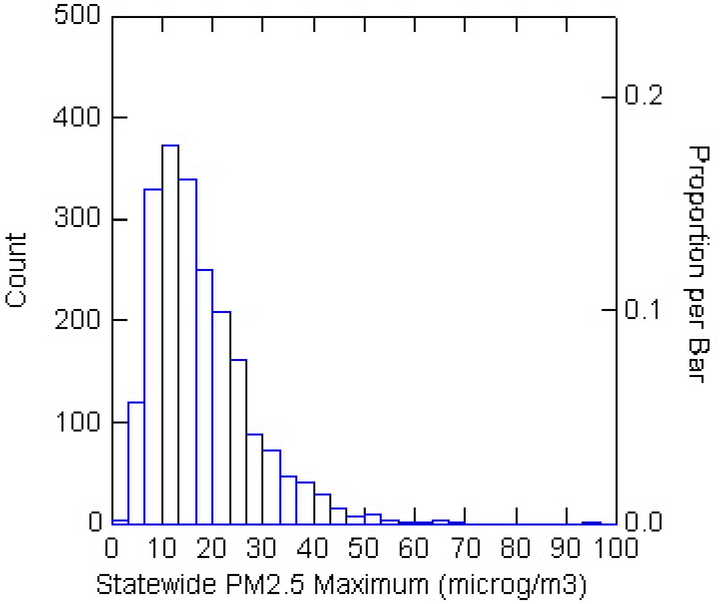


Figure A1. Daily maximum PM$_{2.5}$ concentrations (24-hour average) from all FRM monitors in the State of Maryland.

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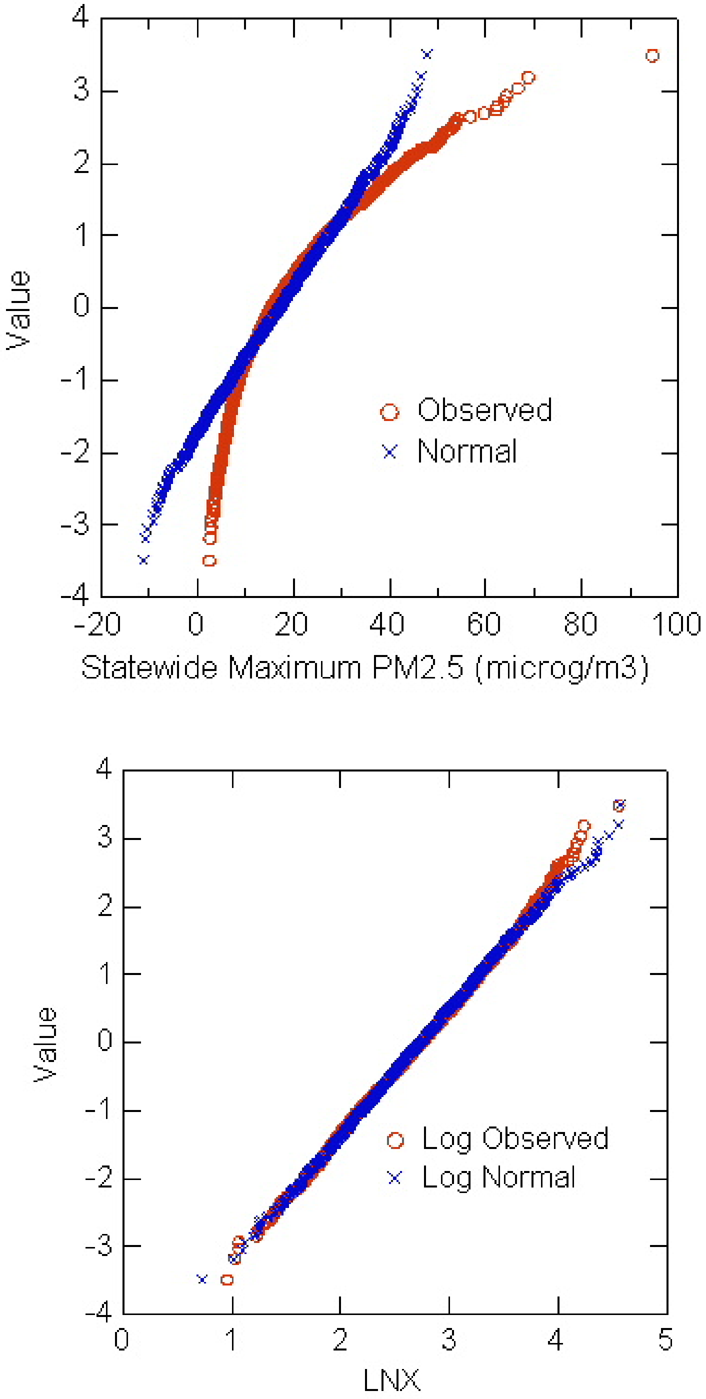

Figure A2. Probability plots for statewide maximum daily $PM_{2.5}$ concentrations and normal distributions given same mean and standard deviation. Top panel: Unmodified statewide $PM_{2.5}$ concentrations. Bottom panel: Statewide $PM_{2.5}$ concentrations transformed by the natural log function. The log-transformed $PM_{2.5}$ data best approximates a normal distribution.

Maryland $PM_{2.5}$ 2000-2005 Basic Statistical Measures		
Statistical Measure	**Statewide**	**Old Town**
N	2107	1918
Median	15.5	14.7
Mean	17.7	16.7
Standard Deviation	9.8	9.2
Skewness	1.49	1.19
Standard Error of Skewness (SES)	0.05	0.06
Kurtosis	3.78	1.67
Standard Error of Kurtosis (SEK)	0.11	0.11
Skewness/SES	29.8	19.8
Kurtosis/SEK	34.4	15.2

Table A2. Statistical summary for statewide daily maximum $PM_{2.5}$ and for the monitor at Old Town in Baltimore.

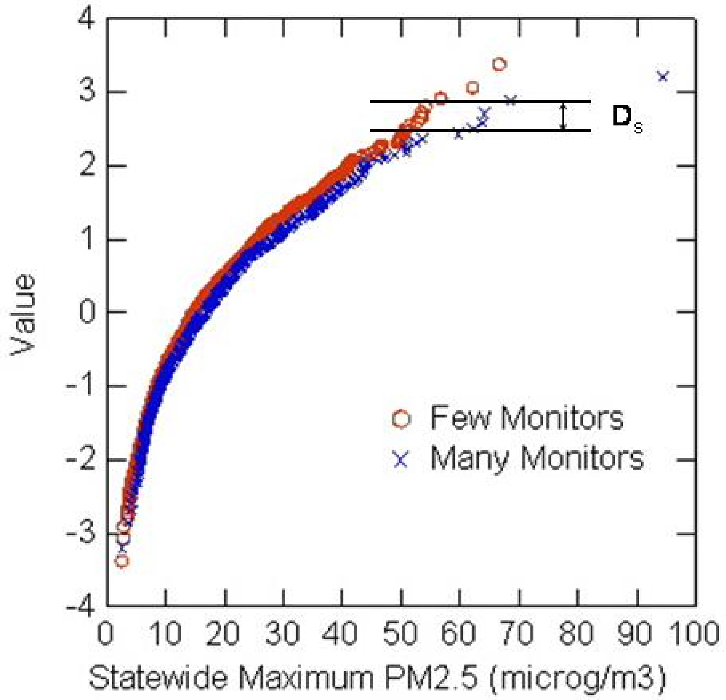

Figure A3. Example of the D$_s$ measure used in the K-S two sample test.

Footnotes

1. The conventional moments based measure of symmetry, the skewness coefficient, is based on the cube of the difference between any data point and the mean. As a result, the measure is criticized as neither statistically robust nor resistant. The measure is, in particular, sensitive to the influence of outliers due to the cubic function. An alternative measure of symmetry that is more resistant is the Yule-Kendall Index:

$$\gamma_{YK} = (q_{0.25} - 2^* q_{0.25} + q_{0.25})/IQR$$

Where q_n is the nth percentile of the data and IQR (inter-quartile range) is the difference between the 75th and 25th percentile.

In this case, $\gamma_{YK} = 11.9$ which corroborates the skewness coefficient results above that concluded that the sample distribution was asymmetric.

References

Wilks, D.S., 2006: *Statistical Methods in the Atmospheric Sciences* (2nd Ed.), Elsevier Press.

SYSTAT, 2002: *SYSTAT 10.2, Statistics II*, SYSTAT Software, Inc, www.systat.com.

Appendix B: FRM Stations

Rural Monitors AQS Code	Locations	State
240430009	Hagerstown	MD
420990301	Little Buffalo SP	PA
420270100	PSU Arboretum	PA
511390004	Luray	VA
540890001	Keeney Knob	WV

Maryland Monitors

240030014	Davidsonville
240251001	Edgewood
240053001	Essex
240150003	Fair Hill
245100035	FMC-Curtis Bay
245100006	North East Police
245100007	North West Police
245100008	South East Police (6/01 - current)
245100049	Westport Elem
240031003	Glen Burnie
240430009	Hagerstown
245100040	Old Town
240051007	Padonia
240032002	Riviera Beach
240313001	Rockville
240330030	HU-Beltsville (8/04 > current)
240338003	Prince Geo. Equest. (5/02 - current)
240330002	Greenbelt GSFC (7/02-4/04)

BCC = Baltimore (Urban) Monitors

240053001	Essex
245100006	North East Police
245100007	North West Police
245100008	South East Police (6/01 - current)
245100035	FMC-Curtis Bay
245100049	Westport Elem
245100040	Old Town

BFA = Baltimore Forecast Area

240053001	Essex
245100006	North East Police
245100007	North West Police
245100008	South East Police (6/01 - current)

245100035	FMC-Curtis Bay
245100049	Westport Elem
245100040	Old Town
240030014	Davidsonville
240251001	Edgewood
240150003	Fair Hill
240031003	Glen Burnie
240051007	Padonia
240032002	Riviera Beach

BMA = Baltimore Metropolitan Area

240053001	Essex
245100006	North East Police
245100007	North West Police
245100008	South East Police (6/01 - current)
245100035	FMC-Curtis Bay
245100049	Westport Elem
245100040	Old Town
240251001	Edgewood
240150003	Fair Hill
240031003	Glen Burnie
240051007	Padonia
240032002	Riviera Beach

DCSUB = Washington DC Suburban

240030014	Davidsonville
240313001	Rockville
240330030	HU-Beltsville (8/04 > current)
240338003	Prince Geo. Equest. (5/02 - current)
240330002	Greenbelt GSFC (7/02-4/04)

MDSUB = Maryland Suburban

240030014	Davidsonville
240313001	Rockville
240330030	HU-Beltsville (8/04 > current)
240338003	Prince Geo. Equest. (5/02 - current)
240330002	Greenbelt GSFC (7/02-4/04)
240251001	Edgewood
240150003	Fair Hill
240051007	Padonia
240032002	Riviera Beach
240031003	Glen Burnie

Appendix C: Location of Selected Maryland FRM Stations

This document is in Power Point format and can be accessed at:
http://www.meteo.psu.edu/~wfryan/mde/frm-monitors.ppt

Appendix D: Episode Selection

Episodes Selected

January 12-15, 2001
June 26-30, 2001
August 5-10, 2001
July 18-22, 2002
February 19-21, 2003
June 25-30, 2003
October 8-10, 2003
July 20-22, 2003
August 11-14, 2005

Criteria:

1. No more than 10 episodes in initial selection.
2. Episode spans ≥ 3 days.
3. Episode days must be within the 90th percentile of the maximum and mean $PM_{2.5}$ distributions statewide.
4. Episodes do not include major (fireworks) holidays of New Years and July 4th.
5. Single monitor Code Orange peak concentrations must occur on at least 2 days during episode.
6. More than 2 monitors must exceed the Code Orange threshold during the episode.

Discussion of Criteria

Criteria 1

A full analysis of multi-day pollution episodes are time consuming. Criteria 1 sets a limit on the number of episodes that is proportional to the effort that can be applied. In this case, nine are selected. As is often the case, full data is sometimes not available to analyze each possible episode so that the final number of episodes analyzed will likely be somewhat smaller - in the range of 7-8.

Criteria 2

As will be noted in more detail in the final report, the bulk of all high $PM_{2.5}$ episodes occur in multi-day episodes. This reflects, in part, the dependence of $PM_{2.5}$ on meteorological conditions. In addition, single day “spikes” in $PM_{2.5}$ concentrations can often be due to local scales effects that are difficult to analyze at the resolution available from archived materials. This also helps to remove cases that are dominated by mainly local scale effects. Longer time scale events can be influenced by synoptic scale (2-5 day) weather patterns that are well resolved by archived weather data. Finally, making the episodes extend at least three days makes sure that at least one large sampling frequency day (every third day is a large sample observation) is included. This is particularly true in Maryland as all the daily monitors are grouped close to center city Baltimore and may not always reflect regional conditions.

Criteria 3

The days in the selected episodes must be within the 90th percentile of the maximum and mean concentrations statewide. Because of the differences in sampling frequency, this criteria is relaxed for maximum concentrations so that if one day within an episode does not reach the 90th percentile but is bounded on both sides by cases which do reach the criteria, the episode is still considered. For example, if July 17, 19, 20 and 21 are above the 90th percentile, and the 18th is not, the episode is considered to extend from July 17-21 as a 4 day episode. For the episodes selected above, 37 of 39 days were within the 90th percentile of the mean statewide concentrations.

Criteria 4

Some of the highest $PM_{2.5}$ cases occur on days of fireworks displays (December 31-January 1, July 4). Although multi-day episodes may still occur that include one of these days and, therefore, not totally influenced by fireworks, it is difficult to separate the different effects and so these cases have been excluded.

Criteria 5-6

A fairly large (~ 16) set of episodes met Criteria 1-4, so that Criteria 5-6 were added to limit the number of episodes. Both Criteria 5 and 6 add a short term severity measure to the selection that is otherwise dominated by longer term, regional effects.