Appendix B: Source Attribution by Receptor-Based Methods

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ABSTRACT

This section summarizes a number of receptor model results for rural and urban sites within and upwind of the MANE-VU region. These include results from multivariate mathematical models applied to speciated aerosol data from individual monitoring sites, as well as ensemble trajectory evaluations, applied to help evaluate and interpret the mathematical model results, and to identify the most prominent regional origins of these sources. A number of common source categories were identified, which have discernable impacts on average $PM_{2.5}$ mass concentrations and visibility impairment at most Northeastern monitoring sites. These include:

Windblown Dust: a minor contributor to average fine mass, but clearly identified at all sites, with highest short term impacts often associated with Sahara dust transport.

Sea Salt: a minor contributor to fine mass, but clearly identified at coastal and near coastal sites. It can have significant visibility impacts at coastal sites like Acadia and Brigantine on the best visibility days.

Oil Burning: a minor contributor to fine mass, but clearly identified at many MANE-VU sites, especially sites within and downwind of the Northeast urban corridor.

Ammonium Nitrate: a small to moderate contributor to average fine mass, with regional influences at rural sites from upwind agricultural ammonia-emitting areas, and significant local source contributions in urban areas.

Wood Smoke: a small to moderate contributor to average fine mass, with contributions typically higher in rural areas than urban areas, winter peaks in northern areas from residential wood burning, and occasional large summer impacts at all sites from wildfires.

Motor Vehicles and Secondary Organics: a moderate to large contributor to average fine mass, with discernable influence from both gasoline and diesel vehicles in urban areas. At forested rural sites, biogenic organics are likely a more important contributor.

Coal Burning: (including primary aerosol and secondary aerosol formation): the largest mass-contributing and visibility-impairing source category at most sites, with contributions primarily from utility and industrial sources in western MANE-VU, northern VISTAS and the Midwest RPO planning regions.

Appendix B: Source Attribution by Receptor-Based Methods

Emissions-based air quality models begin with emissions inventories and act on them in a "forward" direction with atmospheric physical and chemical process to predict downwind concentrations at multiple "receptor locations." Once validated by comparison to ambient measurement data, these models can be used for apportioning ambient pollutant concentrations to specific sources, as well as for evaluating potential effects of future changes in emissions or meteorology. Receptor-based models begin with ambient measurement data at one or more receptor locations and work "backward" to identify sources contributing to historical ambient pollutant concentrations at the receptor locations. Receptor models aren't usually used to predict effects of future emissions changes, but can be applied to long historical records, providing a long-term "climatological" indication of past source-receptor relationships and to evaluate the effects of historical emissions changes, thus providing a valuable complement to emission-based models for determining effective future emissions control strategies.

Two general categories of receptor methods include multivariate mathematical models and ensemble backward trajectory techniques. Multivariate models, such as Chemical Mass Balance (CMB), Principal Component Analysis (PCA), Positive Matrix Factorization (PMF) and UNMIX, are typically driven by the variations in multiple species data in multiple observations at one or more sites. Ensemble trajectory techniques, such as Cluster Analysis, Potential Source Contribution Function (PSCF) and Residence Time Analysis (RTA) are driven by large numbers of backward air trajectory calculations at one or more sites, which are sorted and/or aggregated as a function of measured or modeled pollutant concentrations at the receptor, or grouped as a function of similar upwind locations.

The CMB multivariate model requires input of measured source composition profiles, while PCA, PMF and UNMIX develop the source profiles during model operations. An advantage of CMB is that the identified source contributions are unambiguous, since the named sources are included as model input. A disadvantage is the required assumption that the emissions source profiles are accurate and include all the relevant emissions source influences. PCA, PMF and UNMIX have the advantage that the source profiles need not be known in advance, and the disadvantage that the resulting "sources" require subjective interpretation by the modelers to identify what these source influences actually represent. Resulting sources may represent an individual point source, source category, source region, meteorological influence, measurement or data processing artifacts or various combinations of the above. An additional characteristic of these multivariate models is that the resulting sources have fixed or constant chemical compositions. This presents a particular problem for sources emitting a combination of primary aerosol species (emitted directly in particle phase) and secondary aerosol precursors (converting from gas to particle phase in the atmosphere). The problem is not so much the mix of primary and secondary species, but rather the variable rate of secondary aerosol formation, which can result in a variable "virtual source profile" at downwind receptor locations. Consequently, models like PMF and UNMIX may divide a source influence into 2 or more "source components", each with constant but different chemical compositions, representing different degrees of secondary aerosol formation.

Because of these complexities in source interpretation, and because the multivariate models typically rely entirely on the measured chemical compositions without regard to meteorology, the ensemble trajectory techniques (which rely on meteorology-only) are especially useful for interpreting and/or evaluating the multivariate model results.

B.1. Multivariate Mathematical Results Relevant to the MANE-VU Region

B.1.1. Introduction

This section summarizes source apportionment studies conducted for sites within the Mid-Atlantic/Northeast Visibility Union (MANE-VU) region, and a few neighboring sites within the up-wind or down-wind influence area of MANE-VU. The intent is to provide a general overview of the source categories identified in these various studies, and to provide an indication of their relative contributions to fine mass concentration and visibility impairment in the MANE-VU region. For additional detail, the reader is encouraged to consult the original references, as well as the trajectory interpretations in Section B.2 of this report.

Many of the results presented here were from an exploratory "Phase 1" $PM_{2.5}$ source apportionment study previously sponsored by MANE-VU and the Midwest RPO (Coutant et al. 2002) which was also extensively used in a subsequent U.S. Environmental Protection Agency-sponsored review report (Coutant et al. 2003). These findings were also referenced in a U.S. Environmental Protection Agency Report (Air Quality Data Analysis Technical Support Document for the Proposed Interstate Air Quality Rule, January 2004) and in a recent Clean Air Act Advisory, Science and Technology Subcommittee report (Synthesis of Air Quality Assessments: Identification of Important Contributors to Ozone and PM Nonattainment, and Regional Haze, October 15, 2004). Other studies and peer reviewed journal articles are also cited in this summary and referenced at the end of the document.

B.1.2. Background

A number of mathematical receptor models and ensemble trajectory analysis techniques have commonly been used in the studies summarized below in order to apportion the $PM_{2.5}$ mass concentrations (and, hence, the light extinction values) into components attributable to the most significant source categories, and to indicate the most common origins of these sources. The mathematical models include PMF (Positive Matrix Factorization), UNMIX, APCA (Absolute Principal Component Analysis), and CMB (Chemical Mass Balance). Some studies also used these tools in conjunction with trajectory transport analysis such as PSCF (Positive Source Contribution Function), RTA (Residence Time Analysis), Cluster Analysis and other ensemble back-trajectory techniques, to assist in interpreting and identifying primary locations of these sources. An extensive literature explaining these ensemble trajectory techniques is available, but these explanations are not referenced in this summary. A recently developed "Combined Aerosol Trajectory Tool" (CATT) described by Husar et al. (2004) includes options to calculate a wide range of ensemble trajectory metrics for all aerosol species data, and any "user-submitted" receptor model results derived from these data for any or all IMPROVE and/or EPA STN sites

The main goal of the studies summarized here is to describe and quantify the major source categories contributing to the observed concentrations of fine particulate matter in the atmosphere. This is achieved by mathematically modeling the day to day variation in the $PM_{2.5}$ mass concentration (and 10 to 30 constituent species) as a mixture arriving from the major sources to the receptor point. At least initially, it is assumed that each source contributing to the $PM_{2.5}$ concentration contributes to the observed species concentrations with approximately fixed ratios. The list of the ratios of the species mass to the total mass contributed by the source is referred to as a source profile. Sources can be identified through these profiles, the associated time series (the day-by-day variations in the sources mass contribution), and the magnitude of the source. Further evaluation of the results with local surface meteorological data (for local source influences) and

back trajectory techniques (for more distant source influences) provides additional insights and often leads to refinements or revisions in the original source interpretations.

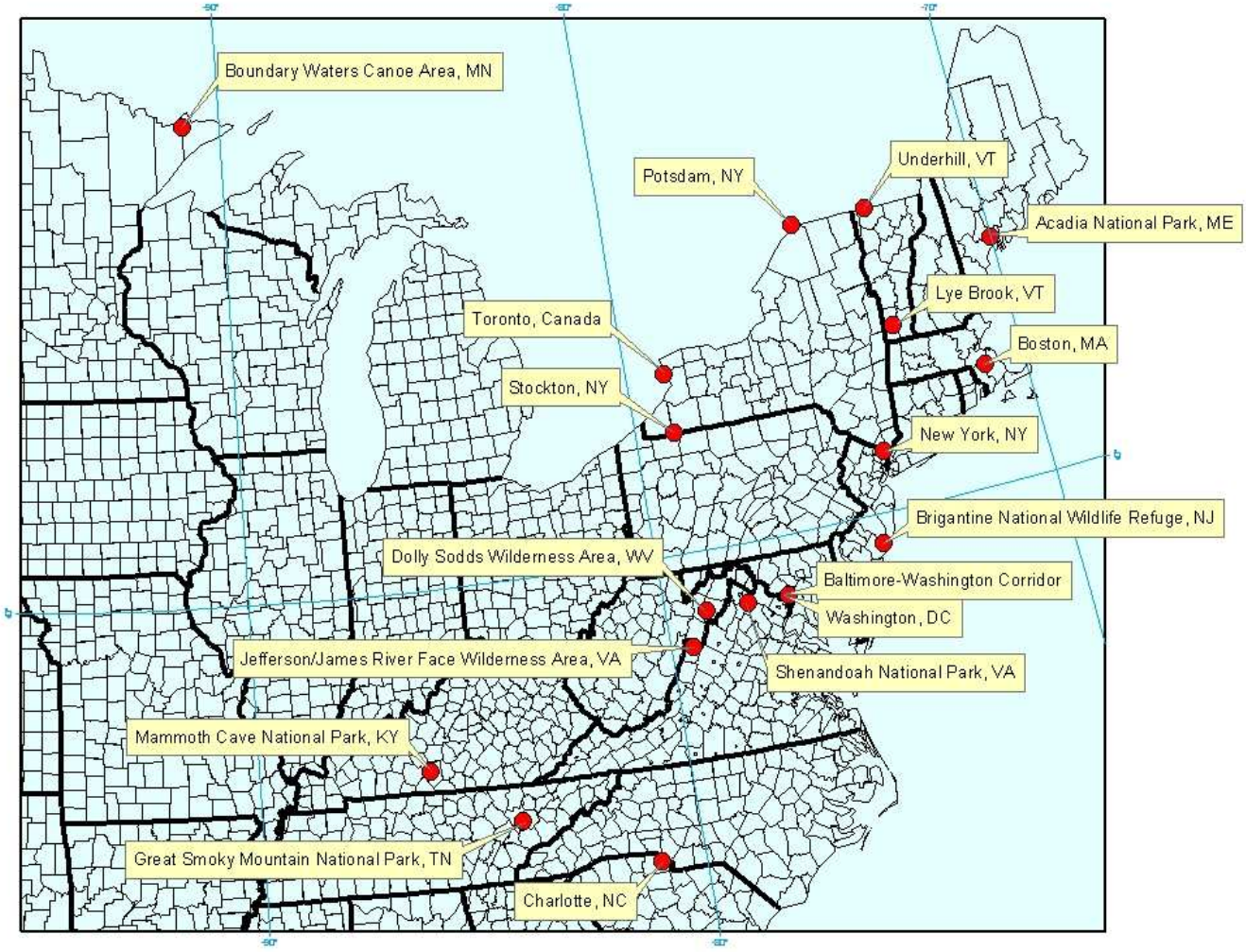
Typically, the studies included in this summary used quality assured and validated data, conducted trends analyses for data consistency, and considered additional meteorological and transport factors, emissions inventory implications and monitoring site specifics to complement the source apportionment results. For any given site, and overall regionally, the results are generally consistent when comparable data sets were used. However, methodologies vary considerably among studies. In addition, the primary goals of apportioning total $PM_{2.5}$ or visibility are quite different. Hence, there are difficulties with making direct comparisons. For example, the modeled source profiles typically include mixtures of several different aerosol species with different extinction efficiencies and/or hygroscopic growth functions. Several of the reviewed studies have included estimates of source contributions to $PM_{2.5}$ mass on best 20% and worst 20% visibility days, but this does not necessarily reflect the visibility impacts of the sources on these days, since sulfates have a much larger impact on visibility than the same mass of the other pollutants.

In this summary, to provide consistency and direct comparability, the data presented are the source apportioned $PM_{2.5}$ mass (and percentage of $PM_{2.5}$ mass). Quoting from the recent Clean Air Act Advisory, Science and Technology Subcommittee report (Synthesis of Air Quality Assessments: Identification of Important Contributors to Ozone and PM Nonattainment, and Regional Haze, dated October 15, 2004):

> "Because regional haze is linked so closely to $PM_{2.5}$, few source apportionment studies look at haze impacts separately. Nevertheless, some observations about the relationship between $PM_{2.5}$ and haze are appropriate. Light extinction is a function of the particular components of $PM_{2.5}$ as well as relative humidity. While the sources responsible for $PM_{2.5}$ are the same as those for regional haze, the relative importance of those sources varies somewhat in relation to their propensity to scatter light (e.g., sulfate contribution to regional haze is greater than to fine particle mass). Work by IMPROVE over the past decades has shown that light extinction almost everywhere across the country is primarily due to sulfate; organic carbon is next most important almost everywhere. Regional differences become important in looking at relative importance of the other species; in the west, crustal material and coarse mass are third in importance. In the east, nitrate is the third-most important, followed by crustal material. However, because the general importance of regional haze species is the same (for most of the country) as that for $PM_{2.5}$, and because impaired visibility has adverse effects on public welfare in both urban and rural areas, control measure priorities for reducing human health and visibility effects of $PM_{2.5}$ are strongly convergent."

This compilation summarizes several reports and articles focusing specifically on source apportionment results in the MANE-VU region and its surroundings. A more detailed review of articles, reports and recent presentations on the nation as a whole can be found in Coutant et al. (2003). In addition to those, the summary below adds a few new articles for the MANE-VU region. Figure B-1 below shows the locations of all sites referred to in this summary. Tables provided throughout this summary reference the original study, period of the data and analytical technique used, mean mass measured, and apportioned mass into source types by mass and percent of the total.

Figure B-1. Locations of the Monitoring Sites Reviewed in This Report



A few receptor sites were studied repeatedly, such as Underhill (Vermont), Brigantine (New Jersey), and Washington (DC). The monitoring data were primarily taken from the IMPROVE and STN networks. NESCAUM (2003) provides a summary and comparison between the sampling techniques employed in data resulting from these networks. Typically, more detailed measurement data leads to more detailed source characterization. For example, inclusion of the thermally stratified TOR carbon fractions (available for IMPROVE sites only), has allowed for separate detection of gasoline and diesel motor vehicle sources – especially in urban areas like Seattle (Maykut et al., 2003), Toronto (Poirot and Brook, 2004), Atlanta and Washington DC (Kim and Hopke, 2003, 2004), and at the "near urban" Brigantine site (Kim and Hopke, 2004). For the recent Toronto studies, the detailed aerosol measurements included additional species including high quality NH4 and a number of organic ions (oxalate, succinate, etc.), which allowed refinement of a secondary sulfate source into neutral and acidic components, with a substantial "secondary organic aerosol" component associated with the acidic sulfates (Lee et al, 2003, Poirot and Brook, 2004).

The general results from many of the studies were found to be similar as the methodologies have become more mature and data sets broader and more comparable, and the collective experience and knowledge of the modeling community advances. Following Coutant (2003) the

sources identified grouped into seven categories: sulfate/coal, secondary organic compounds/mobile, nitrate, biomass burning, industrial, crustal and salt, and other/not identified.

Except in a few rare cases, where a local source of sulfate is known, "sulfate/coal" was identified as regional secondary transport of sulfate primarily attributable to coal-fired power plants in the 'Midwest" (indicated by presence of S and Se). Some studies found a single large "sulfate" or "coal" source influence, accounting for high fractions of both total Se (primary) and SO_4 (secondary) aerosol concentrations. Several other studies tended to split an overall coal burning influence into two "primary" and "secondary" components, each of which have constant compositions, but mixed in different proportions on different sample days. In cases where the analysis was based on longer-term (5-10 year) historical records, the sulfate/coal sources typically showed reductions over time.

A large "secondary organic matter/mobile" source was indicated by the presence of OC, EC and sometimes a small fraction of crustal elements (like Fe, Ca, and Si which may be associated with road dust) was also a major source category for nearly all sites. Generally, the sources of carbonaceous aerosols have not been clearly identified in many of these studies, especially at rural sites, and initial interpretations of "mobile source" influence have frequently been revised following more detailed analyses to indicate other categories like "biomass combustion". So the general term "secondary organic matter/mobile" employed in this summary should not be taken literally. Only a few studies were able to separate mobile source into gasoline and diesel sources, and the contributions of these specific source categories, even in urban areas, are typically smaller than the large general OC sources such as those identified in the exploratory Coutant et al., 2002 studies.

"Nitrate" was also found to be a significant source (in those studies that included NO_3 as an input variable). Typically, most of the NO_3 tends to break out into a separate general "source" category, assumed to be ammonium nitrate, and the model does not associate this pollutant with the specific combustion, motor vehicle or agricultural sources from which its precursors originate. This may be related to the complex combination of mixed emission sources, temperature and atmospheric chemistry conditions needed for accumulation of ammonium nitrate in the ambient air in the Northeast. The receptor models have more difficulty differentiating between sources of complex secondary pollutants than primary pollutants. In the Eastern US, regional ammonium nitrate concentrations are highest in and immediately downwind of agricultural areas in the northern Midwest. There also appear to be significant local urban sources of nitrate precursors in Northeastern urban areas.

The "biomass burning" category includes residential wood smoke and forest fires indicated by the presence of OC, EC and K. Fireworks emit similar species, and are occasionally included with "wood smoke" sources in receptor model results, unless care is taken to screen out dates (July 3-5) of "obvious fireworks impacts." The size of the biomass burning source varies considerably from site to site, but it is usually higher in rural areas, as expected. Winter residential wood burning impacts can also be substantial in small northeastern villages located in deep mountain valleys like Rutland, VT (Allen et al., 2004).

The industrial source category includes a variety of small sources characterized by elemental carbon and trace metals, such as smelters (presence of Cu, Zn, Mn, As, etc), incinerators (presence of OC, EC, PB, and Zn), oil burning (presence of Ni and V), and in some cases industrial salts. Frequently, the industrial sources are associated with known local sources. Residual oil burning impacts from both industrial and utility sources are especially evident along the East Coast urban corridor.

A "crustal" (dust, soil, etc.) source category is indicated by the presence of Si, Al, Ca, Fe, and Ti. A crustal source category is almost always identified in all receptor modeling studies and sites. In the Northeast, it typically accounts for a small fraction of fine mass, but a relatively large fraction of the trace elements listed above (which are also assumed to result predominantly from soil in the IMPROVE soil formula). Highest dust impacts at rural northeastern sites often result from very long-range transport of African, Asian or SW North American dust storms. Reintrained road dust impacts are indicated in some urban areas.

A "sea salt" source was identified by the presence of Na and Cl. Sea salt is consistently identified at Northeastern coastal sites (Acadia, Brigantine) and at near-coastal sites (NYC, Washington DC, Shenandoah, Dolly Sods, Gt Smokey Mtns.). The modeled sea salt compositions at these sites typically exhibit signs of chemical aging, with loss of chloride ion content and excess nitrate and sulfate, compared to fresh marine emissions. A curious feature of the sea salt sources identified (at 6 sites) in the Coutant (2002) studies was that it that it showed a significant increase over time at all sites. Road salt sources, often mixed with crustal elements, are evident at several northern inland urban sites.

B.1.3. Site Summaries

The following summaries provide a brief description of the monitoring site, period of the data used for the analysis, analysis technique(s) used, mean $PM_{2.5}$ mass, source apportioned $PM_{2.5}$ mass according to the identified source types and fractions of the total mass (in parenthesis). The source of the information is referenced. In addition, where available, additional information is provided regarding the major source types and their associated source regions as indicated in the studies summarized. In the tables, source types contributing greater than 20 percent but less than 40 percent of the total mass are shaded yellow; sources contributing greater than 40 percent are shaded pink. In order to present a concise overview, some sources were renamed and/or combined. Some concentration values were calculated based on reported percentages. The sum of the sources may not equal the total due to rounding and/or modeling limitations.

Table B-1. Acadia National Park, ME

Reference	Data Period (Analysis Method)	Total Mass (ug/m^3) (% Mass)	Sulfate/ Coal	Nitrate	Mobile	Biomass Burning	Industrial		Crustal and Salt		Miscell.
			Regional Secondary Transport	General	Secondary OC /General	Wood Smoke	Oil /Diesel Combustion	Other /General	Crustal /Dirt /Soil	Sea Salt	Not Identified
Coutant et al. 2002	1988-1999 (PMF)	7.5 (100)	2.3 (30.7)		3.9 (52.0)	0.3 (4.0)	0.4 (5.3)	0.0	0.1 (1.3)	0.4 (5.3)	0.1 (1.3)

The Acadia National Park IMPROVE site (44 N, 68 W) is located near the center of Mount Desert Island, at an elevation of 150 meters, on the southern slope of McFarland Hill. Upwind of the receptor, there are four small towns with residents that have home heating needs. Park visitation is three million people/year, with more than two-thirds visiting during June-September, creating high volume vehicle traffic. More than 50 large cruise ships visit Bar Harbor during summer and fall, and the number of cruise ships is increasing. $PM_{2.5}$ concentrations at this site tend to be low, averaging 7.5 μg/m3. Initial results from Coutant et al. (2002) indicated that mobile sources dominate at this site, followed by the regional secondary sulfate. However, the reconstructed masses of these modeled sources are inconsistent with the model-apportioned masses, suggesting

that the mobile source contribution has been overestimated while the other sources contributions are underestimated.

Table B-2. Lye Brook Wilderness, VT

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate/ Coal		Nitrate	Mobile	Biomass Burning	Industrial			Crustal and Salt		
			Primary Coal	2ndary Coal	General	2ndary OC /General	Wood Smoke	Oil Burning	Smelter	Incin-erator	Crustal /Dirt /Soil Hi Ca	Crustal /Dirt /Soil Low Ca	Road Salt
Coutant et al. 2002	1991-1999 (PMF)	7.6 (100)	0.36 (5.2)	3.2 (46.3)			2.4 (35.1)	0.38 (5.5)	0.46 (6.6)	0.19 (2.8)	0.13 (1.9)	0.37 (5.3)	0.07 (1)

The Lye Brook IMPROVE site (43 N, 73 W) is located in Southwestern VT at an elevation of 1010 meters. The site is surrounded by mountainous and forested areas and these areas are sparsely populated for about 20 miles in all directions from the site. The area has some home heating activity (in nearby valleys), but no industrial sources of pollution in the vicinity. This is a popular tourist region with substantial vehicle traffic. Coutant et al. (2002) estimated that regional secondary sulfate was the most important source type, followed by biomass burning/wood smoke.

Table B-3. Underhill, VT

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate /Coal	Nitrate	Mobile	Biomass Burning	Industrial				Crustal and Salt			Miscell.
			Regional Secondary Transport	General	General	Wood Smoke	Smelter	Incinerator	Oil/ Diesel Combustion	Other /General	Crustal /Dirt /Soil	Road Salt	Sea Salt	Not Identified
Polissar et al. 2001	1988-1995 (PMF & PSCF)	6.4 (100)	3.7 (57.8)			1.0 (15.6)	0.2 (3.1)		0.4 (6.3)	0.6 (9.4)	0.3 (4.7)	0.1 (1.6)		0.3 (4.7)
Poirot et al. 2001	1988-1995 (UNMIX&RTA)	8.4 (100)	5.8 (69.0)			1.3 (15.5)	0.1 (1.2)		0.7 (8.3)	0.3 (3.6)	0.2 (2.4)			
Poirot et al. 2001	1988-1995 (PMF & UNMIX)	7.9 (100)	4.8 (60.8)			1.2 (15.2)	0.1 (1.3)		0.6 (7.6)	0.9 (11.4)	0.3 (3.8)	0.0		
Song et al. 2001	1988-1995 (PMF)	8.0 (100)	4.9 (61.3)			1.2 (15.0)	0.2 (2.5)	0.6 (7.5)	0.5 (6.3)	0.2 (2.5)	0.3 (3.8)	0.0	0.1 (1.3)	
Gao et al. 2004	2001-2003 (PMF & PSCF)	5.5 (100)	2.6 (47)	0.6 (11)		1.1 (20)			0.1 (1)	0.5 (9)	0.2 (4)	0.4 (7)		
Gao et al. 2004	2001-2003 (best visibility days) (PMF & PSCF)		(47)	(8)		(25)			(1)		(2)	(9)		(8)
Gao et al. 2004	2001-2003 (worst visibility days) (PMF & PSCF)		(80)	(10)		(7)			(3)					

Samples were collected at a remote background site in Underhill, Vermont (45 N, 73 W, elevation 400 m) using the IMPROVE monitoring protocol. The first three studies summarized above (Poirot et al. 2001, Polissar et al. 2001, and Song et al. 2001) used data from the same period but employed different analysis techniques. The last study (Gao et al. 2004) used a more recent data set. Results were very consistent, showing similar chemical composition profiles and temporal variations, providing confidence in the results obtained by the different techniques. The most important source type was found to be regional secondary sulfate, followed by wood smoke. This is a rural northern latitude area with substantial wood burning activities. The effects of oil burning and industrial sources were also found in the area. The analysis of more recent data by Gao et al. (2004) differentiated between two types of sulfur-rich secondary aerosol; in Table B-3 the total of these

two were used. They also separated subsets of the results for the best and worst 20% visibility days. Secondary sulfate was found to be significantly more important during the worst days. Gao et al. also noted a substantial reduction of about 35% in the total fossil fuel (coal + oil) source influence for the 2001-2003 analyses compared to the earlier PMF and UNMIX results based on 1989-95 data.

Table B-4. New York, NY

Reference	Data Period (Analysis Method)	Total Mass (ug/m^3) (% Mass)	Sulfate /Coal	Nitrate	Mobile	Biomass Burning	Industrial		Crustal and Salt		Miscell.
			Regional Secondary Transport	General	Secondary OC /General	General	Oil /Diesel Combustion	Other /General	Crustal /Dirt /Soil	Sea Salt	General
Coutant et al. 2003	2001-2002 (PMF)	16.1 (100)	5.3 (32.9)	4.1 (25.5)	2.5 (15.5)		1.2 (7.5)	1.8 (11.2)	1.0 (6.2)	0.3 (1.9)	
Ito et al. 2004	2001-2002 (APCA & PMF)	15.8 (100)	5.6 (35.4)		2.5 (15.8)		4.2 (26.6)		2.2 (13.9)		
Ito et al. 2004	2001-2002 (APCA & PMF)	16.1 (100)	6.7 (41.6)		6.2 (38.5)		1.8 (11.2)		2.9 (18.0)		
Ito et al. 2004	2001-2002 (APCA & PMF)	15.1 (100)	6.8 (45.0)		5.5 (36.4)		1.8 (11.9)		1.6 (10.6)		

Note: The table summarizes results from four studies of three sites in New York City.

The first and second studies in the table above looked at data from New York Botanical Gardens in the Bronx (an urban Speciation Trends Network site, a Met One sampler). This site is located in the middle of the Bronx (41 N, 74 W), a heavily populated urban area. There are local sources that could potentially have a significant effect on the site. These include mobile emissions, fuel oil (particularly in the winter), two oil-fired power plants, street cleaning, and marine influences. The difference between these two studies is probably attributable to the fact that only the first study distinguished nitrate as a source type.

The third study in the table above looked at I.S. 52 in the Bronx (an urban speciation Trends Network site, R and P sampler) and the fourth study focused on Queens College in Queens (an urban speciation Trends Network site, R and P sampler). These three sites are within six miles of each other.

Results obtained from the four studies summarized above are highly consistent. All four studies found secondary sulfate the most important source type. The studies concluded that the temporal correlation across monitors in NYC varied considerably across individual $PM_{2.5}$ species, indicating that the precision of population exposure estimates for specific elements can vary depending on the species. However, as expected, the constituents of secondary aerosols showed consistently high temporal correlations across the monitors. Other $PM_{2.5}$ species that are constituents of major source types (soil, traffic, oil burning, and incineration) showed low to high correlation (Ito et al., 2004).

Table B-5. Brigantine Wilderness, NJ

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate /Coal	Nitrate	Mobile		Biomass Burning	Industrial			Crustal and Salt		Miscell.
			Regional Secondary Transport	General	Secondary OC /General		Wood Smoke	Incin-erator	Oil /Diesel Combustion	Other /General	Crustal /Dirt /Soil	Sea Salt	Not Identified
					Diesel	Gasoline							
Song et al. 2001	1992-1999 (PMF)	11.4 (100)	7.1 (62.3)	0.9 (7.9)	0.6 (5.3)		0.9 (7.9)	0.5 (4.4)	0.2 (1.8)		0.1 (0.9)	0.9 (7.9)	
Coutant et al. 2002	1992-1999 (PMF)	11.6 (100)	5.7 (49.1)		3.5 (30.2)				1.3 (11.2)	0.3 (2.6)	0.1 (0.9)	0.7 (6.0)	0.0
Lee et al. 2003	1991-1999 (PMF)	11.4 (100)	7.9 (69.3)		1.8 (15.8)			0.2 (1.8)	0.3 (2.6)		0.2 (1.8)	0.9 (7.9)	
Poirot & Wishinski 2002	1991-1999 (UNMIX & RTA)	10.7 (100)	5.3 (50)	0.8 (7)	1.0 (9.2)	1.4 (12.7)	0.2 (1.9)		0.4 (3.9)	0.4 (3.8)	0.5 (4.6)	0.7 (7.0	
Poirot & Wishinski 2002	1991-1999 (Best Visibility Days) (UNMIX & RTA)	(% mass on 20% days)	(29)	(4.3)	(12.1)	(13.5)	(3.4)		(6.3)	(5.6)	(6.0)	(20.1)	
Poirot & Wishinski 2002	1991-1999 (Worst Visibility Days) (UNMIX & RTA)	(% mass on 20% days)	(60.9)	(6.2)	(5.4)	(13.2)	(1.1)		(2.3)	(3.5)	(3.7)	(3.5)	
Kim & Hopke 2004	1992-2001 (PMF&PSCF)	11.2 (100)	6.7 (59.8)	0.4 (3.6)	0.3 (2.7)	1.4 (12.5)		0.2 (1.8)	0.1 (0.9)			1.3 (11.6)	

Five studies analyzed samples that were collected at the IMPROVE site located in the Brigantine Wilderness (New Jersey) since 1991. This site is located near the Atlantic Ocean, 12 km northwest of Atlantic City, 90 km southeast of Philadelphia, and 150 km south of New York City. Highways are closely situated to the north, south, and west of the monitoring site. The last study, in contrast to the previous two-carbon-fraction analyses, included eight temperature-resolved carbon fractions. This helped distinguish between the diesel and gasoline mobile source types.

Sulfate-rich secondary aerosols are the largest $PM_{2.5}$ (and hence regional haze) source, consistently accounting about 60% of the mass in all the studies of Brigantine that included high PM days. The Poirot-Wishinski analysis of the 20% best visibility days showed much lower sulfate influence. The Potential Source Contribution Function (PSCF) analysis (Kim and Hopke, 2004) shows the source areas and pathways of sulfate-rich secondary aerosols, including the regional influences of the biogenic as well as anthropogenic secondary aerosol arriving from the Southeast and Midwest. Back-trajectories indicate that the elevated airborne soil impact on Brigantine is likely to be caused by both Asian and Saharan dust storms. The impacts from local sources (mobile, biomass, and industrial) are also seen using PMF results combined with the conditional probability plots.

Table B-6. Baltimore-Washington Corridor

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate /Coal		Nitrate	Mobile	Biomass Burning	Industrial	Crustal and Salt	Miscell.
			Regional Secondary Transport	Local	General	Secondary OC /General	Wood Smoke	Smelter	General	General
Chen et al. 2002	1999-2001 (UNMIX&BT)	13.0 (100)	5.3 (40.8)	0.9 (6.9)	2.0 (15.4)	1.8 (13.8)	1.6 (12.3)	0.2 (1.5)		

From 1999 to 2001, samples were collected at Fort Meade (39 N, 77 W; elevation 46 m), Maryland. Fort Meade is in a suburban area located between Baltimore and Washington. Fort Meade is generally downwind of the Washington, DC area and the highly industrialized Midwest.

The $PM_{2.5}$ at this site is expected to be from both local and regional sources. Measurements over a two year period include eight seasonally representative months.

The authors conclude the predominate source affecting this site is an aged sulfate source more regional in character, resulting from emissions in the Midwest. The aged sulfate moves into Maryland from the north, while the fresh SO_2/sulfate mixture likely originates from proximate urban areas north of Fort Meade during stagnant air conditions. Wintertime wood burning occurs more in rural areas of Virginia and West Virginia, and the mobile-related factors are dominated by traffic emissions on the nearby highways. A small industrial/smelter source comes from the industrial corridor to the northeast of the site.

Chen et al. 2002, indicate summertime $PM_{2.5}$ at Fort Meade is dominated by the regional sulfate source. The local contribution (mobile sources plus local sulfate) increases from less than 30% in summer to more than 60% in winter. Though high $PM_{2.5}$ episodes were observed in both summer and winter, the relative importance of local and regional sources could be very different.

Table B-7. Washington, DC

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate /Coal	Nitrate	Mobile		Biomass Burning		Industrial		Crustal and Salt		Miscell.	
			Regional Secondary Transport	Gen-eral	Secondary OC /General		Wood smoke	Vegeta-tive burning	Incin-erator	Oil /diesel combus-tion	Crustal /Dirt / Soil	Sea salt	Other	Other defined
					Diesel	Gasoline								
Coutant et al. 2002	1989-1999 (PMF)	17.9 (100)	7.5 (41.9)		6.6 (36.9)			0.3 (1.7)		1.8 (10.1)	1.4 (7.8)	0.3 (1.7)		
Coutant et al. 2003	2001-2002 (PMF)	16.7 (100)	7.7 (46.1)	1.2 (7.2)	4.7 (28.1)		1.1 (6.6)				1.5 (9.0)		0.5 (3.0)	Fire works
Song et al. 2001	1988-1999 (PMF)	17.6 (100)	10.0 (56.8)	3.5 (19.9)	1.6 (9.1)				0.9 (5.1)	0.6 (3.4)	0.5 (2.8)	0.6 (3.4)		
Kim and Hopke 2003	1988-1997 (PMF)	17.9 (100)	10.7 (59.8)	1.6 (8.9)	0.4 (2.2)	3.8 (21.2)			0.7 (3.9)	0.4 (2.2)	0.4 (2.2)	0.4 (2.2)		

Samples in the studies summarized above were collected at the McMillan IMPROVE monitoring site in Washington, DC. This site is located (at 39 N, 77 W) near the Potomac River, 2 km southeast of the Lincoln Memorial, 3 km northeast of the Ronald Reagan Washington National Airport, and 30 m above sea level. Highways are closely situated to the north and west of the site.

The total mass measured was relatively high in all four studies. Source apportioned results consistently showed that the most important source type affecting this site was the regional secondary sulfate, followed by the mobile/secondary OC and crustal sources. In the one study where diesel and gasoline sources were differentiated, gasoline dominated the mobile sources (Kim and Hopke, 2003).

Table B-8. Shenandoah National Park, VA

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate /Coal	Nitrate	Mobile	Biomass Burning	Industrial	Crustal and Salt		Miscell.
			Regional Secondary Transport	General	Secondary OC /General	Vegetative Burning	General	Crustal /Dirt /Soil	Sea Salt	Not Identified
Coutant et al. 2002	1988-1999 (PMF)	11.8 (100)	4.5 (38.1)		3.2 (27.1)	3.5 (29.7)		0.2 (1.7)	0.3 (2.5)	0.1 (0.8)

This is an IMPROVE site (39 N, 78 W, 1098 m) surrounded by forested mountain areas located in the Blue Ridge Mountains. This site is located close to Skyline Drive in Shenandoah National Park. This is an elevated site well above the valley, where most local pollutant sources are located. The site is thought to be subject to long range transport of pollutants. This site generally remains above the valley-based inversion layer at night and early morning.

Results obtained at this elevated site showed the dominating effect of regional secondary sulfate sources. Mobile or other secondary OC sources, secondary organics and vegetative burning sources are also important.

Table B-9. Jefferson/James River Face Wilderness Area, VA

Reference	Data Period (Analysis Method)	Total Mass (ug/m^3) (% Mass)	Sulfate/ Coal	Nitrate	Mobile	Biomass Burning	Industrial			Crustal and Salt	Miscell.
			Regional Secondary Transport	Gen-eral	Secondary OC /General	Wood smoke	Incin-erator	Oil /Diesel Combustion	Other /General	Crustal /Dirt /Soil	General
Coutant et al. 2002	1995-1999 (PMF)	14.7 (100)	7.2 (49.0)		3.7 (25.2)	2.2 (15.0)	0.3 (2.0)	0.4 (2.7)	0.5 (3.4)	0.5 (3.4)	

This is an IMPROVE site located at 38 N, 79 W, at an elevation of 280 m, surrounded by a forested area. There is an interstate highway 4 km from the site and several other local roads nearby. There are several mills and some open mining of gravel and sandstone 10 miles from the site. A fair amount of wood burning to heat homes occurs in this area during the winter. As expected, the results at this site showed the strong influence of regional secondary sulfate followed by mobile sources, secondary organics and wood smoke

Table B-10. Dolly Sods Wilderness Area, WV

Reference	Data Period (Analysis Method)	Total Mass (ug/m^3) (% Mass)	Sulfate /Coal	Nitrate	Mobile	Biomass Burning	Industrial		Crustal and Salt		Miscell.
			Regional Secondary Transport	General	Secondary OC /General	Vegetative Burning	Incin-erator	Oil /Diesel Combustion	Crustal /Dirt /Soil	Sea salt	General
Coutant et al. 2002	1992-1999 (PMF)	12.7 (100)	5.0 (39.4)		4.5 (35.4)	0.7 (5.5)	0.2 (1.6)	0.2 (1.6)	0.8 (6.3)	1.2 (9.4)	

This is an IMPROVE site (39 N, 79 W, 1158 m) at a forested mountainous site in the Dolly Sods Wilderness Area. A highway and local paved and unpaved roads are in the vicinity. There are major power plants to the north and northeast within 10-15 km of the site and a quarry charcoal plant at 0-20 km. Results obtained at this rural site showed the dominating effects of regional secondary sulfate sources followed by "mobile sources" or other secondary organics.

Table B-11. Mammoth Cave National Park, KY

Reference	Data Period (Analysis Method)	Total Mass (ug/m^3) (% Mass)	Sulfate /Coal	Nitrate	Mobile	Biomass Burning	Industrial		Crustal and Salt		Miscell.
			Regional Secondary Transport	General	Secondary OC /General	Wood Smoke	Oil /Diesel Combustion	Other /General	Crustal /Dirt / Soil	Road Salt	General
Coutant et al. 2002	1992-1999 (PMF)	16.0 (100)	4.9 (30.6)		6.1 (38.1)	3.0 (18.8)	0.7 (4.4)	0.1 (0.6)	0.8 (5.0)	0.3 (1.9)	

This IMPROVE site (37 N, 86 W, 248 m) is located on the south boundary of the Mammoth Cave National Park, Kentucky. This is a forested and agricultural area with a major highway within

10 km. Various types of agriculture surround the site. Immediately adjacent to the south are hay fields. Some of the farms within 10 miles of the site have small hog operations, providing some local sources of ammonia. There are also two commercial chicken barns near the site. Nearly all of the former gravel roads in the area are, at a minimum, chip-sealed with asphalt. The terrain is on a level ridge-top area adjacent to forested valley/ridge terrain within the park.

This is one of the rare sites included in this summary where the regional secondary sulfate was not identified as the dominant source type. However (as with the Acadia results), several aspects of the Mammoth Cave model results appear illogical and indicate problems with the initial source interpretations, modeling procedures or input data. For example, the largest modeled source, interpreted as "mobile sources/ secondary OC", is composed of less than 5% OC, and the reconstructed source mass totals only 10% of the apportioned source mass. The source's sulfur: sulfate ratio – which should be 1:3 -- is an irrational 40:1. Using sulfur, rather than sulfate ion for defining the source composition would increase its ammonium sulfate fraction from 0.01% to 60% (compared to 4% OC). This source also correlates strongly with the secondary sulfate source, especially after 1994, where the inter-source correlation (R^2) is 0.91. All of the above suggest major problems with the input measurement data, modeling procedures or source interpretation.

Table B-12. Great Smoky Mountains National Park, TN

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate/ Coal	Nitrate	Mobile	Biomass Burning	Industrial		Crustal and Salt		Miscell.
			Regional Secondary Transport	General	Secondary OC /General	Vegetative Burning	Incinerator	Oil /Diesel Combustion	Crustal /Dirt /Soil	Sea Salt	Not Identified
Coutant et al. 2002	1988-1999 (PMF)	13.4 (100)	4.8 (35.8)		6.6 (49.3)	0.7 (5.2)	0.3 (2.2)	0.2 (1.5)	0.6 (4.5)	0.2 (1.5)	0.1 (0.7)

This IMPROVE site (36 N, 84 W, 815 m) is located in the Great Smoky Mountains National Park, Tennessee. The immediate surroundings of the site are forested areas. Within a ten miles distance there is an airport, a moderately-sized residential areas, and an aluminum plant. There are several local roads in the vicinity of the site. Similar to Mammoth Cave, the largest source category is "mobile sources/secondary organics." As with the Mammoth Cave and Acadia results there are inconsistencies with the source profiles and mass apportionment, although a high "secondary organic" biogenic source contribution may provide a more rational interpretation.

Table B-13. Boundary Waters canoe area, MN

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate /Coal	Nitrate	Mobile	Biomass Burning	Industrial		Crustal and Salt		Miscell.
			Regional Secondary Transport	General	Secondary OC /General	Vegetative Burning	Incinerator	Other /General	Crustal /Dirt /Soil	Road Salt	General
Coutant et al. 2002	1991-1999 (PMF)	5.4 (100)	2.4 (44.4)		2.2 (40.7)	0.2 (3.7)	0.2 (3.7)	0.2 (3.7)	0.2 (3.7)	0.1 (1.9)	

This Midwestern IMPROVE site is located at 48 N, 91 W, at 524 m elevation. The immediate vicinity contains forested sites with local paved and unpaved roads. There are several large power plants within 60 miles. Sulfate/Coal and Secondary Organics sources are of similar magnitude here.

Table B-14. Charlotte, NC

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate/ Coal	Nitrate	Mobile	Biomass Burning	Industrial		Crustal and Salt		Miscell.	
			Regional Secondary Transport	General	Secondary OC /General	General	Smelter	Oil /Diesel Combustion	Crustal /Dirt /Soil	Sea Salt	Other	Other Defined
Coutant et al. 2003	2001-2002 (PMF)	16.2 (100)	5.7 (35.2)	1.2 (7.4)	3.9 (24.1)		0.7 (4.3)	1.9 (11.7)	0.6 (3.7)	0.1 (0.6)	0.5 (3.1)	Fire-works

This EPA Trends site is located at 35 N, 81 W, at 230 m, on the campus of Garinger High School in Charlette, NC. The area surrounding the school is primarily residential, but contains some commercial land uses that would be associated with densely populated residential areas (convenience stores, restaurants, and other small businesses) near intersections along the main thoroughfares. The area also contains some light industrial land uses within relatively close proximity. This site is dominated by the secondary sulfate and mobile sources / secondary organics.

Table B-15. Boston, MA

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate /Coal	Nitrate	Mobile	Biomass Burning	Industrial	Crustal and Salt	Miscell.
			Regional Secondary Transport	General	Secondary OC /General	General	Oil /Diesel Combustion	General	Other
Laden et al. 2000	1979-1988	16.5 (100)	8.3 (50.3)		4.8 (29.1)		0.5 (3.0)		2.9 (17.6)

This site was part of the Harvard Six Cities Study (Laden et al., 2000) at a central residential monitoring site in Watertown, Massachusetts. Sulfate and mobile sources / secondary OC account for the majority of fine particle mass.

Table B-16. Potsdam and Stockton, NY

Reference	Data Period (Analysis Method)	Total Mass (ug/m³) (% Mass)	Sulfate /Coal	Nitrate	Mobile	Biomass Burning	Industrial	Crustal and Salt	Miscell.
			Regional Secondary Transport	General	General	Wood Smoke	Smelter	Crustal /Dirt /Soil	Not Identified
Liu et al. 2003	2000-2001 (PMF & PSCF)	10.8 (100)	6.0 (56.0)	1.0 (9.2)		1.0 (8.8)	0.9 (8.2)	1.6 (14.6)	0.3 (3.2)
Liu et al. 2003	2000-2001 (PMF & PSCF)	18.5 (100)	10.4 (56.2)	0.4 (2.2)		0.3 (1.7)	2.8 (15.3)	4.3 (23.9)	0.1 (0.7)

The first site in the table above is Potsdam, located in St. Lawrence county in northern New York near the Canadian border. The second site is Stockton, located in Chautauqua county, about twelve miles south of Fredonia in New York and six miles from the eastern shore of Lake Erie. Daily sampling was conducted during the summers of 2000 and 2001. Compared to IMPROVE methods, the sampling and analysis methods employed here yielded less concentrated sample deposits and poorer representation of some low detection limit species. However analyses were also conducted for a number of specific PAH compounds, providing additional detail to the input data.

On average secondary sulfate sources contribute over 50% to the summertime mass and the authors identify the Ohio River Valley as the primary source region for both sites. Soil source

regions include the agricultural areas from Ohio to Illinois. Wood smoke was mainly from the area surrounding the Great Lakes, particularly the upper Great Lakes. A copper source (indicative of industrial/smelter) in central Ohio was important at Potsdam, while at Stockton, the smelter source area was further east in Ontario trailing into western Quebec. For Potsdam, the main potential source areas for the zinc smelter were in eastern Quebec. For Stockton, the main potential source areas were along the US-Canada border from central Ontario to southern Manitoba. It appears to be influenced by smelters from outside the domain of trajectories such as the facilities at Flin Flon and Thompson, Manitoba. A nickel smelter source was also obtained at Potsdam. The results showed this source most likely included the smelters at Noranda, Quebec and Falconbridge, Ontario.

Table B-17. Toronto, Canada

Reference	Data Period (Analysis Method)	Total Mass (ug/m^3) (% Mass)	Sulfate /Coal: Coal Related + Organic Acids	Nitrate: Ammo-nium Nitrate	Mobile: MV + Road Dust + Road Salt	Biomass Burning: Wood Smoke	Industrial: Smelter	Crustal and Salt: Crustal /Dirt /Soil	Miscell.: Not Identified
Lee et al. 2003	2000-2001 (PMF)	14.0	5.8	5.1	2.5		0.5		
Poirot & Brook 2004	2000-2001 (UNMIX)	14.0 (100)	4.7 (33.6)	4.8 (34.3)	3.1 (22.1)		0.6 (4.3)		
Poirot & Brook 2004	2000-2001 (Average PMF& UNMIX)	14.0 (100)	5.3 (37.9)	4.9 (35.0)	2.8 (20.0)		0.3 (2.1)		
Poirot 2004 pers. com.	2000-2001 (Average PMF& UNMIX)	%Bext Best 20%	(30.6)	(17.4)	(47.2)		4.8		
Poirot 2004 pers.com.	2000-2001 (Average PMF& UNMIX)	%Bext Worst 20%	(43.3)	(44.1)	(10.5)		2.0		

This is a Canadian site located at the University of Toronto in Canada's largest urban area and just off the Northwest corner of the MANE-VU region. The measurement data were similar to those collected in routine IMPROVE and STN networks, but include more detailed measurements on ammonium and several organic anions (oxalate, succinate, etc.). These additional species allowed for more detailed source resolution than for many of the other sites summarized above. PMF and UNMIX modeling were initially conducted independently by the Canadian and US groups respectively, followed by comparison and reanalysis or re-interpretation of the resulting sources. The model results were very similar, with the exception that the PMF results divided a total Motor Vehicle influence into 2 components (MV exhaust + road dust, and MV exhaust + road salt), while the UNMIX results broke a similar total MV influence into Diesel MV, Gasoline MV and Road Dust. Both models also identified 2 "secondary sulfate" sources: one fully neutralized $(NH_4)_2SO_4$ and one acidic (approximately NH_4HSO_4) which also included a large fraction of several organic acids and other secondary organic matter (consistent with the "acid-catalyzed SOA formation mechanism" identified in chamber studies by Jang et al. (2002). A large "secondary nitrate" source, composed of nearly pure NH_4NO_3 was identified and of similar mass magnitude to the combined sulfate + SOA sources.

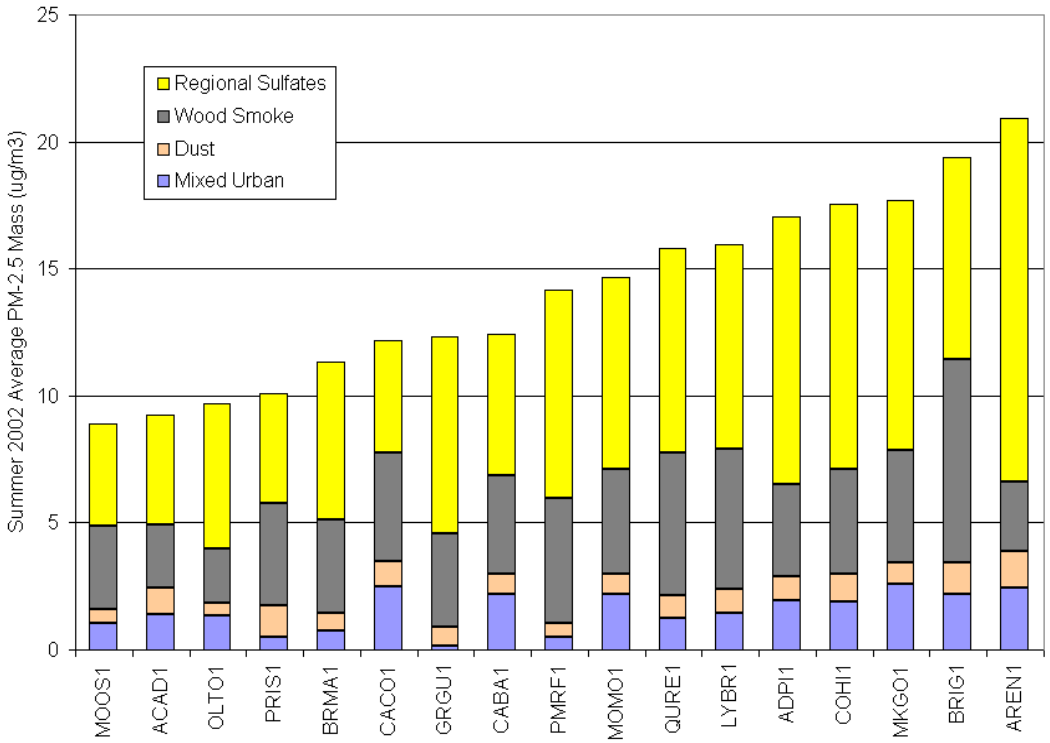
The visibility impacts of the sources were also estimated by applying IMPROVE formulae to the individual source species and adding hygroscopic growth functions for the $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3 fractions, using nearby Toronto airport (hourly) RH data. Local mobile sources were dominant on the cleanest days, and the sulfate and nitrate-related sources were dominant on the haziest days.

Table B-18. MANE-VU Region Multi-Site UNMIX (July and August, 2002)

Reference	Data Period (Analysis Method)	Total Mass (ug/m^3) (% Mass)	Regional Sulfates	Wood Smoke	Mixed Urban	Airborne Dust
Poirot & Husar, 2004	July, August 2002 UNMIX on 17 IMPROVE sites	14.0 (100%	7.4 (53%)	4.1 (29.4%	1.5 (10.9%)	0.9 (6.6%)
Poirot & Husar, 2004	July, August 2002 UNMIX on 43 STN sites	24.6 (100%)	10.1 (41%)	8.0 (32.4%)	4.1 (16.7%)	2.4 (9.9%)

This analysis employed data from all IMPROVE sites and all STN sites in the MANE-VU region for the months of July and August, 2002, in 2 separate UNMIX model runs, one for each network. The input data were constrained to include only major mass-contributing species, selected crustal elements, and trace elements (K and Sr). The objective was to develop a chemical fingerprint for the large Quebec forest fire impacts centered on July 2002, while also accounting for other regional source influences. This required regionally consistent source compositions (the same for all sites in each network), but also yielded variable source contributions for each site and sample date. Results were surprisingly consistent across the MANE-VU sites in the two different networks, and included a large regional sulfate source, a wood smoke source, a (primarily local) "mixed urban" source and a crustal source. The 7/7/02 Quebec fire impacts resulted in the highest 1-day fine mass and light extinction ever recorded across the MANE-VU region, and one of the largest Sahara Dust events ever recorded in the Northeast was detected on the preceding sample day. Averaged over the 2-month summer period, however, the regional sulfate source predominated, but both the wood smoke and crustal sources were proportionately higher than in more "typical" summers. Modeled impacts for the IMPROVE sites are displayed graphically in Figure B-2.

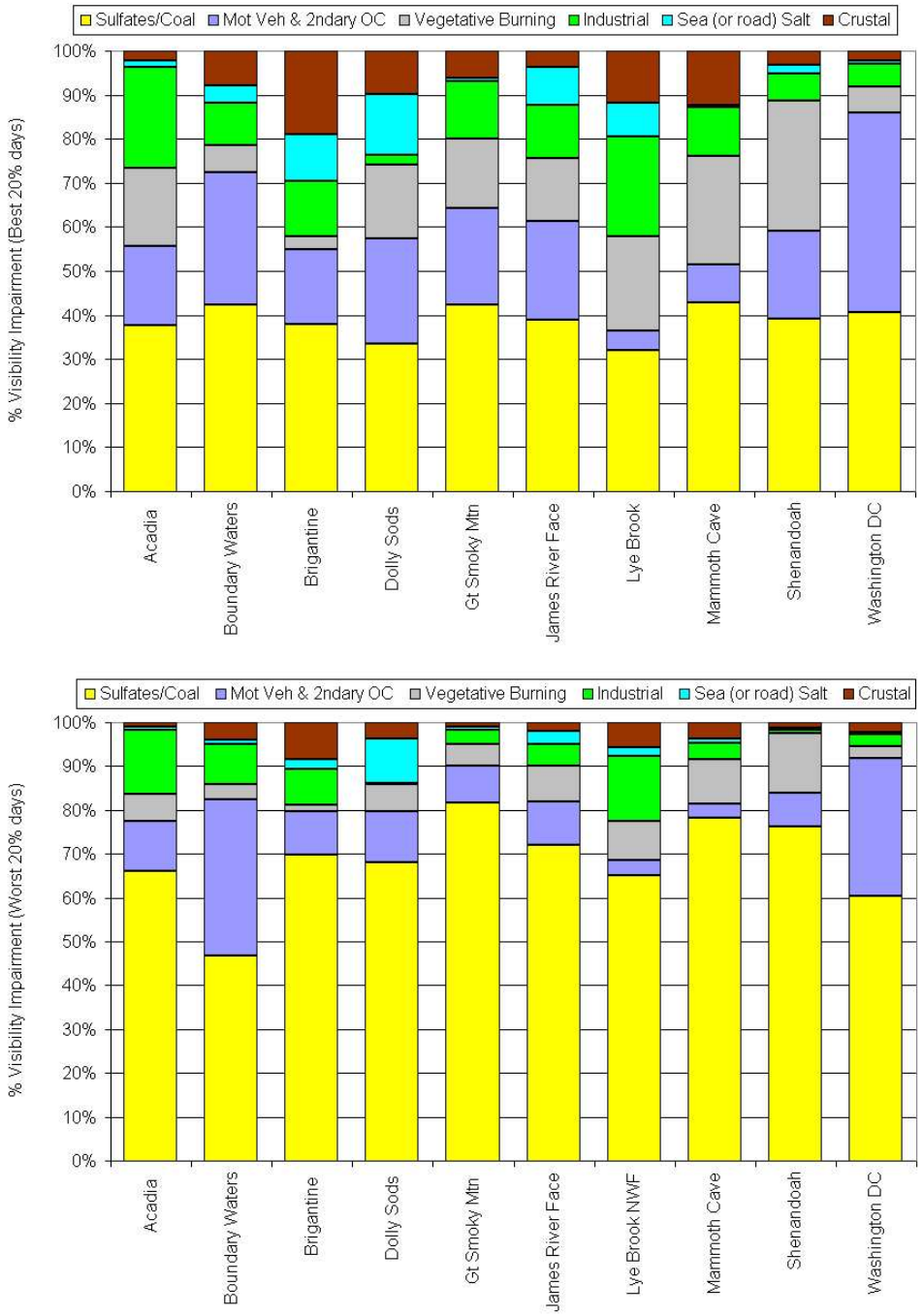
Figure B-2. Modeled Regional Source Impacts for MANE-VU IMPROVE sites, Summer 2002



B.1.4. Estimated Source Visibility Contributions from the Battelle Study

While many of the above studies had a primary objective of apportioning fine mass to source types at selected urban or rural locations, the Battelle analysis (Coutant, 2002) also had the specific objective of estimating source impacts on visibility on best and worst 20% days. This apportionment was estimated by regressing the normalized daily source contributions vs. reconstructed extinction (calculated by IMPROVE formulae), stratified by month (for application of monthly mean f(RH) factors).

Figure B-3. Estimated Visibility Impacts from Battelle PMF sources on IMPROVE sites on Best 20% (top) and Worst 20% (bottom) visibility days (adapted from Coutant, 2002).



Results of this analysis, with sources grouped into 6 summary categories, are presented graphically in Figure B-3. On the best visibility days, regional sulfate sources account for about 30 to 40% of the light extinction, and are usually the largest contributing category (with the exception of the urban Washington DC site, where motor vehicle and secondary OC sources predominate. On the worst visibility days, regional sulfate / coal related sources account for 60 to 80% of the light extinction, with the exception of the most westerly Boundary Waters MN site, which is much less frequently downwind of large SO_2-emitting sources than are the MANE-VU and VISTAS regions.

B.2. Ensemble Trajectory Evaluation of Multivariate Model Results

B.2.1. Background

Trajectory models employ meteorological data to calculate paths of airmass motion over space and time. Commonly employed models include NOAA HY-SPLIT, CAPITA Monte Carlo, and ATAD, which can in turn be driven by gridded wind-field data such as from the ETA, FNL, or MM5 meteorological models, or for the older ATAD model, driven by rawinsonde measurement data. Run in a backward direction from a given starting location and time, they can be considered as a form of "meteorological receptor model" and are commonly employed to evaluate potential origins and transport routes of pollution events observed at ambient monitoring sites.

Compared to more sophisticated photochemical grid models, computational requirements for trajectory calculations are modest, facilitating the generation of long-term (multi-year) trajectory databases. Trajectory databases developed for ambient monitoring sites can then be employed in various "ensemble trajectory techniques" to evaluate common origins and transport of long-term monitoring data, such as the speciated aerosol data collected for many years at IMPROVE sites, or to aid in interpretation and validation of results of multivariate mathematical results generated from these speciated measurement data. Examples of commonly employed ensemble trajectory techniques include: Cluster Analysis, Quantitative Transport Bias Analysis, Residence Time Analysis, and Potential Source Contribution Function. Generally, the above ensemble techniques (and their many variations) involve sorting (screening and/or aggregating) trajectories as a function of resultant receptor concentrations, or sorting receptor concentrations as a function of prior trajectory locations.

The "Combined Aerosol Trajectory Tools" (CATT) is a set of web-based analytical tools that facilitate the application of many various ensemble trajectory techniques for evaluation of speciated aerosol data, multivariate model results derived from these data, or anything else that's been measured at or modeled for ambient monitoring sites in the IMPROVE or EPA Speciation Trends Network. CATT was initially conceived as a tool for trajectory evaluation of the multivariate mathematical model results (PMF & UNMIX) from the Battelle "Phase I" analysis of IMPROVE and CASTNet data[1] from 16 eastern US sites. An initial set of CATT tools was developed in 2003 by the CAPITA group at Washington University, with funding support from the MANE-VU and Midwest RPOs. The CATT tools have since been considerably enhanced over the past year, with additional funding from EPA and the other RPOs, and cooperative technical support from CIRA and NPS. In its current configuration, CATT allows combined aerosol/trajectory analyses of all speciated aerosol data from the IMPROVE and EPA STN networks for their respective periods of record. The aerosol data access is directly linked to VIEWS[2] and the trajectories were provided by NPS (Kristi Gebhart) using the ATAD model. The ATAD trajectories

[1] http://www.marama.org/visibility/SA_report
[2] http://vista.cira.colostate.edu/views

were calculated with 5-day backward duration for 4 start-times/day. The many varied CATT analysis and display options are currently evolving, but are generally described by Husar et al, 2005[3] and in the more recent CATT Illustrated Instruction Manual[4]. The following section presents example applications of several of the CATT tools for evaluation of selected aerosol species data as well as some of the multivariate mathematical model results (summarized in Section B.1 above) derived from those data.

B.2.2. Illustrations of Multivariate Model Source Impacts in MANE-VU Region

Using trajectory analyses of the results of source apportionment studies can identify upwind regions on days when specific source factors predominate. CATT is a tool designed to facilitate these analyses. One of the basic CATT tools allows plotting of Multi-Site, Single Day Trajectories[5] & Aerosol Species Concentrations for all IMPROVE and STN sites, where the aerosol species data symbols can be sized in proportion to concentration, and the trajectories colored (from blue – low to red – high) to emphasize the upwind locations associated with low and high concentrations of the selected species. The Gao et al. (2004) PMF modeling of 2001-2003 IMPROVE data from Underhill, VT and the Poirot & Husar (2004) multi-site UNMIX modeling of July and August 2002 data from all MANE-VU IMPROVE and STN sites identified 3 regional source influences which were interpreted similarly by the two modeling groups, and which showed similar species compositions (for common species), and similar time series and absolute magnitudes (for common dates). These common sources (and their dates of maximum influence in both model runs) included "windblown dust" (7/4/02), "wood smoke" (7/7/02) and "secondary sulfates" (8/12/02). The 7/4/02 dust and 7/7/02 wood smoke have also been identified as resulting from unique large natural emissions from Sahara dust storms and Quebec forest fires respectively, and so represent locational and chemical "tracers of opportunity." Figure B-4 displays the multi-site trajectories for all (Eastern US) IMPROVE and STN sites, with color-weighting to reflect highest concentrations of Al (7/4/02), OC (7/7/02) and SO4 (8/12/02) respectively. It may be noted that the 7/4/02 soil event is also clearly evident in the Ito et al. (2004) APCA and PMF results for several NY City sites. Thus the results from multiple receptor models, modeling groups and MANE-VU receptor sites are consistent with each other, with the back trajectory calculations and with clearly identified "tracers of opportunity."

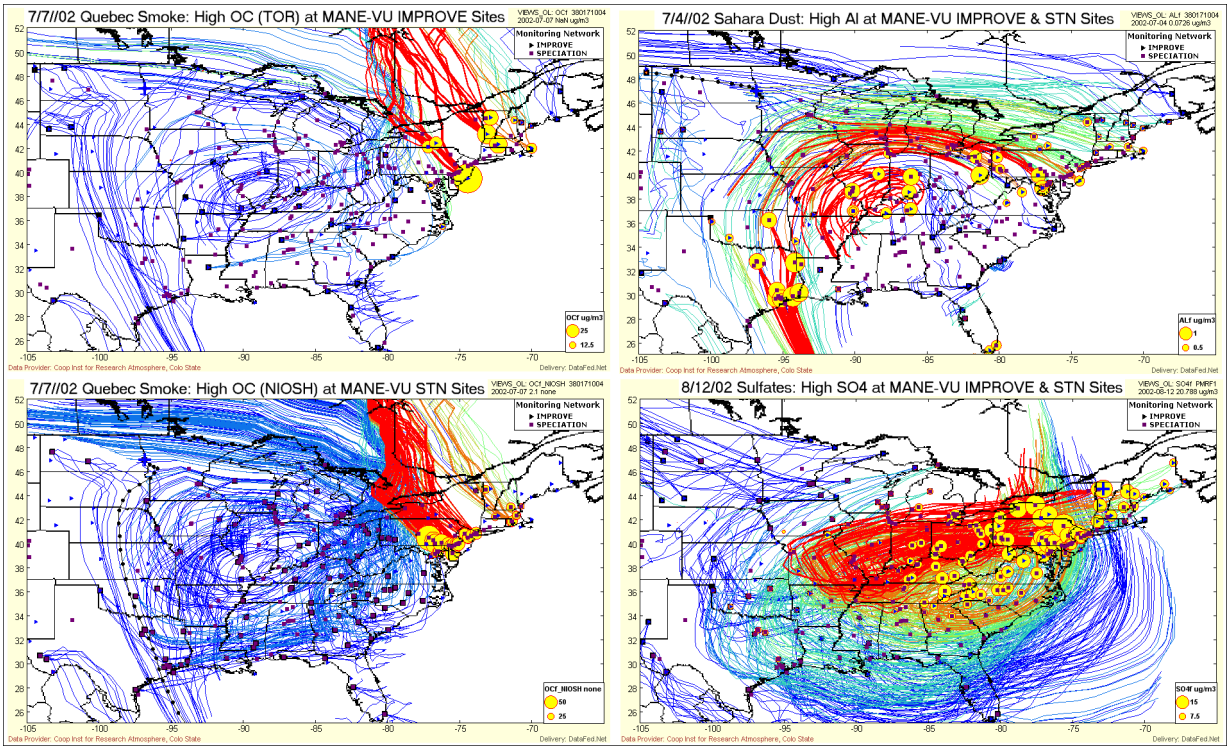
B.2.2.1. Dust

The 7/4/02 "Sahara Dust" event illustrated by highest Aluminum concentrations in Figure B-4 resulted in some of the highest "fine soil" (by IMPROVE formula) concentrations recorded to date at MANE-VU IMPROVE sites. However, soil concentrations are higher in, and trajectories come from, the West and Southwest of MANE-VU – in apparent conflict with the interpretation of a Sahara dust origin far to the Southeast. While visibility and fine mass concentrations in the MANE-VU region are typically less influenced by soil dust than any other RPO region, the highest MANE-VU dust concentrations are typically associated with Sahara dust events, and their transport route into the Northeast typically comes from a southwesterly direction. The 5-day ATAD trajectories don't fully illustrate the much longer transport route for the two reasons that their duration is too short and they exceed the southern and eastern limits of the meteorological domain. A better sense of the full transport route for this event is indicated by the progression of high soil

[3] http://www.anr.state.vt.us/air/Planning/PublicDocs/AWMA97CATT.pdf
[4] http://capita.wustl.edu/capita/capitareports/0411CATTReport/Tutorial/CATT_Manual.htm
[5] http://webapps.datafed.net/dvoy_services/datafed.aspx?page=CATT/CATT_RS

concentrations over the preceding week and longer trajectory duration (Figure B-5) combined with concurrent NAAPS[6] model calculations of global dust emissions, transport and effects on aerosol optical depth.

Figure B-4. Multi-Site, Single Day Trajectories & Species Concentrations for all visible IMPROVE and STN Sites for Wood Smoke, Soil Dust and Sulfate Events



Source: Gao et al. (2004) PMF of PMRF, VT IMPROVE data and Poirot & Husar (2004) Multisite UNMIX for all MANE-VU IMPROVE and STN Sites.

Figure B-5. From Poirot & Husar (2004)

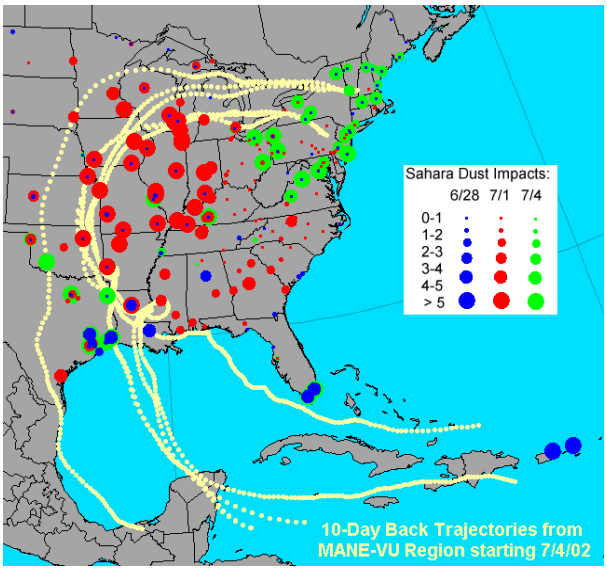
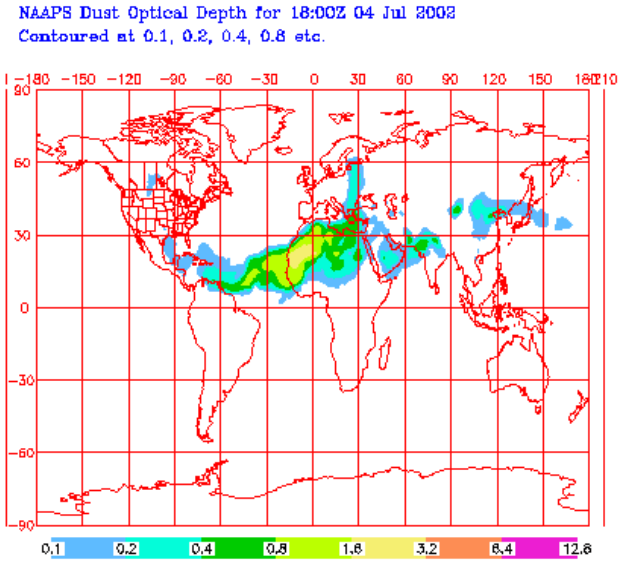


Figure B-6. From NRL Monterrey NAPS model

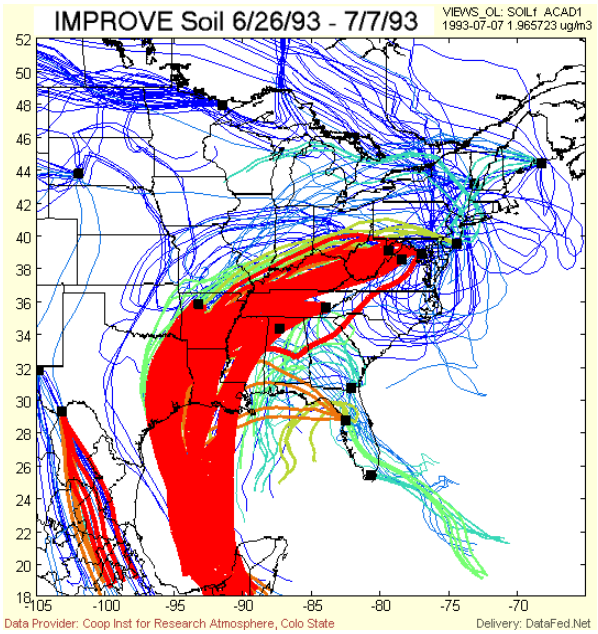


[6] http://www.nrlmry.navy.mil/aerosol/Docs/globaer_model.html

A number of the other mathematical model results summarized in Section A.2.1 also identify "crustal dust" sources at Northeastern sites, and observe that the highest modeled dust contributions in the MANE-VU region are most often associated with Sahara Dust events, with initial easterly transport into the Caribbean, followed by northwesterly transport from the Gulf

Coast across the central US into the Northeast. For example, Kim and Hopke (2003) identify an "airborne soil" source in PMF modeling of 1988-1997 Washington, DC IMPROVE data, for which the highest daily concentration occurred on 7/7/93 with trajectories similar to those in Figure B-5, during a Sahara Dust event previously documented by Perry et al. (1997). The same date also saw the highest "crustal" source contribution in the Battelle Phase 1 PMF and UNMIX modeling of 1988-2000 IMPROVE data at Acadia, ME and was also identified as the highest "soil" source day in PMF and UNMIX analyses of 1988-1995 IMPROVE data at Underhill, VT by Polissar et al. (2001) and Poirot et al. (2001)

Figure B-7. High Soil color-weighted ATADs for Eastern US IMPROVE sites during Summer 1993 Sahara Dust Event.



CATT trajectories for eastern IMPROVE sites, color weighted by (IMPROVE formula) "soil" concentration are displayed in Figure B-7 for this Summer 1993 event, which saw initial impacts on 6/26/93 at the Virgin Islands and Everglades sites, followed by impacts along the TX/LA coast, before progressing toward New England over the following week. At that time, 7/7/93 saw the highest soil levels recorded to date at: Gt Smokey Mtns., TN, Shenandoah, VA, Washington, DC, Dolly Sods, WV, Ringwood, NJ, Mohawk Mtn., CT, Whiteface Mtn., NY, Burlington, VT, Mt. Sunapee, NH, Acadia, ME. Routine Canadian sampling (on 7/6/93) also noted the highest Si levels to date at: Winsor, Egbert, Toronto, Ottawa, Montreal, Sutton and Quebec City. In addition to these fairly routine (nearly every summer) spikes of Sahara dust, occasional Asian dust events are also observed in the MANE-VU region. For example, the well documented continental-scale impacts of the Spring 2001 Asian Dust event are observed in the modeled soil results of Kim and Hopke (2004) at Brigantine, NJ and Gao et al (2004) at Underhill, VT.

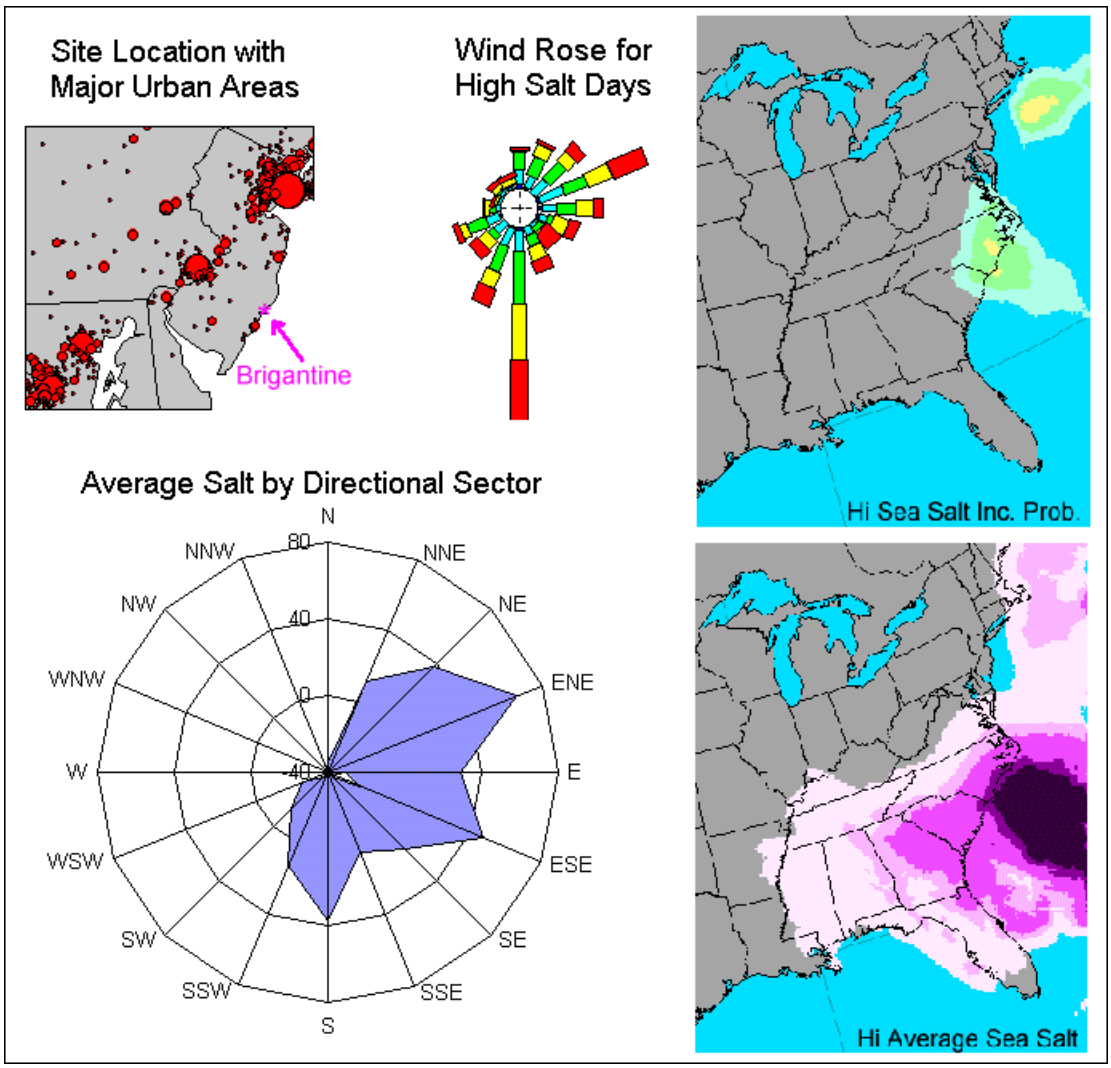
A clear distinction should be drawn between fine "soil" as calculated by the IMPROVE formula (2.2[Al]+2.49[Si]+1.63[Ca] +2.42[Fe]+1.94[Ti]) and "soil, dust or crustal" sources identified by receptor models. The IMPROVE formula represents an idealized form of "pure" crustal material, composed of the most prevalent oxides of the elements used in the equation (all of which are assumed to result predominantly from crustal sources) plus additional minor adjustments to account for oxides of K, Mg, Na and water and carbonate (which also have non-soil sources). Receptor modeled soil sources typically include most of the above "crustal elements", usually in similar relative proportions to those generated by the IMPROVE formula, and may include several crustal sources at locations influenced by nearby calcarious soils, as well as by more distant sources like Sahara dust, which tends to be relatively depleted in Ca and enriched in Al. The above "crustal" elements are also often partially distributed among other modeled sources, as they are

emitted by various combustion and industrial processes, kicked up by motor vehicle traffic, etc. In addition, modeled soil sources are frequently "aged" or "contaminated" by other pollutants like SO_4, NO_3 and/or OC, all of which can react with or "coat" fine soil particles during transport, or which may be present in the soil emission source, as might be anticipated for reentrained road dust, enriched by deposited motor vehicle exhaust, oil leaks, etc. Consequently the modeled soil mass contributions are typically higher than the IMPROVE soil calculations (by about a factor of 2), as they represent "aged" soil and the various natural and anthropogenic contaminants which have been added during transport. In the Northeastern US, sulfate often accounts for up to half of the mass of these soil modeled soil sources, which is not surprising considering the lengthy transport routes. However, even with this "anthropogenic enhancement" fine soil typically accounts for < 5% of $PM_{2.5}$ mass, and an even smaller fraction of extinction on both best and worst visibility days in the Northeast.

B.2.2.2. Salt

Many of the above receptor model studies identify a small mass-contributing, but significant "sea salt" source. This source influence is especially evident at the MANE-VU coastal Class I sites – Acadia and Brigantine, but was also detected at "near coastal" urban sites (Washington DC, New York City) and further inland at Shenandoah VA, Dolly Sods WV and Charlotte, NC. Like the crustal sources, sea salt can be a useful "tracer of opportunity," as its origin should be unambiguous (from the sea). Figure B-8 illustrates applications of local surface meteorology and ensemble

Figure B-8. Meteorological Evaluation of UNMIX Sea Salt Source at Brigantine, NJ.



Note : Top-right: Incremental probability, bottom-left: Upwind average

trajectory methods to identify the most common origins of the Brigantine sea salt source from UNMIX modeling by Poirot and Wishinski (2002). This modeled source, and other sources from that UNMIX application, were also found to be quite similar to the Battelle UNMIX and PMF sources, as well as the PMF sources reported by Song et al. (2001), Lee et al. (2003) and Kim et al. (2004). See Appendix T in Coutant et al. (2002) for a more detailed comparison.

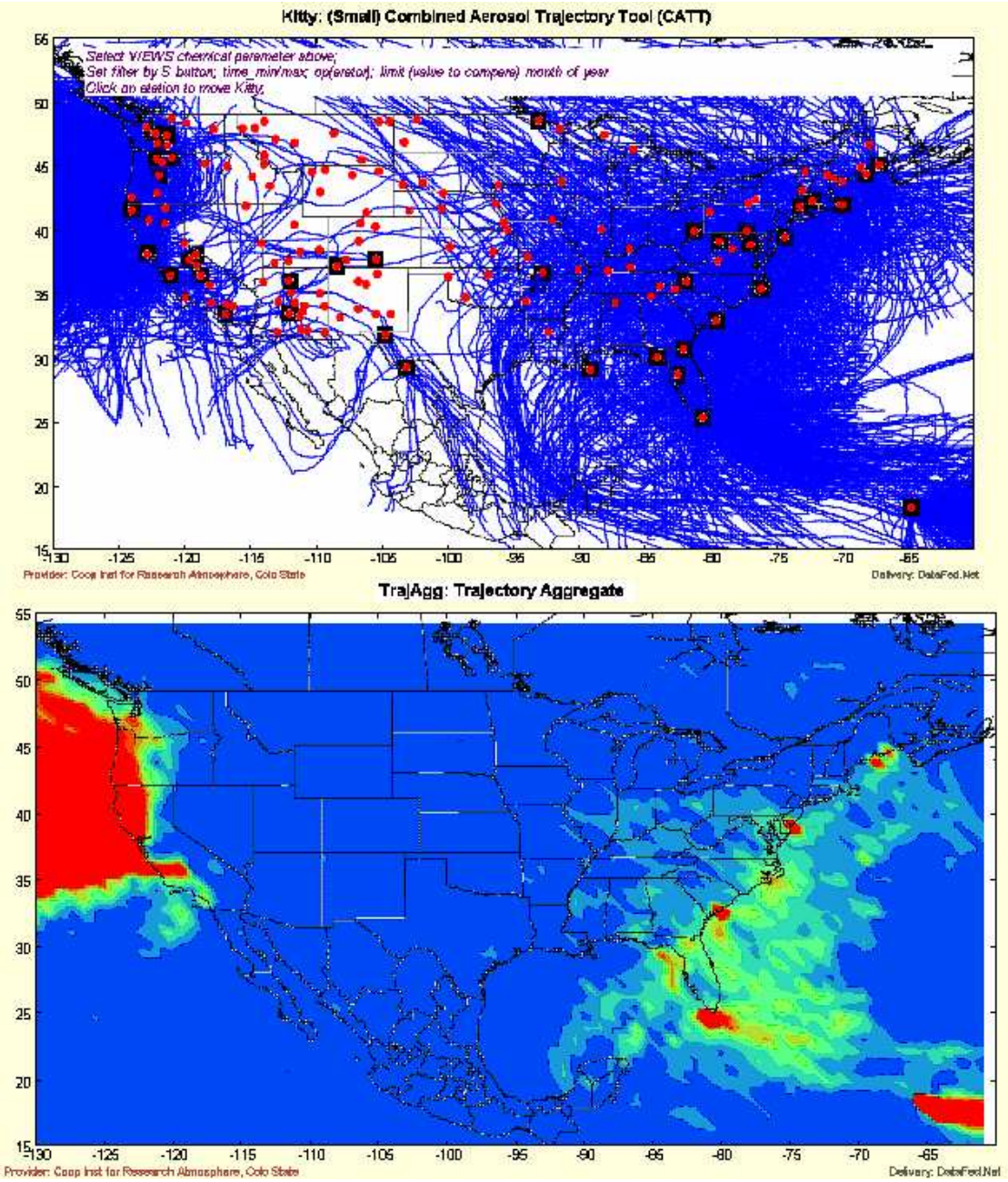
The wind rose is based on local surface wind data, constrained to days when the modeled salt source was high (top 10%). The radial plot is also based on local wind data but shows averages for each directional sector, expressed as % deviations from the mean. The ATAD trajectory based "incremental probability" plot (upper right) shows locations where the trajectories were more frequent on high salt days (top 10%) than on an everyday basis. The "upwind is average" plot (lower right) shows average sea salt at Brigantine as a function of upwind location. Differences between the two trajectory techniques reflect differences in the questions they pose. Incremental probability asks: "if the source contribution was high, where did the air previously reside?" The upwind average asks: "if the air was previously over this location, how high was the source contribution at the downwind receptor?" Incremental probability is influenced by the frequency of contribution, while the upwind average emphasizes areas with the greatest potential to contribute. In the above plot, the very high upwind average off the coast of the Carolinas coincides with the area where the Gulf Stream comes closest to the east coast and where sea salt emissions might be anticipated to be highest. These analyses were conducted prior to development of the CATT tool, but can now be reproduced in CATT for these or any other modeled sources or any of the raw measured species data at Brigantine or any other IMPROVE site.

Like the crustal sources, "sea salt" sources identified by receptor models often reflect an "aged" composition. Over time, chlorine is lost from airborne NaCl and replaced with "excess" NO_3 and SO_4. The Brigantine PMF results from Lee et al. (2003) illustrate this most clearly, as the modelers identified 2 sea salt sources identified as "fresh" and "aged" respectively. Their fresh sea salt contained similar fractions of Na and Cl (on a molar basis) and very little of anything else, while their aged sea salt source contained S, NO_3 and Na but no Cl. The aged source contributed substantially more mass, averaging 8 times higher than the fresh source. Results from all the other Brigantine receptor modeling analyses found a single sea salt source with relatively aged composition.

In all of the Brigantine (and Acadia) modeling studies, the sea salt source accounted for a large fraction of the total sodium at the receptor – typically 90% or more. Thus sodium alone represents a good "tracer" for sea salt, at least at coastal sites, which are in turn most likely to be impacted by marine sources. Figure B-9 illustrates another ensemble trajectory metric created using the CATT tool, in which the entire IMPROVE database – all sites and sample dates – was queried for sites and dates with "high" sodium (> 1.5 ug/m3). CATT then returns the associated trajectories and highlights the site locations where this condition was met. It can be noted in the top half of Figure B-9 that these tend to be coastal or near-coastal sites. For the bottom half of Figure B-9, the "messy" individual trajectories, which for such a large query tend to pile up on top of each other, were further processed by a gridder, which counts and displays the sums of all trajectory endpoints within prespecified grid cells (in this case 1x1 degree of latitude and longitude). Clearly Na is an excellent tracer for sea salt, which comes in turn from marine locations off the east and west coasts. The use of multiple receptor locations and dates tends to correctly identify the "known" source region(s) by "triangulation," even though that region lies outside the domain (continental US) of the receptor sites. An important related point is that since sea salt comes from the sea, it tends to occur at highest concentrations when anthropogenic pollutants (from within the US) are lowest. Thus its

influence on visibility will tend to be greatest on days with lowest "reconstructed extinction," especially since a sea salt component is not currently included in the regional haze equation. It may be noted from Table B-5 in Section B.1.3, that the Poirot & Wishinski (2002) sea salt source averaged 20% of the fine mass at Brigantine on the 20% best visibility days. In addition, sea salt is hygroscopic, and should also include additional mass in the coarse mode. So its fractional contribution to visibility impairment on clean days at coastal sites is likely to be much greater than its fractional contribution to fine mass.

Figure B-9. CATT trajectories for all IMPROVE sites and dates with Na > 1.5 ug/m^3 (top) and gridded, aggregated trajectory endpoint counts for these "High Na" sites and dates (bottom)



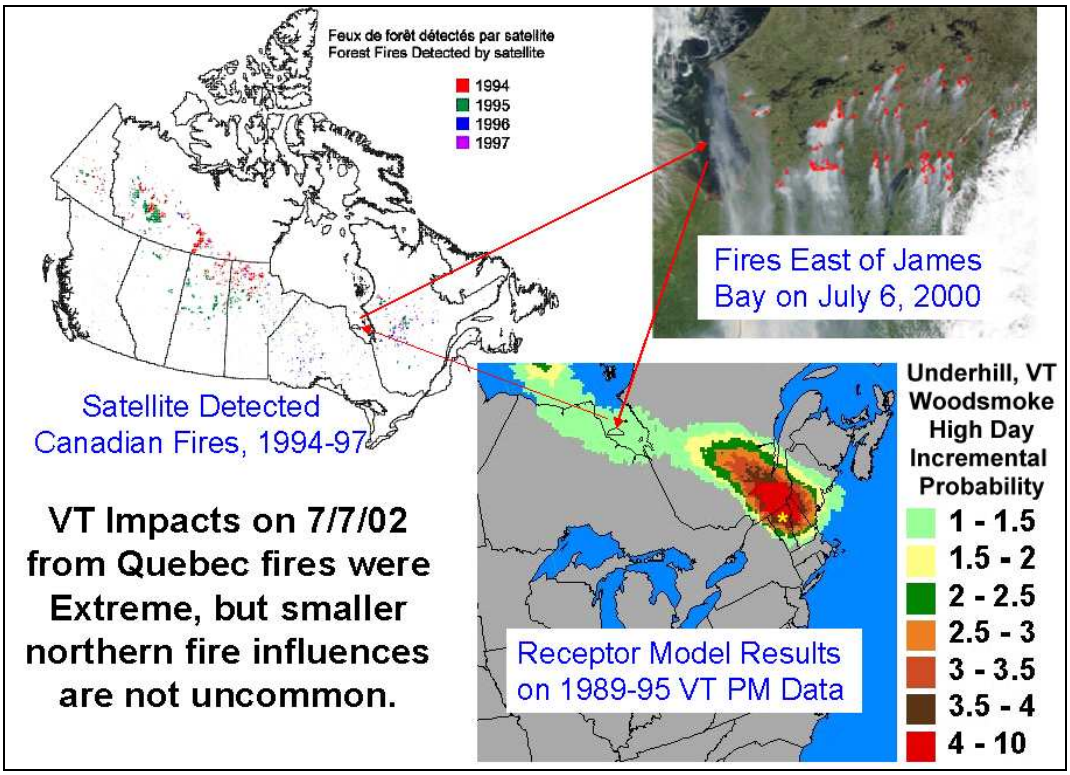
B.2.2.3. Smoke

A "wood smoke" or "biomass combustion" source is identified at most of the rural sites for which model results are available, but is often not detected or of very small magnitude in larger urban areas – for example none of the results for NYC, Toronto and Boston and none in 3 of 4 studies in Washington DC. This makes sense considering the difficulties of storing large piles of fuel wood in densely populated urban centers and/or municipal bans on woodstoves and fireplaces. Due to its relatively abundant rainfall and vegetation types the MANE-VU region is not especially prone to forest fires, compared to other regions further west or south. A notable exception to these generalizations occurred during the 7/7/02 Quebec fires which affected MANE-VU urban and rural sites alike, and which also resulted in the largest 1-day regional fine mass concentrations and visibility impacts recorded in recent years.

Current receptor models (with routine speciation data) are not able to distinguish between wood smoke due to residential wood burning and forest fires. The PMF and UNMIX results from Polissar et al (2001) and Poirot et al. (2001) both identified similar wood smoke sources at Underhill, VT, based on 1989-1995 measurement data, and both also noted a temporal pattern of highest average concentrations (wood stoves) combined with occasional summer spikes (forest fires, several of which were located in roughly the same area as the 2002 fires). The area just east of James Bay Quebec is a relatively chronic summer forest fire area. Figure B-10 shows the incremental probability for the above-mentioned Underhill wood smoke source in comparison with the 7/02 fires and historical pattern of large Canadian fires.

It may be noted that the incremental probability field includes the local region around the receptor site, as might be expected for residential wood burning, but also includes a distinct tail to the north and east, consistent with occasional Canadian wild fire influences.

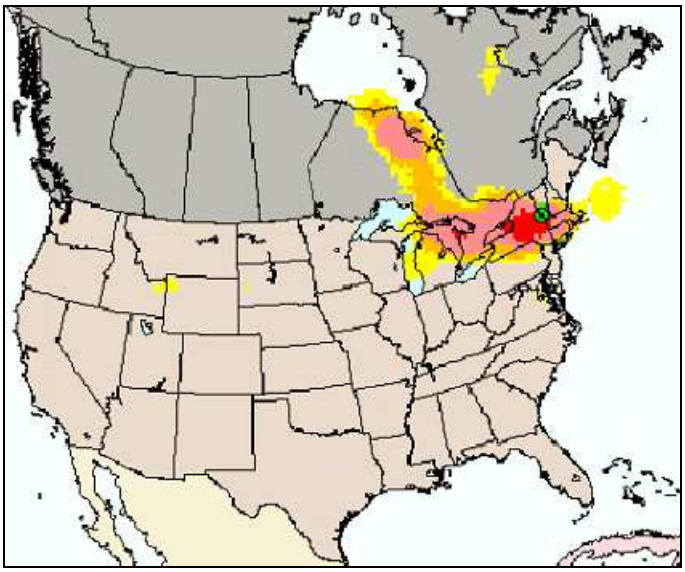
Figure B-10. Incremental probability for 1989-1995 Underhill VT wood smoke compared with Canadian forest fire locations



Gao et al. (2004) also identified a wood smoke source in Underhill, VT, based on 2001-2003 data. It was similar in magnitude to the 1989-95 Underhill wood smoke sources (averaging 1.1 ug/m3), but contributed a higher mass fraction (20% vs. 16%) due to reductions in the magnitude of other source influences, especially sulfates. This source also made a large proportionate contribution (25%) to visibility impairment on the best 20% visibility days but dropped to 7% on the worst visibility days. This might be expected from Canadian fire influences, as air from that direction is typically otherwise very clean. It should also be noted that Gao et al. (2004) intentionally excluded the 7/7/02 sample day from their model input, as the source was clearly known and the huge 1-day impact tended to produce illogical PMF results. However, the chemical composition of Gao's PMF smoke source was very similar to the composition of the Quebec fire smoke identified by the multi-site UNMIX analysis in Poirot and Husar (2004).

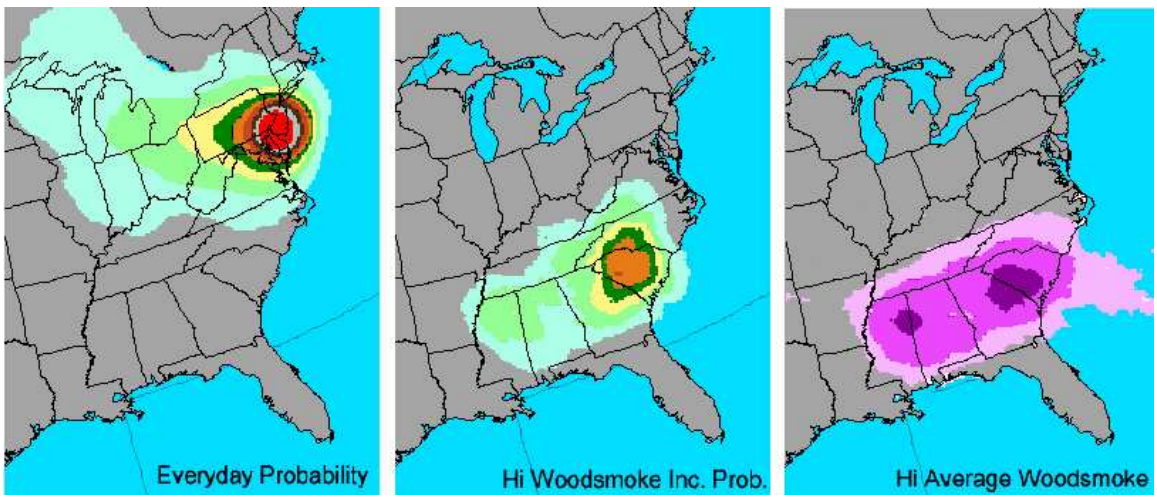
The incremental probability field for the wood smoke source at Lye Brook VT, based on the 1991-99 PMF results in Coutant et al., (2002) is shown in Figure B-11. As was the case in Underhill, Lye Brook shows influence from both local sources as well as more distant Canadian fires. This Lye Brook smoke source contributed a relatively high fraction (25%) of the total fine mass, but was not found to be especially important there on either the best or worst 20% visibility days.

Figure B-11. Incremental probability for Lye Brook wood smoke source (PMF modeling by Coutant et. Al. (2002)



A relatively smaller wood smoke source influence was also noted in several of the Brigantine model results (though not in all studies of Brigantine). Figure B-12 shows the incremental probability field and the upwind average field for wood smoke source contributions from the Poirot and Wishinski (2002) UNMIX model results. It also displays the "everyday probability field for Brigantine (where the air most frequently

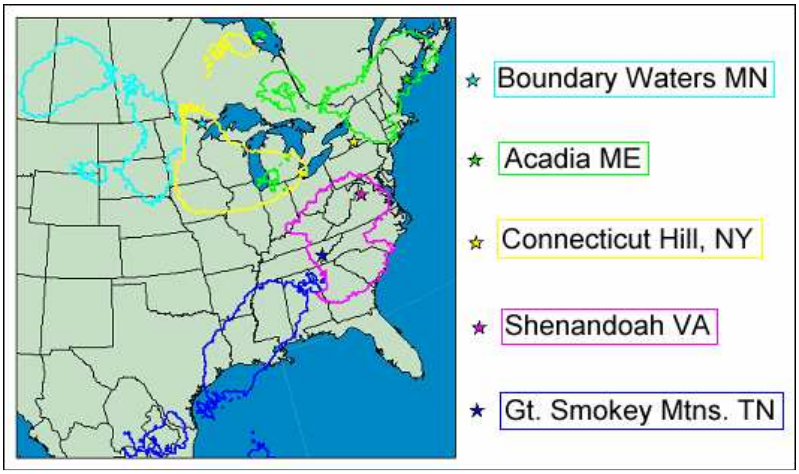
Figure B-12. Everyday probability, incremental probability and upwind average for UNMIX-modeled wood smoke source at Brigantine, NJ (from Poirot & Wishinski, 2002)



resides on all sample days). Unlike the more northern VT sites, there is not strong indication of Canadian fire influence, although that would change if the 7/02 Quebec fire was considered, since Brigantine had the highest impacts of any IMPROVE site for that event, exceeding 100 ug/m3. Also unlike the VT results, there's no indication of strong local wood burning source influences, and a much different regional origin – in the Southeastern US – is indicated.

Figure B-13 displays incremental probabilities for PMF modeled wood smoke sources at selected Eastern US sites from the Coutant et al. (2002) analysis. These were done on an earlier version of the CATT tool which employed HYSPLIT trajectories, rather than ATADs. The gridded results were exported from CATT and imported to ArcView GIS, where additional interpolation and contouring was conducted.

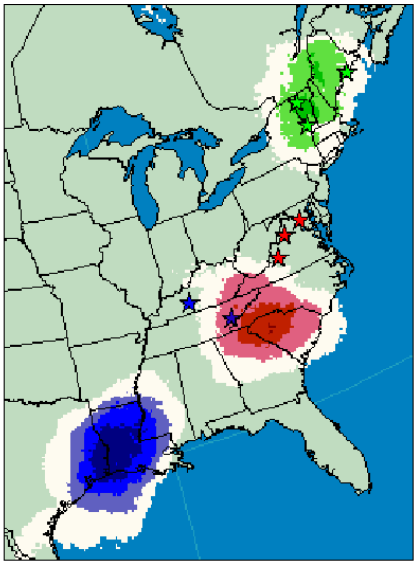
Figure B-13. Incremental probabilities for modeled wood smoke sources at selected sites (PMF sources from Coutant et al., 2002)



Acadia, like Underhill and Lye Brook VT shows highest probabilities for both local New England region and more distant wild fires in eastern Quebec. Shenandoah also shows relatively local influence, as well as more distant effects from an area of the Southeast, similar to that identified for Brigantine. The other 3 sites show influence from regions more offset from the receptors. This may reflect differences in regional forest fire locations, secondary aerosol formation (which requires time & distance), and/or high wind speeds often associated with the spread of large fires.

Figure B-14 is based on a similar approach to that described for Figure B-13, except in this case, the results are aggregated for the New England, Mid Atlantic and Southeast regions.

Figure B-14. Woodsmoke Source Regional Aggregations



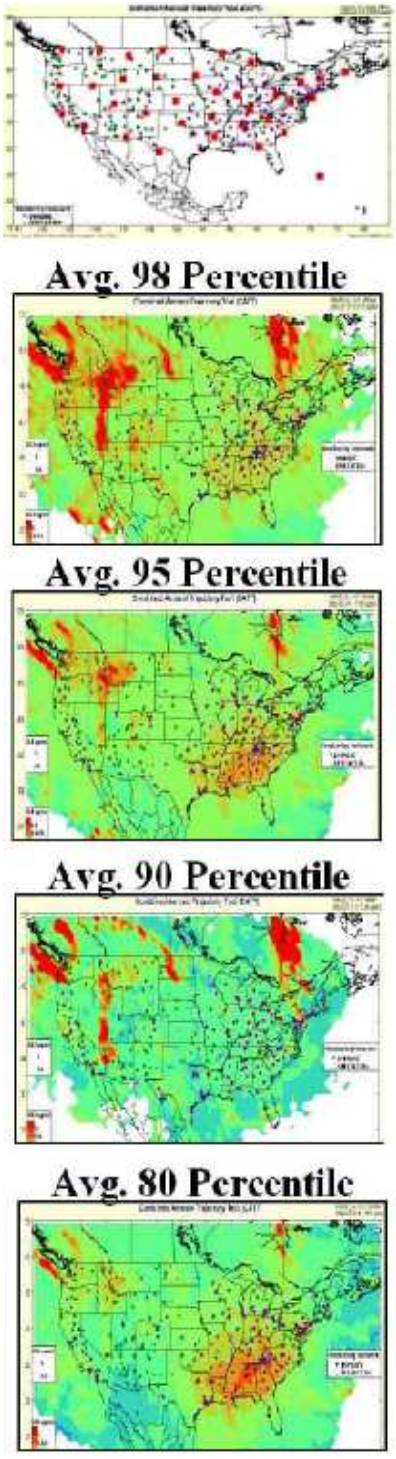
NE: ACAD, PMRC, LYBR

MA: WASH, SHEN, JARI

SE: GRSM, MACA

It should be cautioned that modeling and interpreting sources of primary and secondary carbonaceous sources can be problematic, and our understanding of these sources is currently evolving rapidly. The general grouping of sources into a category of "Mobile and Secondary Organics" – based on the current knowledge in the "dark ages" of 2002 - may be misleading in the sense that in some cases, especially at rural sites there may well be large secondary organic influences that are predominantly biogenic and unrelated to motor vehicle emissions. There may be misinterpretation or mixing of source influences from forest fires and biogenic emissions of gaseous organic precursors in the absence of fires. In the northern half of the MANE-VU region, local and Canadian wood smoke identification is relatively clear, but at southern MANE-VU and

Figure B-15. Multi-site upwind average for high percentile OC



more southeastern sites, the distinction between biogenic fire and non-fire emissions is less clear.

Figure B-15 is adapted from an illustration presented by Husar (2005) in the CATT Illustrated Instruction Manual. Its based on a variation of the "upwind average" trajectory metric, also referred to in CATT parlance as the "Donna Kenski Method," following her GIS development and expansion of the method to multiple sites as described in Kenski (2004). Husar (2005) used OC data for the 2001-2003 period for a large subset of 35 widely distributed IMPROVE sites (top of Figure B-15), and then calculated the "Kenski metric" using only values greater than high (98%) and lower (95%, 90%, 80%) percentiles of the data. He also showed the more traditional "upwind average" using all the OC data from these sites (Figure B-16). At the highest percentiles, locations of well documented large forest fires are evident. But such fires are very episodic in their emission patterns and are not likely to repeat in the same locations within a relatively short multi-year time period. At the 80th percentile (highest 20% of OC measurements at each site), and for the average based on all OC data, the large fire effects are much less evident, and the Southeastern US shows up as a much more chronic OC source area. Although there are fires in the Southeast, they don't burn continuously, and a gaseous biogenic emissions source category is perhaps a more logical interpretation for the "source." This upwind average for all OC data from CATT is quite similar to the pattern displayed in Kenski, 2004 – who also noted a similar pattern for CAMx modeled biogenic secondary organic aerosol as displayed in Figure B-17.

Figure B-16. Multisite Upwind Average OC (from Husar, 2005).

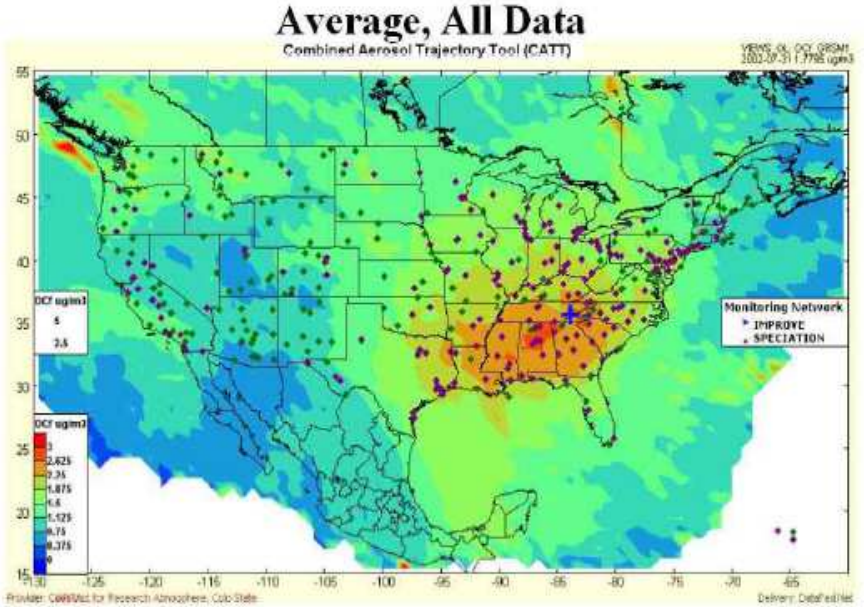
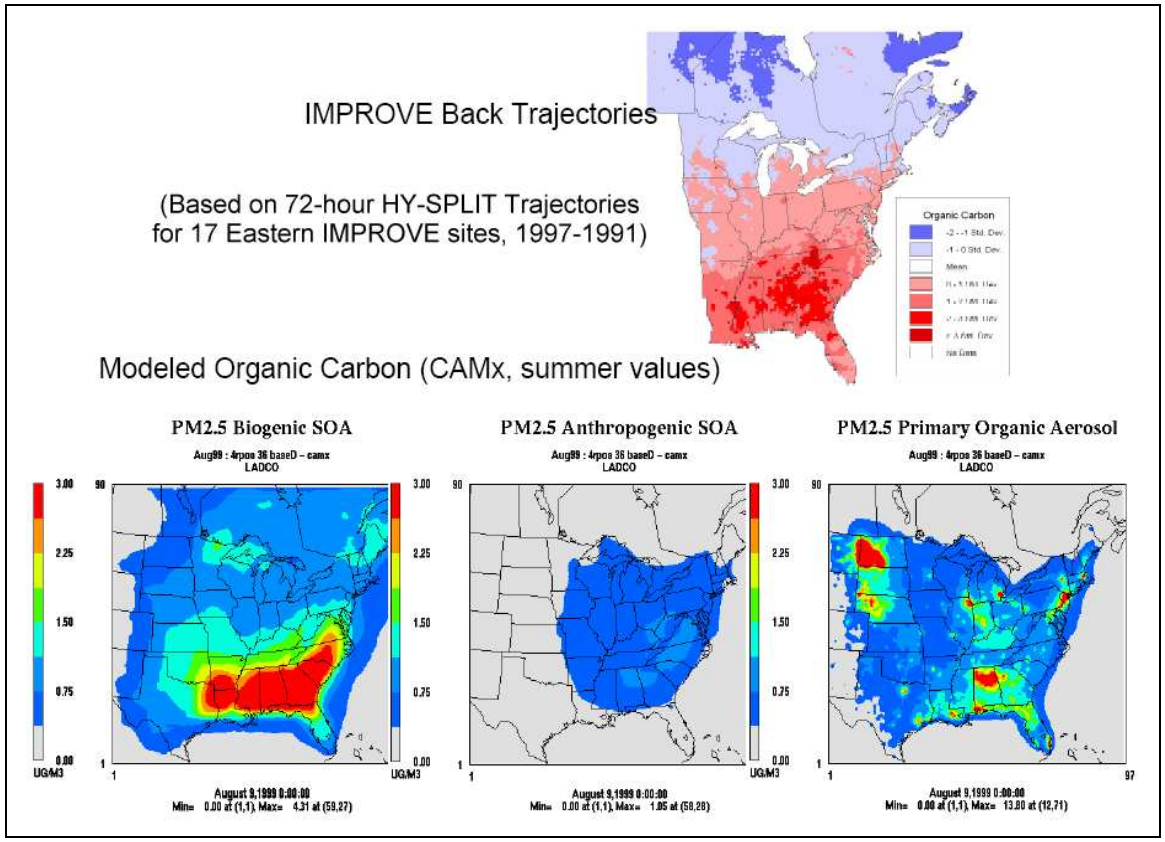


Figure B-17. Average upwind OC for Eastern IMPROVE sites vs. CAMx model results (Kenski, 2004).



It may be noted that the Kenski (2004) analysis is based on 3-day backward HYSPLIT trajectories for 17 eastern IMPROVE sites 1997-2001, while the Husar analysis is based on 5-day ATAD trajectories for 35 nationally distributed sites, 2001-2003.

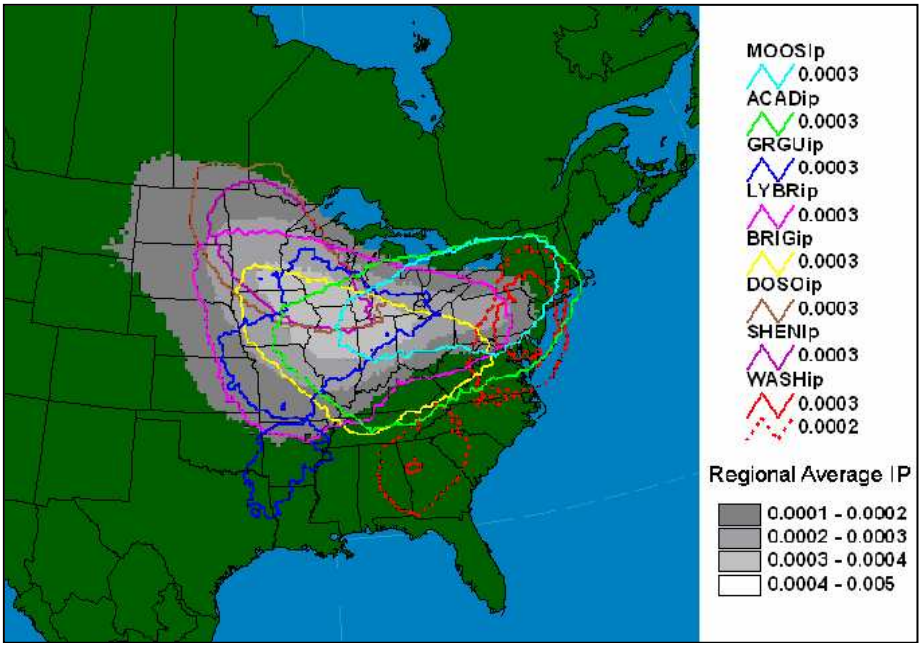
B.2.2.4. Nitrates

The Battelle receptor modeling (Coutant et al., 2002) included both PMF and UNMIX analyses. The PMF results, constrained to 9-source solutions at all sites, generally appeared more reasonable than the UNMIX results (limited to 6-source solutions). But many of the UNMIX sources were quite similar to their PMF counterparts, and nitrate data were included as input to the UNMIX model runs, and therefore apportioned among the resulting sources (nitrate data were omitted from the Batelle PMF analyses). A generally common feature of the Battelle UNMIX results for nitrate was that it tended to mostly break out into a single "nitrate source" at most modeled sites, and this "source," assumed to be mostly ammonium nitrate, accounted for a large fraction (70 to 90%) of the total measured nitrate, with relatively small fractions of other major mass-contributing species or tracer elements. This characteristic of a unique nitrate source, not specifically associated with any emission source category (such as motor vehicles, utilities or industrial sources) was also observed in a number of the other modeling studies - for example in Underhill, Potsdam, Brigantine, New York and Toronto. Fractional mass contributions from these nitrate sources are in the range of 5 to 10% at MANE-VU rural sites, but can be substantially higher in urban areas. In Toronto, an "ammonium nitrate source" identified by Lee et al. (2003) PMF modeling and Poirot and Brook (UNMIX) contributed 35% of the fine mass and accounted for over

40% of the visibility impairment on worst 20% days. Trajectory analyses indicated influence of both agricultural emissions from the "corn belt" region, as well as local urban influences.

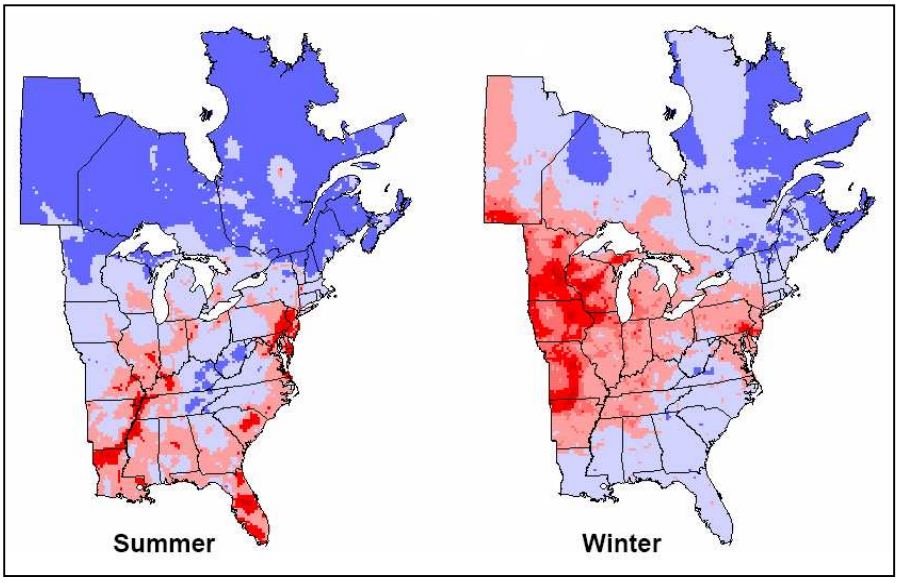
Incremental probability plots for the Battelle UNMIX nitrate sources are displayed in Figure B-18, and suggest a strong influence from Midwestern agricultural emissions at all rural northeastern sites. Note that Washington D.C., the only urban site, shows a markedly different pattern of influence suggestion more local contribution to nitrate at that site.

Figure B-18. Incremental probability fields for high nitrate at selected northeastern sites.



A similar "corn belt" regional influence on average upwind nitrate at 17 eastern IMPROVE sites is also clearly indicated in the Kenski (2004) analysis seen in Figure B-19, particularly for the winter season, when concentrations are highest. During summer, the lower Mississippi valley and east coast urban corridor appear more important. Potentially there is some formation of sodium nitrate in coastal areas and/or competition from acidic sulfates in the Midwest and Southeast during

Figure B-19. Average upwind Nitrate (seasonal) at eastern IMPROVE sites (Kenski, 2004)



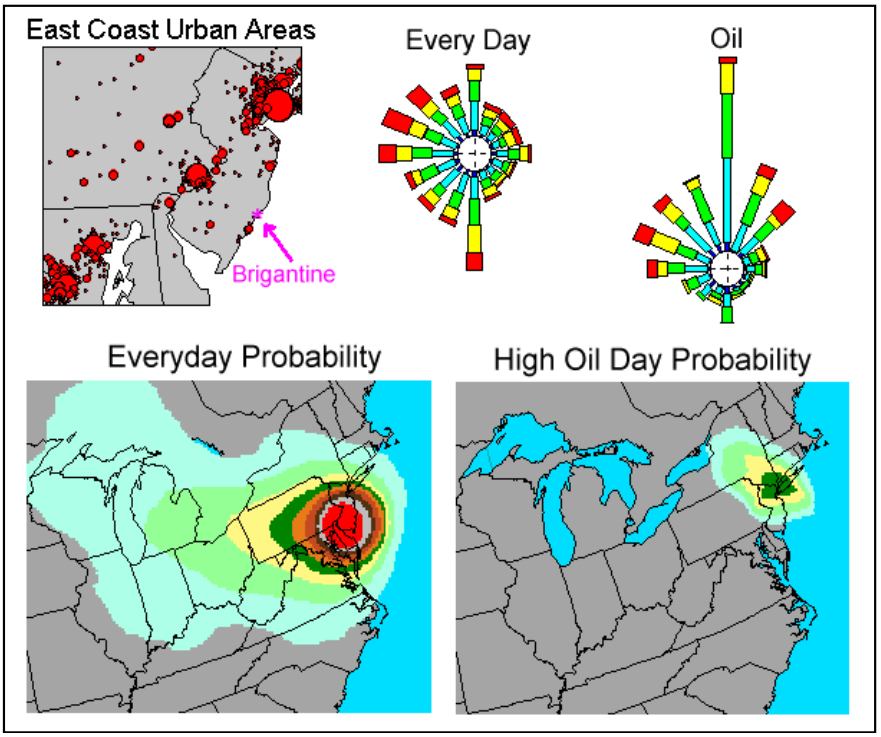
summer.

B.2.2.5. Oil

Many of the referenced modeling studies identify a source identified as "oil combustion" which typically accounts for a high fraction of Ni and/or V at the receptor sites. These trace elements are present in crude oil and tend to become highly concentrated in the "residual" during the refining process. Consequently, "residual oil burning" (rather than distillate oil burning) is the most likely source of these trace (and "tracer") elements. It may also be noted that an oil source is most frequently identified and /or tends to have highest mass concentrations at sites in or near the northeast urban corridor, with the highest reported average source contribution of 4.2 ug/m3 at one of the NYC sites modeled by Ito et al. (2004).

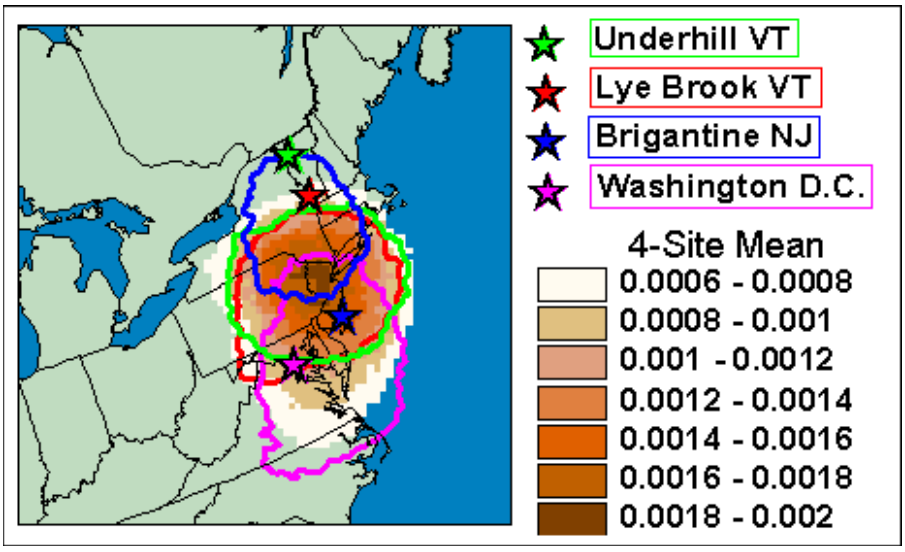
Figure B-20 displays an everyday wind rose based on local surface meteorology data for Brigantine, NJ - along with a similar rose constrained to days when the UNMIX-modeled Oil source from Poirot and Wishinski (2002) was highest. Also shown are ATAD trajectory-based probability fields for every day and for days when the modeled oil source was high. As indicated in Coutant et al. (2002, Appendix T) very similar oil sources were also identified at Brigantine in independent PMF modeling runs by the Battelle, Rutgers and Clarkson modeling groups respectively.

Figure B-20. Meteorological evaluation of Brigantine Oil source.



In Figure B-21, the incremental probability for the Brigantine oil source is compared with similar oil sources identified by Polissar et al. (2001, PMF) and Poirot et al. (2001, UNMIX) at Underhill, VT; and by Coutant et al (2002, PMF) at Lye Brook, VT and Washington DC. The multiple results show a clear convergence on the Northeast urban corridor, where the density

Figure B-21. Incremental Probability for Oil sources at 4 NE sites.



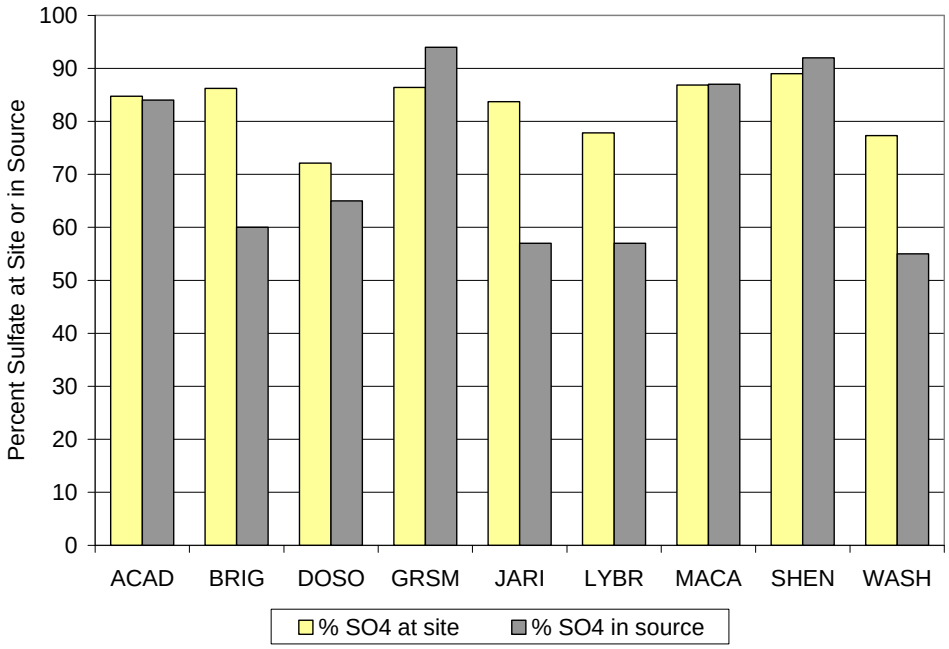
of residual oil combustion sources is highest.

B.2.2.6. Coal

Nearly all of the modeling studies summarized in Section B.1 identify a large "secondary sulfate" or "coal" source which typically accounts for 30 to 60% of the fine mass and 60 to 80% of the visibility impairment on the haziest days in the Northeast. A distinction should be drawn between "sulfate the source" (which is not composed entirely of sulfate) and "sulfate the species" (which is not associated entirely with the source). As indicated in previous discussions of aged windblown dust and sea salt, both of these "natural sources" are also often "contaminated" with anthropogenic sulfate, nitrate or OC. These aerosols of mixed origins raise interesting questions of "causality" (and resultant light extinction characteristics), but typically account for rather small fractions of the contaminant species. Oil burning, industrial sources and motor vehicles also contribute significant amounts of sulfate, and their mass compositions often contain high fractions of sulfate. However, the large, "secondary sulfate" or "secondary coal" sources identified at most sites in most of these receptor modeling studies are typically composed primarily of sulfates and account for high fractions of the total sulfate at the receptors.

Sulfate characteristics of the large sulfate sources identified in the Battelle modeling at eastern IMPROVE sites are summarized in Figure B-22, which shows the percentages of sulfate at the site contributed by the source and the percentages of the sources composed of sulfates.

Figure B-22. Sulfate characteristics of Battelle secondary sulfate/coal sources.



Seventy to ninety percent of the sulfate at these sites is contributed by these large sources, which are in turn composed of fifty to ninety percent sulfate. The regional haze reconstructed extinction equations assume that sulfate is always present as ammonium sulfate, which would have a sulfate to mass ratio of 0.73 (for NH_4HSO_4 and H_2SO_4, the sulfate mass ratios would be 0.83 and 0.98 respectively). At some of the southern sites - like Mammoth Cave, Shenandoah and Gt. Smokey Mts. - the sulfate:mass ratio is greater than 0.83, indicating a sulfate source composition

more acidic than ammonium bisulfate. At other sites such as Brigantine, Lye Brook and Washington DC, with SO_4:mass ratios of 0.55 to 0.60, the sulfate sources must contain species in addition to sulfate and ammonium in order to account for their mass contributions, and there is often a significant organic matter component – in the range of 10 to 15 % in these "sulfate" or "coal" sources.

A number of the studies summarized in section B.1 identified two or more separate "sulfate" or "coal" sources or "source components" which are typically distinguished from each other by very different ratios of sulfate (or sulfur) to selenium. Both species are emitted in the US predominantly by the same sources – coal burning utilities, but Se is a primary aerosol (emitted in particle phase or condensing shortly after emission) while SO_4 is primarily a secondary species (formed at varying rates in the atmosphere). Consequently, the S:Se ratio at downwind receptors varies considerably as a function of the efficiency of secondary aerosol formation in the atmosphere, and S and Se are not well correlated at ambient monitoring sites. This is illustrated in the left panel of Figure B-23, which plots S vs. Se for all IMPROVE sites from 2000 through 2003 (about 50,000 samples) and shows a poor correlation ($R^2 = 0.21$). However, when the incremental probabilities for these same 2000-2003 S and Se data are calculated in CATT, their upwind locations are highly correlated ($R^2 = 0.88$), as displayed on the right side of Figure B-23(based on 4000 common grid locations), and also displayed graphically in Figure B-24.

Figure B-23. Sulfur vs. Selenium at IMPROVE sites (left) and by Incremental Probability (right), 2000-2003

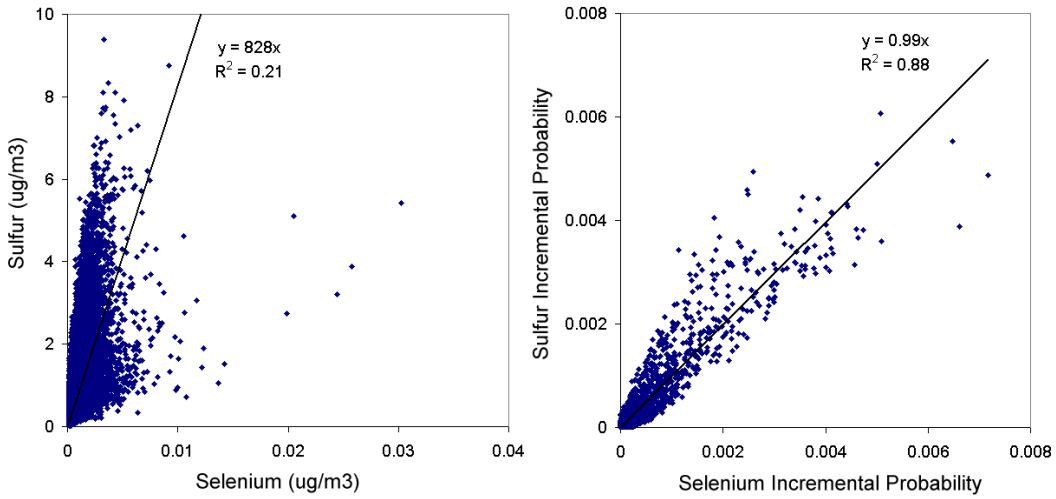
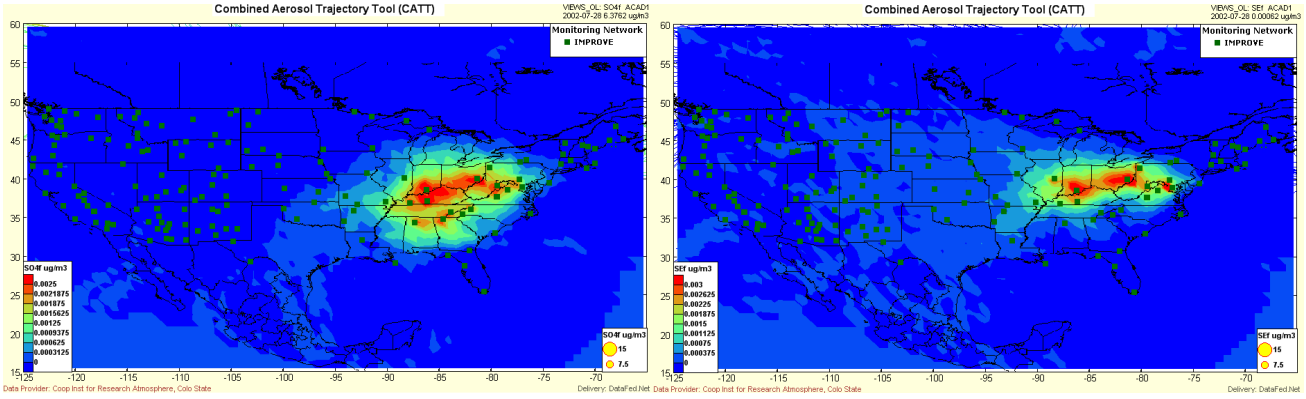
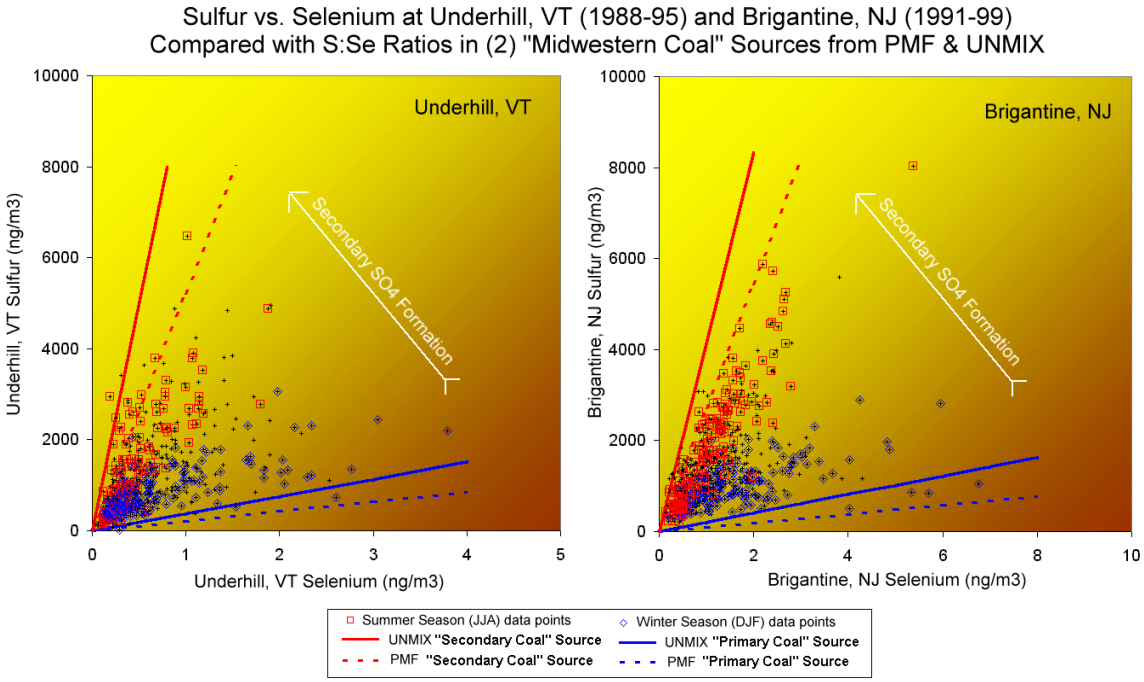


Figure B-24. Incremental Probabilities for High (top 10%) SO4 (left) and Se (right), 2000-2003



Receptor models like PMF and UNMIX identify sources of fixed, constant chemical composition, and so can't find a single source with a variable S:Se ratio at the receptor sites. They can however, break this source influence into two or more "source components" which do have constant ratios. This is illustrated in the Figure B-25 scatter plots of S vs. Se at the Underhill, VT and Brigantine NJ sites, over the time periods of PMF and UNMIX modeling reported by Polissar et al (2001) and Poirot et al (2001) at Underhill (1989-95), and reported by Lee et al. (2003) and Poirot and Wishinski (2002) at Brigantine (1991-1999). Plotted points are colored to summer and winter measurements, showing generally much more efficient segondary formation in the warm season. The solid and dashed lines represent the S:Se ratios of the 2 fixed ratio source components identified by the UNMIX and PMF models respectively. Note that they bound the outer extremes of the varying S:Se ratios of the data ("hard edges" in the scatter plots, which UNMIX specifically seeks and quantifies). These "sources" are then interpreted as representing the primary aerosol component (minimal secondary transformation) and secondary aerosol component (maximal secondary transformation) from coal burning and the daily total source impact is determined by the sum of these components, which are combined in different proportions on different sample days.

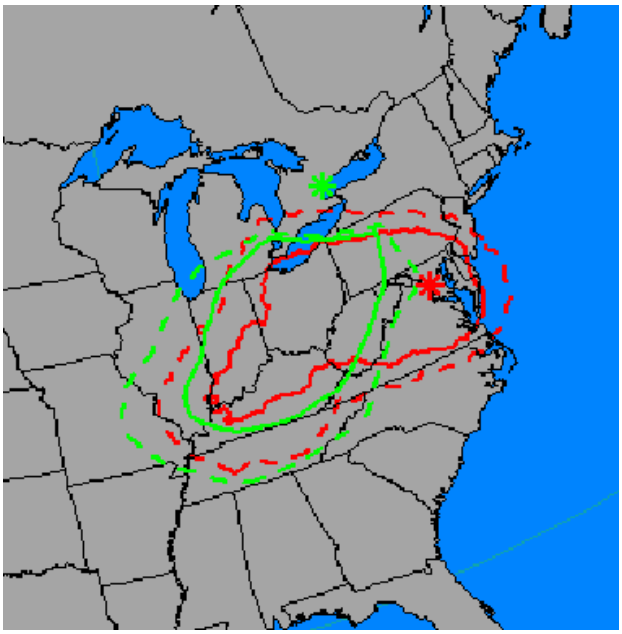
Figure B-25. Illustration of S:Se ratios in "Primary Coal" and Secondary Coal" Source Components by PMF and UNMIX models at Underhill, VT and Brigantine, NJ.



In the Toronto PMF and UNMIX modeling, additional species were measured, including (good quality) NH4 and several organic acids. The PMF modeling at that site identified 3 coal-related source components: primary, secondary neutral ($(NH_4)_2SO_4$), and secondary acidic (NH_4HSO_4). The acidic component also included a significant OC content (while the other 2 components did not). The authors suggested this might be indicative of the "acid-catalyzed secondary organic aerosol formation" mechanism, identified by Jang et al. (2002). Further support for this hypothesis is provided by the surface wind and trajectory analyses which showed the 3 coal-related components tended to come from the same location (of high SO_2 emissions, but not high VOC emissions), and from different locations than other nitrate and motor vehicle source influences.

The secondary OC content of the acidic sulfate component in Toronto may help explain the significant OC fraction identified in "secondary sulfate" sources identified in other modeling studies using less detailed measurement data. For example, a single large "secondary sulfate" source was identified in the Coutant et al. (2002) modeling at Washington, DC (at the southeastern corner of the MANE-VU domain), which included an organic matter content of about 10%. In Figure B-26 the 3 "coal-related" source components in Toronto (at the northwestern corner of MANE-VU) and the single "secondary sulfate" source in Washington DC show upwind incremental probabilities overlapping a common region of source influence, which coincides to the region of the highest density of coal burning and SO_2 emissions.

Figure B-26. Inc. Probs. for "Coal-related sources" at Toronto, Ont. (green) and Washington DC (red)



As results from additional monitoring sites and receptor modeling studies are added (Figure B-27), it becomes clear that many Class 1 and urban sites throughout the eastern US are influenced by this common source region, and that reductions in coal-related SO_2 emissions would have substantial benefits for improved visibility and reduced PM concentrations throughout much of the eastern US (and eastern Canada).

Figure B-27. Incremental Probabilities for "Secondary Sulfate" (Coal) sources at Eastern US sites.

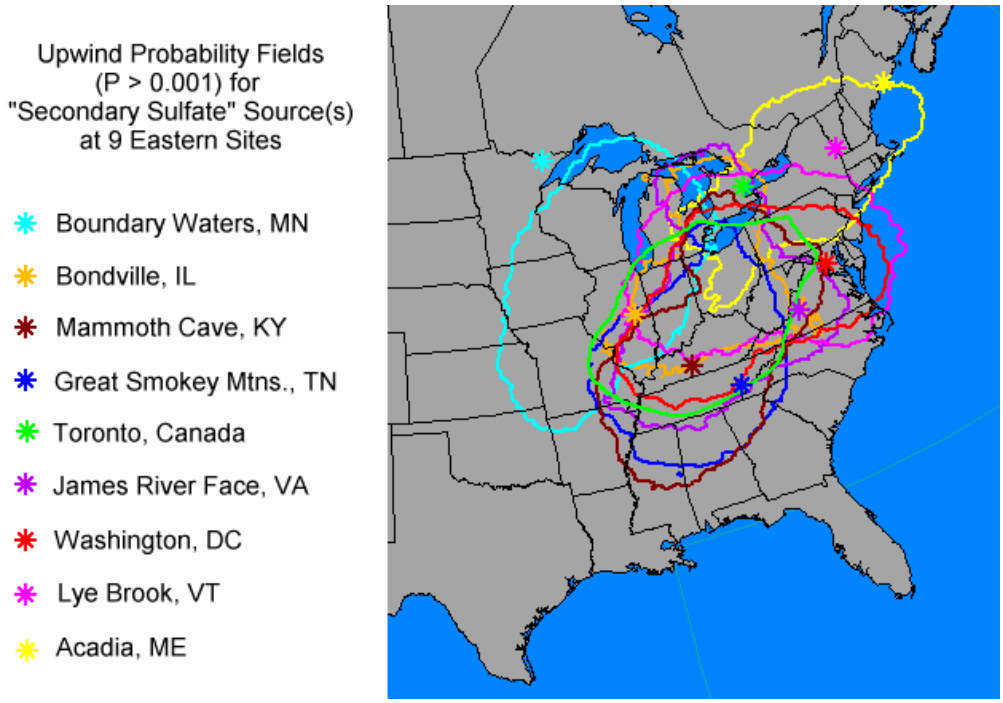
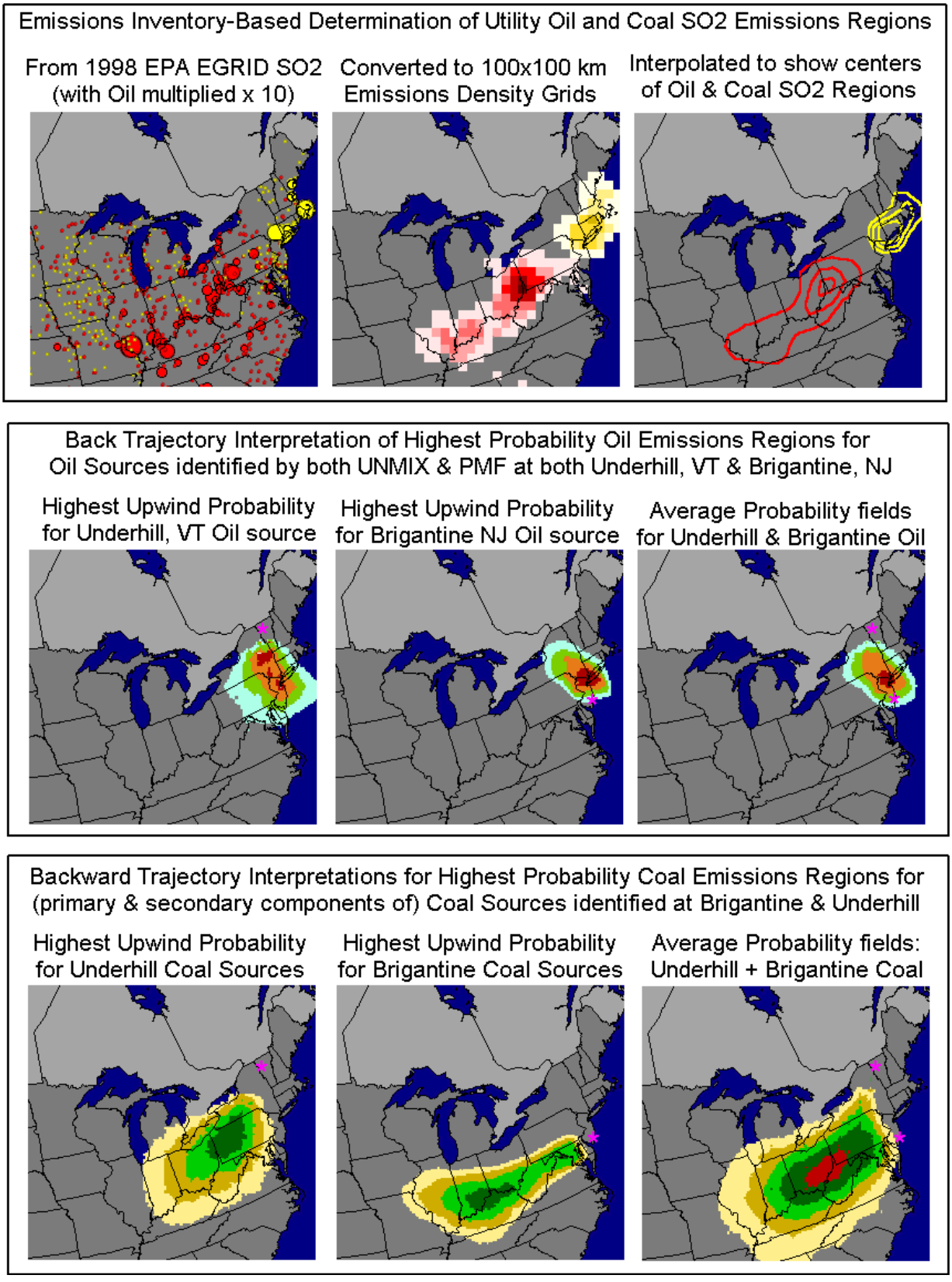


Figure B-28. Comparison of emissions data with oil and coal sources at Underhill and Brigantine



Additional demonstration that the modeled "sulfate sources" are predominantly coal-related is provided in the Figure B-28 comparison of (utility) emissions data from the 1998 EPA EGRID inventory. The top panel shows SO_2 emissions data from oil and coal fired utilities, respectively. These data are gridded and interpolated to show the general northeastern regions where these different fuels predominate. The second panel shows incremental probabilities for "oil" sources, identified by separate PMF and UNMIX model runs (and modeling groups) at the Underhill, VT and Brigantine, NJ sites respectively. These are averaged for the two sites to "triangulate a more accurate source location. The third panel displays similar results for the sum of "primary" and "secondary" coal sources identified in these model runs. The oil source comes from where oil is burned, and the coal source comes from where coal is burned.

Figure B-29 compares a gridded trajectory aggregation of trajectory endpoints from a CATT query of all IMPROVE sites for the past 4 years, for sites and dates where SO_4 exceeded 15 ug/m3 (top panel).

A very similar pattern results from an aggregation of the highest 10% of days for the Battelle "secondary sulfate" sources at the 7 northeastern sites indicated in the middle panel.

The third panel is based on all IMPROVE sites and dates where Deciview values (reconstructed extinction) exceeded 30. Coal sources that most affect MANE-VU sites are associated with the highest sulfate and poorest visibility conditions throughout the eastern US.

This influence is not limited to the Eastern US (and Canada). The consensus results from a variety of dispersion and receptor model results during the BRAVO study (Pitchford et al. (2004) indicated 30% of sulfur at Big Bend National Park in Western TX came from the "Eastern US." While Green et al. (2004) showed occasional eastern sulfate source impacts as far west as the Colorado Plateau.

Figure B-29. Comparative probability fields for Sulfate, Sulfate Sources and Deciviews

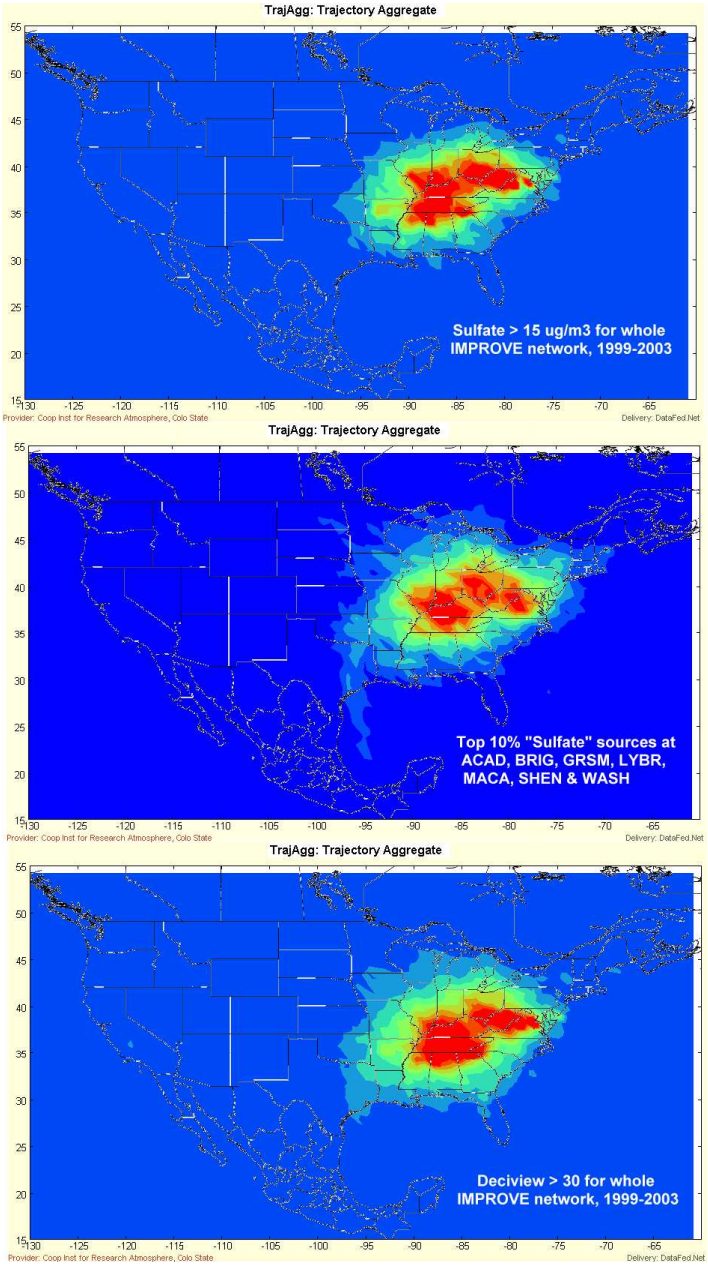


Figure B-30 and Figure B-31 are limited to 2000-2003 data from the MANE-VU Class 1 areas only, and show (Figure B-30) incremental probabilities for high sulfate (by the "Mark Green method)", and (Figure B-31) upwind average sulfate (with calculations constrained to grid cells with > 40 trajectory endpoints). The colored contour lines are for the indicated individual sites, probability levels and/or sulfate concentrations, and the grey shaded areas depict linear averages aggregated for the five MANE-VU Class 1 sites.

Figure B-30. Incremental Probabilities for High SO4 at MANE-VU Class 1 Sites, 1999-2002

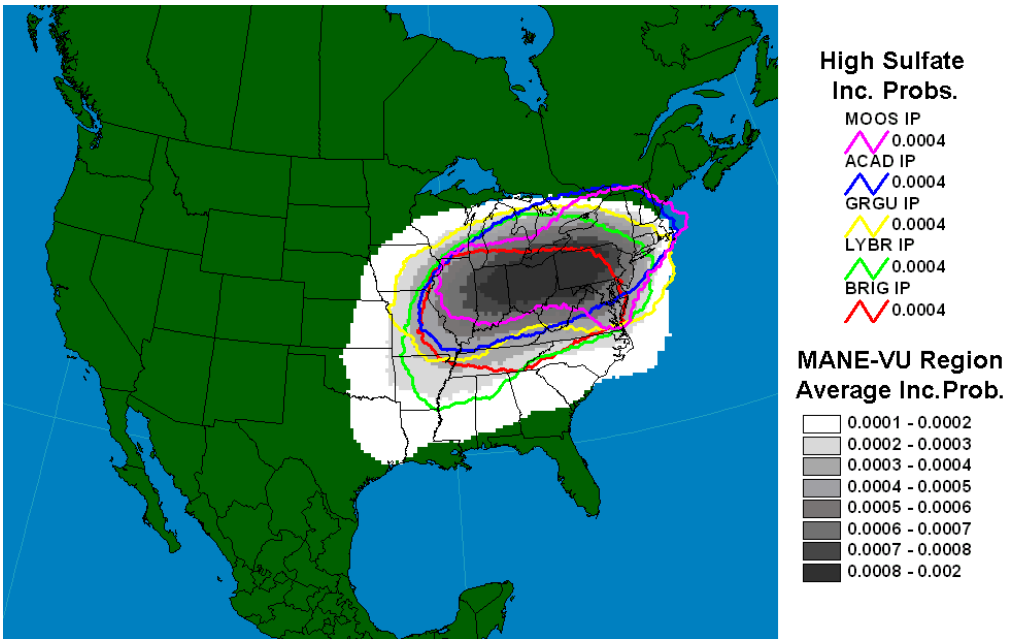
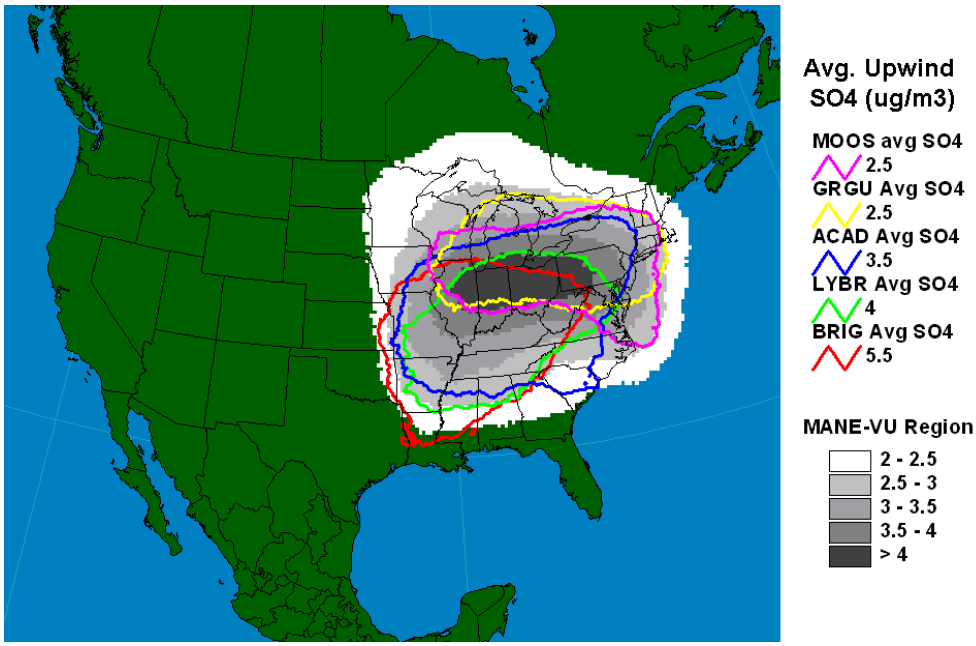


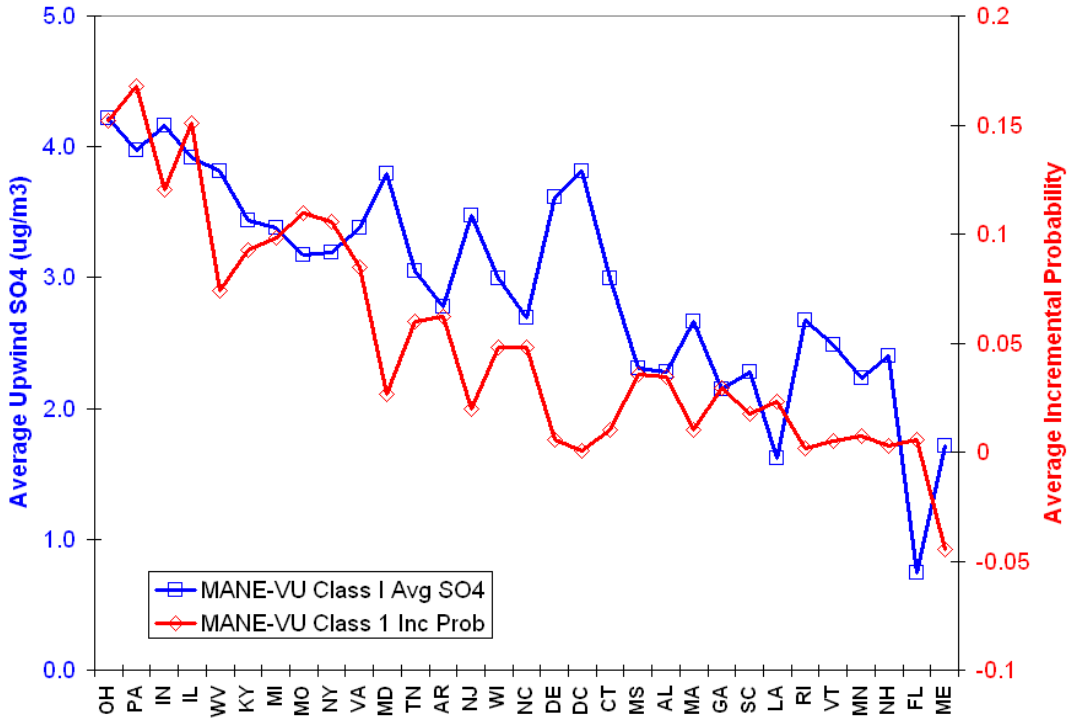
Figure B-31. Average Upwind SO4 at MANE-VU Class 1 Sites, 1999-2002



While the patterns appear "similar" in this case, the two trajectory metrics address different questions. Incremental probability asks "where was the air if sulfate was high at the receptor?" and the upwind average asks "how high is the sulfate at the receptor if the air was over specific upwind locations?" Neither of these provides a quantitative answer to the question "what fraction of the receptor sulfate comes from which upwind locations?" The can however provide a qualitative indication of the relative importance of different contributing regions.

Figure B-32 shows the results of the incremental probabilities and upwind averages in Figure B-30 and Figure B-31 disaggregated into state totals (for the 31 easternmost states) and ranked. The ranks generated for the two different metrics were averaged, and the states on the Y axis are ordered from highest (left) to lowest (right) for these average ranks. It may be noted that the ranking for the two different metrics show largest differences for the physically smallest and nearby (and/or downwind) states in the MANE-VU region (MD, NJ, DE, DC, CT, MA, RI, VT & NH). One reason for this is that the state aggregations were summed for incremental probabilities (which reflects both concentration and frequency) and averaged for the upwind averages (which do not reflect frequency) and this causes the metrics to differ most for the smallest states. In addition, individual grid locations within these small, nearby states are frequently upwind (lots of trajectory endpoints) and the "upwind averages" for locations in these states are moderate (similar to the average concentrations at the receptor sites), but when sulfate concentrations are high, these states are less likely to be upwind than they are on an everyday basis.

Figure B-32. Ranked State Contributions for Incremental Probability and Upwind Average Sulfate for MANE-VU Class 1 Receptors.



It may be noted that the top 10 states are distributed among the MANE-VU, Midwest and VISTAS RPO planning regions, and that coordinated inter-regional strategies will be needed to assure future progress toward the national visibility goals.

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