# Appendix G-11

# Weight of Evidence Report

# Table of Contents

# Table of Contents

# Table of Contents

5. Mark Garrison (ERM) and Dan Riley and Paul Wishinski (VTDEC), ‘Appendix D: Development of Parallel CALPUFF Dispersion Modeling Platforms for Sulfate Source Attribution Studies in the Northeast U.S.”.
6. Jennifer Carrie Hains, ‘A Chemical Climatology of Lower Tropospheric Trace Gases and Aerosols Over the Mid-Atlantic Region. Doctor of Philosophy thesis, University of Maryland, 2007.
7. Robert Carroll Levy, ‘Second Generation Retrieval of Tropospheric Aerosol Properties Over Land from Inversion of Visible and Near-Infrared Spectral Reflectance: Application over Maryland, Doctor of Philosophy thesis, University of Maryland, 2007.
8. Brett F. Taubman, ‘Airborne Characterization of Regional Aerosol Origins and Optical Properties’, Doctor of Philosophy thesis, University of Maryland, 2004.
9. Yu-Jin Choi, ‘A Study of Ground-Level Ozone Over the Baltimore/Washington Ozone Nonattainment Area’, Doctor of Philosophy thesis, University of Maryland, 2004.

# PM2.5 Maryland State Implementation Plan
# Weight of Evidence Report

**By**

**Dr. Russell R. Dickerson[1,3], Dr. Dale Allen[1], Patricia Castellanos[2],**
**Dr. Sheryl Ehrman[2], Hao He[3], Dr. Robert D. Hudson[1], Charles Piety[1], and**
**Dr. Jeffrey W. Stehr[1]**

**[1]Department of Atmospheric and Oceanic Science**
**[2]Department of Chemical and Biomolecular Engineering**
**[3]Department of Chemistry and Biochemistry**
**University of Maryland**
**College Park, MD**

**January 30, 2008**

## Executive Summary

This document summarizes the state of the science of aerosols over the Mid-Atlantic region, and the evidence that Maryland will comply with the annual and 24-hour PM2.5 National Ambient Air Quality Standards (NAAQS) by the 2010 deadline. In 2002 the highest annual PM2.5 design value of 16.6 $\mu g\ m^{-3}$ was observed at the Old Town site located in the city of Baltimore, MD. The EPA approved CMAQ model, using projected emissions for the year 2009 and 2002 meteorology (Section VI), calculated a maximum 2009 PM2.5 design value of 14.4 $\mu g\ m^{-3}$ at the Old Town site; this is below the annual NAAQS of 15 $\mu g\ m^{-3}$, thereby demonstrating attainment. Both model and measurement uncertainty for PM2.5 are substantial (greater than that of ozone), but after evaluating all the supporting evidence the conclusion can be made that Maryland is pursuing an effective and comprehensive strategy of PM2.5 reduction.

- Measurements of the chemical composition of PM2.5 in and around Maryland (Sections I and V) show a consistent makeup with ammonium sulfate (or bisulfate), and organic matter as the major constituents, followed by contributions from black carbon, nitrate, and mineral dust (crustal material).

- Although discernable differences in nitrate and organic matter are observed during the winter months at most urban sites, in the context of a PM2.5 control strategy the mass and composition of PM2.5 shows remarkable spatial uniformity.

- Based on research performed at the University of Maryland (UMD) and gathered from peer-reviewed literature, on surface measurements, UMD aircraft measurements, and on modeling results, it can be concluded that most of the mass of aerosols is secondary and that PM2.5 has a regional signal.

- Modeling results and measurements of sulfates and nitrates are in reasonable agreement, suggesting that major sources of particles, their most important precursors, and the dominant processes have been identified, at least for surface concentrations.

- Examination of PM2.5 ambient speciation data and modeled concentrations suggests that the source categories (e.g., stationary sources, motor vehicles, biogenic and anthropogenic VOC's, primary BC, biogenic $NH_3$) are generally correct (Section II and V). Reported emissions of VOC's and reported concentrations of particulate OM have decreased in parallel. Comparison of trends in emissions to trends in concentrations or deposition (Sections II – V) show reasonable linearity – the reported decrease in emissions of $SO_2$ and $NO_x$ correlate well with the observed decreases in sulfate and nitrate.

- Long term monitoring in the Baltimore/Washington Nonattainment areas (Section III) shows a steady, significant decrease of 0.25 $\mu g\ m^{-3}\ yr^{-1}$ in total PM2.5 and

parallel decreases in sulfate, OM, nitrate, BC and dust suggesting that the emphasis on regional controls of $SO_2$, VOC's, NOx, and primary OC and BC emissions has led to a steady reduction in PM2.5 that should bring Maryland into annual PM2.5 NAAQS compliance by 2009.

# Section I.

# The Composition of PM2.5

Dr. Russell Dickerson, Charles Piety
Department of Atmospheric and Oceanic Science
The University of Maryland
Hao He
Department of Chemistry and Biochemistry
The University of Maryland

February 3, 2008

### 1. Why is this section important?

The observations show that the chemical composition, spatial distributions, and seasonal cycles of PM2.5 are reasonably well understood, and this information can be used to determine if emissions of the right aerosols and PM2.5 precursors are being controlled on the appropriate temporal and spatial scales.

### 2. What questions are answered in this section?

This section examines the observations of PM2.5 composition to address the following questions: What are the typical values and variability in the chemical composition, spatial distribution, and seasonal cycle? Is MDE focusing on the most efficacious strategy for lowering PM2.5 and its precursors?

### 3. What are the take-away messages from this section?

Measurements of PM2.5 show, in the context of abatement strategy, uniformity in composition and concentration across the Mid-Atlantic region. Sulfate peaks in the summer and nitrate peaks in the winter, but regionally during the course of a year the makeup and levels of aerosols are reasonably consistent with the bulk of the mass identified. In round numbers, and in decreasing importance, the main known contributors based on IMPROVE data are ammonium sulfate (50%), organic matter (30%), ammonium nitrate (10%), mineral dust (5%), and BC (5%). Examining the data from EPA/State Chemical Speciation Network (CSN) sites these values are ammonium sulfate (40%), organic matter (40%), ammonium nitrate (10%), with mineral dust and BC at roughly (5%) each.

### 4. What conclusions are reached in this section with respect to Maryland's attainment demonstration?

The winter peak in nitrate indicates that NOx controls should be in effect year-round. The small fraction of total PM2.5 mass attributable to mineral dust suggests that control of local emissions of crustal elements from construction activities for example, have apparently only a minor impact of the annual PM2.5 value. Maryland and the surrounding States have been working to lower year-round regional emissions of $SO_2$, $NO_x$, primary OC (including BC), and

VOC’s, and this strategy appears to be targeting the right species at the appropriate temporal and spatial scales.

## Abstract

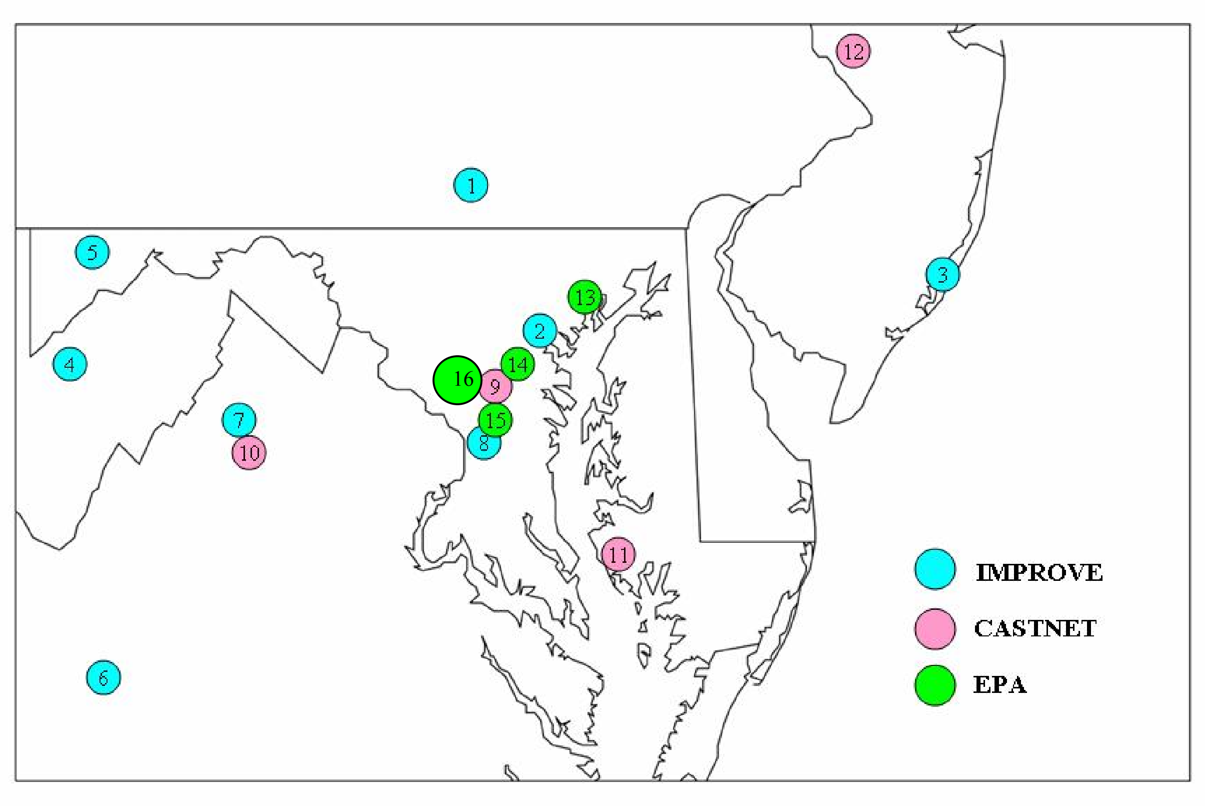
The observations discussed in this Section indicate that the chemical composition, spatial distributions, and seasonal cycles of PM2.5 are reasonably well understood. This information can be used to determine if the right aerosols and PM2.5 precursors are being controlled in the right places and at the right times. This section examines the typical values and variability in chemical composition, spatial distribution, and seasonal cycle of PM2.5 and its major chemical constituents. Measurements of PM2.5 show, in the context of abatement strategy, uniformity in composition and concentration across the Mid-Atlantic region. Sulfate peaks in the summer and nitrate peaks in the winter, but regionally during the course of the year the makeup and levels of aerosols are reasonably consistent with the bulk of the mass identified. In round numbers (to the nearest 5%), and in decreasing importance, an analysis of the IMPROVE data identifies the main contributors to PM2.5 as ammonium sulfate (50%), organic matter (30%), ammonium nitrate (10%), mineral dust (5%), and BC (5%). The EPA/State CSN data show ammonium sulfate (40%), organic matter (40%), ammonium nitrate (10%), mineral dust (5%), and BC (5%). The winter peak in nitrate indicates that NOx controls should be utilized year-round. The small fraction of total PM2.5 mass attributable to mineral dust suggests that control of local emissions of crustal elements from construction activities for example, can have only a minor impact of the annual PM2.5 concentrations. Maryland and the surrounding States have been working through various programs to lower year-round regional emissions of $SO_2$, $NO_x$, primary OC (including BC), and VOC’s, and this approach appears to be targeting the right species on the appropriate spatial and temporal scales.

### a. Introduction

Published studies as well as the experimental evidence made recently available provide extensive data on the chemical composition of the fine particulate matter over the Mid Atlantic region and can be examined to evaluate sources, transformations, and sinks of the aerosols and their precursors. Here, we evaluate the absolute concentration as well as the relative importance of major constituents as a function of season and location in an attempt to determine if the biggest contributors are identified and if the bulk of the mass of PM2.5 is accounted for. Sampling and analytical differences can contribute to variability across platforms, and records from IMPROVE (Interagency Monitoring of PROtected Visual Environments), CASTNET (Clean Air Status and Trends Network), and EPA/State CSN sites are examined. Variations by species, by location, and by season are examined to determine representative concentrations. The variability indicates the lifetime and nature of the aerosols with more uniform distributions indicative of well-mixed, secondary pollutants. Results can guide abatement strategies in terms of the most effective species, locations, and seasonal controls.

The following paragraph provides some basic information on the data sets used in this study. CASTNET (see web site http://www.epa.gov/castnet/) is the nation's primary source for data on dry acidic deposition and rural, ground level ozone. Operating since 1987, CASTNET is used in conjunction with other national monitoring networks to provide information for evaluating the effectiveness of national emission control strategies. CASTNET consists of over 80 sites across the United States [*Sickles and Shadwick*, 2007]. Each CASTNET dry deposition station measures: weekly average atmospheric concentrations of sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid, hourly concentrations of ambient ozone levels and meteorological conditions required for inferring dry deposition rates. The IMPROVE (http//vista.cira.colostate.edu/improve) program is a co-operative measurement effort governed by a steering committee composed of representatives from Federal and regional-state organizations. The objectives of IMPROVE are: to establish current visibility and aerosol conditions in mandatory Class I PSD areas; to identify chemical species and emission sources responsible for existing man-made visibility impairment; to document long-term trends for assessing progress towards the national visibility goal; and to provide regional haze monitoring representing all visibility-protected federal Class I areas where practical. Date from the CSN

EPA/State network was obtained from the Air Explorer website (http://www.epa.gov/mxplorer/index.htm). Air Explorer is a collection of user-friendly visualization tools for air quality analysts. The tools generate maps, graphs, and data tables dynamically. Currently, the tools access ambient concentration data from EPA's Air Quality System (AQS). Figure I-1 and Table I-1 show the locations of the monitors discussed here.



1. Arendtsville, PA
2. UMBC, MD
3. Brigantine, NJ
4. Dolly Sods, WV
5. Frostburg, MD
6. James River, VA
7. Shenandoah, VA
8. Hains Point, DC
9 & 16. Beltsville, MD
10. Big Meadows, VA
11. Blackwater, MD
12. Washington Crossing, NJ
13. Essex, MD
14. Fort Meade, MD
15. McMillan Reservoir, DC

Figure I-1 A map showing the locations of IMRPOVE, CASTNET and EPA/State monitors used in the analysis of PM2.5 composition. Tables I-1 and I-2 present more detailed monitor information.

Table I-1 Summary Information for Monitors used in the Composition analysis.

| Monitoring Site | State | Classification | Elevation (meters) | Latitude, Longitude (degrees) | Sampling Period | Parameters Measured |
|---|---|---|---|---|---|---|
| | | | | | | |
| 1. Arendtsville | PA | IMPROVE | 267 | 39.9, -77.3 | 2001-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 2. UMBC | MD | IMPROVE | 78 | 39.2, -76.7 | 2004-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 3. Brigantine | NJ | IMPROVE | 5 | 39.9, -77.3 | 1991-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 4. Dolly Sods | WV | IMPROVE | 1182 | 39.1, -79.4 | 1991-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 5. Frostburg | MD | IMPROVE | 767 | 39.7, -79.0 | 2004-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, |
| 6. James River | VA | IMPROVE | 289 | 37.6, -79.5 | 2000-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 7. Shenandoah | VA | IMPROVE | 1079 | 38.5, -78.4 | 1988-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 8. Hains Point | DC | IMPROVE | 15 | 38.9, -77.0 | 1989-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 9. Beltsville | MD | CASTNET | 46 | 39.0, -76.6 | 1989-2006 | $NH_4$, $NO_3$, $SO_4$ |
| 10. Big Meadows | VA | CASTNET | 1073 | 38.5, -78.4 | 1989-2006 | $NH_4$, $NO_3$, $SO_4$ |
| 11. Blackwater | MD | CASTNET | 4 | 38.3, -76.0 | 1995-2006 | $NH_4$, $NO_3$, $SO_4$ |
| 12. Washington Crossing | NJ | CASTNET | 61 | 40.3, -74.9 | 1989-2006 | $NH_4$, $NO_3$, $SO_4$ |
| 13. Essex | MD | EPA | 6 | 39.3, -76.4 | 2001-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 14. Fort Meade | MD | EPA | 46 | 39.1, -76.8 | 2001-2004 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 15. McMillan Reservoir | DC | EPA | 44 | 38.9, -77.0 | 2001-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 16. Beltsville | MD | EPA | 46 | 39.0, -76.6 | 2004-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |

Notes: $NH_4$ = ammonium (inferred for IMPROVE sites), $NO_3$ = nitrate, $SO_4$ = sulfate, EC = elemental carbon, OC = organic carbon.
IMPROVE: http://vista.cira.colostate.edu/improve/Default.htm
CASTNET: http://www.epa.gov/castnet/
EPA: http://www.epa.gov/mxplorer/index.htm

## b. Species

There are eight IMPROVE sites, four CASTNET, and four EPA/State CSN monitoring sites in or near the Baltimore/Washington area. Figures I-2 to I-16 show relative contributions; Table I-2 shows the total PM2.5 in μg $m^{-3}$ for each of the IMPROVE sites in the Baltimore, MD – Washington, DC region for 2004-2006. The IMPROVE network is supported by the EPA, BLM, NPS, USFS, USDA-FW, NOAA, and State air agencies, and all of the sites are on national parkland, and most are rural. The IMROVE site on the National Mall, near downtown Washington, DC is an urban site. The CASTNET sites are rural, and monitor only sulfate, ammonium, and nitrate; these sites are dedicated to deposition monitoring. The EPA/State CSN samplers are located in urban (Essex, MD and McMillan Reservoir, in Washington, DC) or suburban (Fort Meade, MD and Beltsville, MD) sites; see

*http://www.epa.gov/cgi-bin/htmSQL/mxplorer/query_spe.hsql*

At all locations where all species are monitored, ammonium sulfate (or bisulfate) dominates followed by organic carbon (OC) with smaller contributions from nitrate, elemental carbon (EC; also called black carbon, BC), and mineral dust (also called crustal material). Note that organic matter is generally 1.6 to 2.2 times higher than OC, due the presence of other elements such as N, H, and O, in the organic compounds. “Other” is the difference between the gravimetric mass and the reconstructed mass. When OC is converted to OM, little of the mass of aerosol is unidentified or “other”.

**Table I-2 Annual Average PM2.5 Values from the IMPROVE Monitors Presented in this Analysis**

| Site/Year | 2004 (μg $m^{-3}$) | 2005 (μg $m^{-3}$) | 2006 (μg $m^{-3}$) | Average 2004-2006 (μg $m^{-3}$) |
|---|---|---|---|---|
| Arendtsville, PA | 11.92 | 12.95 | 10.05 | 11.64 |
| Brigantine, NJ | 9.55 | 9.91 | 9.64 | 9.70 |
| Dolly Sods, WV | 9.48 | 10.05 | 8.46 | 9.33 |
| Frostburg, MD | 11.32 | 10.80 | 9.51 | 10.54 |
| James River, VA | 10.50 | 11.40 | 10.65 | 10.85 |
| Shenandoah, VA | 9.35 | 9.36 | 9.25 | 9.32 |
| Hains Point, DC | 13.25 | 15.20 | 12.65 | 13.70 |
| UMBC, MD | 14.25 | 13.59 | 11.77 | 13.20 |

At the IMPROVE sites, the contribution of sulfate ranges from 34% to 44%; assuming this is fully neutralized, ammonium sulfate would account for 47% to 60% of the total mass. IMPROVE sites do not in general measure ammonium, and we have shown inferred $NH_4^+$, assuming sulfate and nitrate are fully neutralized, on the figures in this Section and Section III. The CASTNET sites measure only sulfate, nitrate, and ammonium, but the concentrations and ratios are similar to those measured by nearby IMPROVE sites with roughly 63% sulfate, 15% nitrate and 22% ammonium by mass.

The range for OC is 12% to 18% of the total fine aerosol mass at the IMPROVE sites. At the urban site in Washington, DC, OC comprises the largest fraction (18%), but the difference in composition between urban and rural is small – OC was 13% of the mass at Frostburg, MD and 12% at Shenandoah National Park; these sites are located at 800 and 1100 m (all altitudes in this document are expressed as above mean sea level, msl). If one assumes a conversion factor of 1.8, then OM accounts for 22% to 32% of the total mass.

The EPA/State CSN sites, using the most recent 2004-2006 data, show similar allocation by species, with somewhat smaller ratio of sulfate to OC. Sulfate ranges from 27% to 34%, OC are nearly a constant 25% at all sites, ammonium ranges from 10% to 12%, and nitrate from 9% to 12%. If one assumes that all of the sulfate is neutralized with ammonium then ammonium sulfate accounts for ~35% of the mass and using a factor of 1.8 for conversion of OC to total organic matter, then OM accounts for about 45% of the total PM2.5 mass in this data set. Nitrate, if full neutralized, accounts for 12%; EC and dust for ≤ 5% of the PM2.5 mass. There is no strong pattern of suburban to urban in the chemical make up of the fine particles for these four stations. Differences in sampling protocol and analytical techniques can account for the differences in distribution seen between the IMPROVE and CSN sites, as demonstrated by experiments with monitors run side-by-side [*Hains, et al.*, 2007]. Elemental carbon likewise presents an analytical challenge, but both EC and dust are typically each about 5% of the total mass. The policy implication is that control of local emissions of crustal elements, from construction, for example, can have at best a minor impact of the annual PM2.5 value.

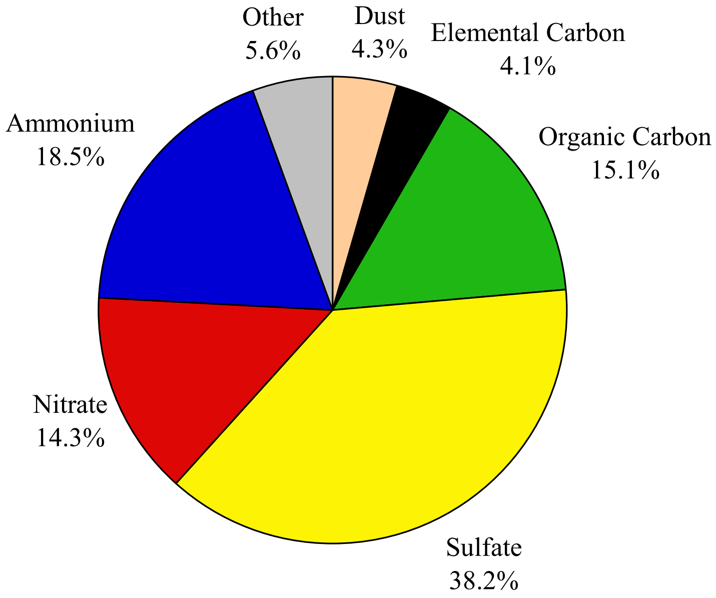


Figure I-2. Relative contributions of PM2.5 species at the Arendtsville, PA IMPROVE monitor for the 2004-2006 time period. Total mass of PM2.5 for individual years is given in Section III. The IMPROVE network does not generally provide ammonium; shown here is the percentage assuming sulfate and nitrate were fully neutralized. "Other" is the difference between gravimetric and reconstructed mass without converting OC to OM.

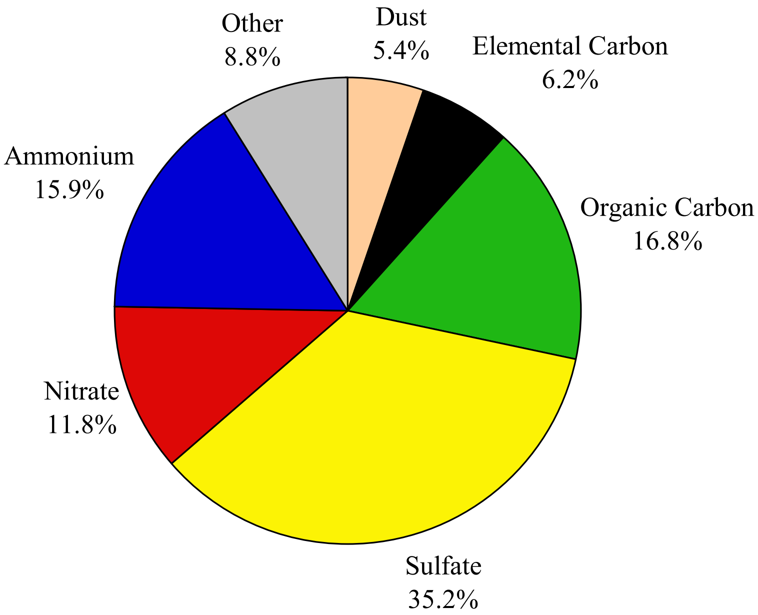


Figure I-3. Relative contributions of PM2.5 species at the UMBC IMPROVE monitor (located in Catonsville, SW of Baltimore, MD) for the 2004-2006 time period. For details see caption to Figure I-2.

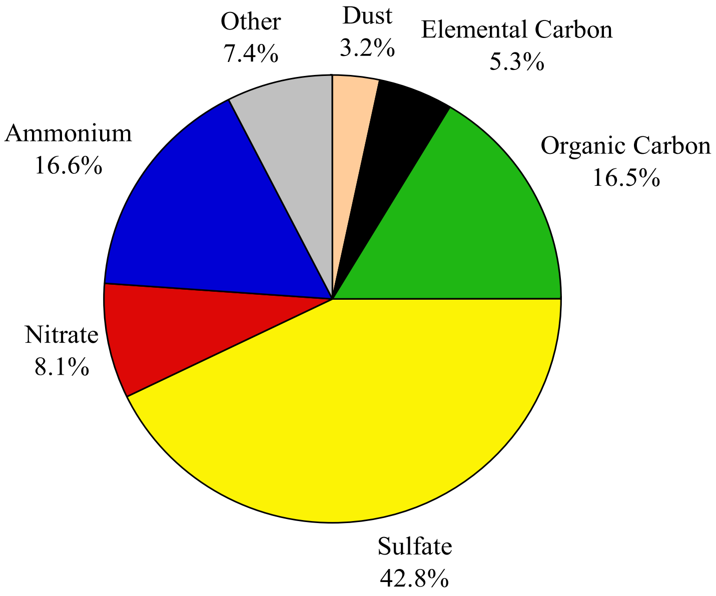


Figure I-4a. Relative contributions of PM2.5 species at the Brigantine, NJ IMPROVE monitor for the 1991-1993 time period. For details see caption to Figure I-2.

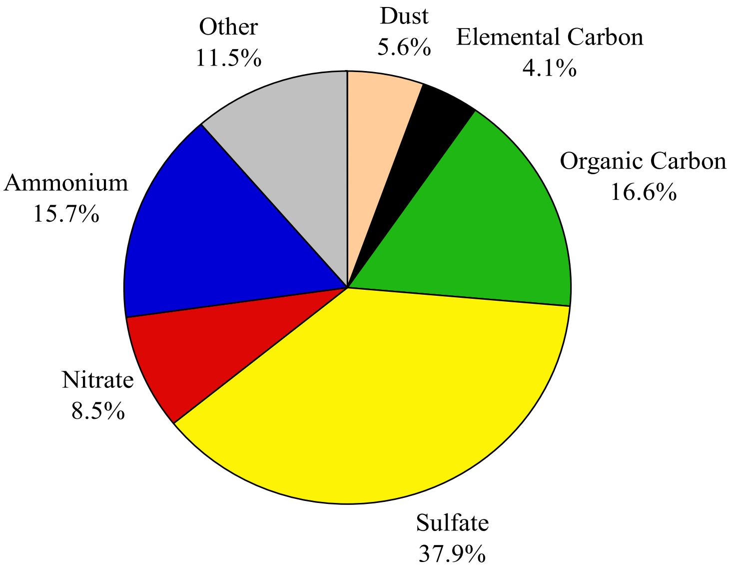


Figure I-4b. Relative contributions of PM2.5 species at the Brigantine, NJ IMPROVE monitor for the 2004-2006 time period. For details see caption to Figure I-2.

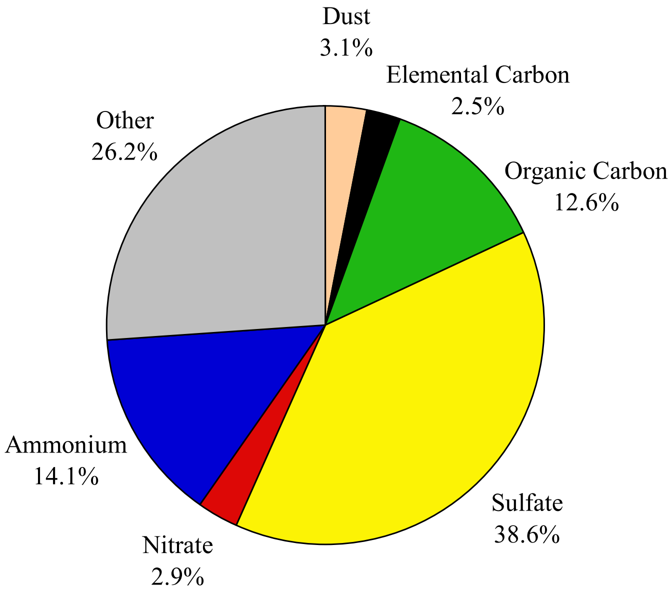


Figure I-5a. Relative contributions of PM2.5 species at the Dolly Sods, WV IMPROVE monitor for the 1991-1993 time period.

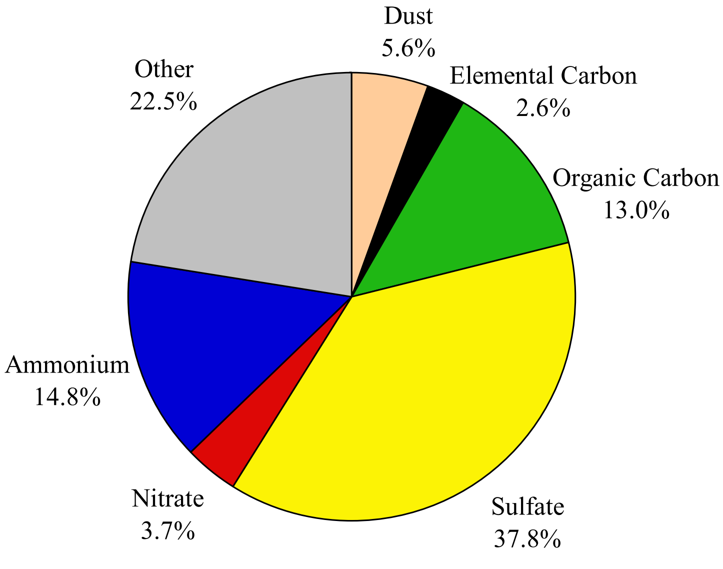


Figure I-5b. Relative contributions of PM2.5 species at the Dolly Sods, WV IMPROVE monitor for the 2004-2006 time period. For details see caption to Figure I-2.

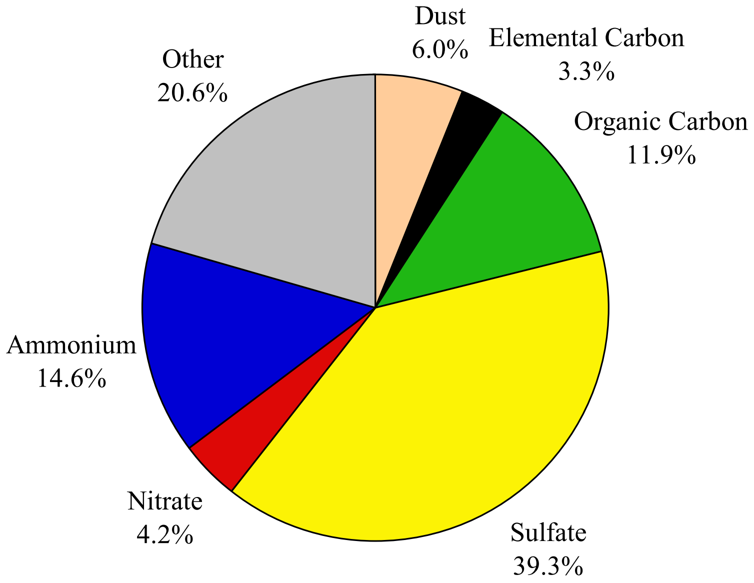


Figure I-6. Relative contributions of PM2.5 species at the Frostburg, MD IMPROVE monitor for the 2004-2006 time period. For details see caption to Figure I-2.

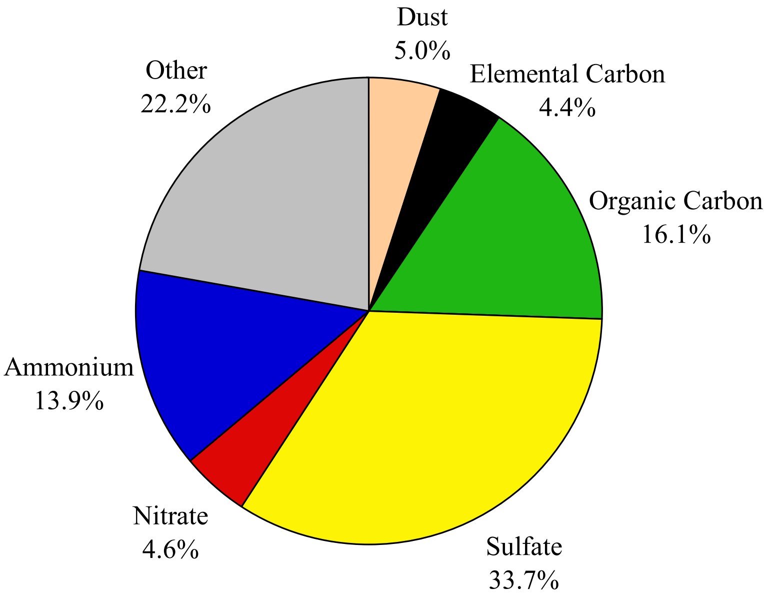


Figure I-7. Relative contributions of PM2.5 species at the James River, VA IMPROVE monitor for the 2004-2006 time period. For details see caption to Figure I-2.

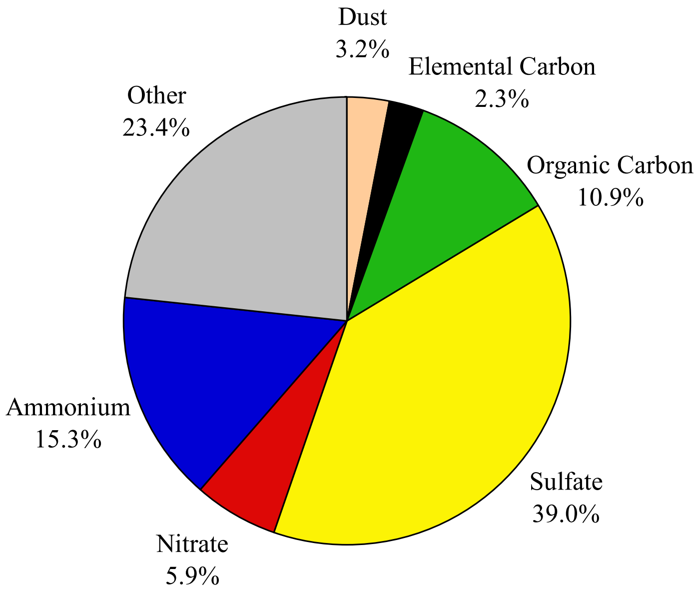


Figure I-8a. Relative contributions of PM2.5 species at the Shenandoah, VA IMPROVE monitor for the 1991-1993 time period.

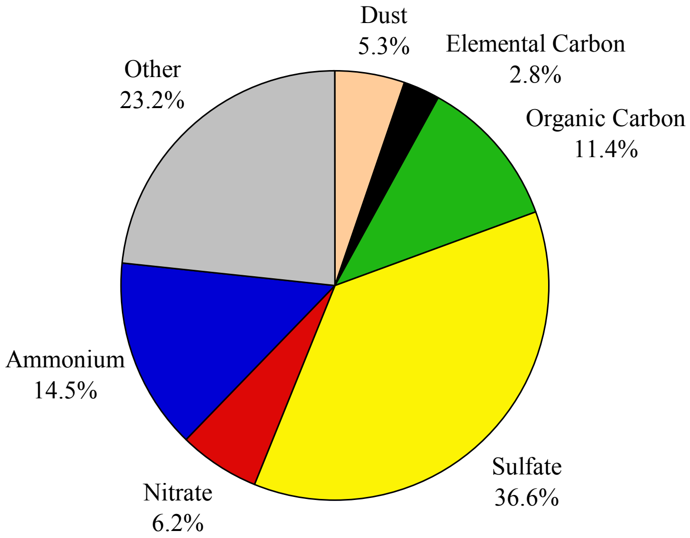


Figure I-8b. Relative contributions of PM2.5 species at the Shenandoah, VA IMPROVE monitor for the 2004-2006 time period. For details see caption to Figure I-2.

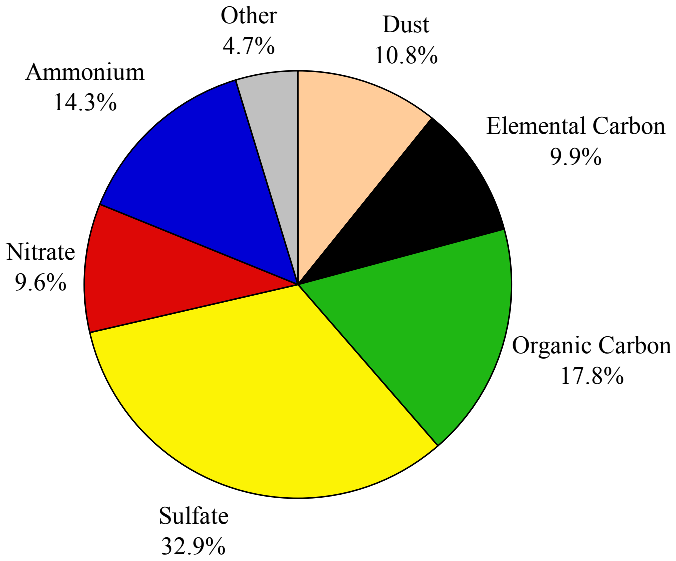


Figure I-9a. Relative contributions of PM2.5 species at the Hains Point (located in Washington, DC) IMPROVE monitor for the 1989-1991 time period.

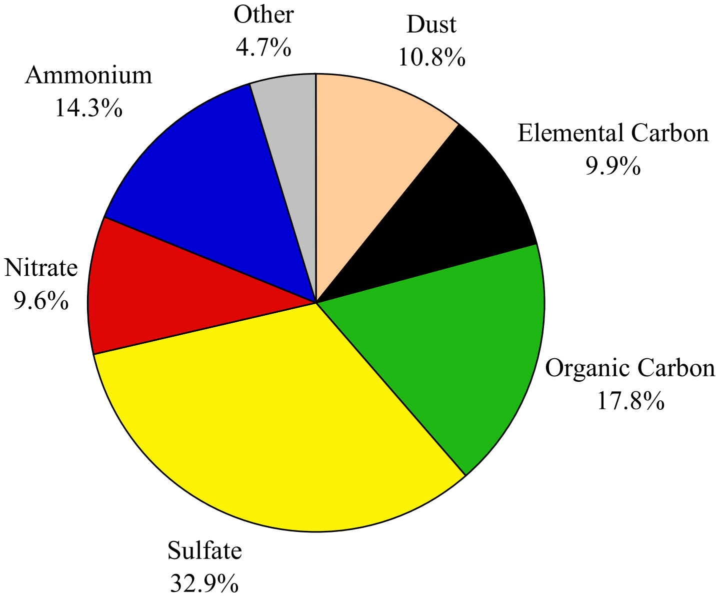


Figure I-9b. Relative contributions of PM2.5 species at the Hains Point (located in Washington, DC) IMPROVE monitor for the 2004-2006 time period.

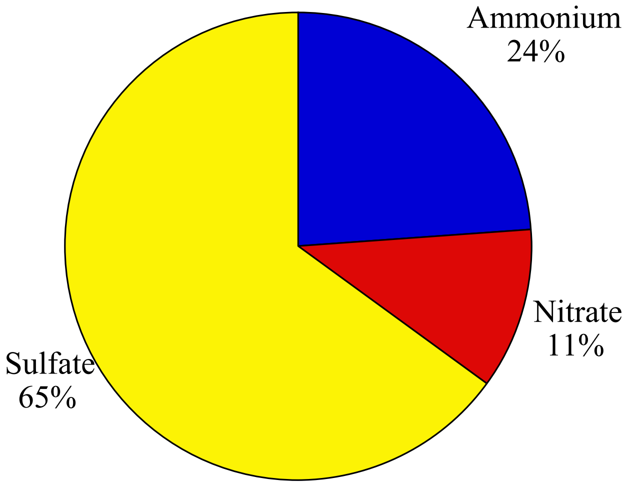


Figure I-10a. Relative contributions of PM2.5 species at the Beltsville, MD CASTNET monitor for the 1991-1993 time period. Percentages shown are of measured mass.

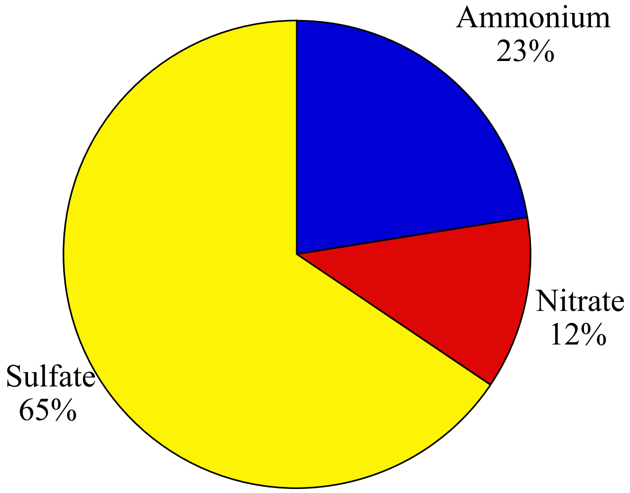


Figure I-10b. Relative contributions of PM2.5 species at the Beltsville, MD CASTNET monitor for the 2004-2006 time period.

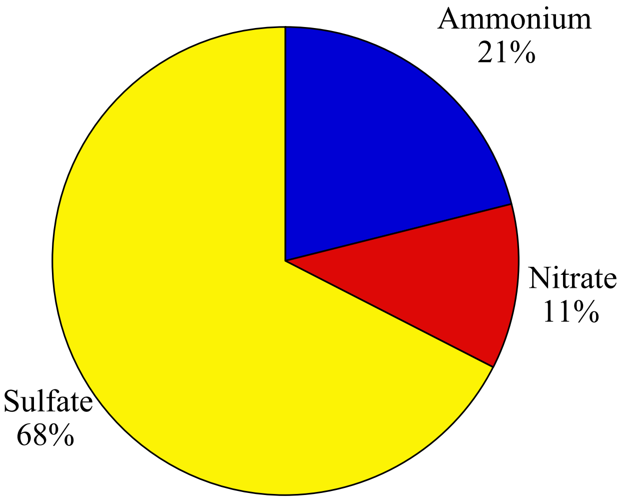


Figure I-11a. Relative contributions of PM2.5 species at the Blackwater, MD CASTNET monitor for the 1995-1997 time period.

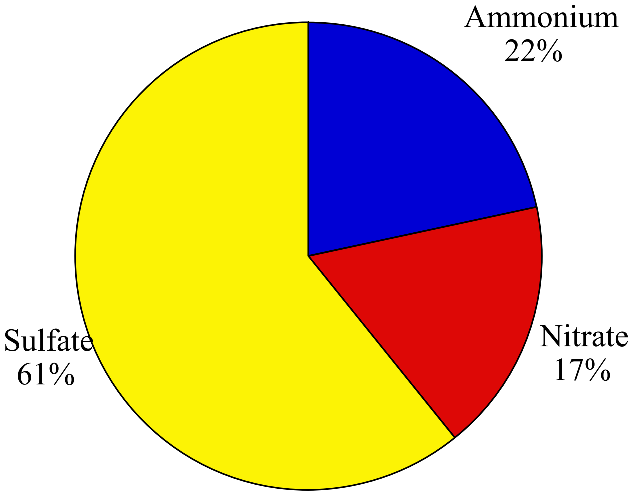


Figure I-11b. Relative contributions of PM2.5 species at the Blackwater, MD CASTNET monitor for the 2004-2006 time period.

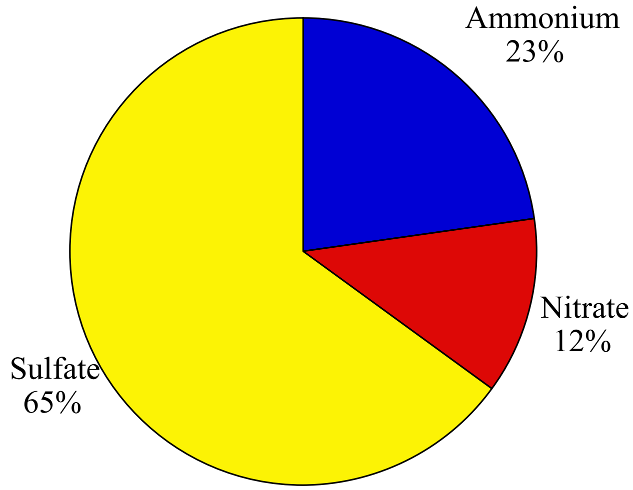


Figure I-12a. Relative contributions of PM2.5 species at the Washington Crossing, NJ CASTNET monitor for the 1991-1993 time period.

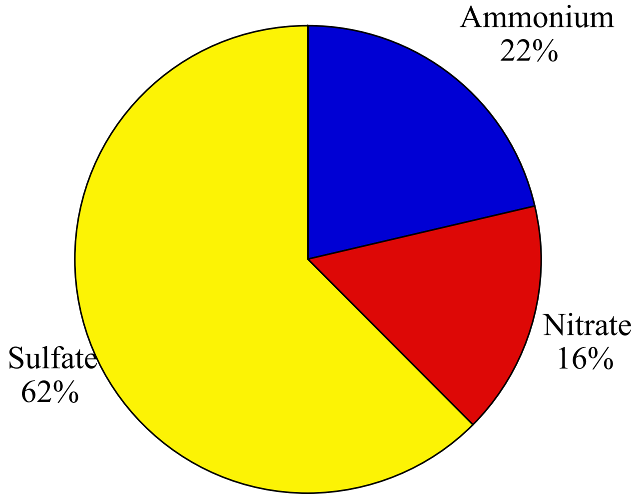


Figure I-12b. Relative contributions of PM2.5 species at the Washington Crossing, NJ CASTNET monitor for the 2004-2006 time period.

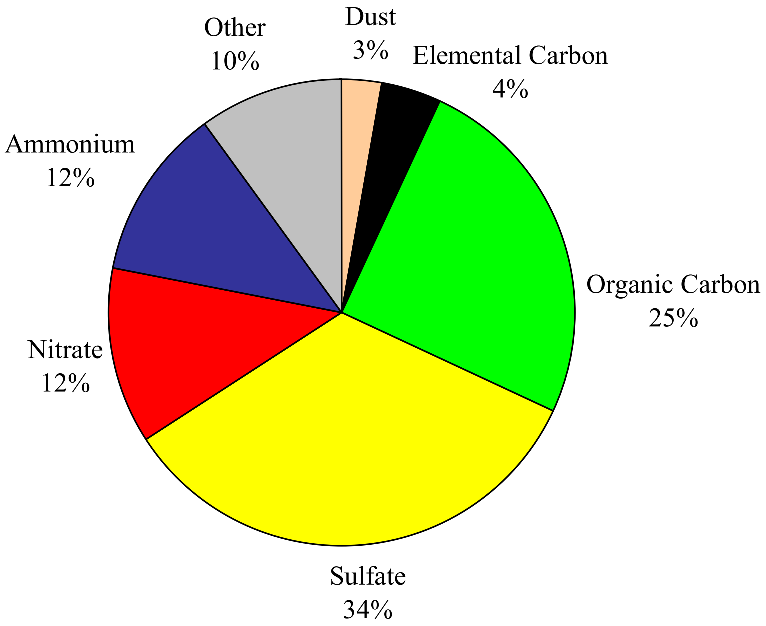


Figure I-13. Relative contributions of PM2.5 species at the Fort Meade, MD CSN EPA/State monitor for the 2004-2006 time period.

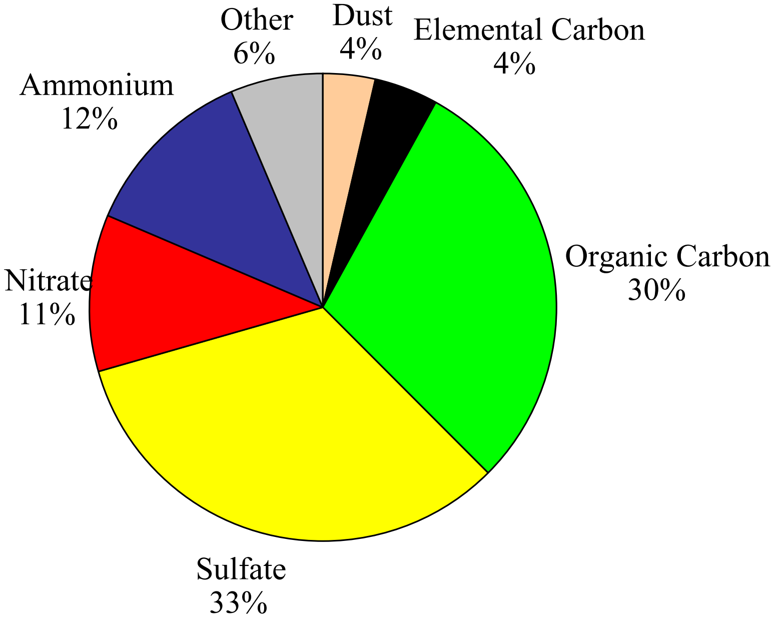


Figure I-14a. Relative contributions of PM2.5 species at the Essex, MD EPA/State CSN monitor for the 2001-2003 time period.

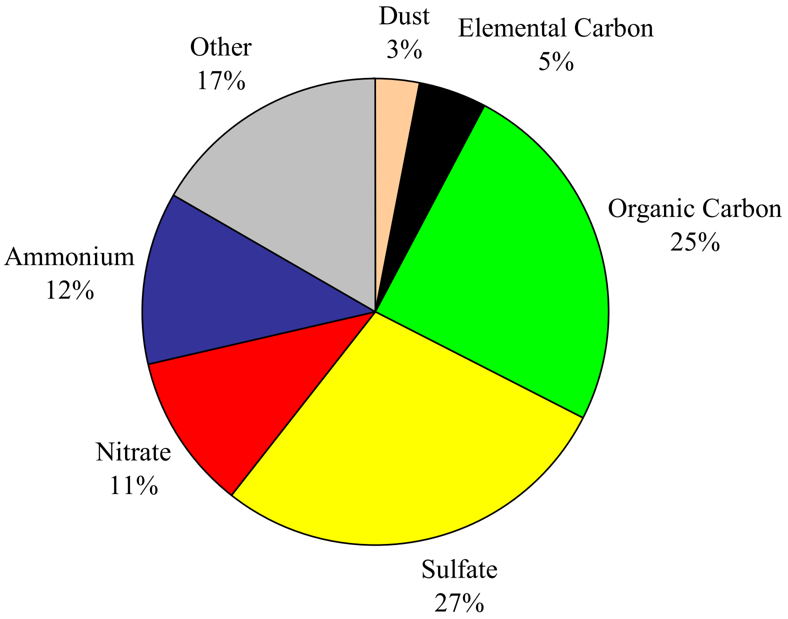


Figure I-14b. Relative contributions of PM2.5 species at the Essex, MD EPA/State CSN monitor for the 2004-2006 time period.

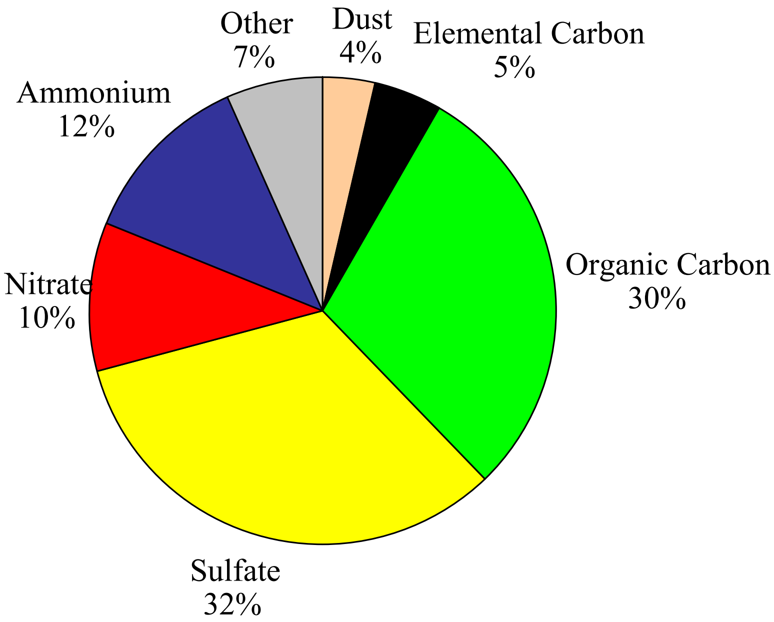


Figure I-15a. Relative contributions of PM2.5 species at the McMillan Reservoir (located in Washington, DC) EPA/State CSN monitor for the 2001-2003 time period.

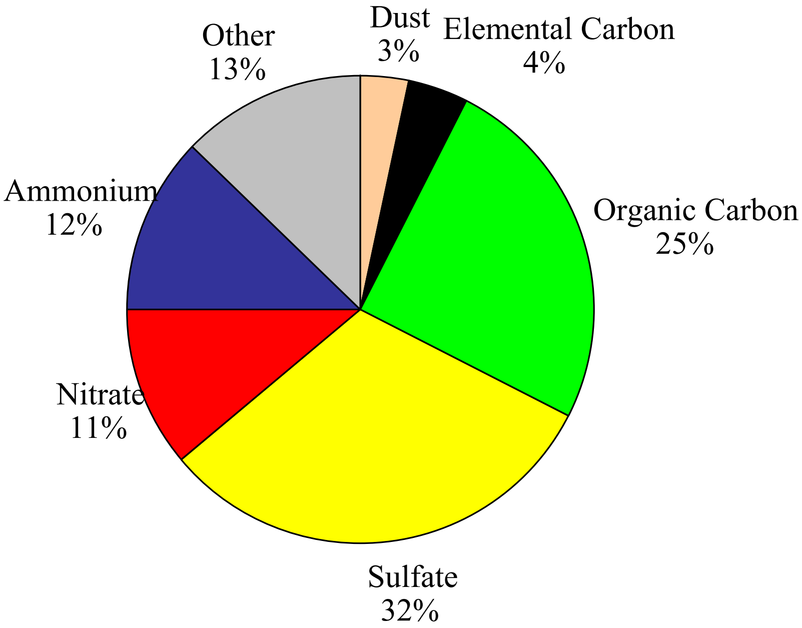


Figure I-15b. Relative contributions of PM2.5 species at the McMillan Reservoir (located in Washington, DC) EPA/State CSN monitor for the 2004-2006 time period.

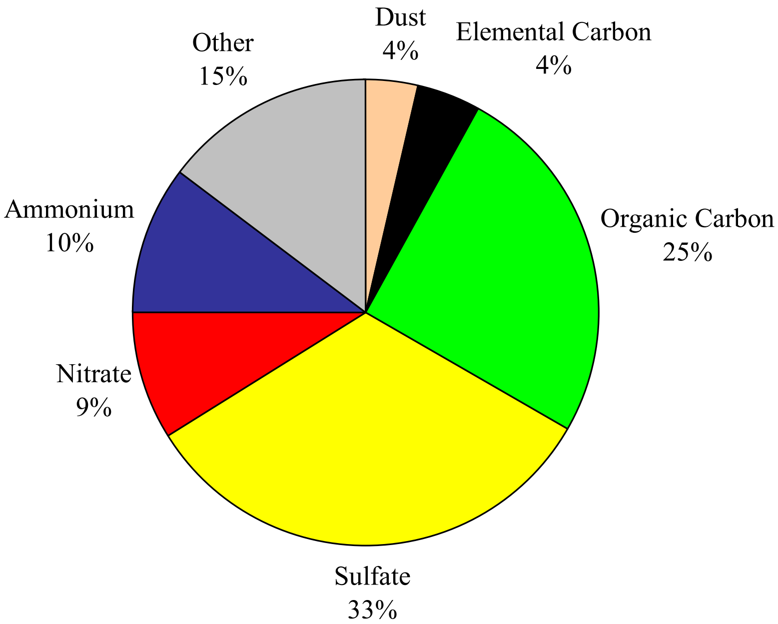


Figure I-16. Relative contributions of PM2.5 species at the Beltsville, MD CSN monitor for the 2004-2006 time period.

### c. Location

Within Maryland, and indeed in the surrounding region, the annual mean concentration of PM2.5 shows little spatial variation. The total mass of PM2.5 shows this regional uniformity because the principal components of the aerosol are in large part secondary particles formed at some distance from the origins of their precursors. For evidence of this we show several examples of the most recent available data from urban and rural sites in Maryland (Figure I-17). Little difference was observed from the Blackwater, MD site on the rural part of Maryland east of the Chesapeake Bay to the urban sites near Baltimore, MD (UMBC) and in Washington, DC (Hains Point). Nitrate, with the larger rural to urban gradient varied only from 1.30 to 1.54 $\mu g\ m^{-3}$, while sulfate concentrations varied from 4.49 to 4.85 $\mu g\ m^{-3}$; the range is about 8% of the mean and probably within the precision of the measurements.

The MARAMA-sponsored study [*Gillespie and Davis*, 2006] investigated eleven sites in the Maryland airshed for an earlier period, 2001-2003 (see Section V and Appendix MARAMA). The region-wide annual average sulfate was 5.11 $\mu g\ m^{-3}$ and varied by only about $\pm$ 1 $\mu g\ m^{-3}$ from the maximum observed in Arendtsville, PA to the minimum in Kinston, NC. Somewhat greater variability was observed in average level of organic material (MARAMA estimated OM as 1.6 x OC), but all monitored sites still fell within $\pm 1.8\ \mu g\ m^{-3}$ of the mean, 5.41 $\mu g\ m^{-3}$. The maximum OM was observed in Elizabeth, NJ and the minimum in Dover, DE. The range for nitrate was higher in the relative sense (mean 1.76 $\mu g\ m^{-3}$, maximum 2.48 $\mu g\ m^{-3}$, and minimum 0.94 $\mu g\ m^{-3}$), but small in the absolute sense, $< 1\ \mu g\ m^{-3}$. In the context of abatement strategy, these are uniform concentrations. The MARAMA study concluded that controlling emissions on a regional scale appears to favorably impact the PM2.5 concentrations for the whole airshed including sites in Maryland.

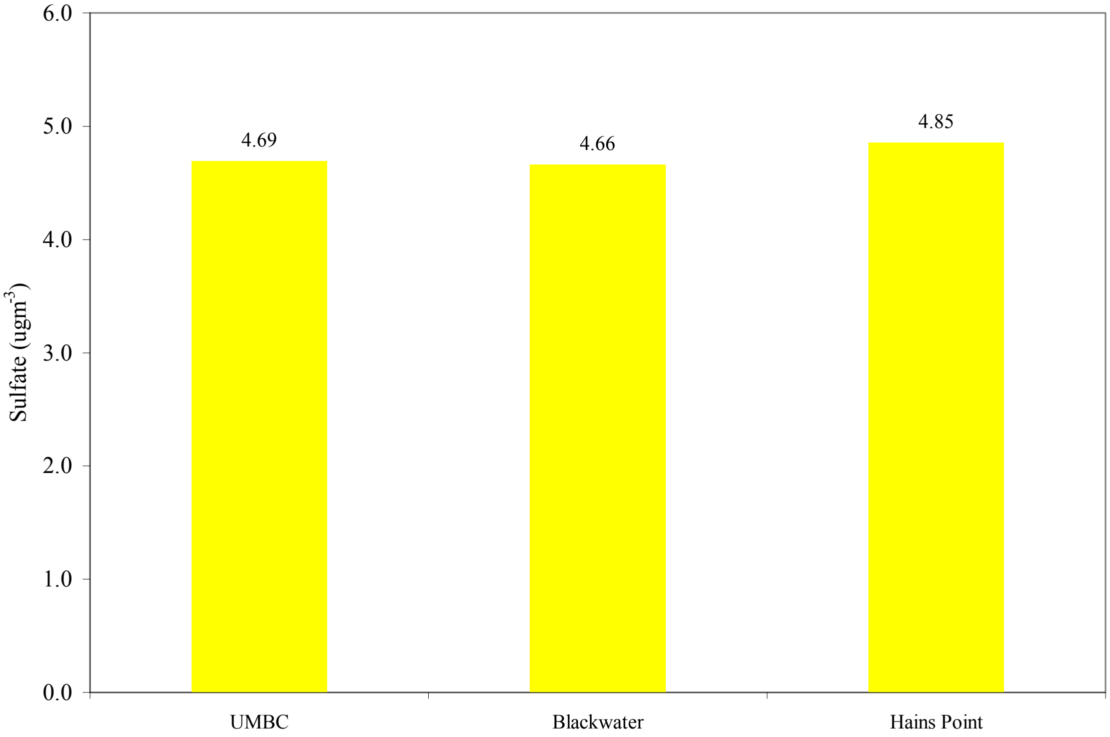


Figure I-17a. Mean concentration of sulfate at two urban (UMBC and Hains Point) and one rural (Blackwater is on Maryland's Eastern Shore) for the years 2004-2006. Because sulfate is a secondary pollutant distributed regionally, little spatial variability is observed in long-term averages.

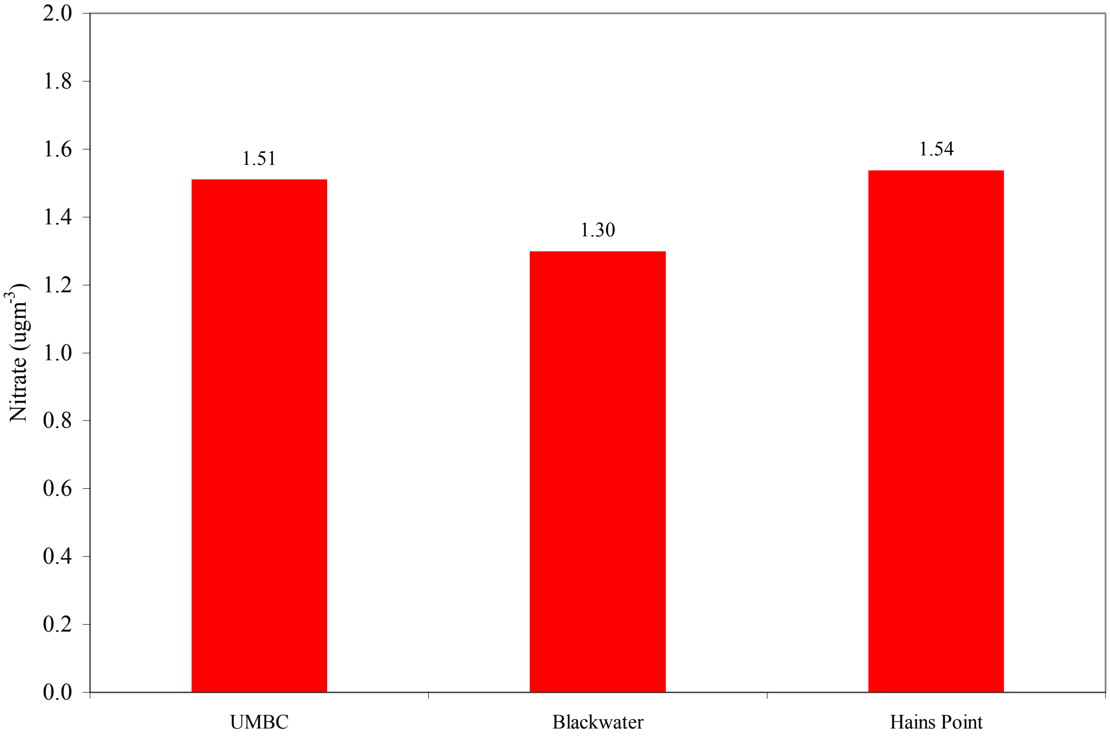


Figure I-17b. Mean concentration of nitrate at two urban (UMBC and Hains Point) and one rural (Blackwater is on Maryland's Eastern Shore) for the years 2004-2006. Because nitrate is a secondary pollutant distributed regionally, little spatial variability is observed in long-term averages.

### d. Time of Year

The seasonal cycle of total PM2.5 mass (Figure I-18) shows a summer peak at all sites reporting; some of the sites show a weaker winter peak as well. The cold-season secondary peak is observed primarily with urban monitors that have relative high concentrations of nitrate such as UMBC (Catonsville, MD) and Hains Point in Washington, DC. Most of the summer maximum is driven by the seasonality in the rate of oxidation of $SO_2$ to sulfate (Figure I-19) reflecting the annual maximum in OH and $H_2O_2$ concentrations in June, July, and August (JJA). Organic matter OM is composed of both primary and secondary pollutants with both biogenic and anthropogenic sources. The biogenic sources are strongest in summer, but anthropogenic sources show only a weak seasonality, thus OM makes a lesser contribution to the summer maximum (Figure I-20). The greater JJA values corroborate the contention of *Robinson et al.* (2007) that most of the OM over the eastern US is produce *in situ* by atmospheric photochemistry making it secondary organic aerosol (SOA).

Although some sites show a weak secondary winter maximum in OM, the driving force for this cold season peak is nitrate (Figures I-20 and I-21). The thermodynamic equilibrium among gaseous nitric acid, gaseous ammonia, and condensed ammonium nitrate favors the vapor state at high temperatures and the solid state at lower temperatures; observations made in Fort Meade, MD were consistent with calculations based on chemical thermodynamics [*Chen, et al.*, 2002]. Ammonium (Figure I-22) shows only a weak seasonality because it is the counter ion to both sulfate and nitrate, and without an anion to bind with ammoniacal N tends to stay in the vapor phase.

We can average the signal to get a smoother view of the seasonal cycle in PM components. Using the mean of the most recent three years available (2004-2006) at Blackwater, MD we can better quantify the seasonality of the major PM species (Figures I-23 – I-25). This site, situated east and generally downwind of Baltimore and Washington, is characteristic of the region. Sulfate varies by more than a factor of two from summer to winter, while nitrate shows an even stronger seasonality with winter concentrations more than five times greater than the summer concentrations. The summer peak in ammonia is 2.24 $\mu g\ m^{-3}$ compared to the minimum in fall of 1.40 $\mu g\ m^{-3}$

for a modest ratio of 1.6:1. Using the Hains Point site, three year smoothing reveals an unusual cycle in EC with a spring minimum and fall maximum (Figure I-26). Planetary boundary layer (PBL) depths are greater in summer making for faster dilution of primary pollutants such as CO and EC, but higher temperatures are conducive to higher emissions of EC [*Chen, et al.*, 2001]. In summary, the seasonal cycle is driven primarily by the secondary nature of sulfate and OM – faster oxidation in the summer months leads to a maximum concentration of total PM2.5 mass in that season.

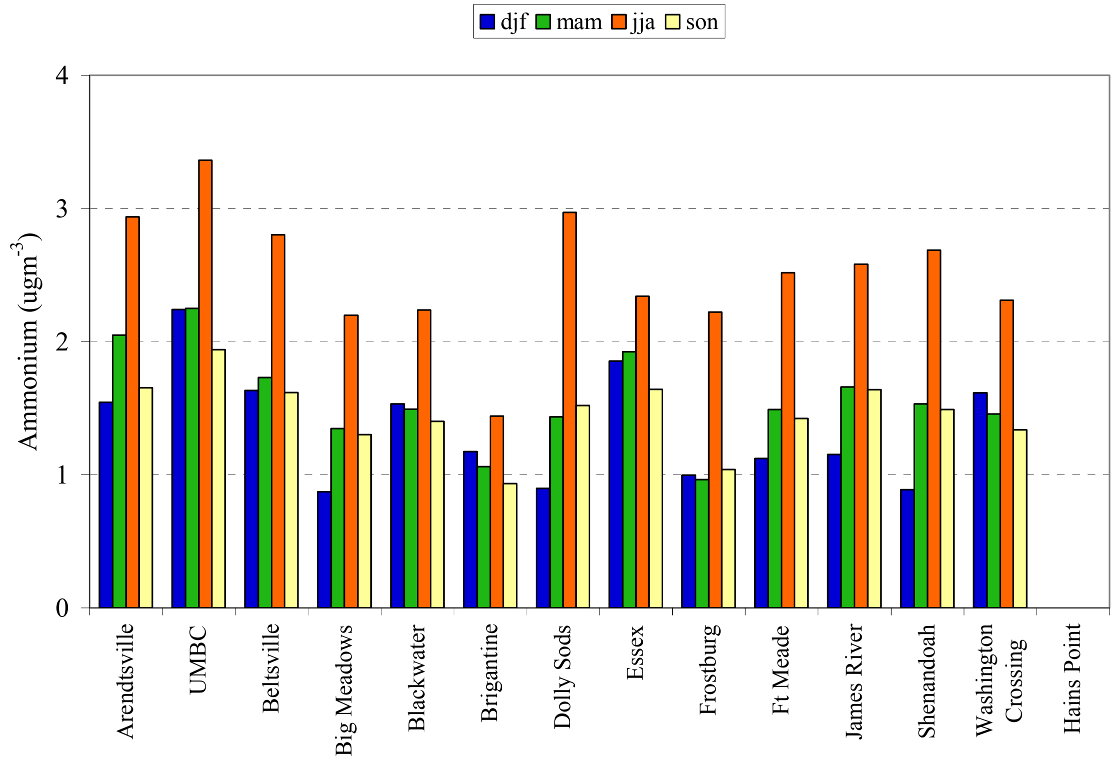


Figure I-18. Seasonal cycles of total PM2.5 mass at the sites in and around the Baltimore nonattainment area. All sites show a summer maximum, due primarily to increased sulfate. The urban sites (Brigantine, UMBC, Essex, and Haines Point) show a secondary peak in the winter, due primarily to nitrate. The seasonal averages cover various years and monitoring networks. For details concerning years encompassed for each monitor and monitor network reference Table I-1.

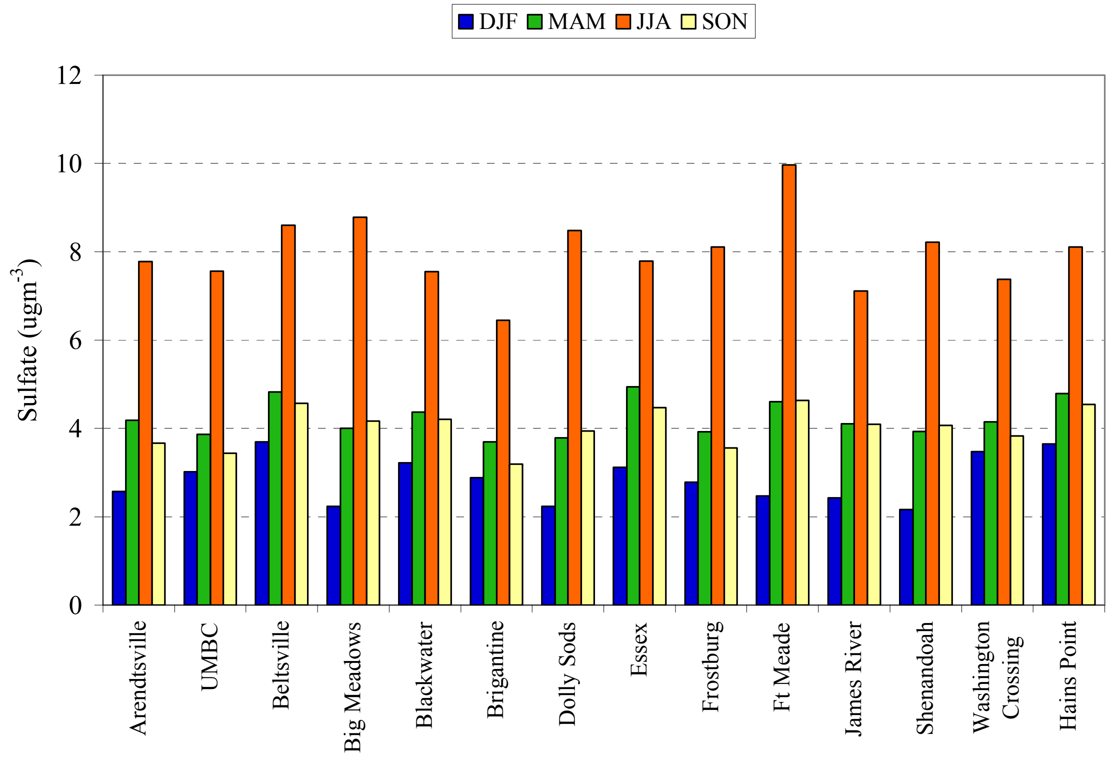


Figure I-19. Seasonal cycles of sulfate concentration at the sites in and around the Baltimore nonattainment area. All sites show a summer maximum, due primarily to increased rate of oxidation. The urban sites (UMBC, Essex, and Hains Point, DC) show little increase relative to rural sites. The seasonal averages cover various years and monitoring networks. For details concerning years encompassed for each monitor and monitor network reference Table I-1.

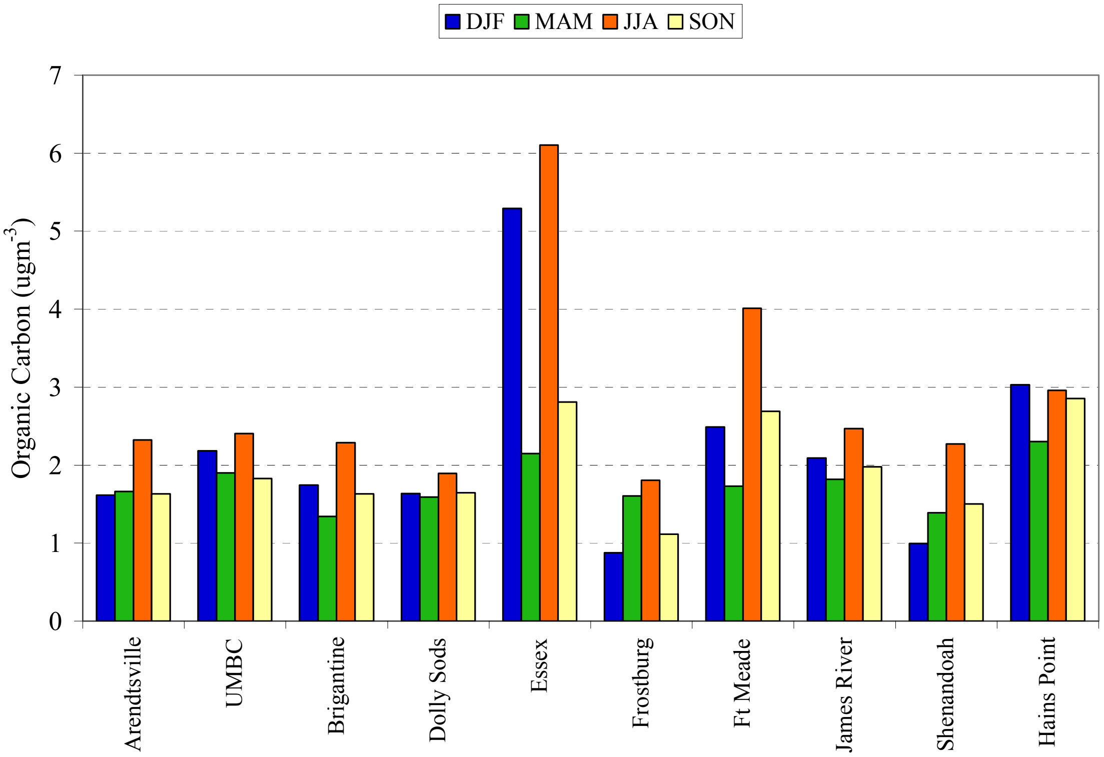


Figure I-20. Seasonal cycles of OC concentration at the sites in and around the Baltimore nonattainment area. Most sites show little seasonal signal although Essex, an urban site, shows a clear double maximum – summer and winter. The seasonal averages cover various years and monitoring networks. For details concerning years encompassed for each monitor and monitor network reference Table I-1.

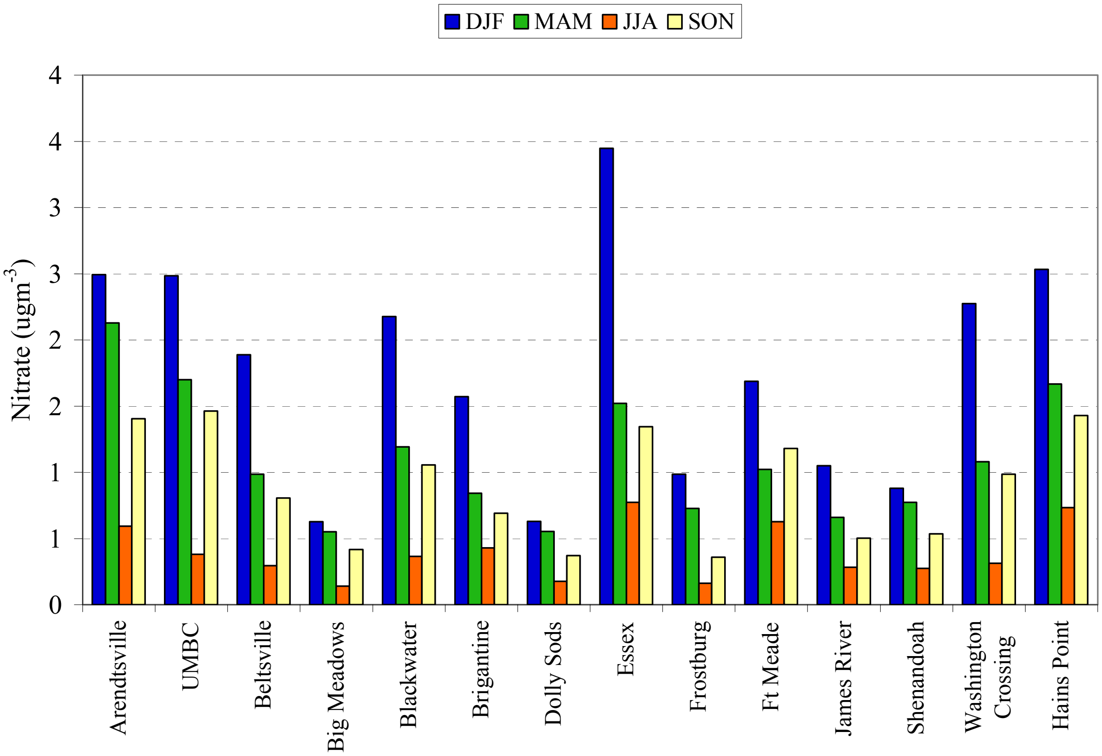


Figure I-21. Seasonal cycles of nitrate concentration at the sites in and around the Baltimore nonattainment area. All sites show a winter maximum due to the thermal instability of ammonium nitrate. The seasonal averages cover various years and monitoring networks. For details concerning years encompassed for each monitor and monitor network reference Table I-1.

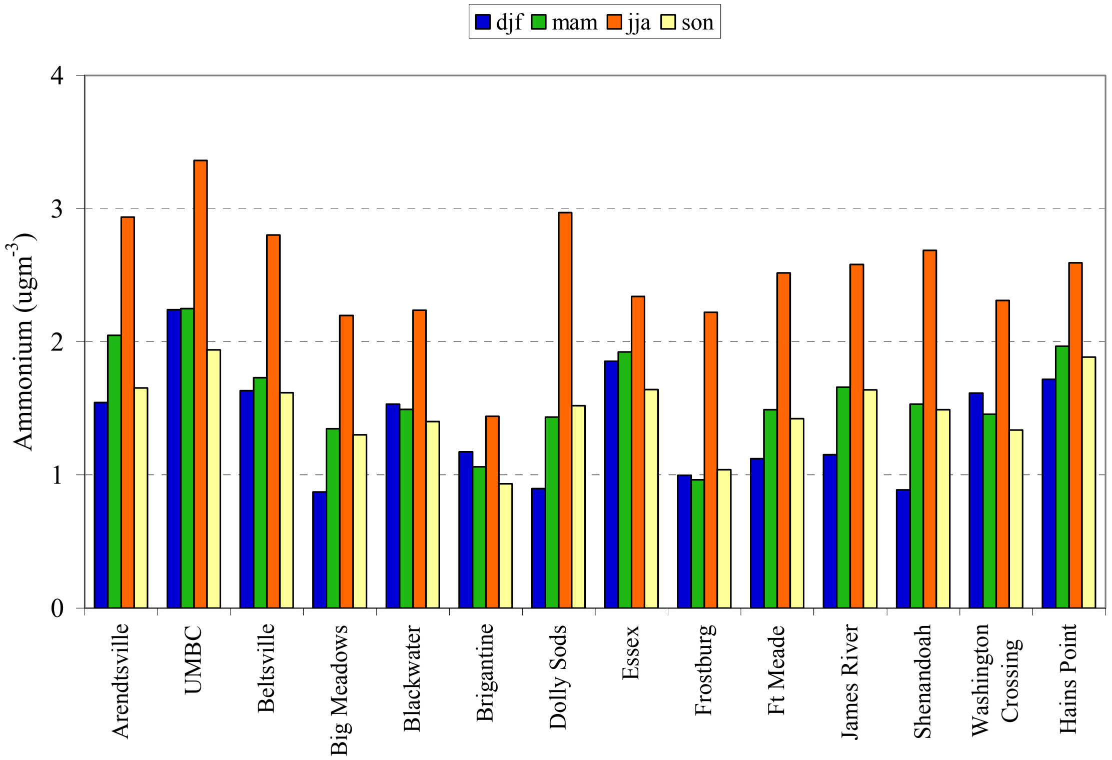


Figure I-22. Seasonal cycles of ammonium concentration at the sites in and around the Baltimore nonattainment area. A weak summer maximum, probably related to ammonium sulfate, is generally observed. The seasonal averages cover various years and monitoring networks. For details concerning years encompassed for each monitor and monitor network reference Table I-1.

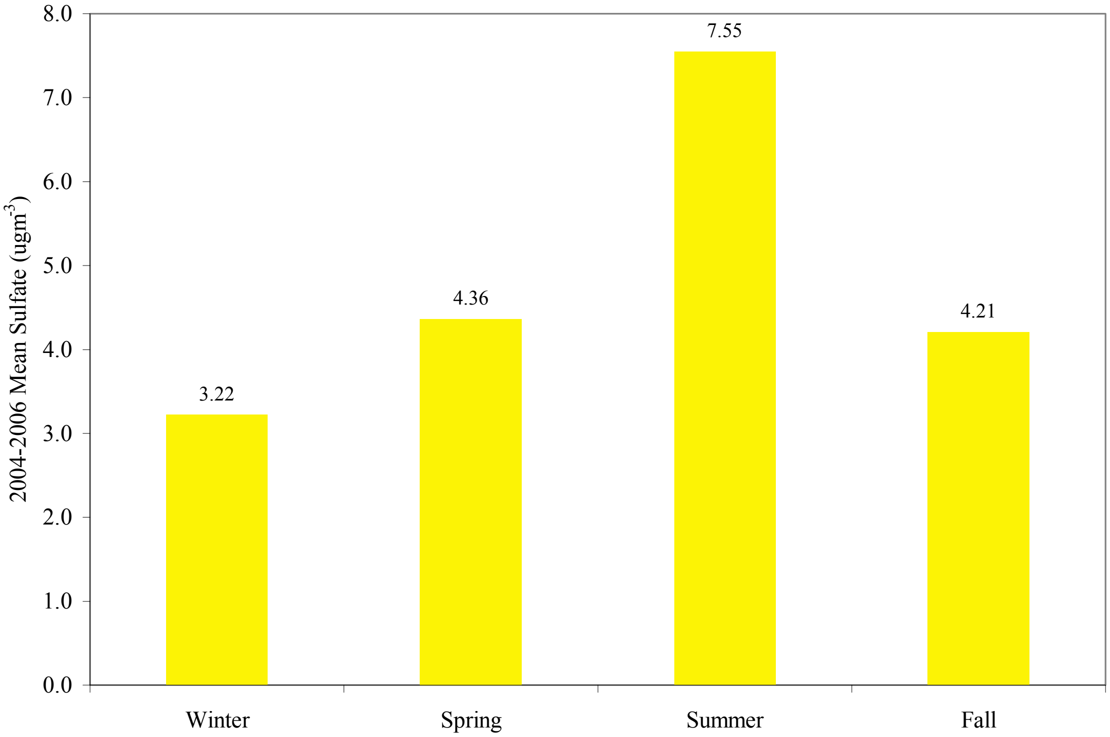


Figure I-23. Seasonal cycle in sulfate observed 2004 to 2006 at the CASTNET site in Blackwater, MD. The concentration of sulfate reflects the rate of oxidation of $SO_2$, which peaks in the sunniest months – summer.

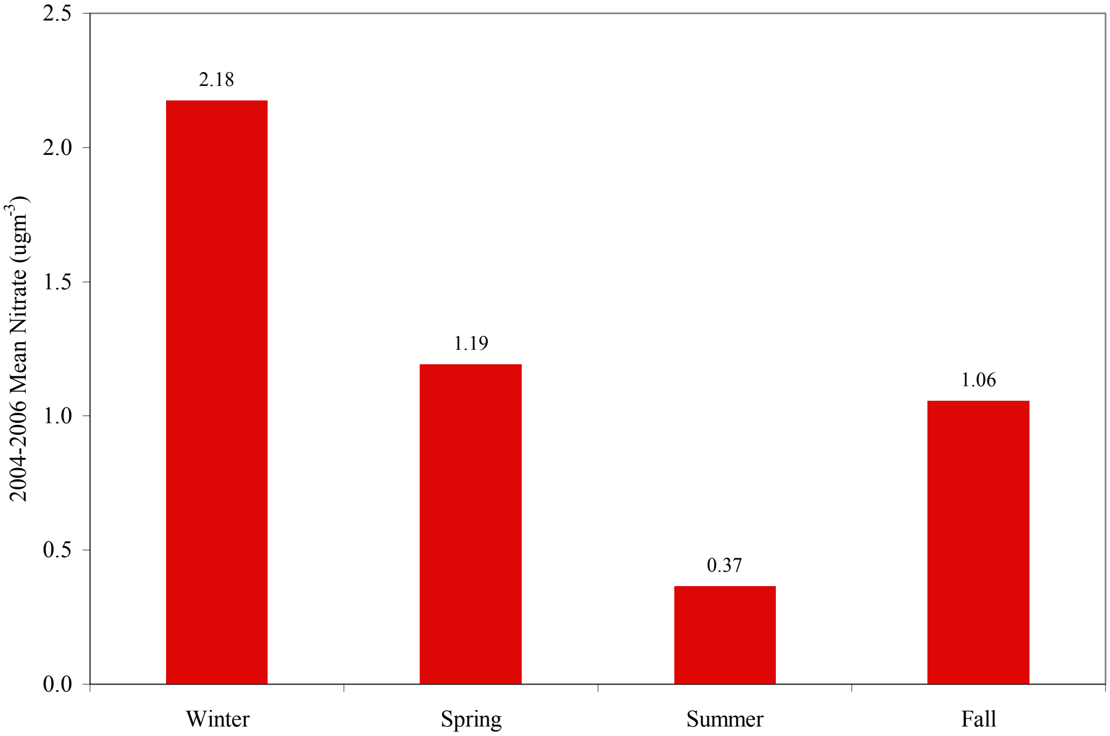


Figure I-24. Seasonal cycle in nitrate observed 2004 to 2006 at the CASTNET site in Blackwater, MD. The concentration of condensed phase nitrate reflects the thermodynamics of solid ammonium nitrate dissociation into vapor phase nitric acid and ammonia. Note minimum in the warmest months.

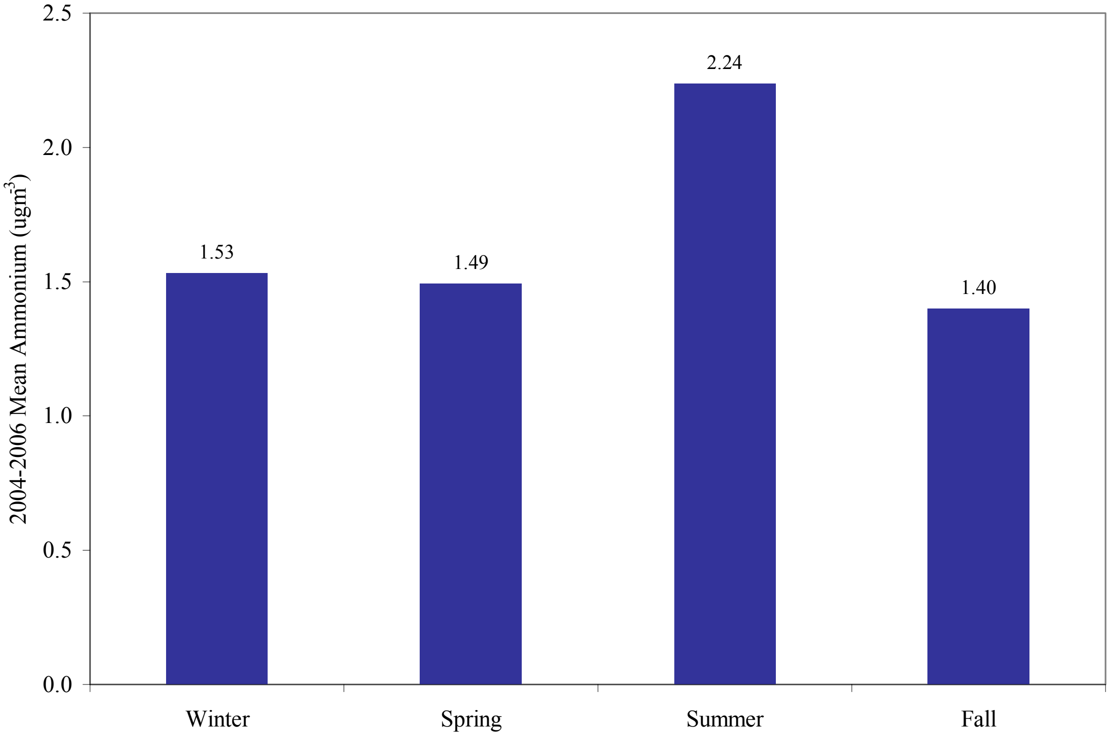


Figure I-25. Seasonal cycle in ammonium observed 2004 to 2006 at the CASTNET site in Blackwater, MD. The concentration of condensed phase ammonium reflects the concentration of sulfate and nitrate. The summer sulfate peak drives the summer ammonium peak.

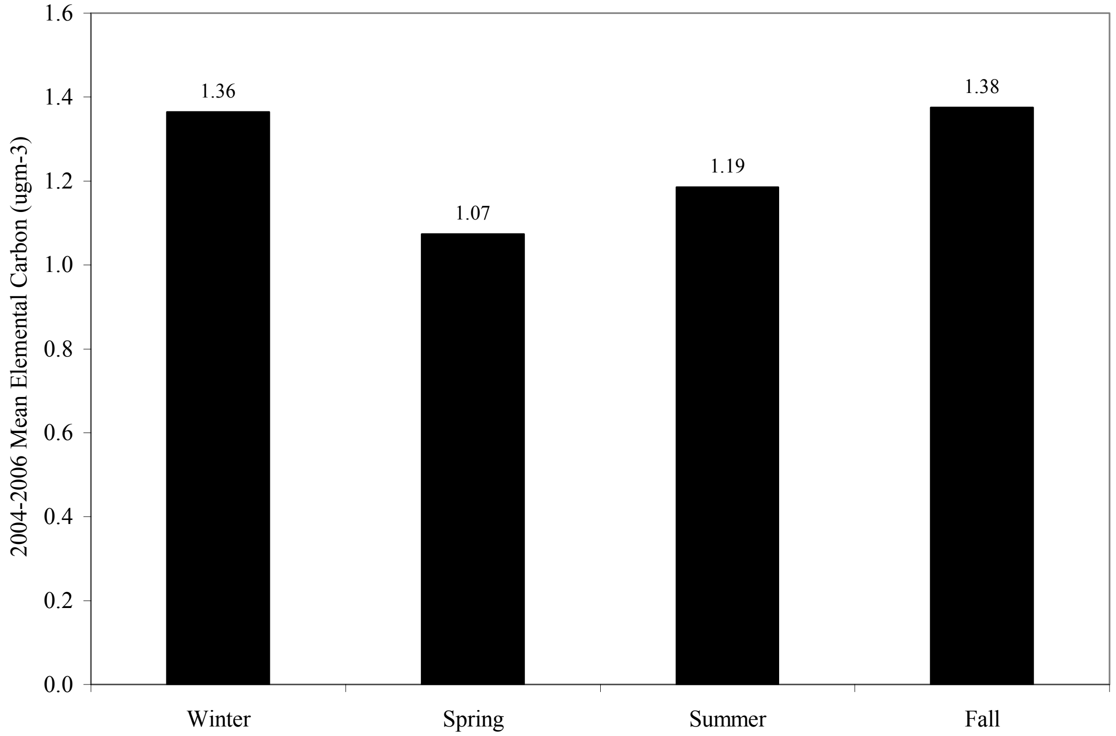


Figure I-26. Seasonal cycle in elemental carbon observed 2004 to 2006 at the IMPROVE Hains Point site (located in Washington, DC). Note weak peak in fall and winter.

### e. Conclusions

In summary, the composition of PM2.5 depends moderately on time of year with a seasonal cycle of individual components that varies from a strong summer maximum for sulfate to a winter maximum for nitrate. These observations imply that $SO_2$ controls are important year-round, but possibly more effective in JJA. Summer controls on NOx may be successful in reducing photochemical smog (ground-level ozone), but are less effective for PM2.5 reduction, because most of the particulate nitrate is found in the winter. At most sites, total PM2.5 concentration shows a primary peak in summer and a secondary peak in winter. OM peaks in summer, and this may be a function of biogenic and evaporative VOC emissions that scale with temperature. Observations indicate that year-round controls of anthropogenic VOC's (as well as primary aerosols) are most likely to be beneficial. Published studies and the experimental evidence made recently available show that the absolute concentration as well chemical composition of the fine particulate matter over the Mid Atlantic region are reasonably well understood and reflect the sources, transformations, and sinks of the aerosols and their precursors. The relative importance of major constituents varies by season and location, but the fundamental properties are, for purposes of abatement strategy, fairly uniform in time and space. Ammonium sulfate or bisulfate is the biggest contributor with organic material a close second. With the addition of nitrate, black carbon, and crustal material, individually measured species account over 90% of the total aerosol mass, and "other" or unidentified compounds generally play only a minor role. Total PM2.5 concentration shows a modest tendency towards higher magnitudes in more urban areas although much of the distribution is regional in nature, especially in summer.

## References

Chen, L.-W. A., et al. (2001), Seasonal variations in elemental carbon aerosol, carbon monoxide, and sulfur dioxide: Implications for sources, *Geophys. Res. Lett.*, *28*, 1711-1714.

Chen, L. W. A., et al. (2002), Origins of fine aerosol mass in the Baltimore-Washington corridor: Implications from observation, factor analysis, and ensemble air parcel back trajectories, *Atmospheric Environment*, *36*, 4541-4554.

Gillespie, W. G., and P. Davis (2006), An Analysis of Speciated PM2.5 Data in the MARAMA Region, 254 pp, Mid-Atlantic Regional Air Management Association.

Hains, J. C., et al. (2007), A Side-by-Side comparison of Filter-Based PM2.5 Measurements at a Suburban Site: A Closure Study, *Atmos. Environ.*

Sickles, J. E., and D. S. Shadwick (2007), Seasonal and regional air quality and atmospheric deposition in the eastern United States, *Journal of Geophysical Research-Atmospheres*, *112*.

# Section II

# Review of Literature on PM2.5: Focus on Maryland

Dr. Russell R. Dickerson, Dr. Jeffrey W. Stehr
Department of Atmospheric and Oceanic Science
The University of Maryland
Patricia Castellanos, Dr. Sheryl Ehrman
Department of Chemical and Biomolecular Engineering
The University of Maryland

February 6, 2008

### 1. Why is this section important?

A careful appraisal of the peer-reviewed literature on PM2.5 can provide technical insight into the concentrations of aerosols in Maryland and the processes that affect them. This review examines the nature of the PM2.5 problem in Maryland; it summarizes published scientific evidence on the relative importance of the individual components of PM2.5, their origins, and their spatial and temporal trends.

### 2. What questions are answered in this section?

How does the peer-reviewed literature (and other studies) support the conceptual model of PM2.5 in Maryland? What species should Maryland focus on controlling in order to be in PM2.5 attainment? Where do the precursors of these species come from? Is the PM2.5 problem local or regional? Do the highest PM2.5 episodes throughout the year have the same characteristics?

### 3. What are the key takeaway messages from this section?

The largest portion of the PM2.5 nonattainment problem in Maryland stems from secondary sulfate (as ammonium sulfate or bisulfate), with a large fraction of that coming from $SO_2$ emissions from the Ohio River Valley. The current emphasis on $SO_2$ controls is therefore entirely justified due to sulfate's dominance of the regional PM2.5 burden. Controls in upwind states are essential in addressing the PM2.5 problem in Maryland. The highest PM2.5 episodes are typically dominated by high sulfate, especially in summer. Even in winter, sulfate usually has the largest contribution to total PM2.5 of any single species. The next greatest contributor to PM2.5 is OM, and this review indicates that reductions of emissions of VOC's and primary particles have resulted in reductions of concentrations of OM and should continue to do so.

### 4. What conclusions are reached in this section with respect to Maryland attainment demonstration?

The peer-reviewed literature cannot provide exact numbers for EPA's model attainment test, but it does support Maryland's approach as scientifically justified. Emissions of $SO_2$, $NO_x$, VOC's and primary PM are all being reduced, but by emphasizing regional $SO_2$ controls to reduce sulfate, Maryland is applying the most effective controls at the right time and place. Furthermore, the highest PM2.5 levels occur on days when sulfate is highest, so future attainment of the daily standard will benefit from the current emphasis on sulfate.

## Abstract

This section summarizes the scientific literature on PM2.5, especially as it relates to PM2.5 in Maryland. In this review, a picture emerges of a regional PM2.5 burden, with sources hundreds of km's away providing much of the burden of the aerosols. Sulfate dominates the regional picture, though local PM2.5 and precursor sources are also important. Because the PM2.5 problem in Maryland is part of a broader regional problem, the focus on regional controls in the Maryland SIP is supported, especially regional $SO_2$ controls, though local and regional VOC controls as well as $NO_x$ controls should also have some impact on PM2.5. In this review, experimental campaigns in Maryland are discussed first, then proceeding to regional campaigns and data analysis efforts. In all, direct observations, modeling, source apportionment, back trajectory and clustering techniques are used to create a coherent picture of the PM2.5 problem in the East, especially as it applies to Maryland. Sulfate emerges as the dominant contributor, with a large share of the PM2.5 problem and an even larger share of the visibility problem, while OC and nitrate are smaller, but still significant contributors. Reductions in $SO_2$ and $NO_x$ emissions have been conclusively linked to reductions in sulfate and nitrate. From this literature review, we conclude that control of $SO_2$ (especially on the regional scale), VOC's, and $NO_x$ should lead to continued significant reductions in PM2.5 over Maryland.

## a. Chemistry and Precursors

### i. Published Evidence that Concentrations are Proportional to Emissions

The State Implementation Plan for PM2.5 is predicated on the assumption that reducing emissions of PM2.5 precursors will reduce concentrations of individual aerosol species. Several studies have addressed the issue of the relationship between $SO_2$ and NOx emissions and sulfate and nitrate concentrations in aerosol concentration or in deposition [*Likens et al.*, 2005; *Malm et al.*, 2002; *Malm et al.*, 2004; *Polissar et al.*, 2001; *West et al.*, 1999]. Although some models have suggested nonlinearities, observations over decades indicate that nitrate and sulfate respond proportionally to emissions of precursors. Investigators in New England found a highly significant second-order polynomial relation between $SO_2$ emissions and sulfate concentrations during the period 1970 - 2000 and a linear relation between NOx and nitrate concentrations measured in bulk precipitation in the Hubbard Brook Experimental Forest, NH during the period 1991 – 2000 [*Butler, et al.*, 2005; *Likens, et al.*, 2005]. In these studies, they used 24-hour back-trajectories to determine source areas of emissions. Earlier periods had poorer linear relations, and the authors attribute this to frequent and significant changes in the methodology used by the US Environmental Protection Agency for calculating emissions data during these decades. The relationship between NOx and nitrate for the period 1991-2000 was the best when vehicular and Canadian emissions were included in the analysis.

A recent review of Clean Air Status and Trends Network (CASTNET) and National Acid Deposition Program (NADP) data [*Sickles and Shadwick*, 2007a; *Sickles and Shadwick*, 2007b] analyzed the seasonal and regional behavior of concentration and deposition of a variety of primary and secondary pollutants including nitrate and sulfate and determined trends from 1990 to 2004 for the US east of the Mississippi River. They investigated observations from more than 50 sites in the eastern States. Little trend in nitrate was observed between in the first ten years of the study, but significant reductions ($p = 0.05$) were found between the 1990-1994 period and the 2000-2004 period, commensurate with emissions reductions in the NOx SIP Call implemented in 2003 and 2004. The concentration of nitric acid fell from 1.99 to1.74 $\mu g\ N\ m^{-3}$ or by 13%, and total nitrate deposition fell by 0.56 $kg\ N\ ha^{-1}yr^{-1}$ or 11%. NOx emissions controls were implemented primarily in the ozone season (May to September) and greatest reductions in N deposition were observed in the summer. Area average sulfate concentration in the period 2000-

2004 was 21% lower than in the period 1990-1994; $SO_2$ emissions decreased by 39% over the same time. For ammonium, the average concentration fell from 1.83 to 1.61 μg N $m^{-3}$ probably as a result of lower sulfur emissions – no change was observed in wet ammonium deposition.

Sickles and Shadwick [2007b] attributed the reduction in nitrate concentrations and deposition to reductions in NOx emissions. They reported that the relationship between emissions and deposition was less than 1:1, in other words emissions were reduced by about 22%, but deposition fell by only about 11%. Analysis is complicated by the brief period of monitoring since the emissions controls were implemented. The second five-year period averages from 2000-2004, but reductions went into effect over the 24-month period 2003-2004.

Satellite observations [*Kim, et al.*, 2006] showed declining regional $NO_2$ levels between 1999 and 2005 in response to the recent (2003 & 2004) implementation of pollution controls (NOx SIP Call) by utility companies in the eastern U.S. Remotely sensed summertime $NO_2$ columns and bottom-up emission estimates show large NOx reductions in the Ohio River Valley, where power plants dominate $NO_x$ emissions. In the Northeastern urban corridor, where local, vehicular sources of NOx dominate, the trend was weak.

Malm et al. (2002) examined spatial and temporal trends in ambient sulfate concentrations from 1988 to 1999 and $SO_2$ emissions from 1990 to 1999 using the Interagency Monitoring of Protected Visual Environments (IMPROVE) and the CASTNET sites located across the continental United States. The 90th percentile of summer sulfate concentrations was found along the Ohio River Valley and in central Tennessee where the emission density of $SO_2$ is the greatest. In the Eastern U.S., the largest sulfate decreases in the 80th percentile concentrations occurred north of the Ohio River Valley, while most monitoring sites south of Kentucky and Virginia showed no statistically significant trends. The 1990-1999 annual 80th percentile sulfate time series were compared to the annual $SO_2$ emissions over several regions, including the Northeast where both the sulfate and $SO_2$ emissions decreased by about 28%.

In a continuation of the study using data from the IMPROVE network, Malm et al. (2004) assessed visibility and aerosols for the purpose of tracking spatial and temporal trends. This paper focused on fine aerosol data collected in the year 2001 at 143 sites. The major PM2.5 species, sulfates, nitrates, organics, black carbon, and wind-blown dust, as well as coarse gravimetric mass were monitored; at some sites, light scattering and/or extinction were also measured. Sulfates, carbonaceous, and crustal material were responsible for most of the fine mass (diameter less than 2.5 μm) at most of locations in the United States; only at sites in southern California and the Midwestern United States did nitrates contribute significantly. Here in the East, they reported that sulfates accounted for between 50% and 60% of the fine mass. Sulfate concentrations were generally highest in the summer months while organic concentrations peaked in other seasons, depending upon fire-related emissions. They reported that at two urban sites, Phoenix, Arizona, and Puget Sound, Washington, organics and nitrates peaked during the winter months, and similar results have been seen in more recent analyses of PM2.5 in the Washington/Baltimore NAA (Section I). In summary, the IMPROVE studies showed that the regions of the greatest emissions of $SO_2$ and NOx are also the regions of greatest sulfate and nitrate concentrations.

### ii. Published Evidence that PM2.5 is a Secondary Pollutant and Regional in Nature

The relative contribution of primary vs. secondary organic aerosols is important for understanding whether controls on local or regional emissions will be most effective. Recent combined laboratory and model studies [*Robinson, et al.*, 2007] suggest that a large fraction of the anthropogenic organic aerosol is secondary. Primary organic-particulate emissions are for the most part semivolatile, and they can evaporate upon dilution in the atmosphere, creating substantial amounts of VOC's with low vapor pressures. Laboratory experiments described in this paper show that *in situ* oxidation of diesel exhaust can generate organic aerosol faster than was previously thought and make substantially more secondary organic-aerosols than had been previously suspected. The authors attributed this SOA production to rapid atmospheric oxidation of low-volatility gas-phase species. The results suggest that organic aerosols are more regional in nature and inclusion of these findings brings models and observations into better agreement (see also the regional nature of aerosol scattering reported by Hains et al., 2007). The policy implication of this study is that stronger regulation of VOC emissions from vehicles will help reduce organic particulate-matter concentrations.

Aircraft observations [*Taubman*, 2004; *Taubman, et al.*, 2004] show that transport between the planetary boundary layer (PBL) and lower free troposphere (LFT) plays an important role in aerosol formation and properties. Although most pollutants are injected into the PBL, those emitted directly into the free troposphere (FT) or transported there are exposed to greater UV flux, have a longer lifetime, and demonstrate a greater range of influence.

In a case study involving aircraft flights made near the maximum depth of the collapsing daytime mixed layer [*Taubman et al.,* 2004], chemical, meteorological, and dynamical analyses provided evidence for the buoyant interplay of air parcels between the LFT (where photochemical processes are accelerated and removal via deposition does not occur) and the PBL, where PM2.5 concentrations are monitored. Late afternoon bubbles of air lifted from urban and industrial sources were rich in CO and $SO_2$, but not ozone, and contained large numbers of externally mixed sulfate and black carbon (BC) particles. Rising PBL air in these bubbles often form fair weather cumulus clouds, where aqueous phase reaction with $H_2O_2$ converts $SO_2$ to sulfate.

A statistical analysis (autocorrelation) revealed that approximately 12 discrete air parcels were observed during the flight. Backward trajectories indicate source regions in the Midwest and East Coast urban corridor, The results of this study [*Taubman*, 2004] suggest that a two-reservoir system, composed of the LFT and the PBL, may realistically represent the physics and chemistry of severe, multi-day haze and ozone episodes over the eastern U.S. Exchange between the two reservoirs is apparently governed by small-scale dynamics, but this supposition merits future aircraft studies of mass flux measurements before numerical model simulations can accurately represent the reported observations. The conclusion (*Taubman et al.* 2004) that PM2.5 is formed in part by cloud processes involving exchange between the PBL and LFT adds to the evidence that these aerosols are regional in nature. The policy implication is that regional $SO_2$ controls will be efficient in reducing sulfate aerosols and thus PM2.5 Maryland.

In a statistical analysis of hundreds of summertime aircraft flights made between 1997 and 2003 during poor air quality episodes over the Mid-Atlantic U.S. (34.7° - 44.6°N, 68.4° - 81.6°W). The purpose of the aircraft flights was to make measurements of ozone, CO, $SO_2$, and aerosol properties. These data were examined to provide insight into origins, transport, and properties of trace gases, aerosols and their precursors [*Taubman, et al.*, 2006]. Examination of the ensemble of profiles supports the two-reservoir theory put forth by Taubman et al. (2004). A cluster analysis of back trajectories in conjunction with the vertical profile data was used to identify source regions and characteristic transport patterns during summertime air quality episodes. When the greatest trajectory density lay over the northern Ohio River Valley, the result was large ozone concentrations, large $SO_2$/CO ratios, more highly scattering particles, and large aerosol optical depths. When the maximum trajectory density was over the southern Ohio River Valley, the result was less pollution over the Mid-Atlantic. North-northwesterly and northerly flow brought the least pollution into Maryland. Little diurnal variation was identified in the CO, $SO_2$, and the size spectrum of the particles as indicated by the Ångström exponent profiles. Boundary layer ozone was greater in the afternoon, while lower free tropospheric ozone was invariant at ~55 ppbv. The single scattering albedo increased from morning to afternoon (0.93 ± 0.01 to 0.94 ± 0.01), reflecting increased secondary aerosols and/or water content. Both ozone and PM2.5 decreased at the highest altitudes; all altitudes here are expressed as m above mean sea level (amsl).

Comparing ambient concentrations to the CMAQ modeling results for VOC's [*Choi*, 2004; *Choi, et al.*, 2006] showed that SMOKE is in general capturing the correct ratios of VOC's, CO, and NOx, but may generate excess solvent emissions of toluene. The ratio of toluene to NOx as well as absolute concentrations of these species revealed overestimates of solvent sources by a factor of 1.5 to 3 at the three sites McMillan Reservoir in Washington, D.C., Essex, Maryland, and Camden, New Jersey. In addition, overestimates of solvent source emissions were corroborated by comparing ratios of VOC solvent source contribution to NOx to the ratio from SMOKE at the Essex, MD PAMS site. Similar results were found for New York, Los Angeles, and Boston [*Warneke, et al.*, 2007]. CMAQ modeling indicated that this overestimate of toluene had little impact on ozone formation, but could substantially alter estimates of SOA's on the haziest days (Figure II-1). As a result of the study, investigators recommended further analysis of the emissions inventory of solvent sources and their emission factors.

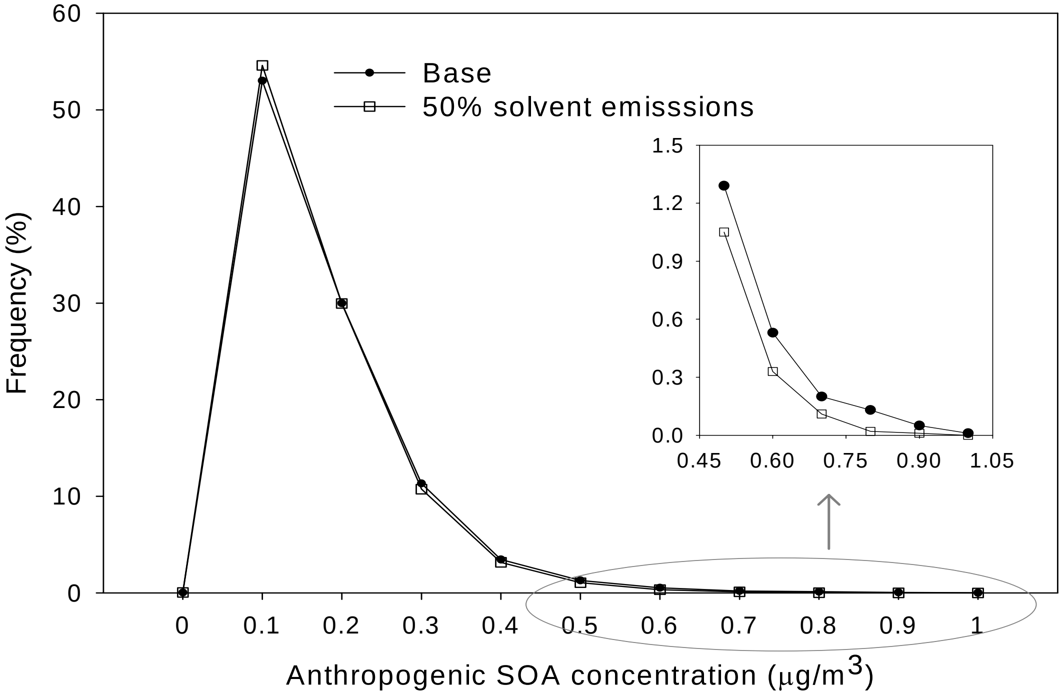


**Figure II- 1.** Comparison of the frequency distributions of hourly surface anthropogenic SOA concentrations calculated by CMAQ for the period 8 July to 20 July 1997. The base case is indicated by filled circles, the case with a 50% reduction of the total solvent VOC emissions is indicated by the line with open boxes. Results represent all days in the period modeled and all surface grid cells in the inner domain covering the Mid-Atlantic area. Although model predicts that a 50% reduction in solvent VOC emissions would have little impact on ozone, the concentration of PM at the high extreme (insert) was reduced substantially (*Choi,* 2004).

By examining aircraft profiles of aerosol optical properties and aerosol precursors, Hains et al. were able to show how upwind sources of $SO_2$ play a crucial role in aerosol loading in the lower troposphere over the Mid-Atlantic region; see Figures II-2 to II-4 [*Hains*, 2007; *Hains, et al.*, 2007b]. All flights analyzed for this study were conducted in the summertime (June, July, and August) and were specifically designed to characterize episodes of poor air quality. In this study a hierarchical clustering method was used to separate distinct chemical and meteorological events from over 200 aircraft vertical profiles in the lower troposphere measuring $O_3$, $SO_2$, CO, and particle absorption and scattering in the Mid-Atlantic U.S. Cluster analyses were performed for 48-hr back trajectories ending at altitudes of 1, 2, and 3 km (amsl), encompassing most of the vertical range covered by the aircraft soundings. These HY-SPLIT trajectories trace a 3-

dimensional path through time to the receptor site. By clustering the trajectories at several altitudes, any variations in the atmospheric circulation patterns in the lower atmosphere and the impacts on regional transport could be identified, but the results of the three cluster analyses for the three altitudes were similar, and we conducted all further analysis with just the clusters of back trajectories ending at 2000 m altitude. To determine quantitatively the similarity among individual trajectories, the total variability between each trajectory pair was determined as the scalar distance between trajectories. Appendix 8 [*Hains*, 2007; *Hains, et al.*, 2007b] provides details of the clustering technique.

For aerosol scattering, a cluster analysis was performed for the summers of 2001-2003, and four clusters were identified (Figure II-2). Two of these, Clusters 3 and 4, corresponded to a forest fire in Canada and will not be discussed further. The remaining two, Clusters 1 and 2, represent the bulk of the data and show substantive differences. Cluster 1 with 139 members represents flow from the SW while Cluster 2 with 34 members represents flow from the WNW. Back trajectories for Cluster 2 show more frequent encounters with the major $SO_2$ sources. The $SO_2$ emissions integrated over the course of the 48 hr back trajectories (Figure II-3) shows that the emissions encountered by the air parcels of Cluster 2 were nearly double those of cluster 1, and the aerosol scattering, driven primarily by sulfate particles, is more than double that of Cluster 1 (*Hains et al., 2007*).

An examination of the statistics for the entire collection of scattering profiles (Figures II-4 and II-5) shows that there is a modest increase in scattering from the surface to a few hundred meters altitude and a decrease above about 1000 m corresponding to the top of the planetary boundary layer. Separation of the profiles into those collected in the morning (before noon EST, average time 09:30 EST) and afternoon (after noon EST, average time 13:30 EST) reveals slightly greater scattering extending to slightly higher altitudes later in the day. The profiles shown were generated by calculating the median value at each altitude layer from all of the measured profiles. Note the morning flights were generally conducted west of the Baltimore/Washington area and the afternoon flights east of the urban centers. These studies support the assertion that the PM2.5 loading for the Mid Atlantic is regional in nature and driven by the integrated sum of emissions more than by local sources.

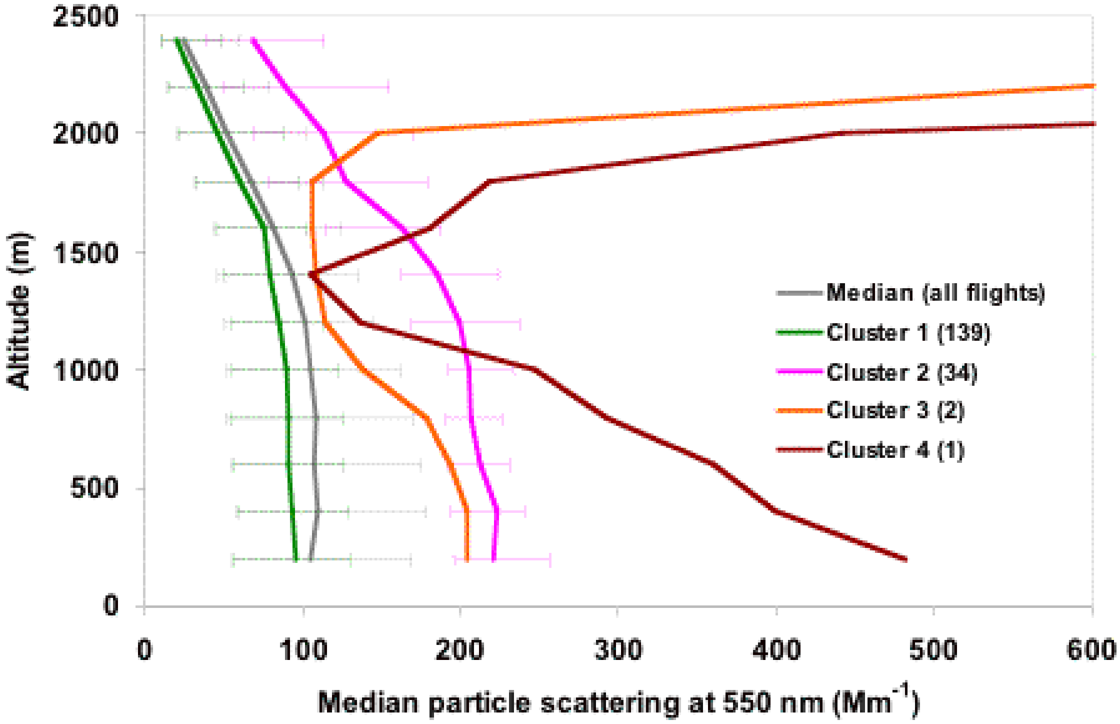


**Figure II-2.** Median profiles of scattering for each cluster, all altitudes in this and following figures are expressed as height above mean sea level. Error bars represent the 25th and 75th percentiles. The number of profiles in each cluster is shown in parentheses in the key. Cluster 2 with a greater component of flow over the Ohio River Valley has profiles with twice the scattering value as Cluster 1. Profiles from clusters 3 and 4 were measured when the Canadian forest fires impacted the region (*Hains et al.* 2007).

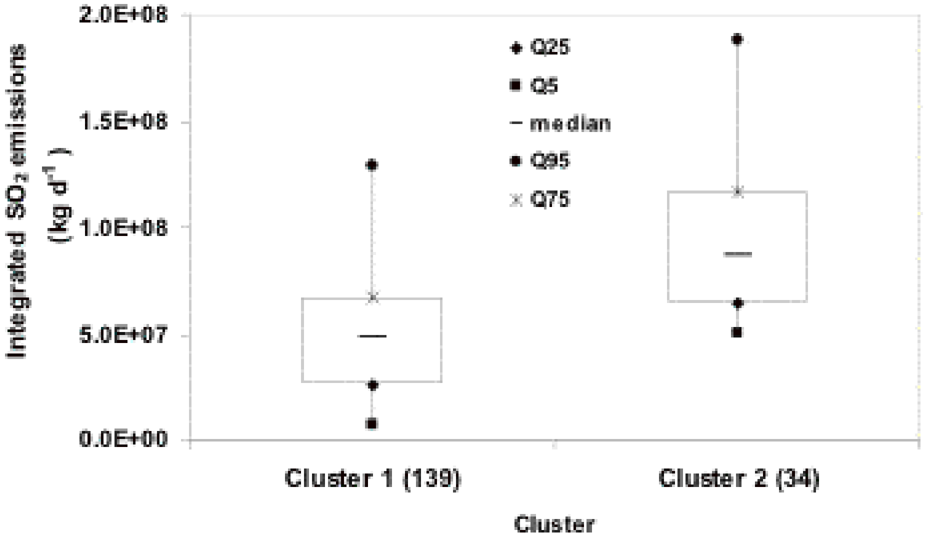


**Figure II- 3.** Statistics for $SO_2$ emissions encountered by back trajectories for each scattering cluster. The $SO_2$ emissions are sums of all emissions (kg $d^{-1}$) encountered by a back trajectory (ending at 750 m). Cluster 2 is associated with almost double the emissions of cluster 1, partially explaining why cluster 2 profiles have twice the scattering values as cluster 1, above (*Hains et al.,* 2007).

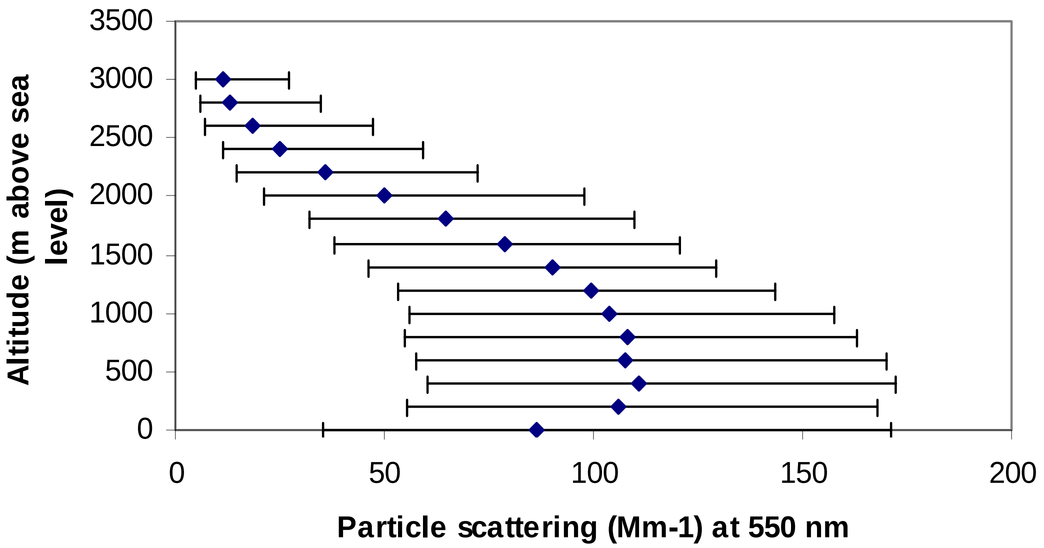


**Figure II-4.** Average (diamonds) and quartiles (error bars) of aerosol scattering of light at 550 nm wavelength for 354 aircraft profiles flown 2001- 2005. Observations made in area inside 34.7-44.6° N latitude and 81.6-68.4° W longitude. Note small increase above surface followed by fairly uniform values until the top of the PBL (*Hains*, 2007).

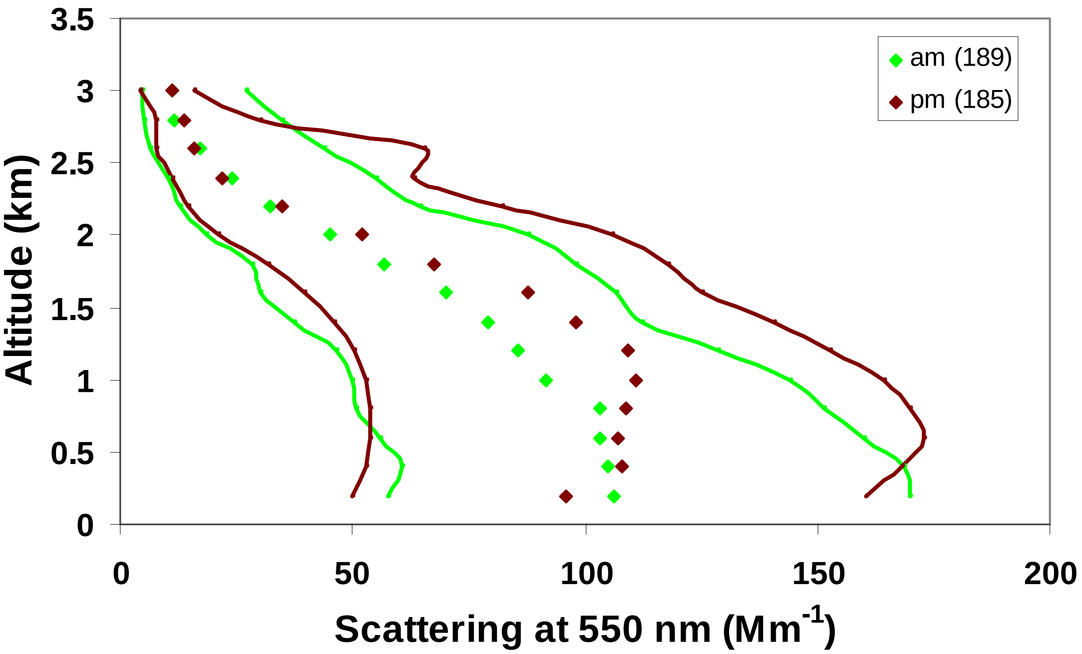


**Figure II-5.** Aerosol scattering measured during morning and afternoon profiles. Except in the lowest layer, afternoon profiles show greater extinction than morning profiles. The values in the legend indicate the number of profiles that went into each plot. The solid lines represent the quartiles.

A deeper examination of the differenced between morning and afternoon profiles for aerosol optical properties and related variables is presented in Figures II-5 to II-9 and provides insight into the characteristic properties of the particles contributing most to PM2.5 over the Eastern US [*Hains*, 2007; *Hains, et al.*, 2007a]; additional profiles can be found in Appendix 8. From 1995 through 2005, there were 658 summertime flights, which included 305 morning and 353 afternoon spirals. Because relative humidity impacts scattering, we have separated RH profiles into morning and afternoon flights (Figure II-6). Water vapor is more evenly distributed in the vertical in the morning than in the morning, and the local RH maximum probably contributes somewhat to the local scattering maximum found around 1000 m altitude in the afternoon.

The Ångström exponent (α) represents the relative size of particles and was calculated using:

$$A = [\log(\sigma_{450}) - \log(\sigma_{700})] / [\log(450) - \log(700)]$$

Where $\sigma_{450}$ and $\sigma_{700}$ are the scattering coefficients at 450 and 700 nm wavelengths respectively. The larger the value of A the smaller the mean diameter of the particles. The single scattering albedo represents the relative contribution of scattering to total optical extinction from particles and was calculated using:

$$\text{Single scattering albedo} = \sigma_{550} / (\sigma_{550} + \text{abs}_{550})$$

where $\sigma_{550}$ is the scattering coefficient at 550 nm and $\text{abs}_{550}$ is absorption coefficient at 550 nm, both in units of $m^{-1}$. Sulfate particles have a single scattering albedo near unity while soot particles have a value well below 0.7, and organic matter shows intermediate values. The similarities of means and statistical distributions of these morning and afternoon subsets indicate that the optical properties of Mid-Atlantic aerosols, scattering coefficient, Angstrom exponent, absorption, and single scattering albedo, demonstrate reasonable spatial uniformity and support the contention that much of the aerosol loading is secondary and disbursed throughout the region.

Hains (2007) also found a pervasive “background” $SO_2$ profile over the eastern U.S. with mixing ratios decreasing smoothly from about 3.5 ppb near the surface to 0.2 ppb at 2400 m. An average lifetime for $SO_2$ of 18 ± 9 hours was calculated using in-situ measurements made during the summer daylight hours in the Mid-Atlantic on days when air quality events were predicted. The CMAQ and GOCART numerical models overestimated $SO_2$ concentrations by about 60%, due perhaps to insufficient cloud processing in the models. If models are indeed under predicting the rate at which $SO_2$ is oxidized to sulfate then they may be under predicting PM2.5. The policy implication of the rapid conversion of $SO_2$ to sulfate and regional nature of aerosol optical properties is that these findings provide evidence to support regional controls of emissions of PM2.5 precursors.

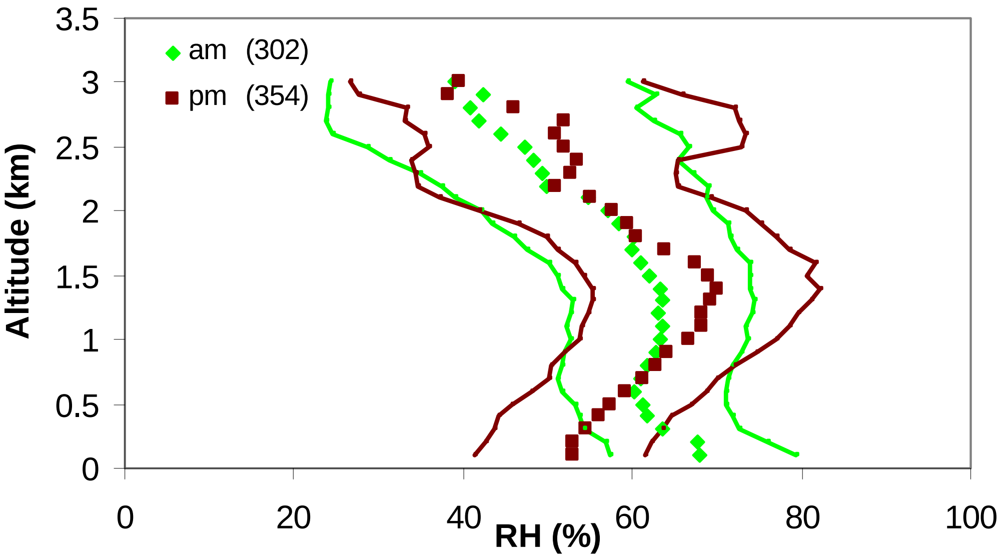


**Figure II-6.** Profiles of relative humidity separated into morning and afternoon flights. The greater scattering in the afternoon (above) is seen despite the lower RH observed below about 600 m altitude.

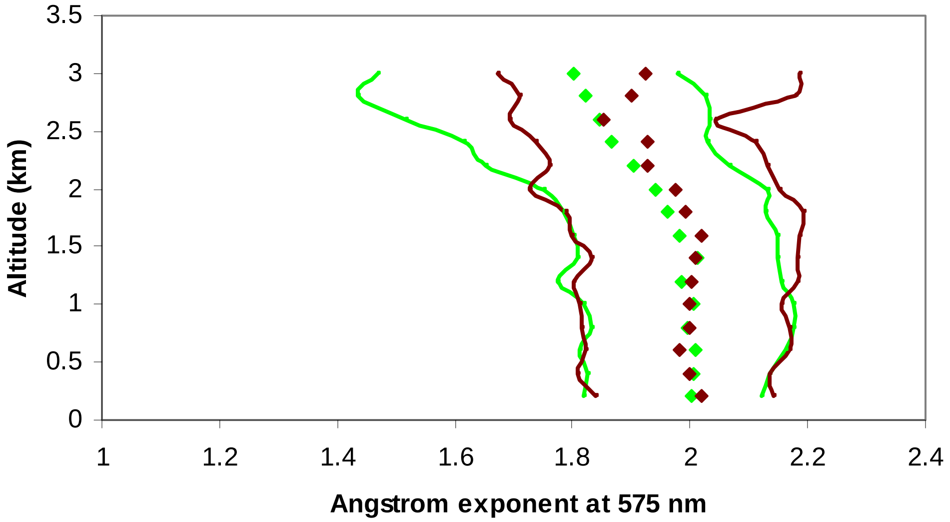


**Figure II-7.** Morning and afternoon Angstrom exponent showing little difference between times of day and suggesting that the size of the particles does not have a strong daily cycle. Greater values for the Angstrom exponent indicate smaller particles.

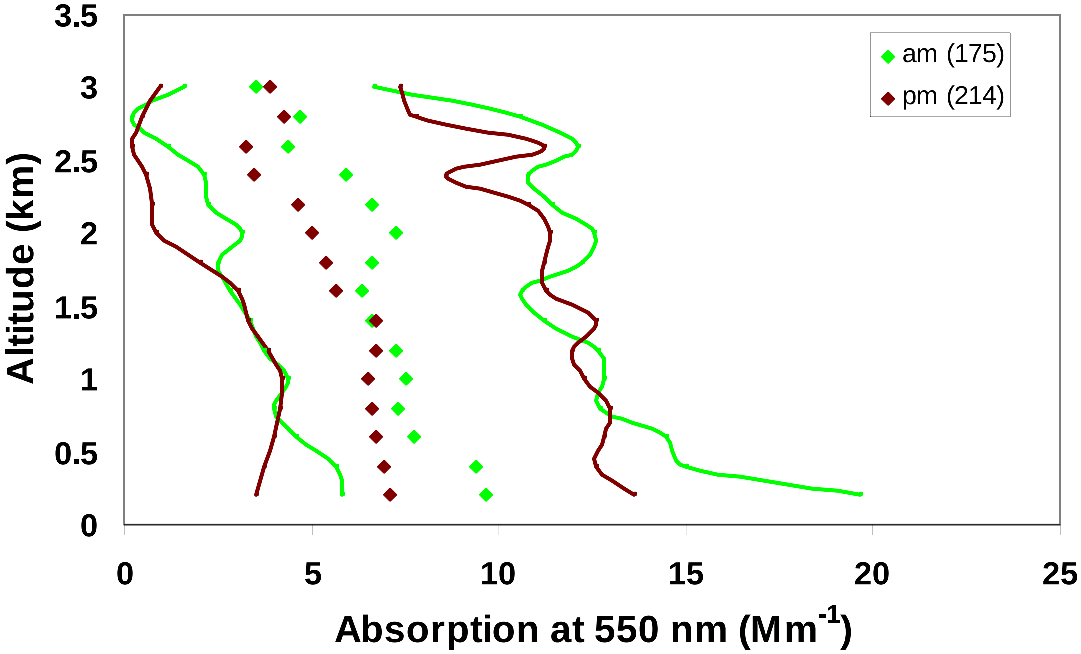


**Figure II-8.** Morning and afternoon profiles of aerosol absorption in the visible. The values in the legend indicate the number of profiles that went into each plot. Note greater absorption in the early hours due to greater emissions and a shallower boundary layer.

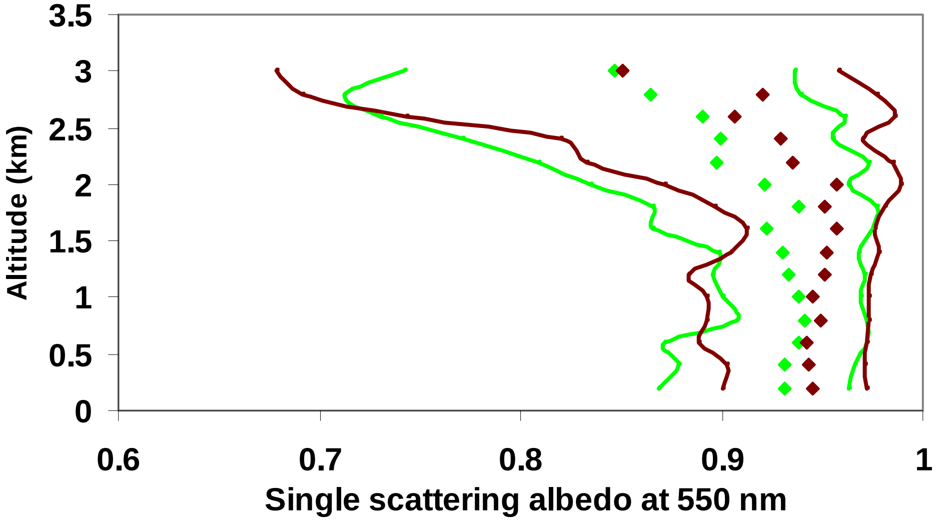


**Figure II-9.** Morning and afternoon single scattering albedo. Slightly greater scattering in the afternoon probably reflects the greater contribution of secondary particles such as sulfates and SOA.

## b. Speciation and Source Fingerprints

Several field campaigns have been conducted in and around the Baltimore-Washington corridor with the goal of determining sources of fine particulate matter (PM2.5). Over the period 1999-2001, 24 hour average PM2.5 measurements were taken at Fort Meade, MD, using sequential filter samples during the months of July, October, January and April (except April 2001). This site is located in between Washington, D.C. and Baltimore, MD, and there are no significant point sources located within a radius of 1 km around the site. A combination of receptor modeling and ensemble back trajectory analysis was used to identify sources. Distinct regional and local sulfate, wood smoke, copper/iron processing, mobile and secondary nitrate sources were resolved [*Chen, et al.*, 2002]. Significant seasonal variations were observed. In summer, based on July observations, the dominant PM2.5 sources were regional sulfate and mobile emissions sources, with regional sulfate contributing the most to total mass of PM2.5. In the winter, based on January observations, the dominant PM2.5 sources were secondary nitrate associated with mobile sources, regional sulfate and wood smoke in decreasing order of contribution to total mass of PM2.5 [*Chen, et al.*, 2002]. Mobile-related emissions are local in nature, but the other dominant sources are regional in nature. The regional sulfate source is believed to result from the Midwest, and the wintertime wood burning is thought to originate from more rural areas in Virginia and West Virginia [*Chen, et al.*, 2002].

Intensive field campaigns in the Baltimore area, part of the Supersites studies sponsored by the Environmental Protection Agency, were conducted over the 2001-2003 period, with a focus on time resolution and chemical speciation [*Ogulei, et al.*, 2005; *Ogulei, et al.*, 2006; *Park, et al.*, 2005; *Park, et al.*, 2006]. In one period during the study, samples were taken at 299 Ponca Street, Baltimore, MD (latitude 39.29°N, longitude 76.55°W, 40 m amsl). The Ponca St. site is situated in an urban residential area, east of downtown Baltimore, and north of the industrialized area of south Baltimore; the site is adjacent to Rt. I-895, an interstate with heavy traffic. Data were collected at time resolutions ranging from 30 minutes to 24 hours over the period from 19 March through 26 November 2002 [*Ogulei, et al.*, 2005; *Park, et al.*, 2005]. A receptor modeling approach was developed to analyze the observations taken over different time intervals. The sources identified, with percent contributions to total PM2.5 mass given in parentheses, were spark-ignition emissions (26%), secondary sulfate (23%), secondary nitrate (23%), steel plant

(12%), incinerator (9%), coal-fired power plant (3%), oil-fired power plant (2%), diesel emissions (1%) and sea salt (1%). Conditional probability function plots were used to identify geographical origin. The most significant source, spark-ignition vehicle emissions, is local; however, secondary sulfate was believed to have formed from sulfur dioxide emissions originating in the Ohio River Valley. Secondary nitrate is thought to form by reaction of precursor $NO_x$ originating from both local interstate highways Rt. I-895 and Rt. I-95 and from industrial and urban cities of Pennsylvania [*Ogulei, et al.*, 2005]. Additional analysis of highly time and size resolved measurements made on the following days, 6,7,18, 19 July 2002 and 21 August 2002, using a bilinear receptor model (PMF2) revealed two additional sources, airborne soil/road-way dust, and nucleation, contributing to 3.5% and 0.88% of the mass respectively, as well as a temporary source associated with the Quebec forest fires on 6-7 July [*Ogulei, et al.*, 2006]. Contributions from other sources were somewhat different than those observed in the full data set, for example the contribution of emissions from a steel plant was 1.9% rather than 12% as observed from the full data set. Distinct regional and local nitrate sources were also resolved. This is easily attributable to the variable nature of PM2.5, [*Ogulei, et al.*, 2006] as discussed below in greater detail.

From the observations made at the Ponca Street site, the varied nature of high PM2.5 episodes could be explored [*Park, et al.*, 2006]. Over the 9.5 month period between 14 February and 26 November, 2002, the average of the 30-minute TEOM PM2.5 mass measurements was $16.9 \pm 13\ \mu g/m^3$. During the sampling period, the US EPA National Ambient Air Quality Standard for the 24-hour PM2.5 ($65\ \mu g/m^3$ at the time) was exceeded only once, 6-8 July 2002. This air quality episode was dominated by long-range transport of PM2.5 emitted from forest fires in Quebec, Canada. Thirteen episodes of high PM2.5 were identified, based upon the criteria of the daily average PM2.5 concentration exceeding the 9.5 month average by one standard deviation ($\geq 30\ \mu g/m^3$). Park et al. (2006) discusses in detail five of these episodes. In addition to the forest fire episode, three of these episodes took place during the summer season: 24-25 June, 18-19 July and 12-14 August, 2002. Ozone concentrations were also elevated during the summer episodes, $\geq 70$ ppb, averaged over all measurements made between 10 am and 8 pm EDT. Two additional episodes in the fall of 2002 were discussed in detail, and for these (2-5 October and 20-21 November), ozone was not elevated. From time series and regression analyses, and consideration of the meteorology, the probable causes of each episode were determined. In the case of the summer episodes, there was a strong regional haze component for the June and July episode, while the August episode was likely a result of both regional haze and local traffic. There were strong low-level nocturnal inversions associated with this episode that persisted between 6 am and 9 am during the morning, which favored trapping of local pollutants including motor vehicle emissions. The episode in October was associated with higher than normal temperatures (maximum of 30°C, average temperature 25.5°C), high relative humidity and moderately high ozone with ozone maxima of 60 ppb on each afternoon during the episode. The contributors to the observed PM2.5 were secondary sulfate, likely from Ohio River Valley emissions, and traffic related organic matter. The probable cause of the November episode was local traffic. This episode was characterized by a low-lying early morning boundary layer, with winds aligning with the direction of Rt. I-895. With the winds from this direction, as noted by the authors, Rt. I-895 becomes a 7 km long line source of vehicle emissions with emissions from Rt. I-95 contributing from beyond 7 km [*Park, et al.*, 2006].

### c. PM2.5 Transport

Most studies of fine particle pollution deal, in some way, with transport of PM2.5, so this section is not meant to detail every study that ever showed long-range transport of PM2.5 in the eastern United States, but rather to present a survey of several representative techniques, projects and publications that illustrate several of the basic techniques and findings. Many of these studies focus on sulfate, which is appropriate since it is the largest single component of PM2.5 in much of the East and sulfate also dominates regional haze. Many of these studies also focus on the transport of PM2.5 from the Ohio River Valley. Since Maryland's highest PM2.5 days often occur under westerly transport, several studies of transport to non-Maryland sites have also been included here. Furthermore, the largest reduction in any single constituent of PM2.5 by 2009 is expected to be that of sulfate. Owing to its dominance of PM2.5 and visibility and because its chemistry is thought to be better understood than that of the other PM2.5 components, sulfate is the focus of this section.

#### i. MANE-VU Study Findings

The Mid-Atlantic/Northeast Visibility Union (MANE-VU) prepared an extensive report including modeling, observations and data analysis techniques and developed a conceptual model of visibility obstruction throughout the MANE-VU region [*NESCAUM*, 2006]. In this report, the authors conclude that sulfate is the single most important constituent of haze-forming particle pollution and the principal cause of visibility impairment throughout the region. The report emphasizes that haze is a regional pollutant, with sulfate accounting for half to two thirds of the fine particle mass at Class I areas on the 20% worst visibility days. The fraction of the visibility impairment is still larger at 70%-82% on the 20% worst visibility days. Even on the best visibility days, sulfate is usually the dominant constituent, contributing 40% or more of the total fine particle mass at these sites.

The role of the industrialized Midwest is also prominent, as visibility impairment (and by extension sulfate) is at its worst in the southern and western portions, namely Maryland and western Pennsylvania, of MANE-VU. These regions are closest to the large $SO_2$ emissions of the Ohio River Valley and the industrial Midwest. Summertime visibility impairment is almost exclusively driven by the concentration of sulfate, especially the regional sulfate load.

Wintertime haze is more complex, depending on the combination of local and regional emissions as driven by the distinct meteorology of winter.

In the report, sulfate is implicated as the main focus for control efforts, with organics in second place. Regional $SO_2$ controls will help most when sulfate is at its peak in summer, and will also help in winter, though not as much as in summer owing to the smaller contribution of sulfate to PM2.5 in winter. Local $SO_2$ controls should help in winter, and VOC controls should help bring down PM2.5 levels year round. In areas with high wintertime PM2.5 levels, local $NO_x$ controls will also help.

Analysis of monitoring data indicates that regional $SO_2$ emissions reductions have produced substantial reductions in secondary sulfate levels. Control of primary PM2.5 emissions has also produced reductions in PM2.5, though these reductions do not cover as large an area as for secondary species.

The report does not rely heavily on any one technique, instead building a picture of regional haze and PM2.5 by using different modeling and data analysis techniques and synthesizing those results. For example, contributions to sulfate at Brigantine Wildlife Refuge in New Jersey, downwind of Maryland, were determined using the REMSAD model, two different implementations of the CALPUFF model, and two very simple techniques, dividing the source emissions strength by the distance from Brigantine to the source and the fraction of the time the source is upwind of Brigantine. All these methods produce very similar results as shown in Figure II-10.

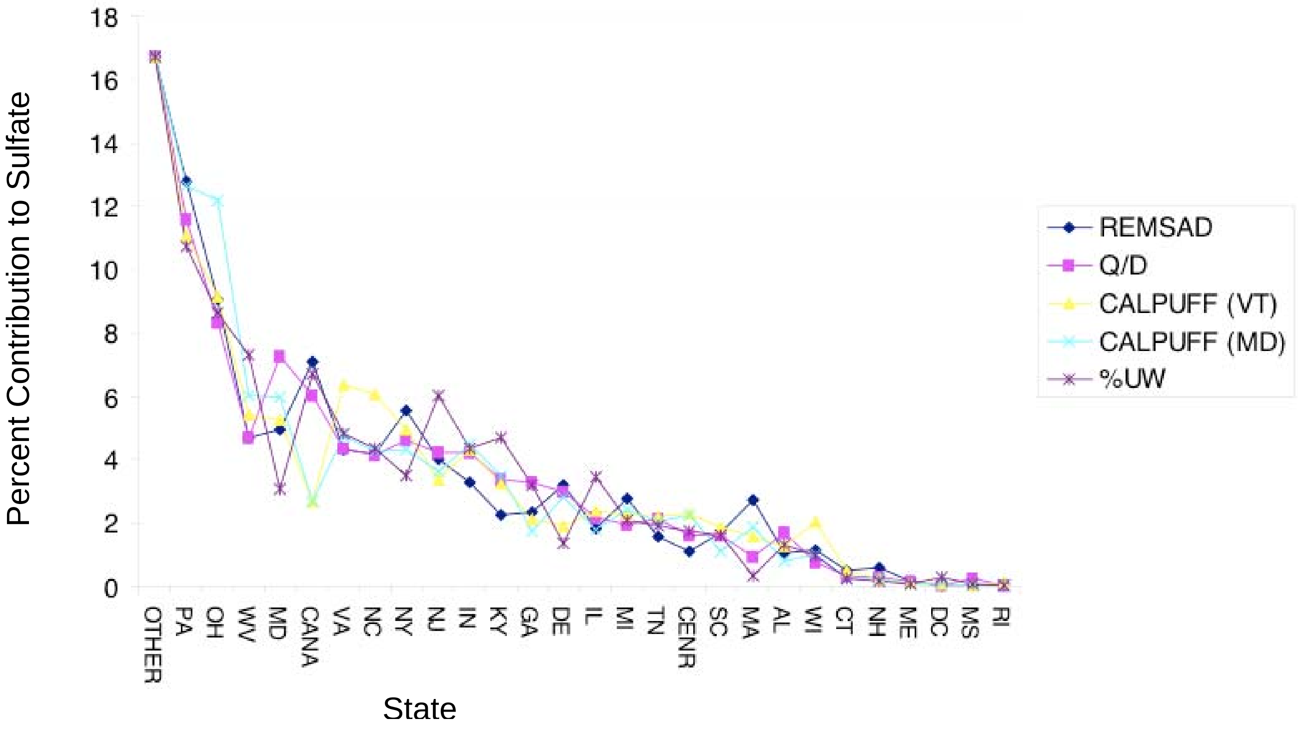


**Figure II- 10.** Contributions to sulfate at Brigantine National Wildlife Refuge by state, using several different techniques. Two modeling techniques were used; CALPUFF and REMSAD, and two different implementations of CALPUFF (one by Vermont and the other by Maryland) were also used. Two simplified techniques were used as well; source over distance (Q/D) and percent upwind (%UW). All five techniques agree rather well. Notably, the three largest contributors are states and regions that are well upwind of Brigantine, pointing to the regional nature of sulfate. [*NESCAUM*, 2006]

Notably, the largest contributions to sulfate mass at Brigantine were from Pennsylvania, Ohio and West Virginia, three of the largest $SO_2$ emitting states in the U.S., and the largest category was not a state at all, but rather the summed contributions of all states outside of the domain. New Jersey itself ranked well down the list, illustrating the long-range, regional nature of PM2.5.

Source apportionment techniques combined with back-trajectory analyses provided powerful demonstrations of the source regions for some of these pollutants. Two different data analysis techniques arrived at very similar conclusions. One used a source apportionment technique and found a substantial contribution from secondary sulfate and coal combustion; back trajectories then revealed that when the contribution from that source category was high, the air had come largely through the Ohio River Valley. Similarly, all days with high sulfate at Brigantine were grouped together and the back trajectories were calculated, revealing that sulfate peaked when air traveled through the same region (Figure II-11).

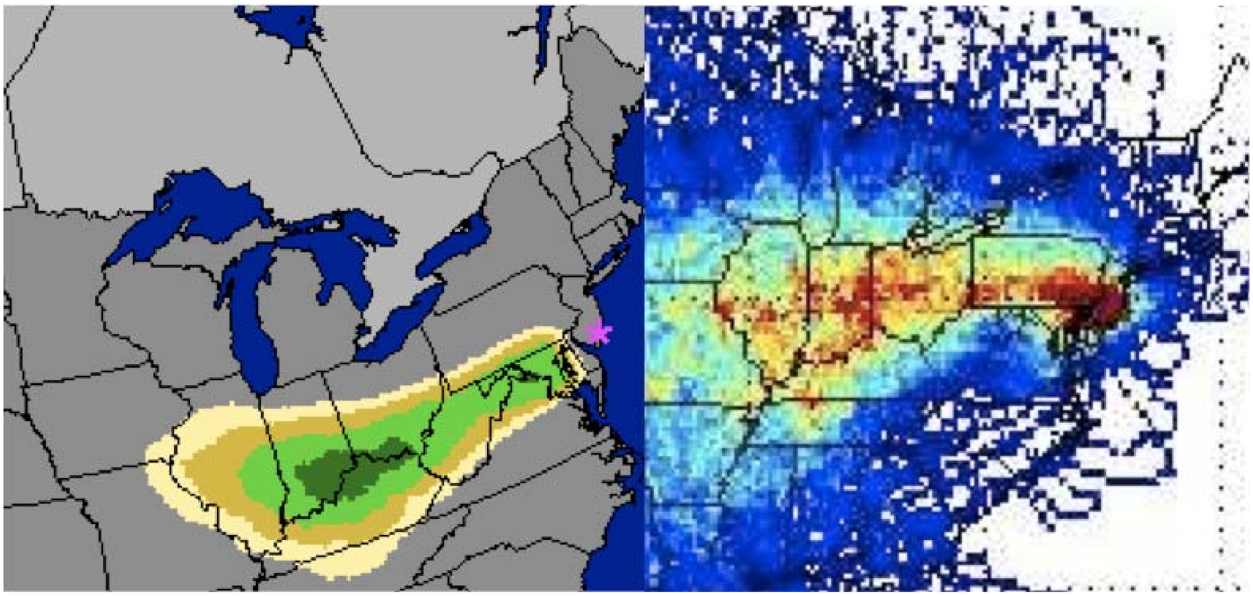


**Figure II- 11.** Source regions for Brigantine National Wildlife refuge as identified using two different methods. In the left panel, a source apportionment technique performed on the Brigantine data identified a significant contribution from a secondary sulfate/coal combustion source. The source region was identified above, using back-trajectories. On the right, all days with high sulfate were identified, and back trajectories were calculated and gridded on the map for those days. The two techniques complement each other and serve to show the influence of long-range transport, especially from the Ohio River Valley, and especially for secondary species like sulfate, on PM2.5 in the East. [*NESCAUM*, 2006]

The techniques are similar, though not identical and arrive at complementary results, again reinforcing the idea that multiple techniques identify similar sources, both with considerable regional, long-range transport signatures.

An incremental probability technique was also used, whereby the probability of transport to a site on days with a high contribution from secondary sulfate/coal was compared with the climatological transport to that site. In this way, one can construct a picture of where the air comes from when conditions are dirtiest and how that compares with transport patterns on the rest of the days. After compiling results from one observing site, one can then proceed to combine the results from several. As might be expected for a secondary pollutant, the source areas are rather large. When the areas are combined from several different sites, much as a surveyor uses triangulation to identify the precise position and elevation of a feature, the data from these sites combine to identify the Ohio River Valley as the center of the secondary sulfate source (Figure II-12).

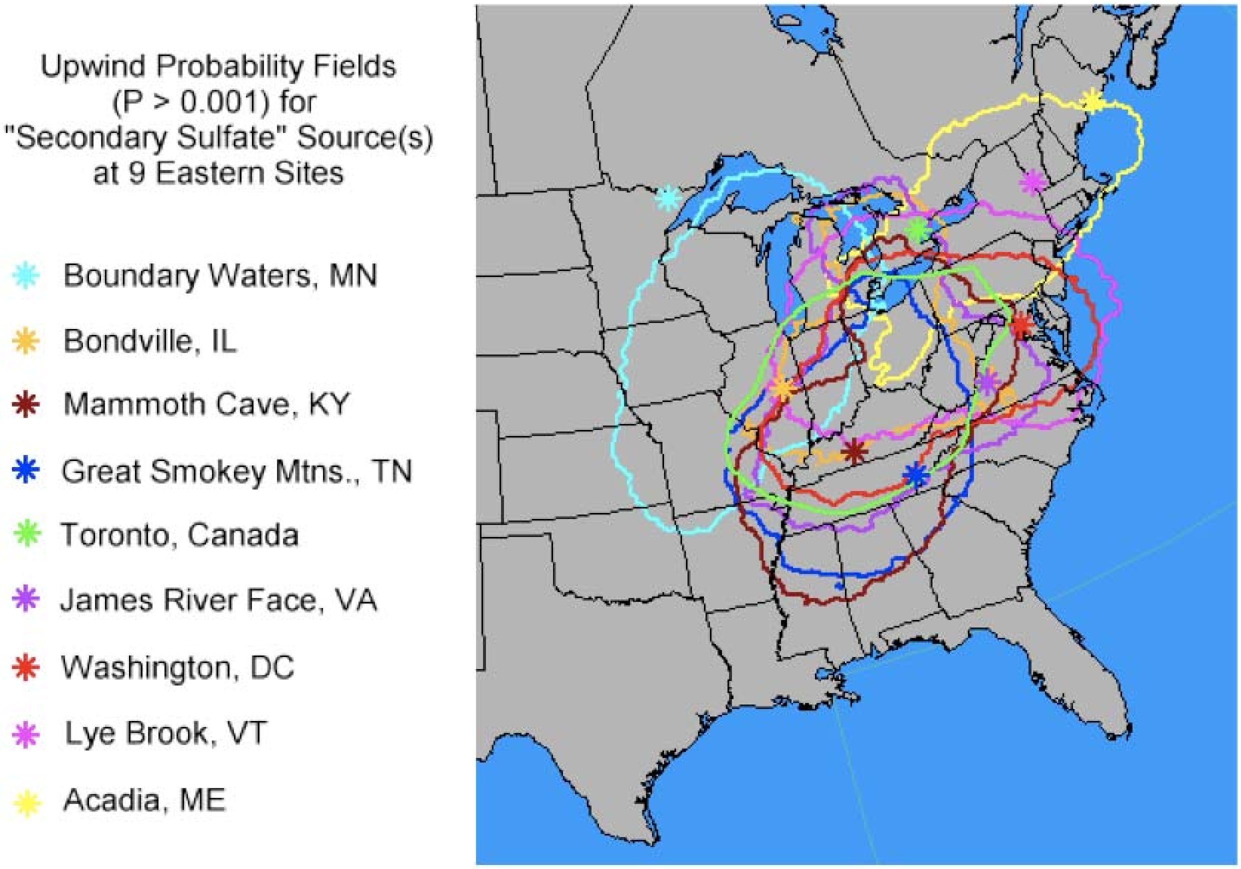


**Figure II- 12.** Results of the incremental probability technique, indicating source regions for several Class I areas in the East. Notable are the size of the areas and the fact that all contain some portion of the Ohio River Valley, with most containing a sizeable fraction of the Valley. When these regions combined (not shown) to produce a common source region, the Ohio River Valley stands out as the dominant source region across many different receptor sites for PM2.5 sulfate in the East. [*NESCAUM*, 2006]

Multiple techniques, involving data analysis, direct observation, and models ranging from the simple to highly complex were brought together to illustrate the regional nature of the PM2.5 problem. Some of those techniques are outlined in some more detail in the following sections, which delve into the peer-reviewed literature on PM2.5 transport.

ii. **Air Quality Changes During a Blackout**

A dramatic illustration of the range and the impact of power plant emissions on fine particle concentrations come from a detailed study of the 2003 Northeast blackout. On August 14, 2003, in the midst of a heat wave, a number of power plants in the Great Lakes region and the Northeast shut down. On the next day, the University of Maryland's instrumented aircraft flew into and out of the area affected by the blackout to investigate the influence of transported air pollution, especially that from power plants, on Maryland air quality. The aircraft first flew to western Maryland, outside the area affected by the blackout, then northeast into the area affected by the blackout, near Selinsgrove, Pennsylvania, and finally south to Fort Meade, Maryland, again outside the area affected by the blackout (Figure II-13).

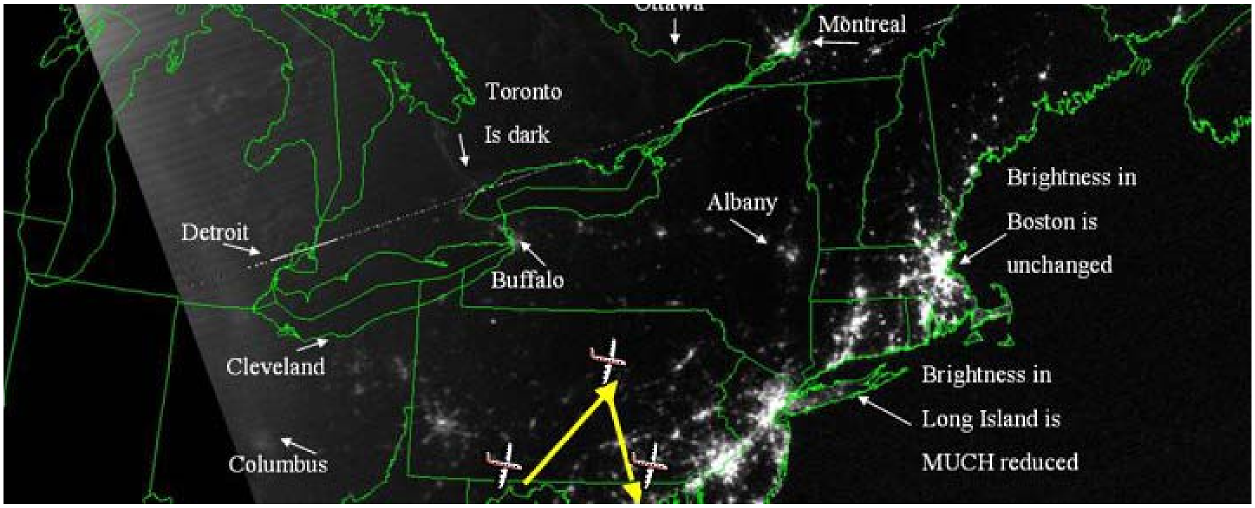


**Figure II-13.**The afternoon flight path of the UMD aircraft on August 15, 2003 from Cumberland, MD to Selinsgrove, PA and on to Ft. Meade, MD is shown in yellow arrows against a backdrop of the visible satellite image from that day.

As shown in Figure II-14, areas affected by the blackout were considerably cleaner than areas outside the blackout, exhibiting considerably greater visibility (indicated by less light scattered by particles).

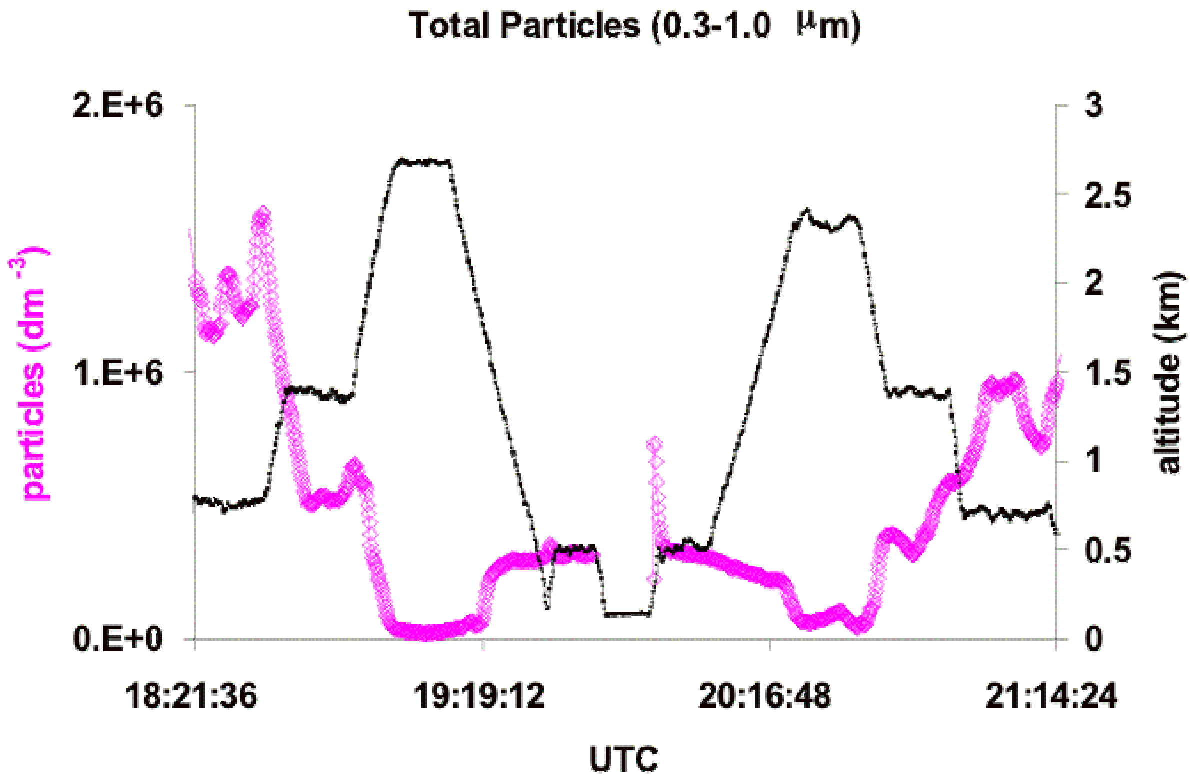


**Figure II- 14.** Total fine particles below 1 μm detected on the entire flight the day after the blackout started, August 14, 2003, are plotted in pink diamonds. In black is the aircraft altitude. The two altitude peaks represent the beginning of a spiral down to Selinsgrove, PA and the end of the spiral up away from Selinsgrove, PA. Particle counts near the ground in Selinsgrove, PA were well below those observed on the rest of the flight, indicating the contrast between areas near Selinsgrove that were affected by the blackout and those outside the area (e.g., Fort Meade, MD and Cumberland, MD) that were not.

The University of Maryland aircraft has been flying a package of similar instruments for over a decade, and continues to fly, allowing for comparisons to other flights under similar meteorological conditions. Comparisons of the data obtained from the blackout flight with flights over Selinsgrove on other days that were similar meteorologically, but when the power plants were operating normally, indicated that air quality improved dramatically when the power plants were not operating [*Marufu, et al.*, 2004]. When compared with a meteorologically similar day, August 4, 2002, ozone dropped by 50%, and $SO_2$ dropped by 90%, while light scattered by particles, indicative of sulfate, dropped by 70%. A more recent comparison day, occurring after the $NO_x$ SIP Call, showed that ozone, $SO_2$, and scattering from fine particles were still lower during the blackout than on this new comparison day, August 3, 2005 (Figure II-15).

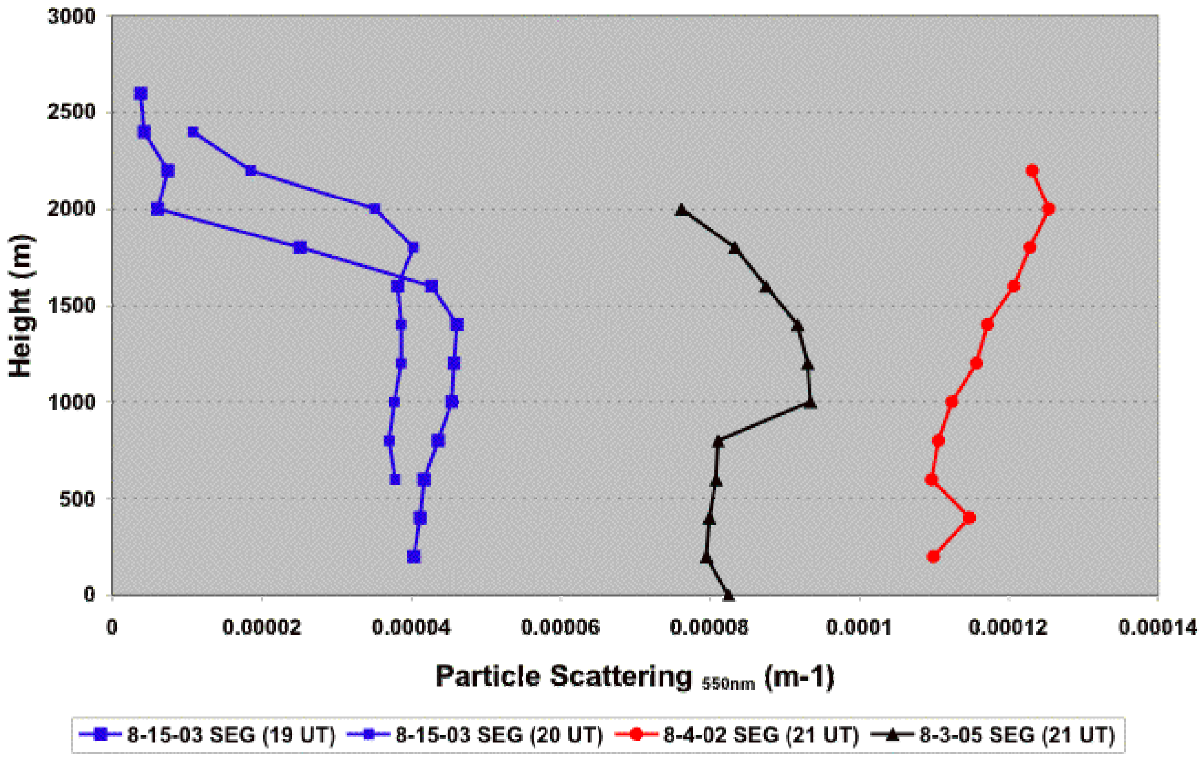


**Figure II- 15.** Comparisons of particle scattering over Selinsgrove between the two spirals flown on the blackout day (blue), another flown on August 3, 2005 (black) and one flown on August 4, 2002 (red). Both reference days were meteorologically similar to August 15, 2003, the day after the blackout began, though back-trajectories on August 3, 2005 were nearly identical to those during the blackout, while the trajectories on August 4, 2002 were less similar. August 3, 2005 also falls after the implementation of the $NO_x$ SIP call, while August 4, 2002 does not.

Observations of carbon monoxide and soot particles, associated with emissions from sources other than power plants, were unchanged from flights on both reference days. The unchanged levels of black carbon (soot) and carbon monoxide are strong indicators that emissions from other sources remained relatively constant across the different reference days. Further utilizing the extensive database of Maryland aircraft flights, back trajectories were computed for every flight day in the entire history of the aircraft program. Those trajectories were clustered using an objective clustering technique, forming clusters of similar meteorology. The observations on the day of the blackout were compared with those from all the other aircraft profiles that fell within that cluster. In this comparison, the blackout stands out as singularly exceptional. Black carbon absorption was entirely unspectacular, falling on or near the median for all 62 flights in this cluster (Figure II-16), while scattering from particles falls in the 5th percentile of those same days (Figure II-17).

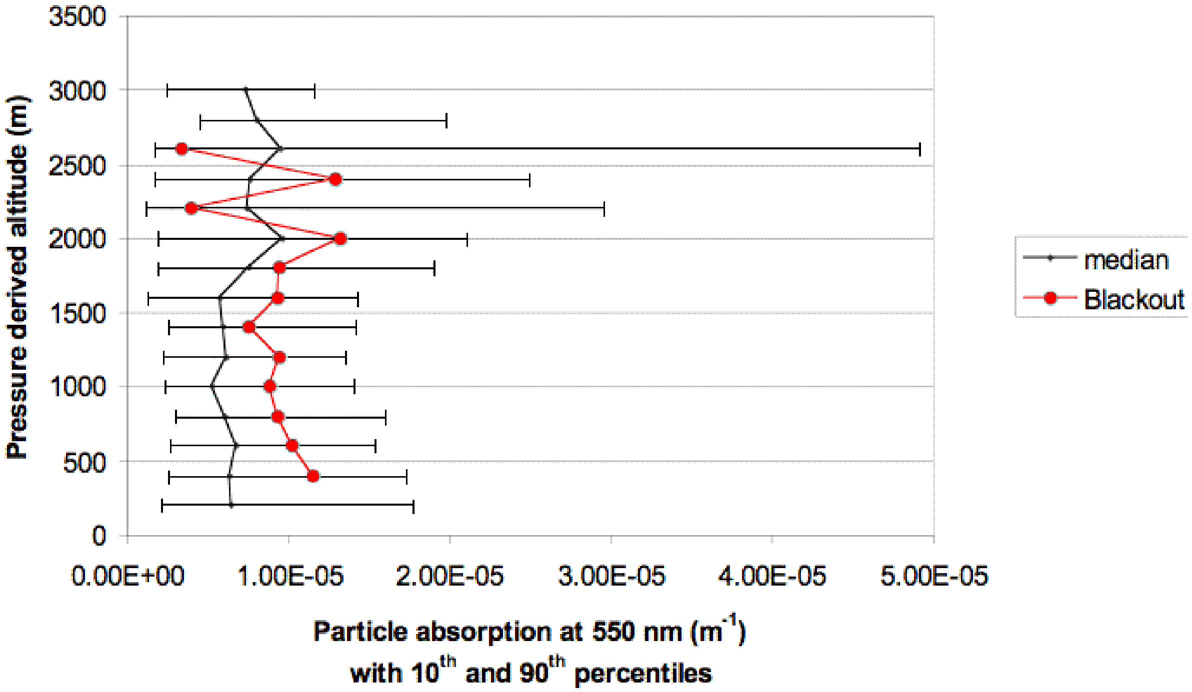


**Figure II- 16.** Fine particle absorption from the day of the blackout as compared with the median, 10th and 90th percentiles from other flights. Back-trajectories were run for the entire flight history of the University of Maryland aircraft and clustered. The blackout day was compared with the 62 other days within its cluster, revealing that absorption on the day of the blackout might have been somewhat higher than the median, but was well within the norms established from previous flights.

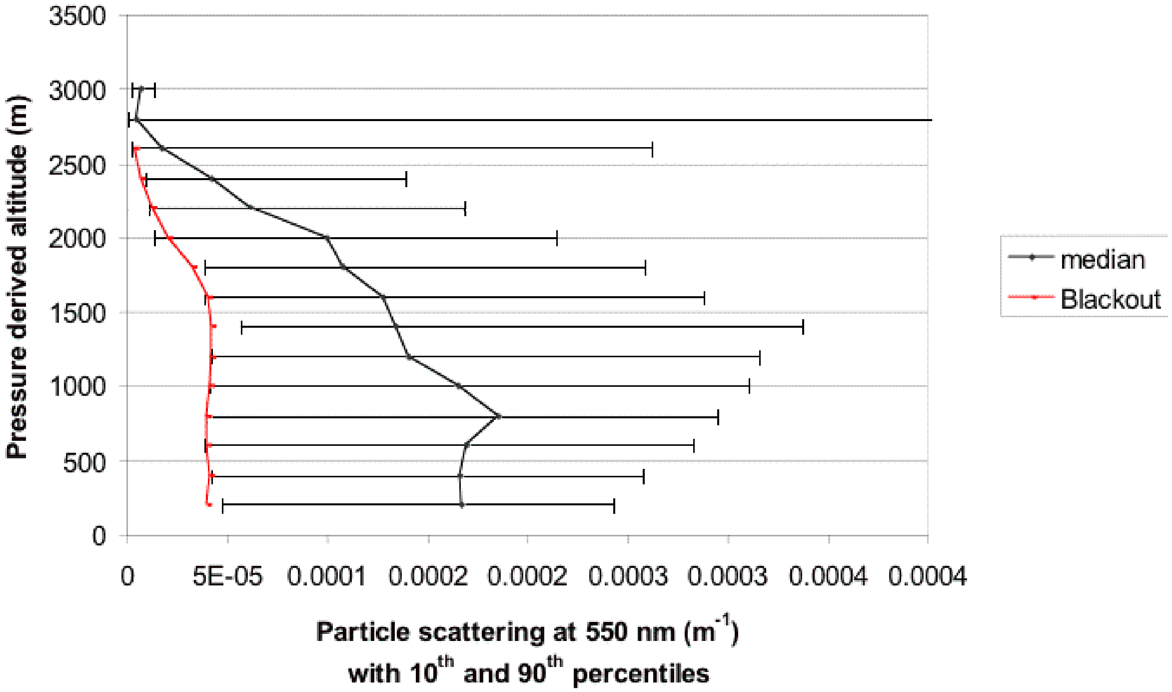


**Figure II- 17.** Fine particle scattering from the day of the blackout as compared with the median, 10th and 90th percentiles from other flights. Back-trajectories were run for the entire flight history of the University of Maryland aircraft and clustered. The blackout day was compared with the 62 other days within its cluster, revealing that scattering on the day of the blackout was rather unusual, falling below the 10th percentile at every level when compared with all flights that fell within that cluster.

The inadvertent shutdown of so many power plants dramatically improved air quality, most notably in ozone and PM2.5 on the days following the blackout. As power plants were shut down, $SO_2$ emissions dropped dramatically, and visibility and air quality improved dramatically well downwind. The power plants that shut down in 2003 were hundreds of miles upwind of Selinsgrove, PA, illustrating that the particles that form as a result of these power plant emissions could travel over considerable distances to affect communities well downwind.

### ii. Impacts of Ohio River Valley Emissions Throughout the Eastern United States

As part of the New York supersite program, measurements were made in Queens, New York, at Pinnacle State Park in south central New York near the Pennsylvania border, and at Whiteface Mountain in the Adirondack Mountains in northern New York State *[Dutkiewicz, et al., 2004]*. Sulfate concentrations were measured from July 2001 through June 2002 at all three locations, and then segregated according to where the air came from when the measurements were made. The trajectories were grouped into 12 sectors, and the sulfate concentration associated with each trajectory was then lumped into 12 categories—one for each sector. The results are plotted on maps of New York in Figure II-18. The greater the amount of sulfate (top plot), the farther the shaded outline extends from the center of these bull's-eye plots. These plots in essence point a finger at the region that gives each site its highest sulfate values. For example, in Figure II-18A approximately 7 $\mu g/m^3$ of sulfate was associated with transport from the west and southwest, while in (Figure II-18B, 44% of the sulfate at the Queens site was associated with flow from the west (two sectors combined). The authors also find that sulfate concentrations at sites throughout the Northeast are highly correlated, indicating the regional nature of the problem, and that over half of the sulfate at the Queens site came from sources more than 160 km distant. Similarly, over 60% of the sulfate at the Pinnacles and Whiteface Mountain sites came from sources farther than 160 km away.

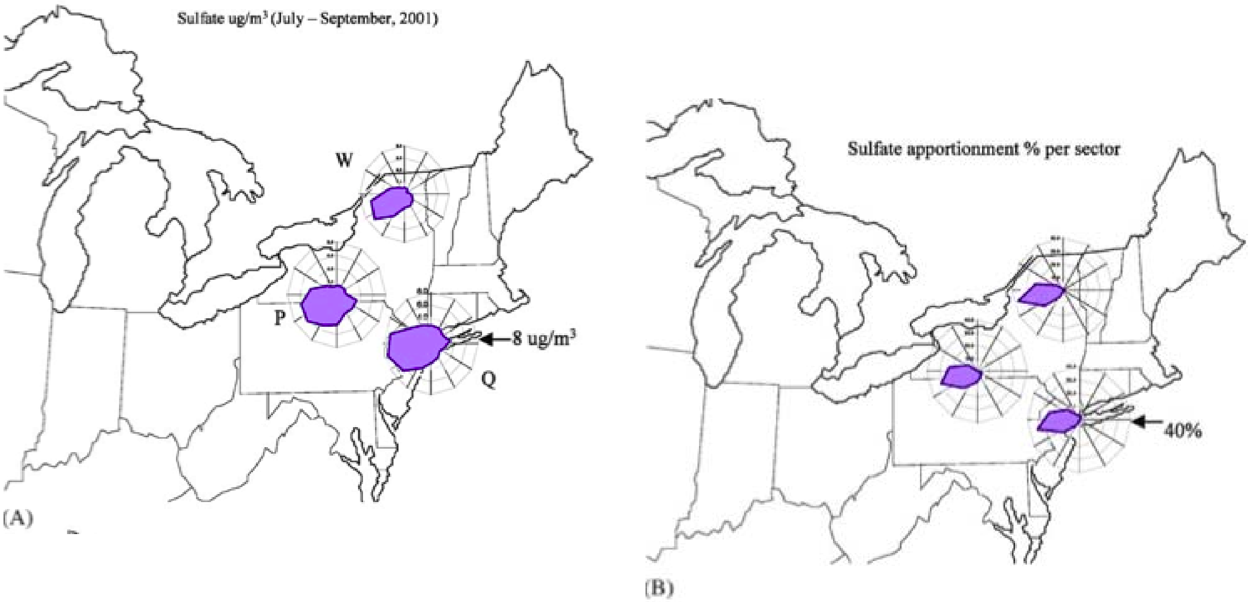


**Figure II- 18. (A)** Radial plot of sulfate vs. the sector where the air came from as superimposed on a map of the Northeast. The largest ring at each site is 8 $\mu g/m^3$ and there are 2 $\mu g/m^3$ between each ring. **(B)** Same as A except sulfate is normalized to the frequency of the air masses in each sector and expressed as a percent. The largest ring at each site is 40% and there is 10% between each ring. Higher concentrations or fractions in a sector indicate that air arriving from that sector had a greater concentration of sulfate on average than when it arrived from others. Reprinted from Atmospheric Environment, Vol 38, *Dutkiewicz et al.*, "Sources of Fine Particulate Sulfate in New York," pp 3179-89, Copyright 2004, with permission from Elsevier.

A study at a site in northern Vermont analyzed measurements of fine aerosol composition taken from 1988 to 1995, using several techniques to determine mass, aerosol absorption, the elemental composition of the aerosols, and their hydrogen content [*Poirot et al.*, 2001]. These measurements were broken down into several categories, also called factors, using two statistical techniques that look for patterns in the concentrations of different chemical species. The central idea is that each source type has a certain characteristic chemical makeup, and since the contribution from each source type varies with time, those variations can be used to sort out the influences of different sources. Some factors point to specific sources, such as a large Canadian smelting operation, while others point to wood smoke or the products of coal combustion. These factors are then used in conjunction with back-trajectory analysis to assign areas of influence to each factor. The trajectories were examined to determine which areas each source came from. The analysis revealed a large contribution from coal-fired processes in the Midwest, especially in summer. The contributions of midwestern coal averaged 65% of the mass at this site, year-round. The region of peak contribution from coal-fired processes corresponds to the Upper Midwest and much of the Ohio River Valley (Figure II-19).

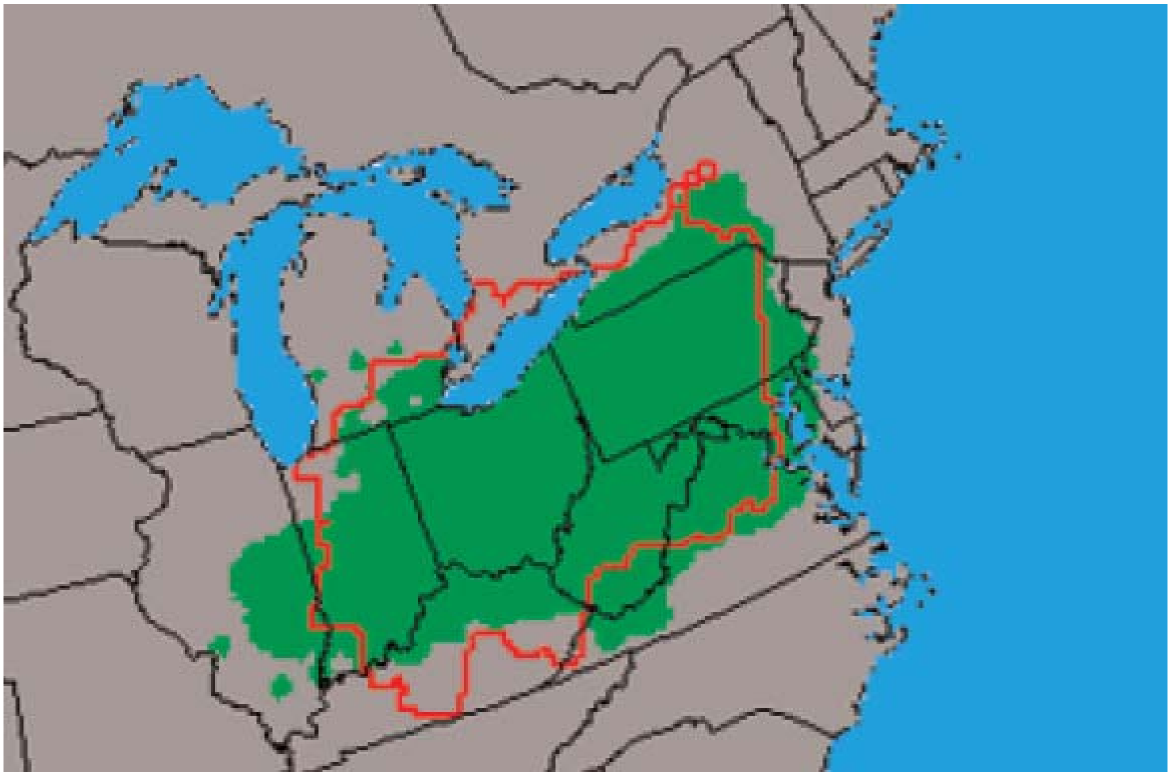


**Figure II- 19.** Regions of peak contributions from the coal-fired source identified from observations at Underhill, Vermont. The two regions correspond to the results from two different techniques. Reprinted in part with permission from *Poirot et al.*, *Environ. Sci. Technol.*, Vol 35, pp 4622-4636 [*Poirot, et al.*, 2001]. Copyright 2001 American Chemical Society.

A follow-on study examining the data from Underhill, Vermont used in the previous study and new data from Brigantine National Wildlife Refuge in New Jersey, came to similar conclusions [*Hopke, et al.*, 2005]. The techniques used in this study were the same as those used in the Poirot study [2001], but new methods were added. The emissions footprint from the Brigantine data is shown in Figure II-20. This study combined the results of the Vermont study with the New Jersey study to arrive at a combined source contribution for both sites. The area corresponds to the Ohio River Valley. The coal-fired emissions from 1998 were also calculated, and overlain on Figure II-21 as contours. The area of peak emissions coincides nicely with the combined area of peak influence. Another paper, using similar observations from a site in far western New York and another in the northeast corner of New York also found that the upper Ohio River Valley is a likely source region for sulfate *[Zhou, et al., 2004]*.

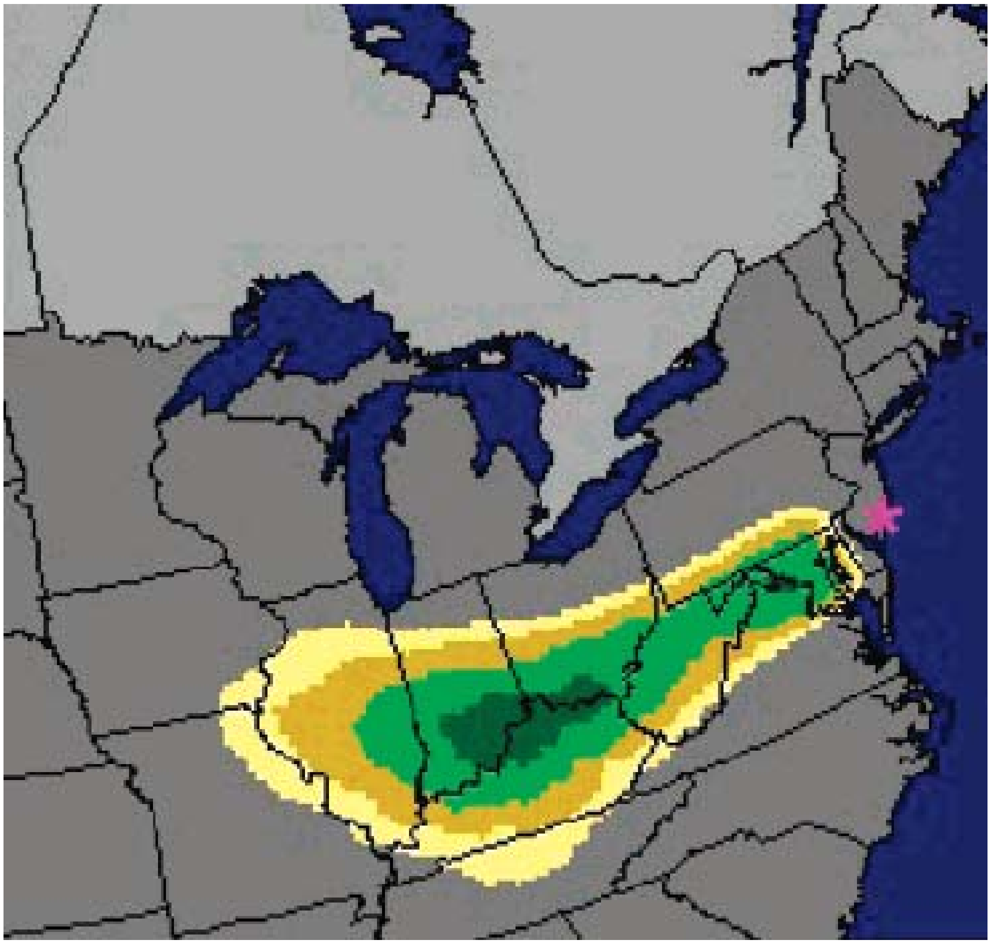


**Figure II- 20.** The area of influence (higher probabilities shown in darker green, lower in yellows) from coal-fired processes as determined from measurements taken at the Brigantine National Wildlife Refuge in New Jersey. Reprinted in part with permission from Hopke *et al.*, *Environ. Sci. Technol.*, Vol 39, pp 7980-83. Copyright 2005 American Chemical Society.

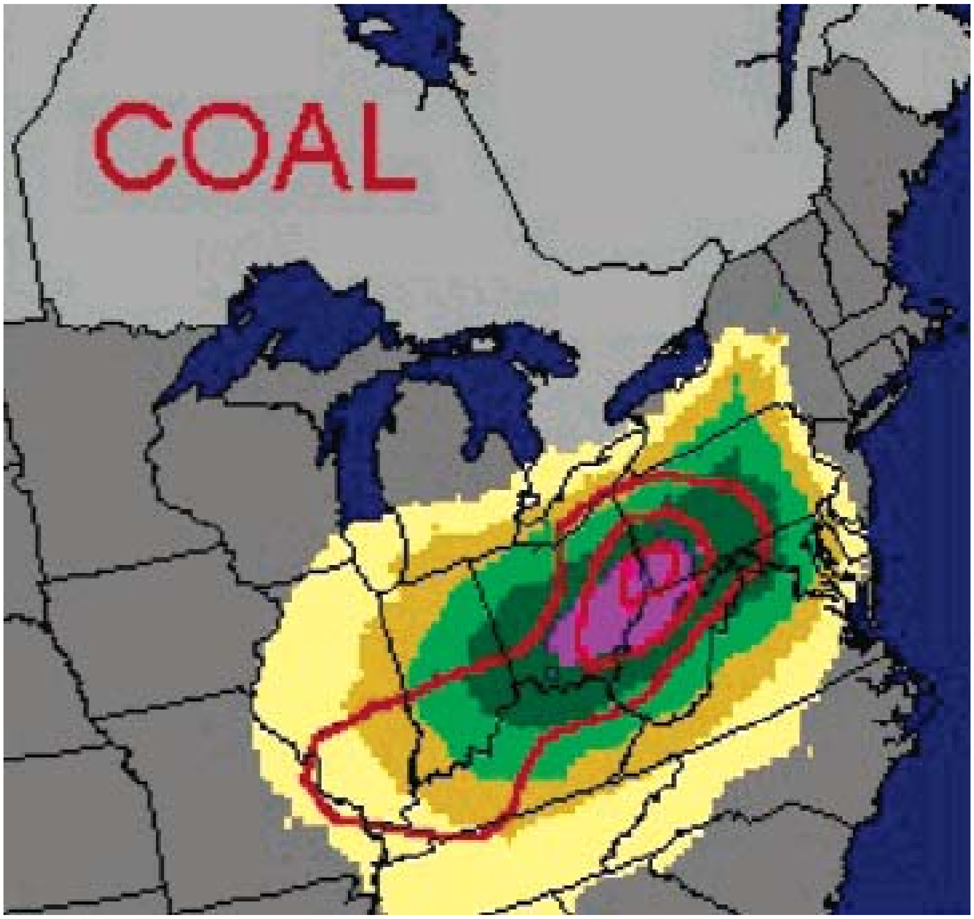


**Figure II-21.** The combined source contributions for the Underhill, Vermont and Brigantine National Wildlife Refuge in New Jersey, with contoured emissions from coal-fired units overlain on the plot. Reprinted in part with permission from *Hopke et al.*, *Environ Sci Technol*, Vol 39, pp 7980-83. Copyright 2005 American Chemical Society.

A study of 12 sites throughout Canada and the United States employed measurements of total PM2.5 mass and back trajectories to determine the origins of the airmasses reaching these sites when weighted by the PM2.5 concentrations on those days [*Brook, et al.*, 2004]. The technique was applied for May through September of 2000 and 2001. The tapered element oscillating microbalance (TEOM) instruments used measure PM2.5 mass; they respond best to the nonvolatile component of fine particles, and relatively poorly to volatile components such as nitrate and some organics. In the analysis technique used in this paper, trajectories for the entire period of interest are assembled, and where they travel is logged on a grid. This builds up a climatology of transport patterns to that site. PM2.5 mass from TEOM observations is then averaged over 6-hour periods, and trajectories are weighted according to the mass reaching the site in each 6-hour period. The ensemble of all these mass-weighted trajectories is divided by the climatology, so that areas are emphasized that contribute greatly to PM2.5 mass observed at each site. Finally, the results from ten sites were aggregated to reveal the source regions that all ten had in common (three were too close to each other to offer distinct perspectives, and therefore had redundant source regions, so one was selected to represent all three). The source region common to all ten (Figure II-22) was the Ohio River Valley, meaning that all these sites had an above average probability of receiving high PM2.5 when air came from the Ohio River Valley.

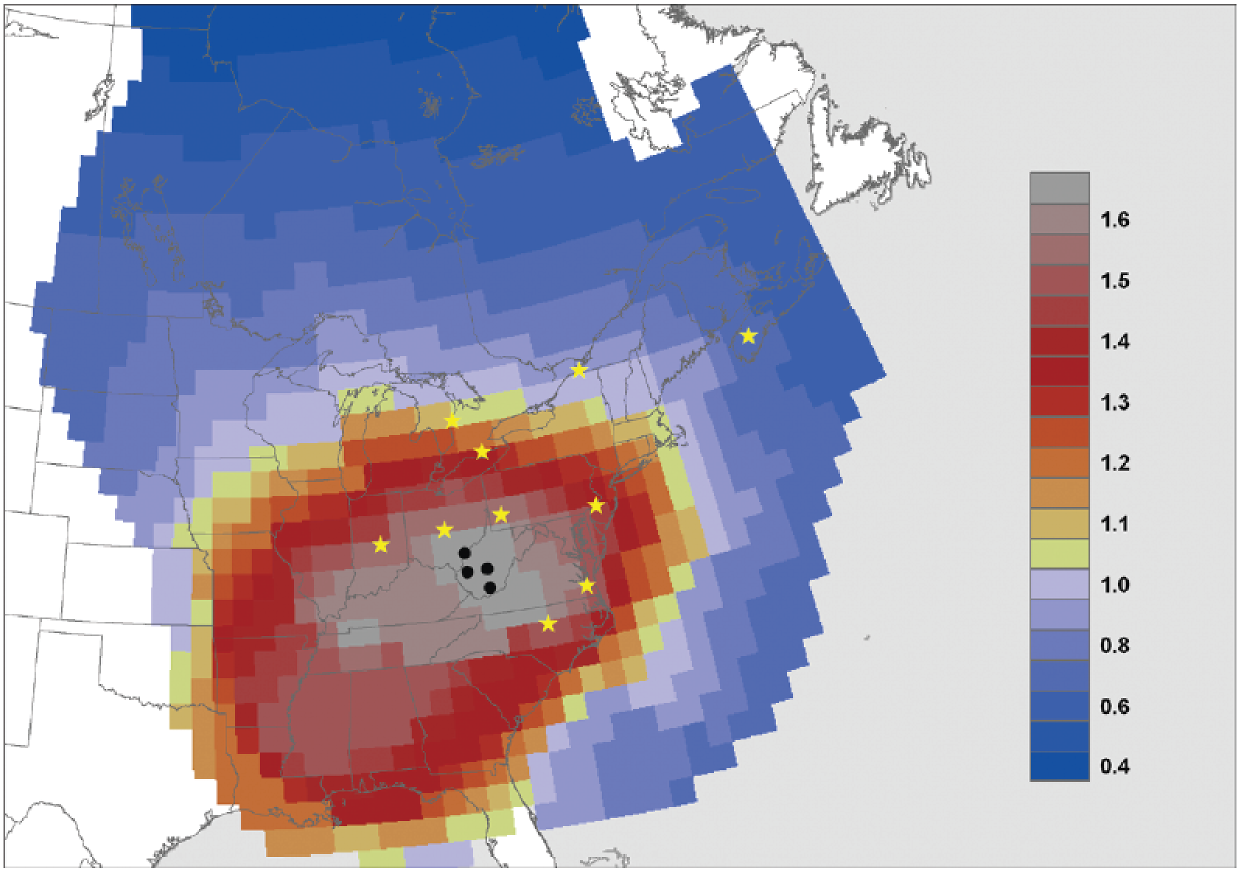


**Figure II-22.** The source region common to ten North American PM2.5 mass sites in the months of May through September of 2000 and 2001 as illustrated by dimensionless Quantitative Transport Bias Analysis (QTBA) plots. Reproduced with permission from [Brook *et al.*, 2004].

A modeling study investigated the effects of 10% cuts in emissions from broad regions *[Mueller, et al., 2004]*. The regions were the Midwest (Wisconsin, Michigan, Illinois, Indiana, Ohio, and Kentucky), the Mid-Atlantic (Pennsylvania, New Jersey, Maryland, Delaware, West Virginia, and Virginia), the Northeast (all states to the north and east of New York), the Southeast (Tennessee, North Carolina, South Carolina, Georgia, Alabama, and Mississippi), and the West (states to the west of the Mississippi River). The study employed the URM1-ATM model, and utilized the Direct Decoupled Method (DDM) to examine the sensitivity of atmospheric concentrations in one region to 10% changes in emissions from all the others and from itself. DDM is an efficient modeling method in that only one simulation is required to generate multiple sensitivity calculations. The results compare very favorably with the results from multiple simulations whereby the emissions from each region would be reduced by 10% and compared with a base case. The results from 10% reductions in $SO_2$ emissions were particularly dramatic, since they showed that a 10% reduction in emissions from the Midwest had a larger effect on sulfate concentrations in both the Mid-Atlantic and the Northeast than a 10% reduction in $SO_2$ emissions within those regions themselves. The large contribution from the Midwest is not surprising since $SO_2$ emissions there are large and it is frequently upwind of both the Mid-Atlantic and the Northeast, especially on high PM2.5 and haze days. In each case, changes in sulfate concentrations were more sensitive to changes in $SO_2$ emissions than they were to changes in other emissions. Emissions were projected to 2010, using the meteorological conditions present during several episodes in 1992, 1993, and 1995.

### iv. Response of Sulfate to Emissions Controls

Emissions of $SO_2$ have declined in recent years in response to legislative and regulatory initiatives. A study covering emissions trends and concentrations over the 1990's [*Malm et al.*, 2002] indicates that the strong downward trends in sulfate observed at IMPROVE (Interagency Monitoring of PROtected Visual Environments) monitoring sites maintained mostly by the National Park Service and at CASTNET sites maintained by the EPA are strongly correlated with emissions changes over the same period. In particular, this study investigated the 80th and 90th percentiles of sulfate concentrations and found that they correlated well with emissions reductions. Reductions in sulfate were highest in the Ohio River Valley and Tennessee, where emissions density was also the highest.

Another study [*Malm et al.*, 1994] that also used the IMPROVE data set investigated changes in visibility due to changes in sulfate. In this study, it was found that two thirds of the visibility impairment in the eastern United States was due to sulfate. A subsequent study *[Ames and Malm, 2001]* indicated that sulfate's contributions to visibility impairment on the worst visibility days are far greater, especially in the eastern United States, than its contributions on days with median visibility. This was particularly true of the Dolly Sods site in West Virginia, where 80% of the visibility obstruction on the haziest days was due to sulfate.

## References

Ames, R. B., and W. C. Malm (2001), Chemical species' contributions to the upper extremes of aerosol fine mass, *Atmospheric Environment*, *35*, 5193-5204.

Brook, J. R., et al. (2004), Determination of the source areas contributing to regionally high warm season PM2.5 in eastern north America, *Journal of the Air & Waste Management Association*, *54*, 1162-1169.

Butler, T. J., et al. (2005), The impact of changing nitrogen oxide emissions on wet and dry nitrogen deposition in the northeastern USA, *Atmospheric Environment*, *39*, 4851-4862.

Chen, L. W. A., et al. (2002), Origins of fine aerosol mass in the Baltimore-Washington corridor: Implications from observation, factor analysis, and ensemble air parcel back trajectories, *Atmospheric Environment*, *36*, 4541-4554.

Choi, Y. J. (2004), A study of ground-level ozone over the Baltimore/Washington ozone nonattainment area, 158 pp, The University of Maryland, College Park.

Choi, Y. J., et al. (2006), A combined approach for the evaluation of a volatile organic compound emissions inventory, *Journal of the Air & Waste Management Association*, *56*, 169-178.

Dutkiewicz, V. A., et al. (2004), Sources of fine particulate sulfate in New York, *Atmospheric Environment*, *38*, 3179-3189.

Hains, J. C. (2007), Measurements and Models of Pollutants over the Mid Atlantic: A Chemical Climatology, Ph.D. thesis, The University of Maryland, College Park.

Hains, J. C., et al. (2007a), A side-by-side comparison of filter-based PM2.5 measurements at a suburban site: A closure study, *Atmospheric Environment*, *41*, 6167-6184.

Hains, J. C., et al. (2007b), Origins of chemical pollution derived from Mid-Atlantic aircraft profiles using a clustering technique, *Atmospheric Environment*, *in press*.

Hopke, P. K., et al. (2005), Reconciling trajectory ensemble receptor model results with emissions, *Environmental Science & Technology*, *39*, 7980-7983.

Kim, S. W., et al. (2006), Satellite-observed US power plant NOx emission reductions and their impact on air quality, *Geophysical Research Letters*, *33*.

Likens, G. E., et al. (2005), Long-term relationships between $SO_2$ and $NO_x$ emissions and $SO_4^{2-}$ and $NO_3^-$ concentration in bulk deposition at the Hubbard Brook Experimental Forest, NH, *Journal of Environmental Monitoring*, *7*, 964-968.

Marufu, L. T., et al. (2004), The 2003 North American electrical blackout: An accidental experiment in atmospheric chemistry, *Geophysical Research Letters*, *31*.

Mueller, S. F., et al. (2004), Geographic sensitivity of fine particle mass to emissions of SO2 and NOx, *Environmental Science & Technology*, *38*, 570-580.

NESCAUM (2006), Contributions to Regional Haze in the Northeast and Mid-Atlantic United States: Mid-Atlantic/northeast Visibility Union (MANE-VU) Contribution Assessment, 122 pp. pp, Boston, MA.

Ogulei, D., et al. (2005), Receptor modeling for multiple time resolved species: The Baltimore, supersite, *Atmospheric Environment*, *39*, 3751-3762.

Ogulei, D., et al. (2006), Source apportionment of Baltimore aerosol from combined size distribution and chemical composition data, *Atmospheric Environment*, *40*, S396-S410.

Park, S. S., et al. (2005), Highly time-resolved organic and elemental carbon measurements at the Baltimore Supersite in 2002, *Journal of Geophysical Research-Atmospheres*, *110*.

Park, S. S., et al. (2006), Characteristics of PM2.5 episodes revealed by semi-continuous measurements at the Baltimore Supersite at Ponca St, *Aerosol Science and Technology*, *40*, 845-860.

Poirot, R. L., et al. (2001), Comparative application of multiple receptor methods to identify aerosol sources in northern Vermont, *Environmental Science & Technology*, *35*, 4622-4636.

Robinson, A. L., et al. (2007), Rethinking organic aerosols: Semivolatile emissions and photochemical aging, *Science*, *315*, 1259-1262.

Sickles, J., and D. S. Shadwick (2007a), Changes in air quality and atmospheric deposition in the eastern United States: 1990-2004, *Journal of Geophysical Research-Atmospheres*, *112*.

Sickles, J. E., and D. S. Shadwick (2007b), Seasonal and regional air quality and atmospheric deposition in the eastern United States, *Journal of Geophysical Research-Atmospheres*, *112*.

Taubman, B. F. (2004), Airborne Characterization of Regional Aerosol Origins and Optical Properties, 242 pp, The University of Maryland, College Park.

Taubman, B. F., et al. (2006), Aircraft vertical profiles of trace gas and aerosol pollution over the mid-Atlantic United States: Statistics and meteorological cluster analysis, *Journal of Geophysical Research-Atmospheres*, *111*.

Taubman, B. F., et al. (2004), Airborne characterization of the chemical, optical, and meteorological properties, and origins of a combined ozone-haze episode over the eastern United States, *Journal of the Atmospheric Sciences*, *61*, 1781-1793.

Warneke, C., et al. (2007), Determination of urban volatile organic compound emission ratios and comparison with an emissions database, *Journal of Geophysical Research-Atmospheres*, *112*.

Zhou, L. M., et al. (2004), Comparison of two trajectory based models for locating particle sources for two rural New York sites, *Atmospheric Environment*, *38*, 1955-1963.

# Section III

# PM2.5 Trends over the Mid Atlantic Region

Charles A. Piety, Dr. Russell R. Dickerson,
Department of Atmospheric and Oceanic Science
The University of Maryland

February 4, 2008

### 1. How is this section important?

Assessing trends in PM2.5 and its constituents over the Mid Atlantic region is an important part of describing the current state, and future projections regarding air quality over Maryland.

### 2. What questions are answered in this section?

What are the long-term trends and seasonal cycles regarding concentrations of PM2.5 and PM2.5 species? What are the long-term trends of PM2.5 from monitors over the Mid Atlantic region locations? What is the variability in this trend from monitor to monitor? Is a species or a set of species responsible for the bulk of the temporal trend? Have concentrations in some seasons changed more than in others?

### 3. What are the key take-away messages of this section?

Monitors over the Mid Atlantic region show a decrease in PM2.5 concentrations ranging from 0.117 to 0.360 micrograms per-cubic meter per-year ($\mu g\ m^{-3}\ yr^{-1}$), with a mean decreasing trend among sites with a sufficiently long history of observations of ~0.25 $\mu g\ m^{-3}\ yr^{-1}$. The trend is significant for each individual site ($p < 0.05$) and for all sites together ($p < 0.01$). At all locations investigated in this study, the PM2.5 species that contributed the most to the decrease in PM2.5 was sulfate which is responsible for ~50% of the PM2.5 decrease on average. Similarly, organic carbon accounts for ~25% and ammonium ~15% of the decrease. The homogeneity in the trend of PM2.5 and PM2.5 species suggests all monitors studied share a common regional “load” of PM2.5, which may account for roughly 60%-75% of the total observed PM2.5. Inspection of seasonal cycles suggests the regional contribution may increase during parts of the summer season, but the seasonality of the species distribution has changed little over the past ten years. The analysis shows that the highest PM2.5 observations represent a small percentage (5%-10%) of the total days during the year and occur primarily over the warm months (May-September). Recently implemented regional control strategies, which target sulfur, nitrogen and VOC emissions, should continue the current trends to further reduce PM2.5 concentrations on the worst pollution days in Maryland.

### 4. What conclusions are reached in this section with respect to Maryland's attainment demonstration?

The results from this analysis show that, on a regional scale, average PM2.5 levels are decreasing with time at a rate of 0.25 µg $m^{-3}$ $yr^{-1}$, significant at $p<0.05$; when data from all sites are considered together the significance is $p<0.01$. While there is site-to-site and year-to-year variability in PM2.5 readings, this consistent decrease in concentration suggests that Maryland and the surrounding areas are targeting the appropriate species at the appropriate locations. Considering that the site with the maximum annual 2002 Design Value was Old Town in Baltimore, MD with 16.64 µg $m^{-3}$, it is more then likely that Maryland will comply with the annual and 24-hr PM2.5 NAAQS by 2009.

## Abstract

This section assesses temporal trends in PM2.5 over the Mid Atlantic region in order to describe the current state and future projections regarding air quality over Maryland. Described here are long-term (≥ 5 yr) trends and seasonal cycles regarding concentrations of PM2.5 and individual PM2.5 species seen at monitors over the Mid Atlantic region locations. Monitors over the Mid Atlantic region show a decrease in PM2.5 concentrations ranging from 0.117 to 0.360 micrograms per-cubic meter per-year ($\mu g\ m^{-3}\ yr^{-1}$), with a mean trend of ~0.25 $\mu g\ m^{-3}\ yr^{-1}$. Trends are statistically significant at each site ($p < 0.05$) and at all sites overall ($p < 0.01$). At all locations investigated in this study, the PM2.5 species that contributed the most to the decrease in PM2.5 was sulfate which is responsible for ~50% of the PM2.5 decrease on average. Similarly, organic carbon accounts for ~25% of the decrease and ammonium ~15%. Nitrate, dust and elemental carbon contribute to the trend in a smaller way. While definitively quantifying the regional signal of PM2.5 is a complex problem, the homogeneity in the trend of PM2.5 and PM2.5 species suggests all monitors studied share a common regional "load" of PM2.5. Comparison of the urban and rural monitors suggests the regional load may account for roughly 60%-75% of the total observed PM2.5 (see http://www.epa.gov/air/airtrends/aqtrnd03/pdfs/2_chemspecofpm25.pdf). Inspection of seasonal cycles suggests the regional contribution may increase during parts of the summer season, but the seasonality of the species distribution has changed little over the past ten years. The analysis also shows that the highest PM2.5 observations represent a small percentage (5%-10%) of the total days during the year and occur primarily over the summer months (May-September). Recently-implemented regional control strategies, which target sulfur, nitrogen and VOC emissions, should continue the current trends to further reduce PM2.5 concentrations on the worst pollution days in Maryland. While there is site to site and year to year variability in PM2.5 readings, this consistent decrease in concentration suggests that Maryland and the surrounding areas are targeting the appropriate PM2.5 species at the appropriate locations. Given that the Old Town site in Baltimore, MD has the maximum 2002 Baltimore NAA design value (16.6 $\mu g\ m^{-3}$), the area will likely comply with the annual PM2.5 annual NAAQS by 2009.

### a. Introduction

This analysis summarizes what, if any, changes in annual PM2.5 concentrations have occurred over the recent past, i.e. the last 5-10 years at each PM2.5 monitor. PM2.5 data from the Clean Air Status and Trends Network (CASTNET) and Interagency Monitoring of PROtected Visual Environments (IMPROVE) aerosol monitoring network were used to assess the annual trend of PM2.5 and PM2.5 species over the Mid Atlantic region. The analysis is relevant because year-to-year variability at any given site can be high, but by examining long-term trends in PM2.5 and individual PM2.5 species we can discern the effectiveness of control measures and attempt to forecast likely air quality improvements and future PM2.5 levels.

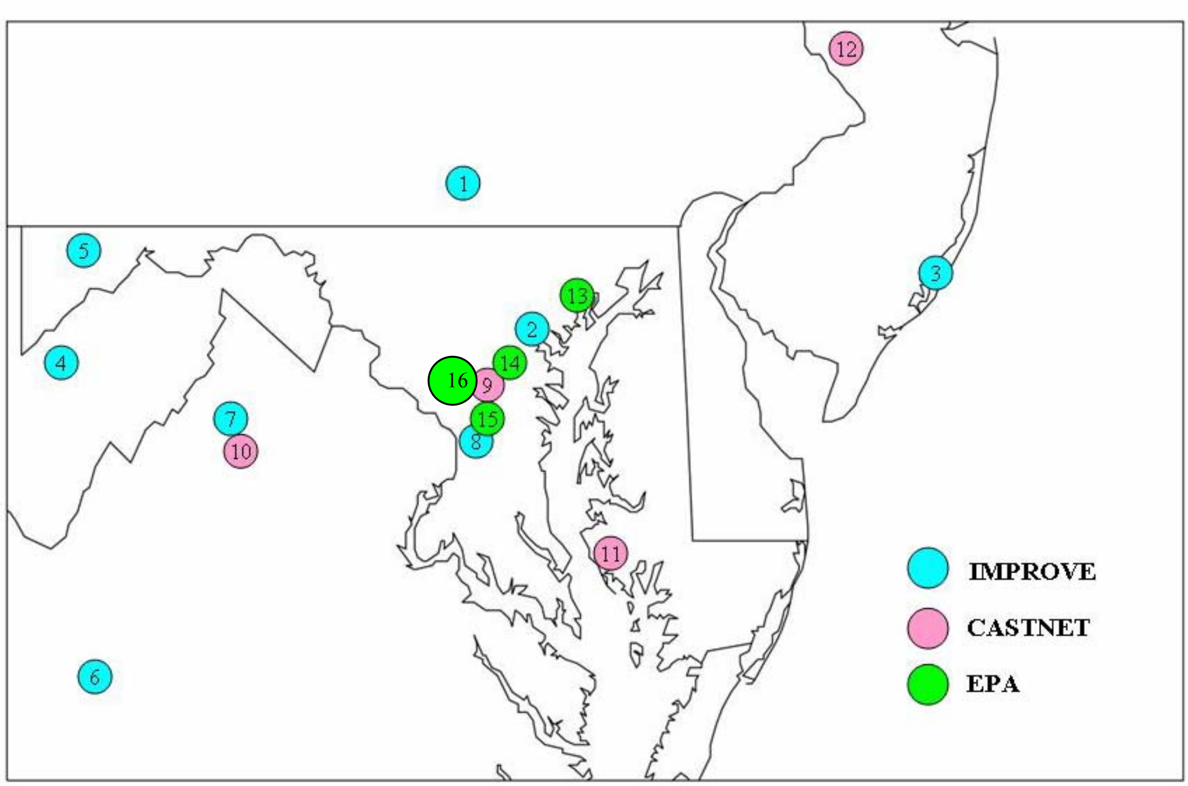
Although this investigation focuses on long-term trends, PM2.5 does also vary seasonally with the highest concentrations during the summer (May-September). Mostly in urban areas, a secondary PM2.5 maximum occurs during the winter (December-February) months. Summer-time peaks are associated with warmer temperatures, favorable pollution transport patterns and light winds which lead to increases in sulfate concentrations. Winter season maxima are driven more by increases in nitrogen and carbon compounds associated with lower mixing heights and general stagnant weather conditions. On a time scale smaller still PM2.5 does fluctuate diurnally with the highest concentrations typically during the morning and evening rush hours and the lowest concentrations during the well-mixed afternoon hours. While daily and seasonal fluctuations in PM2.5 are in part a function of weather conditions, longer-term trends should be less dependent on meteorology and are more likely to reflect changes associated with emissions.

### b. Methods

Two monitoring networks, CASTNET and IMPROVE, were the main sources of long-term data for this analysis. The IMPROVE and CASTNET monitors used in this analysis are listed in Table III-1 and Table III-2; see also Figure I-1. IMPROVE data sets typically contain PM2.5 mass, and several of the PM2.5 species. The particular species investigated were ammonium, nitrate, sulfate, elemental carbon, organic carbon, and dust.

The IMPROVE network employs a 1-in-3-day sampling protocol in which 24-hour samples are collected every third day. Average trend values were calculated using data sets from IMPROVE monitors that have been in operation for at least five years. For completeness, other shorter time period data (i.e., Catonsville, MD and Piney Run, MD) are also shown. The CASTNET measurements used in this analysis were sulfate, nitrate and ammonium. The atmospheric sampling for sulfur and nitrogen species was integrated over weekly collection periods.

Long-term trends in PM2.5 mass and PM2.5 species were obtained by calculating linear trends from the time series data. IMPROVE ammonium data are inferred from nitrate and sulfate concentrations, assuming complete neutralization with $NH_4^+$. A linear trend line was plotted with the time series data to show the overall trend over the entire time period. Additionally, to highlight the seasonal nature of the PM2.5 a line was plotted showing approximately a 90-day running average. This corresponds to a 30-point running average for the IMPROVE data and a 12-point running average for the CASTNET data.



| | | |
|---|---|---|
| 1. Arendtsville, PA | 2. UMBC, MD | 3. Brigantine, NJ |
| 4. Dolly Sods, WV | 5. Frostburg, MD | 6. James River, VA |
| 7. Shenandoah, VA | 8. Hains Point, DC | 9 & 16. Beltsville, MD |
| 10. Big Meadows, VA | 11. Blackwater, MD | 12. Washington Crossing, NJ |
| 13. Essex, MD | 14. Fort Meade, MD | 15. McMillan Reservoir, DC |

Figure III-1 A map showing the locations of IMRPOVE, CASTNET and EPA/State monitors used in the analysis of PM2.5 composition. Tables III-1 and III-2 present more detailed monitor information.

Table III-1 Summary Information for Monitors used in the Composition analysis.

| Monitoring Site | State | Classification | Elevation (meters) | Latitude, Longitude (degrees) | Sampling Period | Parameters Measured |
|---|---|---|---|---|---|---|
| | | | | | | |
| 1. Arendtsville | PA | IMPROVE | 267 | 39.9, -77.3 | 2001-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 2. UMBC | MD | IMPROVE | 78 | 39.2, -76.7 | 2004-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 3. Brigantine | NJ | IMPROVE | 5 | 39.9, -77.3 | 1991-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 4. Dolly Sods | WV | IMPROVE | 1182 | 39.1, -79.4 | 1991-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 5. Frostburg | MD | IMPROVE | 767 | 39.7, -79.0 | 2004-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, |
| 6. James River | VA | IMPROVE | 289 | 37.6, -79.5 | 2000-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 7. Shenandoah | VA | IMPROVE | 1079 | 38.5, -78.4 | 1988-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 8. Hains Point | DC | IMPROVE | 15 | 38.9, -77.0 | 1989-2006 | PM2.5, $NH_4$,$NO_3$, $SO_4$, EC , OC, Dust |
| 9. Beltsville | MD | CASTNET | 46 | 39.0, -76.6 | 1989-2006 | $NH_4$, $NO_3$, $SO_4$ |
| 10. Big Meadows | VA | CASTNET | 1073 | 38.5, -78.4 | 1989-2006 | $NH_4$, $NO_3$, $SO_4$ |
| 11. Blackwater | MD | CASTNET | 4 | 38.3, -76.0 | 1995-2006 | $NH_4$, $NO_3$, $SO_4$ |
| 12. Washington Crossing | NJ | CASTNET | 61 | 40.3, -74.9 | 1989-2006 | $NH_4$, $NO_3$, $SO_4$ |
| 13. Essex | MD | EPA | 6 | 39.3, -76.4 | 2001-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 14. Fort Meade | MD | EPA | 46 | 39.1, -76.8 | 2001-2004 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 15. McMillan Reservoir | DC | EPA | 44 | 38.9, -77.0 | 2001-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |
| 16. Beltsville | MD | EPA | 46 | 39.0, -76.6 | 2004-2006 | PM2.5, $NH_4$, $NO_3$, $SO_4$, EC, OC, Dust |

Notes: $NH_4$ = ammonium (inferred for IMPROVE sites), $NO_3$ = nitrate, $SO_4$ = sulfate, EC = elemental carbon, OC = organic carbon.
IMPROVE: http://vista.cira.colostate.edu/improve/Default.htm
CASTNET: http://www.epa.gov/castnet/
EPA: http://www.epa.gov/mxplorer/index.htm

Table III-2. Summary Table of Annual Trends in $\mu g\ m^{-3}\ yr^{-1}$ for PM2.5 and PM2.5 Species

| IMPROVE Monitors | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Monitoring Site | PM2.5 | Ammonium | Nitrate | Sulfate | Elemental Carbon | Organic Carbon | Dust | Period of Trend |
| Arendtsville | -0.360 | -0.075 | 0.000 | -0.194 | 0.000 | -0.194 | -0.056 | 2001-2006 |
| UMBC | -1.750 | -0.280 | -0.150 | -0.684 | 0.032 | -0.033 | -0.001 | 2004-2006 |
| Brigantine | -0.167 | -0.018 | -0.013 | -0.013 | -0.015 | -0.011 | -0.011 | 1991-2006 |
| Dolly Sods | -0.117 | -0.048 | -0.040 | -0.110 | -0.067 | -0.037 | 0.060 | 1991-2006 |
| Frostburg | -0.167 | -0.040 | -0.050 | -1.000 | -0.010 | -0.137 | -0.071 | 2004-2006 |
| James River | -0.300 | -0.047 | -0.043 | -0.183 | 0.003 | -0.025 | 0.033 | 2000-2006 |
| Shenandoah | -0.210 | -0.018 | 0.006 | -0.094 | -0.006 | -0.041 | -0.002 | 1988-2006 |
| Hains Point | -0.344 | -0.017 | -0.022 | -0.022 | -0.053 | -0.067 | -0.031 | 1989-2006 |
| CASNET Monitors | | | | | | | | |
| | PM2.5 | Ammonium | Nitrate | Sulfate | Elemental Carbon | Organic Carbon | Dust | Period of Trend |
| Beltsville | NA | -0.059 | -0.036 | -0.152 | NA | NA | NA | 1989-2006 |
| Big Meadows | NA | -0.006 | 0.015 | -0.127 | NA | NA | NA | 1988-2006 |
| Blackwater | NA | -0.011 | 0.019 | -0.230 | NA | NA | NA | 1995-2006 |
| Washington Crossing | NA | -0.044 | -0.011 | -0.130 | NA | NA | NA | 1989-2006 |
| Mean Value | 0.250<br>(±0.100) | -0.042<br>(±0.041) | -0.019<br>(±0.023) | -0.103<br>(±0.070) | -0.023<br>(±0.030) | -0.063<br>(±0.067) | -0.001<br>(±0.042) | |

**c. Results**

Figure III-2 shows the mean annual trend in PM2.5 concentrations from seven different locations over the Mid Atlantic region. PM2.5 trends range from -0.117 μg $m^{-3}$ $yr^{-1}$ over Dolly Sods, WV to -0.360 $μgm^{-3}yr^{-1}$ at Arendtsville, PA. The average trend of all plotted monitors was -0.250 (±0.1) $μgm^{-3}yr^{-1}$. The data from UMBC IMPROVE monitor (located in Catonsville, SW of Baltimore, MD) and Frostburg, MD were not included in the summary plot because the sampling period for each location was relatively brief (2004-2006 for UMBC, MD and 2004-2006 for Frostburg, MD). However, it is important to note that both trends were negative with the UMBC trend being substantially higher than the average of -1.70 $μgm^{-3}yr^{-1}$ and Frostburg trend slightly below the average of -0.167 $μgm^{-3}yr^{-1}$. Figure III-3 presents the mean annual trends in sulfate for the IMPROVE and CASTNET monitors with sampling periods longer than 5 years. Sulfate trends range from -0.013 $μgm^{-3}yr^{-1}$ over Brigantine, NJ to -0.22 $μgm^{-3}yr^{-1}$ at Blackwater, MD. The average standard deviation trend of all plotted sulfate monitors was -0.126 (±0.070) μg $m^{-3}$ $yr^{-1}$.

Figure III-4 presents the mean annual trends in ammonium for the IMPROVE and CASTNET monitors with sampling periods longer than 5 years. Ammonium trends range from +0.003 $μgm^{-3}yr^{-1}$ over Shenandoah, VA to -0.092 $μgm^{-3}yr^{-1}$ at James River, VA. The average and standard deviation trend of all plotted ammonium monitors was -0.041 (±0.036) $μgm^{-3}yr^{-1}$. Figure III-5 presents the mean annual trends in nitrate for the IMPROVE and CASTNET monitors with sampling periods longer than 5 years. Nitrate trends range from +0.006 $μgm^{-3}yr^{-1}$ over Shenandoah, VA to -0.043 $μgm^{-3}yr^{-1}$ at James River, VA. The average trend, and standard deviation, of all plotted monitors was -0.013 (±0.023) $μgm^{-3}yr^{-1}$. Figure III-6 presents the mean annual trends in organic carbon for the IMPROVE monitors with sampling periods longer than 5 years. Organic carbon trends range from -0.011 $μgm^{-3}yr^{-1}$ over Brigantine, NJ to -0.194 $μgm^{-3}yr^{-1}$ at Arendtsville, PA. The average trend for all plotted monitors was -0.063 (±0.067) $μgm^{-3}yr^{-1}$. Figure III-7 presents the mean annual trends in elemental carbon for the IMPROVE monitors with sampling periods longer than 5 years. Elemental carbon trends range from +0.003 $μgm^{-3}yr^{-1}$ over James River, VA to -0.063 $μgm^{-3}yr^{-1}$ at Dolly Sods, WV. The average trend of all plotted monitors was -0.063 (±0.067) μgm$^{-3}$yr$^{-1}$. Figure III-8 presents the mean annual trends in Dust for the IMPROVE monitors with sampling periods longer than 5 years. Dust trends range from +0.060 μgm$^{-3}$yr$^{-1}$ over Dolly Sods, WV to -0.056 μgm$^{-3}$yr$^{-1}$ at Arendtsville, PA. The average trend for all plotted dust monitors were -0.001 (±0.042) μgm$^{-3}$yr$^{-1}$.

Figures III-9a to III-9c show time series plots of weekly data from the Beltsville, MD CASTNET monitor of ammonium, nitrate and sulfate respectively. A linear trend is also presented along with a 12-point running average. The data show steady, slightly decreasing values throughout the entire time period for all species.

Figures III-10a to III-10c show time series plots of weekly data from the Big Meadows, VA CASTNET monitor of ammonium, nitrate and sulfate respectively. A linear trend is also presented along with a 12-point running average. The data show steady, slightly decreasing values for ammonium and sulfate while the nitrate trend is slightly positive. Because particulate nitrate concentrations are so sensitive to temperature and gaseous ammonia concentration an explanation for this positive trend must await further analysis. For much of the year, most of the nitrate remains in the gas phase; decreases in total nitrate have been reported [*Sickles and Shadwick*, 2007].

Figures III-11a to III-11c show time series plots of weekly data from the Blackwater, MD CASTNET monitor of ammonium, nitrate and sulfate respectively. A linear trend is also presented along with a 12-point running average. The data show steady, slightly decreasing values for ammonium and sulfate while the nitrate trend is slightly positive.

Figures III-12a to III-12c show time series plots of weekly data from the Washington Crossing, NJ CASTNET monitor of ammonium, nitrate and sulfate respectively. A linear trend is also presented along with a 12-point running average. The data show steady, slightly decreasing values throughout the entire time period for all species.

Figures III-13a to III-13g show time series plots of weekly data from the Arendtsville, PA IMPROVE monitor of Total PM2.5, ammonium, nitrate and sulfate, elemental carbon, organic carbon and dust respectively. A linear trend is also presented along with a 30-point running average. The data show steady, slightly decreasing values for PM2.5 and all species except nitrate and elemental carbon for which there is no apparent trend.

Figures III-14a to III-14g show time series plots of weekly data from the Brigantine, NJ IMPROVE monitor of Total PM2.5, ammonium, nitrate and sulfate, elemental carbon, organic carbon and dust respectively. A linear trend is also presented along with a 30-point running average. The data show steady, slightly decreasing values for PM2.5 and all species.

Figures III-15a to III-15g show time series plots of weekly data from the Dolly Sods, WV IMPROVE monitor of Total PM2.5, ammonium, nitrate and sulfate, elemental carbon, organic carbon and dust respectively. A linear trend is also presented along with a 30-point running average. The data show steady, slightly decreasing values for PM2.5 and all species with the exception of dust, which has a slightly positive trend.

Figures III-16a to III-16g show time series plots of weekly data from the James River, VA IMPROVE monitor of Total PM2.5, ammonium, nitrate, sulfate, elemental carbon, organic carbon and dust respectively. A linear trend is also presented along with a 30-point running average. The data show steady, slightly decreasing values for PM2.5 and all species with the exception of elemental carbon and dust which each have a slightly positive trend.

Figures III-17a to III-17g show time series plots of weekly data from the Shenandoah, VA IMPROVE monitor of Total PM2.5, ammonium, nitrate and sulfate, elemental carbon, organic carbon and dust respectively. A linear trend is also presented along with a 30-point running average. The data show steady, slightly decreasing values for PM2.5 and all species with the exception of ammonium, which has a slightly positive trend.

Figures III-18a to III-18f show time series plots of weekly data from the Hains Point (Washington, DC) IMPROVE monitor of total PM2.5, nitrate and sulfate, elemental carbon, organic carbon and dust respectively. A linear trend is also presented along with a 30-point running average. The data show steady, slightly decreasing values for PM2.5 and all species.

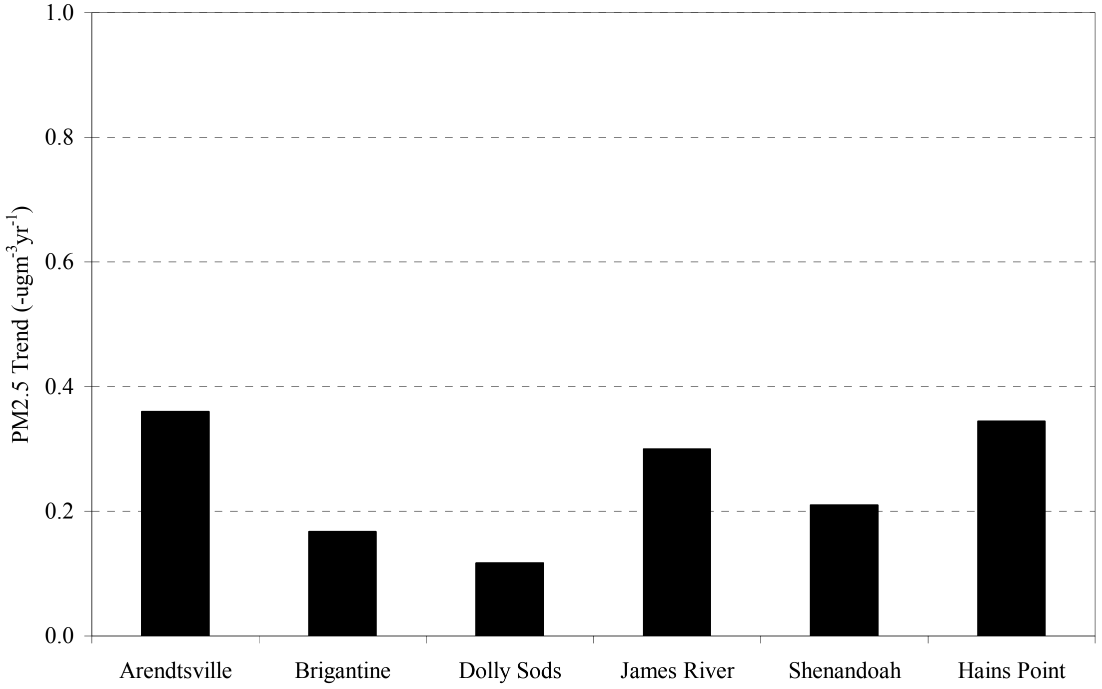


Figure III-2 The mean annual trend of PM2.5 for selected IMPROVE monitors. The UMBC, MD and Frostburg, MD monitors were not included because of the short sampling duration (see Table III-1 for sampling time periods). Note that data are plotted as the negative of the trend.

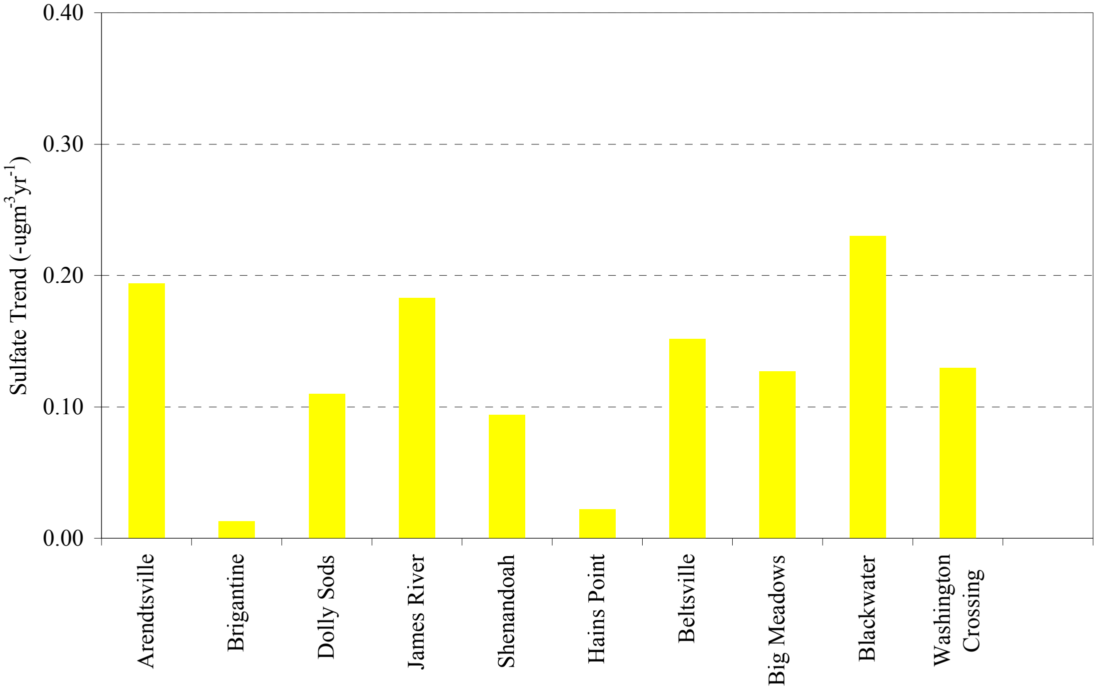


Figure III-3 The mean annual trend of Sulfate for selected IMPROVE and CASTNET monitors. The UMBC and Frostburg, MD monitors were not included because of the short sampling duration (see Table III-1 for sampling time periods). Note that data are plotted as the negative of the trend.

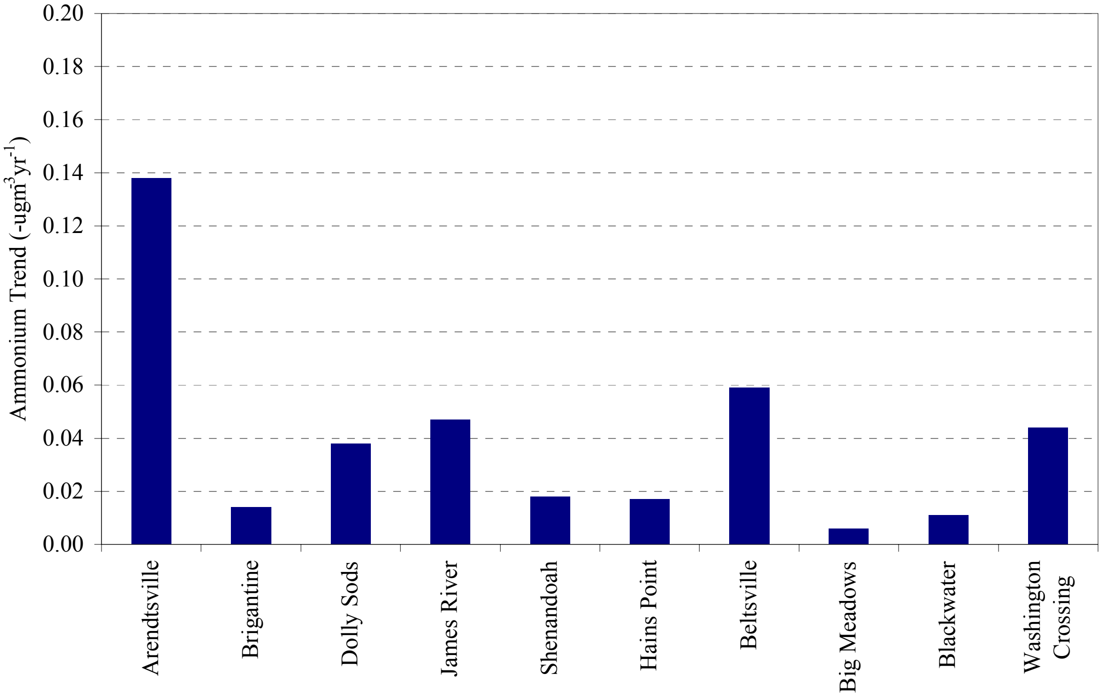


Figure III-4 The mean annual trend of ammonium for selected IMPROVE and CASTNET monitors. The UMBC and Frostburg, MD monitors were not included because of the short sampling duration (see Table III-1 for sampling time periods). Note that data are plotted as the negative of the trend.

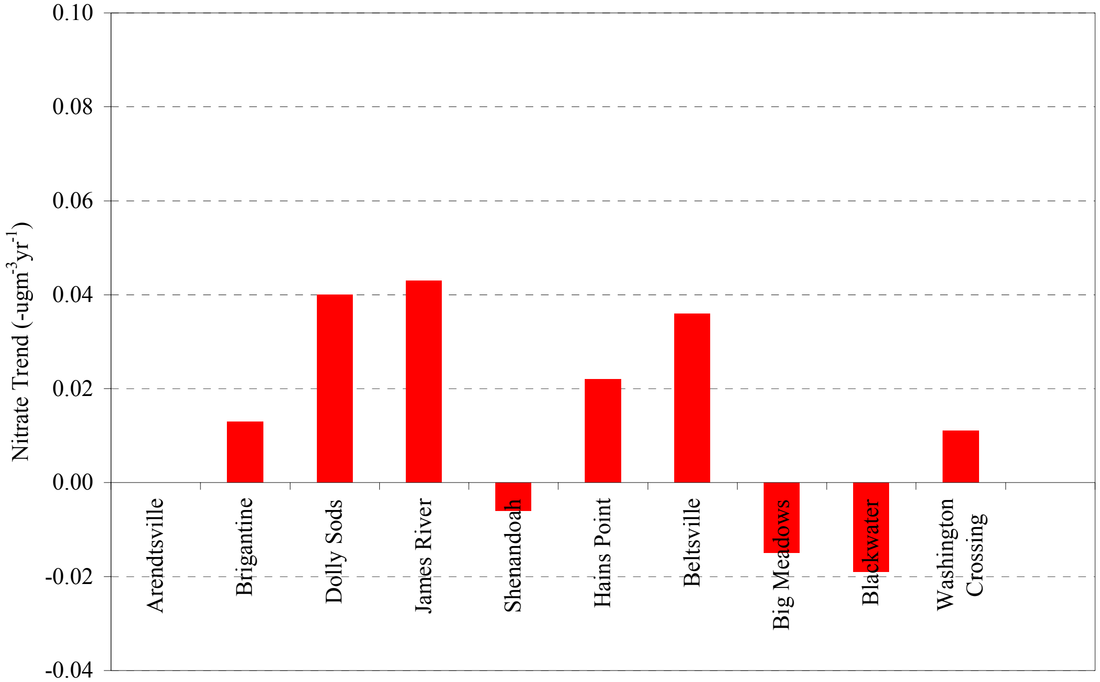


Figure III-5 The mean annual trend of nitrate for selected IMPROVE monitors. The UMBC, MD and Frostburg, MD monitors were not included because of the short sampling duration (see Table III-1 for sampling time periods). No statistically significant trend was detected for the Arendtsville monitor. Note that data are plotted as the negative of the trend.

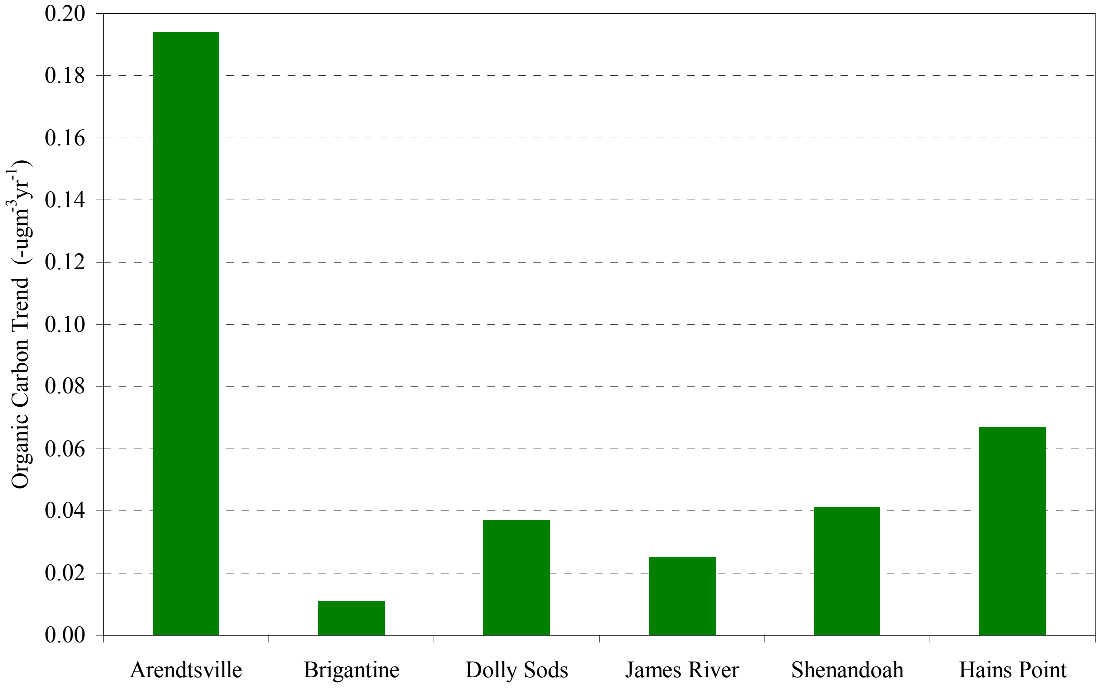


Figure III-6 The mean annual trend of organic carbon for selected IMPROVE monitors. The UMBC, MD and Frostburg, MD monitors were not included because of the short sampling duration (see Table III-1 for sampling time periods). Note that data are plotted as the negative of the trend.

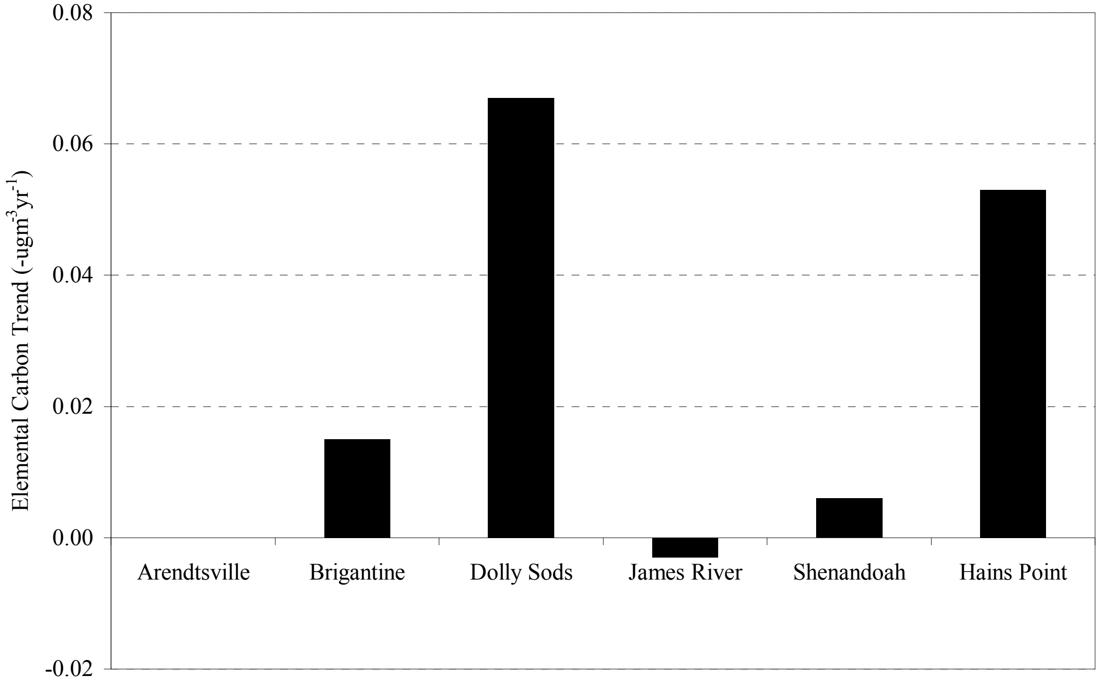


Figure III-7 The mean annual trend of elemental carbon for selected IMPROVE monitors. The UMBC, MD and Frostburg, MD monitors were not included because of the short sampling duration (see Table III-1 for sampling time periods). Note that data are plotted as the negative of the trend.

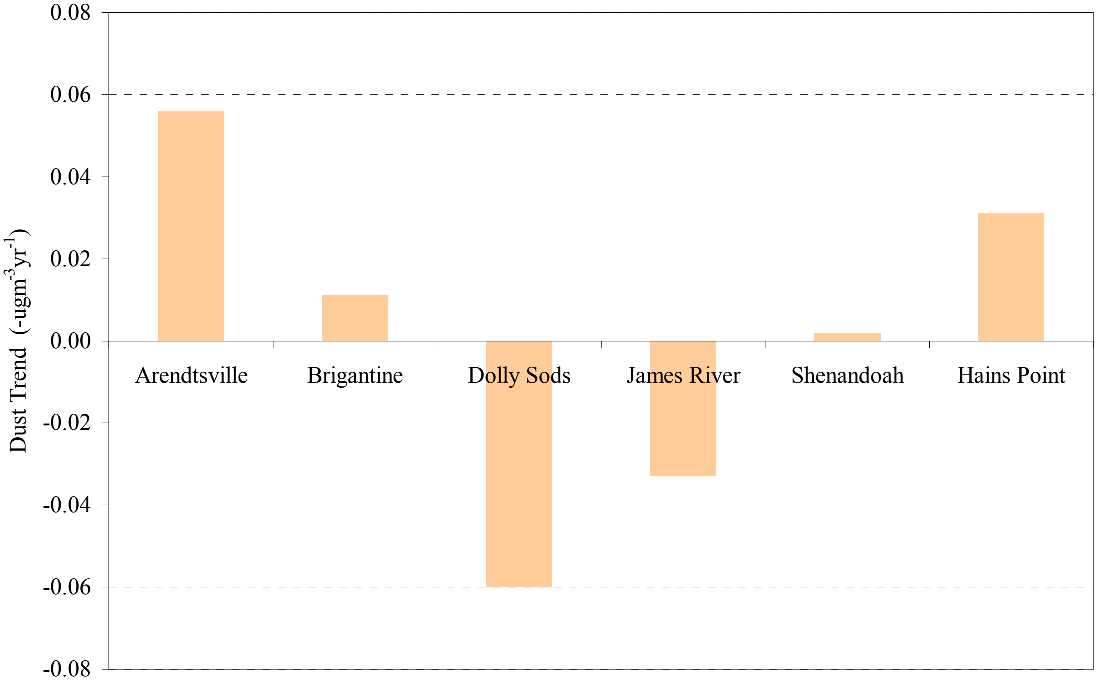


Figure III-8 The mean annual trend of Dust for selected IMPROVE monitors. The UMBC, MD and Frostburg, MD monitors were not included because of the short sampling duration (see Table III-1 for sampling time periods). Note that data are plotted as the negative of the trend.

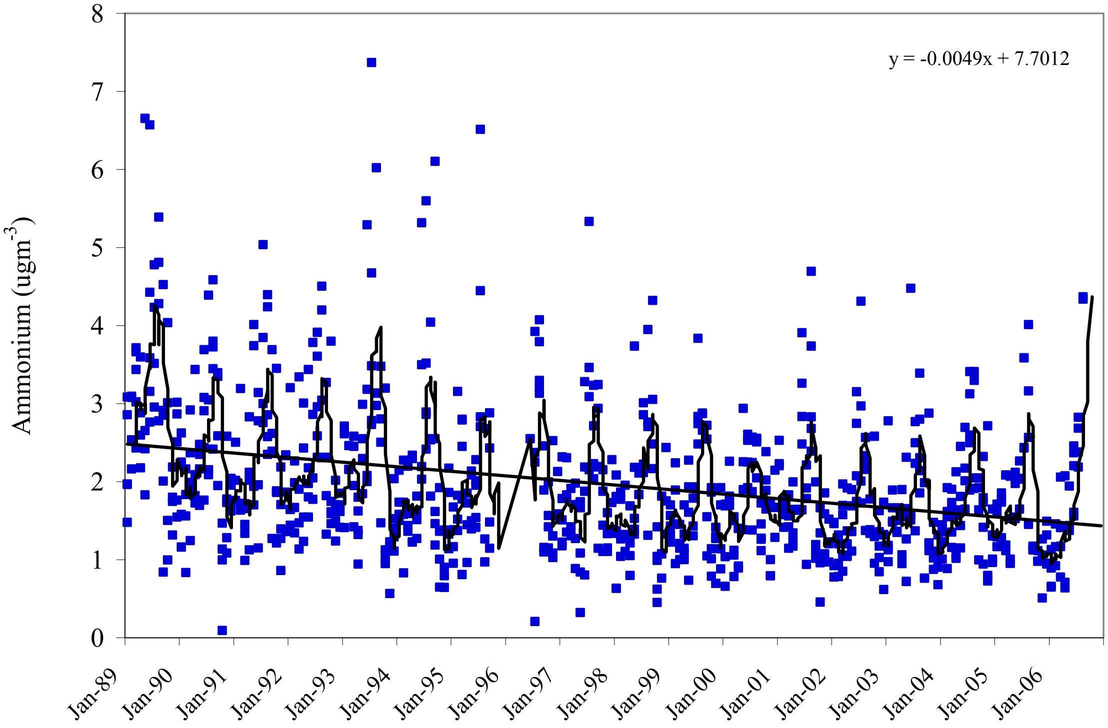


Figure III-9a. Ammonium from the Beltsville, MD CASTNET site. Weekly data from 1989-2006. The mean trend in ammonium is -0.059 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -0.0049x + 7.70. A 12-point running mean is also presented.

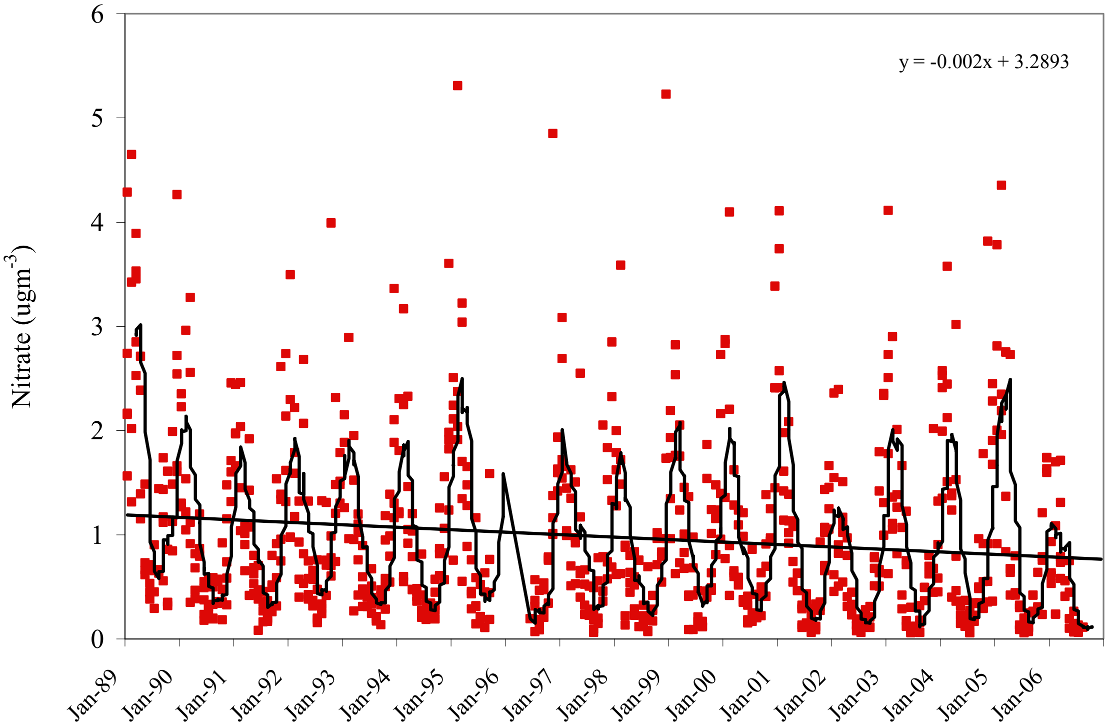


Figure III-9b. Nitrate from the Beltsville, MD CASTNET site. Weekly data from 1989-2006. The mean trend in nitrate is -0.036 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -0.002x + 3.29. A 12 point running mean is also presented.

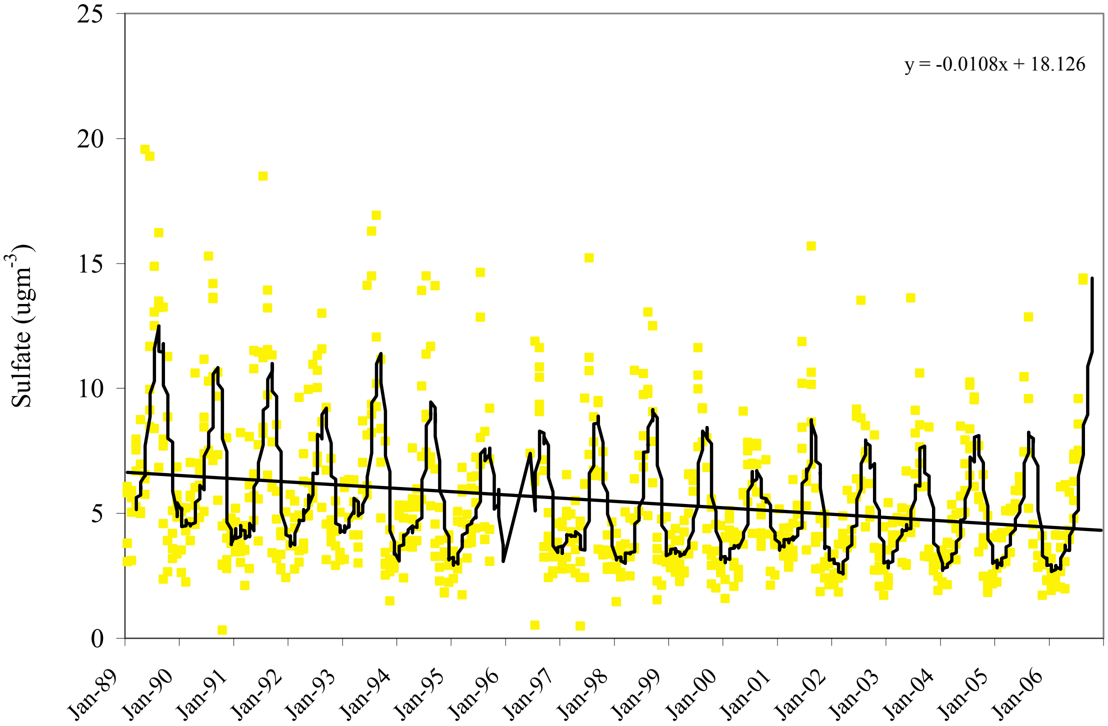


Figure III-9c. Sulfate from the Beltsville, MD CASTNET site. Weekly data from 1989-2006. The mean trend in sulfate is -0.152 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0108x + 18.13. A 12-point running mean is also presented.

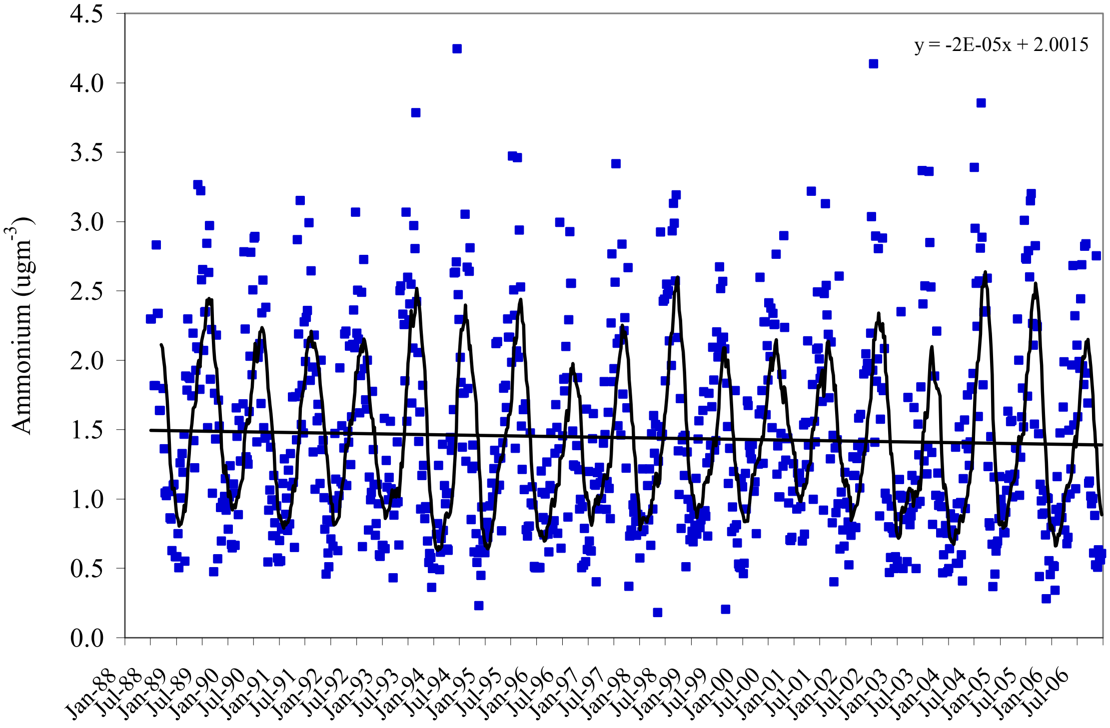


Figure III-10a. Ammonium from the Big Meadows, VA CASTNET site. Weekly data from 1988-2006. The mean trend in ammonium is -0.006 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -2E-05x + 2.003. A 12 point running mean is also presented.

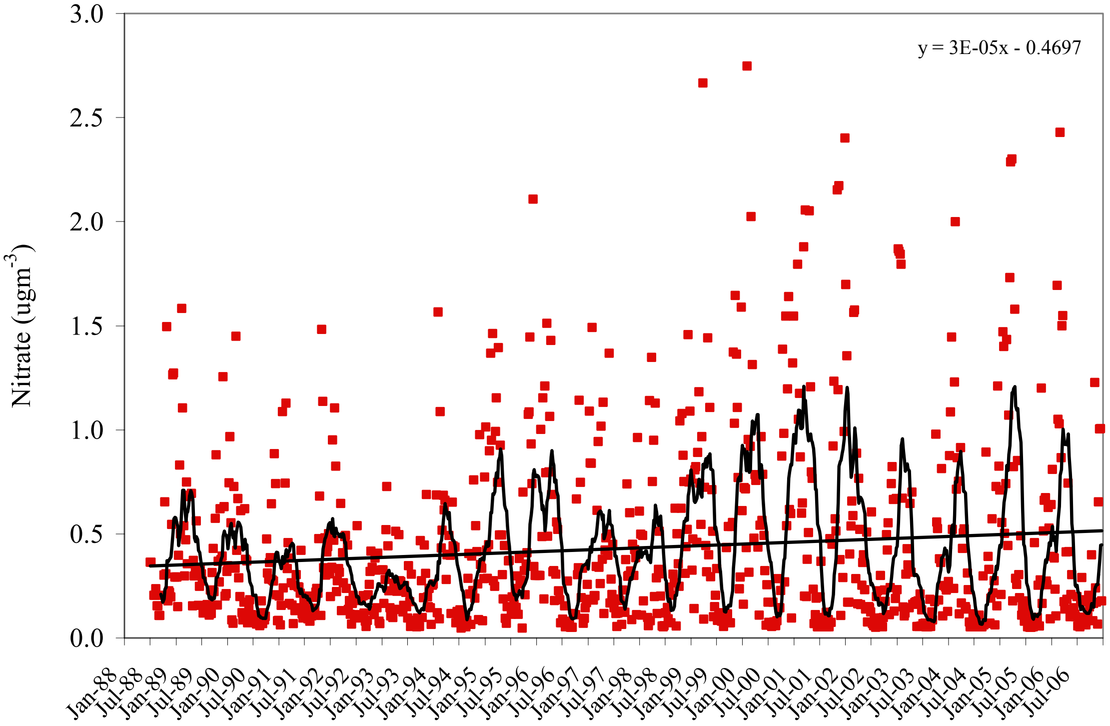


Figure III-10b Nitrate from the Big Meadows, VA CASTNET site. Weekly data from 1988-2006. The mean trend in nitrate is 0.015 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = 3E-05x - 0.467. A 12 point running mean is also presented. Total nitrate (vapor and condensed phases) decreased in the eastern US over this time period (*Sickles and Shadwick, 2007)*.

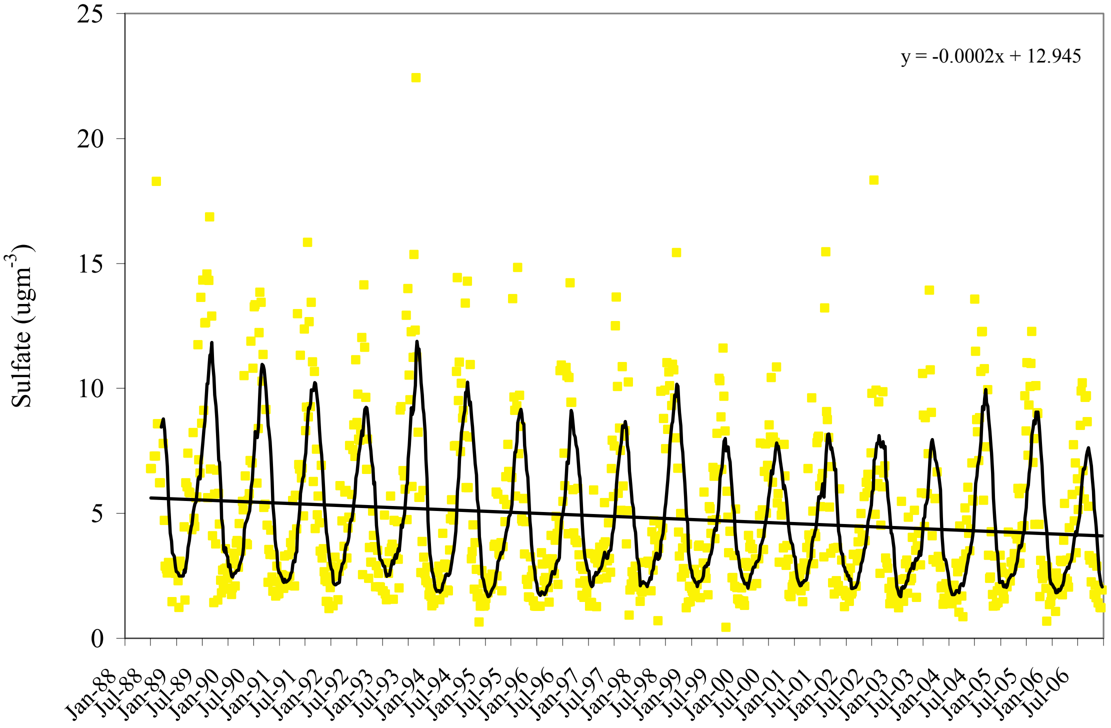


Figure III-10c. Sulfate the Big Meadows, VA CASTNET site. Weekly data from 1988-2006. The mean trend in sulfate is -0.127 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -0.0002x + 12.94. A 12 point running mean is also presented.

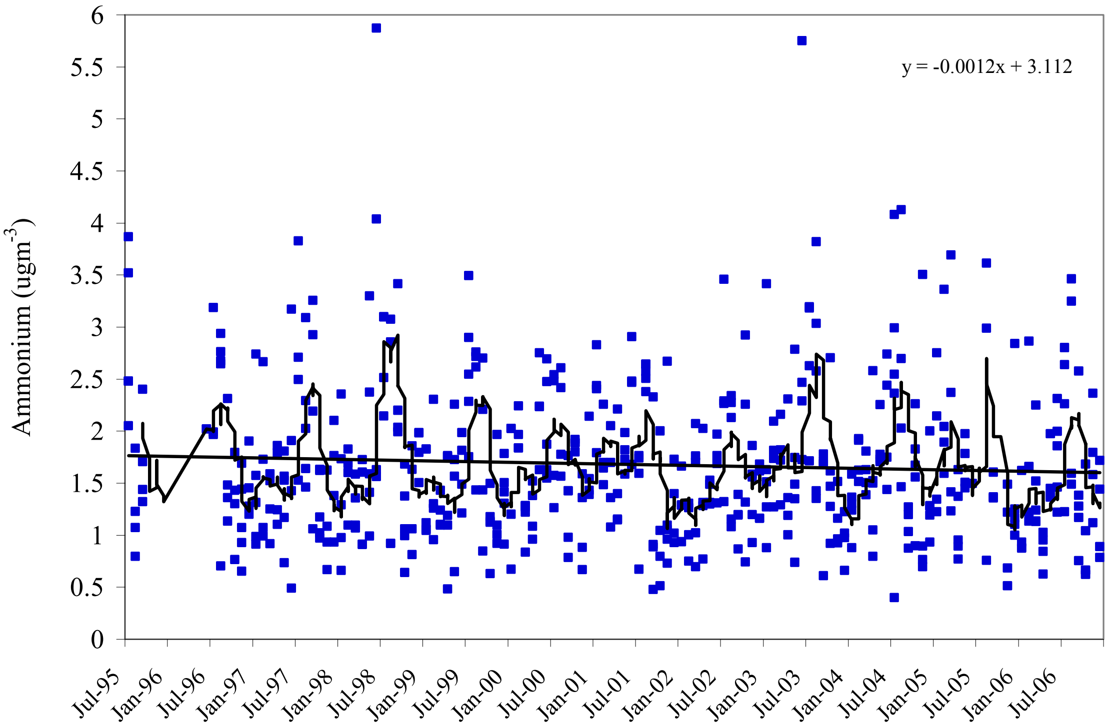


Figure III-11a. Ammonium from the Blackwater, MD CASTNET site. Weekly data from 1995-2006. The mean trend in ammonium is -0.011 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -0.0012x + 3.11. A 12 point running mean is also presented.

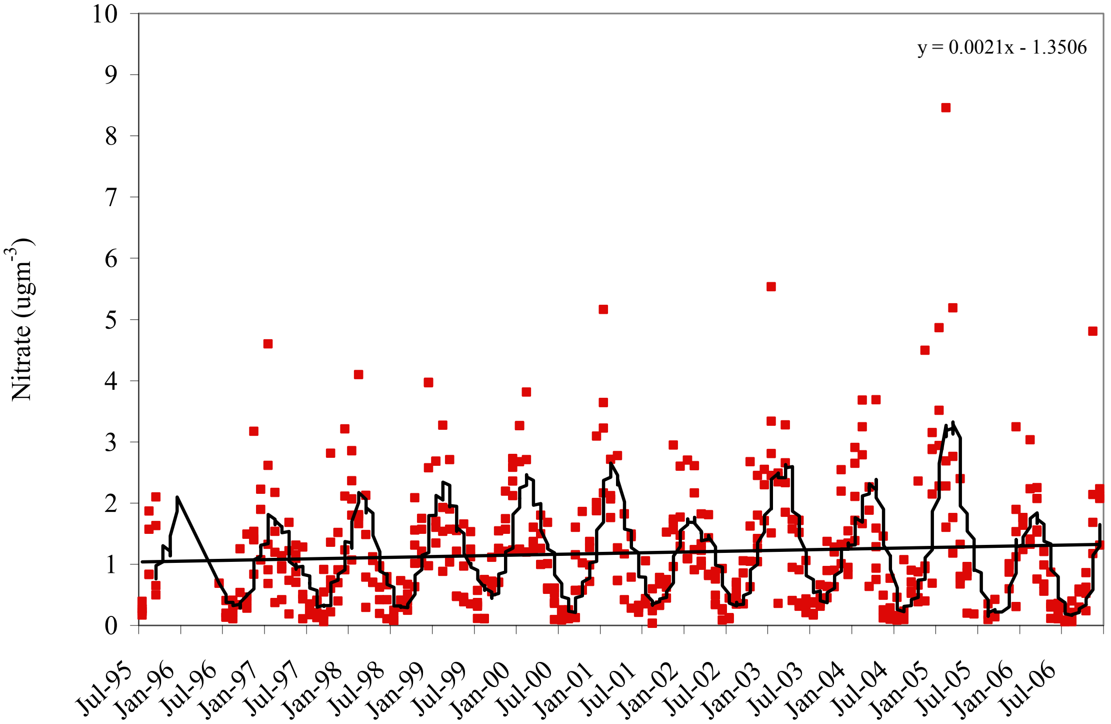


Figure III-11b. Nitrate from the Blackwater, MD CASTNET site. Weekly data from 1995-2006. The mean trend in nitrate is 0.019 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = 0.0021x - 1.35. A 12 point running mean is also presented.

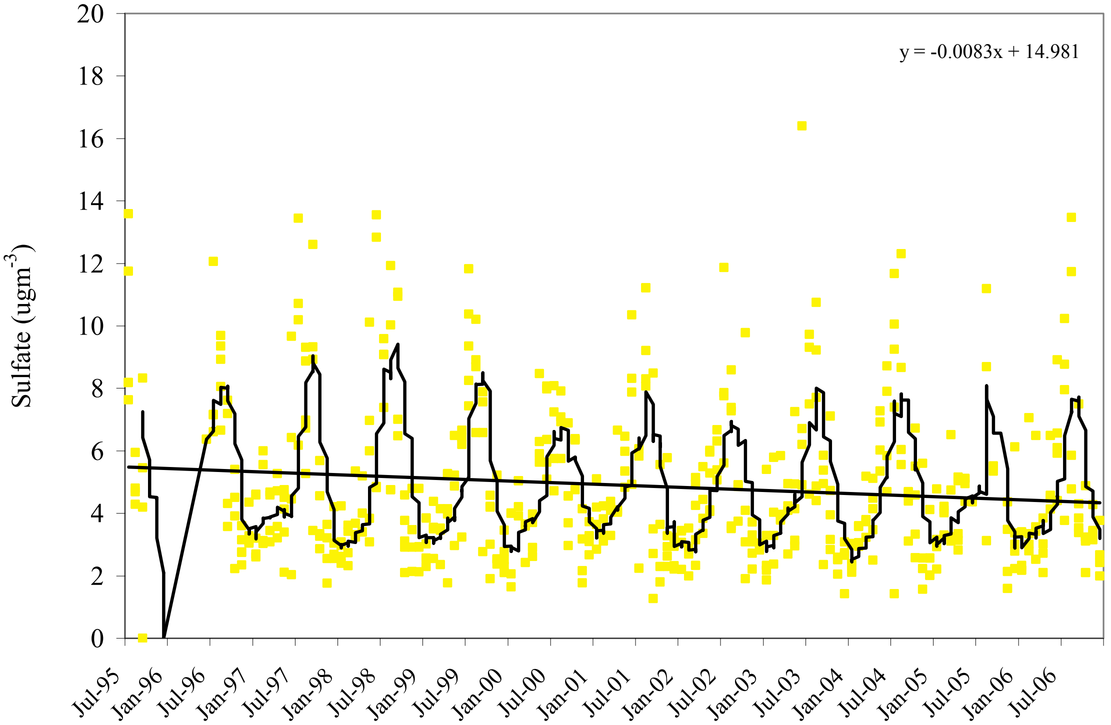


Figure III-11c. Sulfate from the Blackwater, MD CASTNET site. Weekly data from 1995-2006. The mean trend in sulfate is -0.230 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0083x + 14.98. A 12 point running mean is also presented.

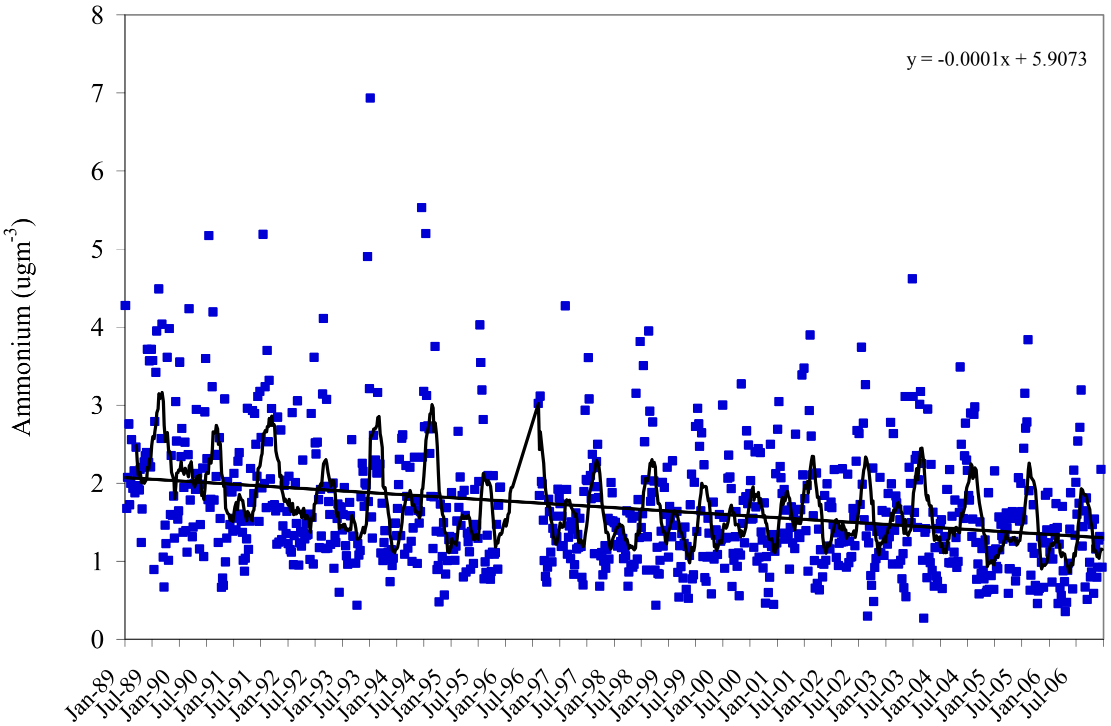


Figure III-12a. Ammonium from the Washington Crossing, NJ CASTNET site. Weekly data from 1989-2006. The mean trend in ammonium is -0.044 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0001x + 5.90. A 12 point running mean is also presented.

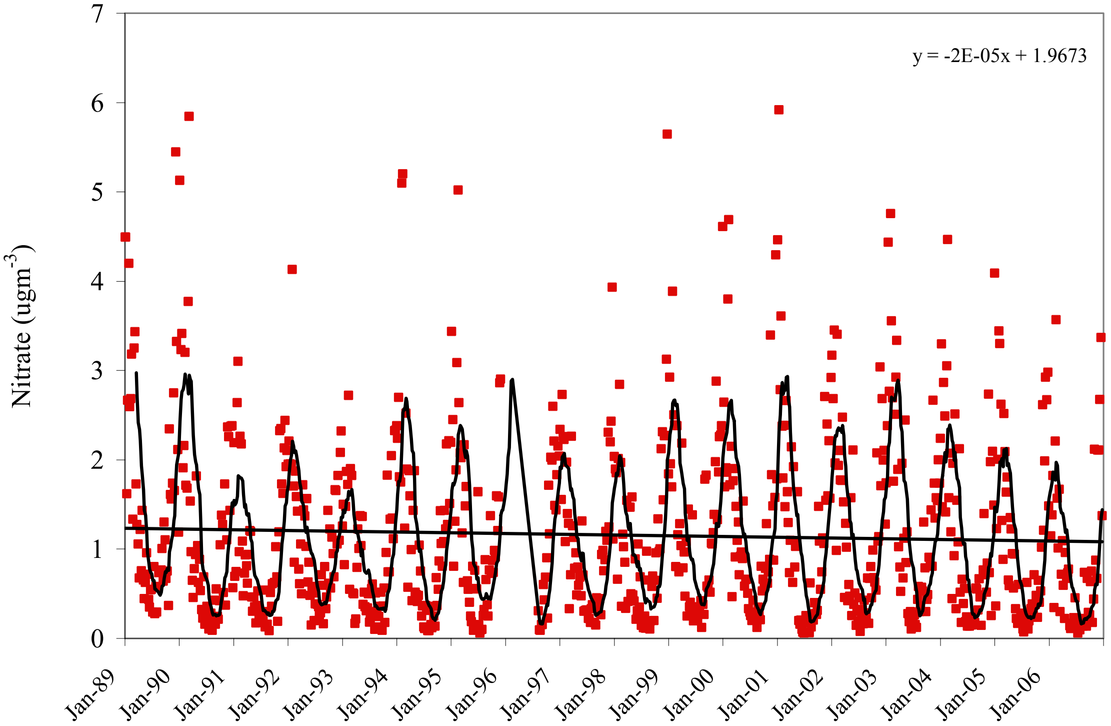


Figure III-12b. Nitrate from the Washington Crossing, NJ CASTNET site. Weekly data from 1989-2006. The mean trend in nitrate is -0.011 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -2E-05x + 1.97. A 12 point running mean is also presented.

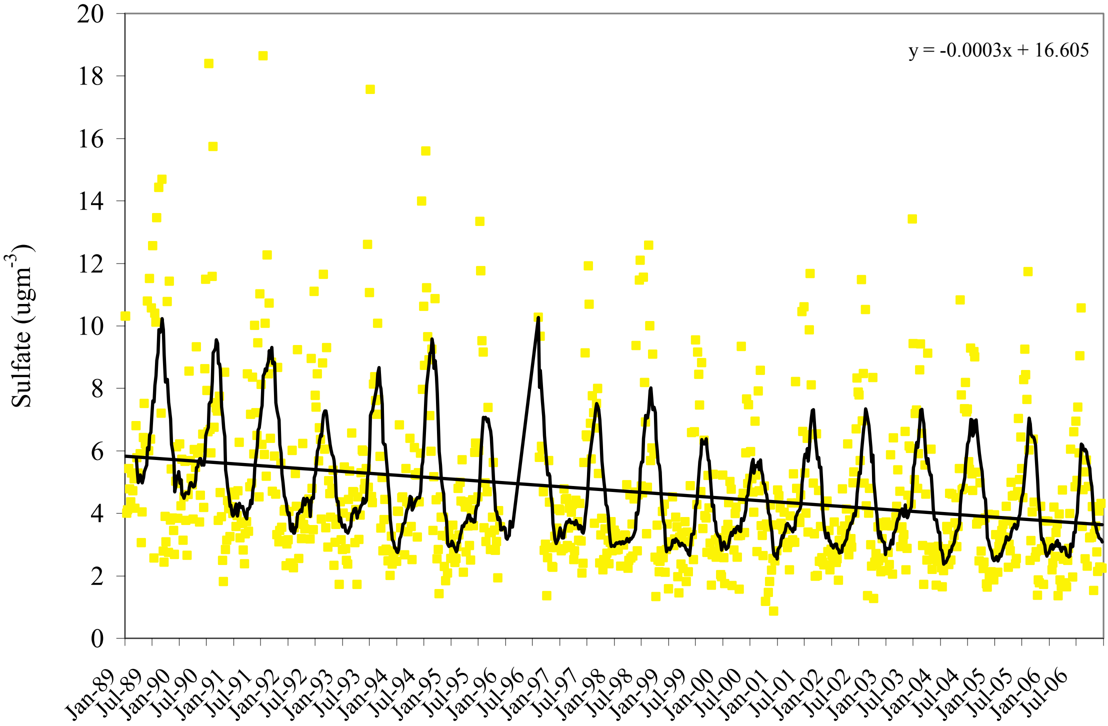


Figure III-12c. Sulfate from the Washington Crossing, NJ CASTNET site. Weekly data from 1989-2006. The mean trend in sulfate is -0.130 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -0.0003x + 16.60. A 12 point running mean is also presented.

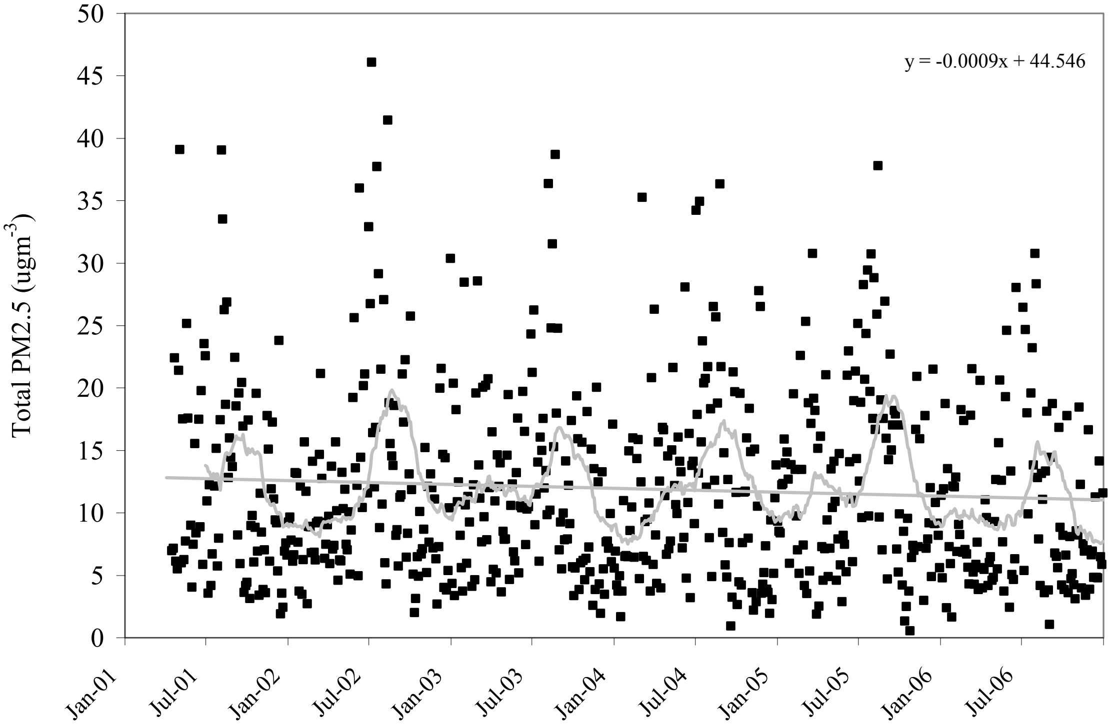


Figure III-13a. PM2.5 from the Arendtsville, PA IMPROVE site. Every 3rd day data from 2001-2006. The mean trend in PM2.5 is -0.360 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is $y = -0.0009x + 44.55$. A 30 point running mean is also presented.

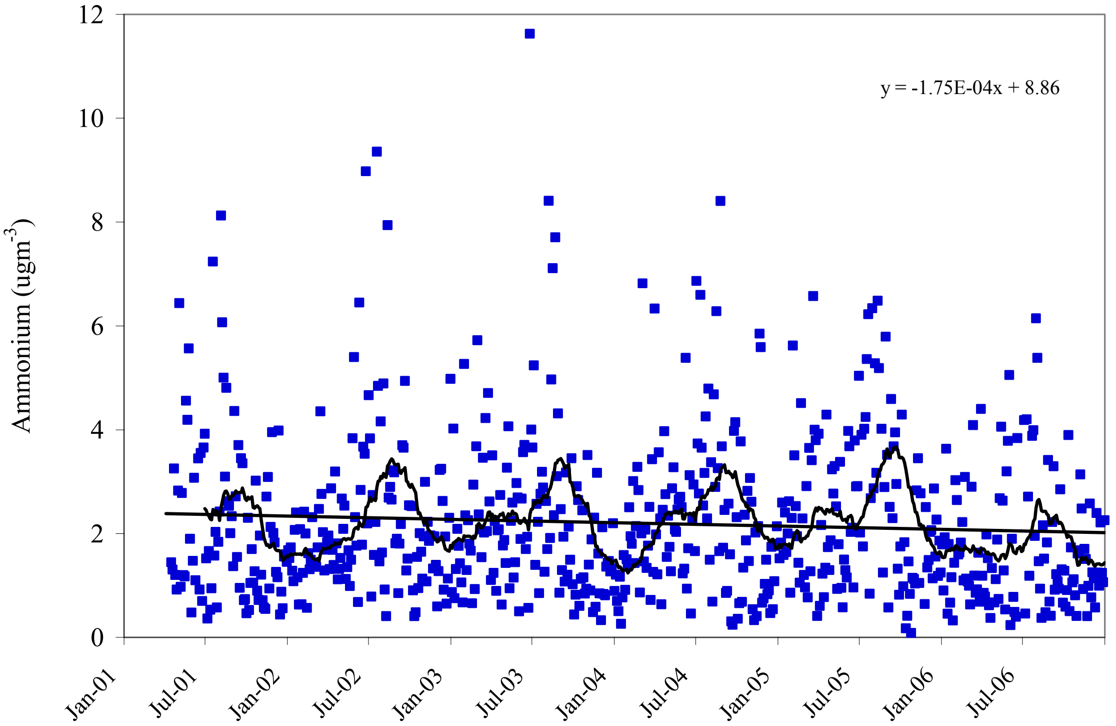


Figure III-13b. Ammonium from the Arendtsville, PA IMPROVE site. Every 3rd day data from 2001-2006. The mean trend in ammonium is -0.075 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -1.75E-4x + 8.86. A 30 point running mean is also presented.

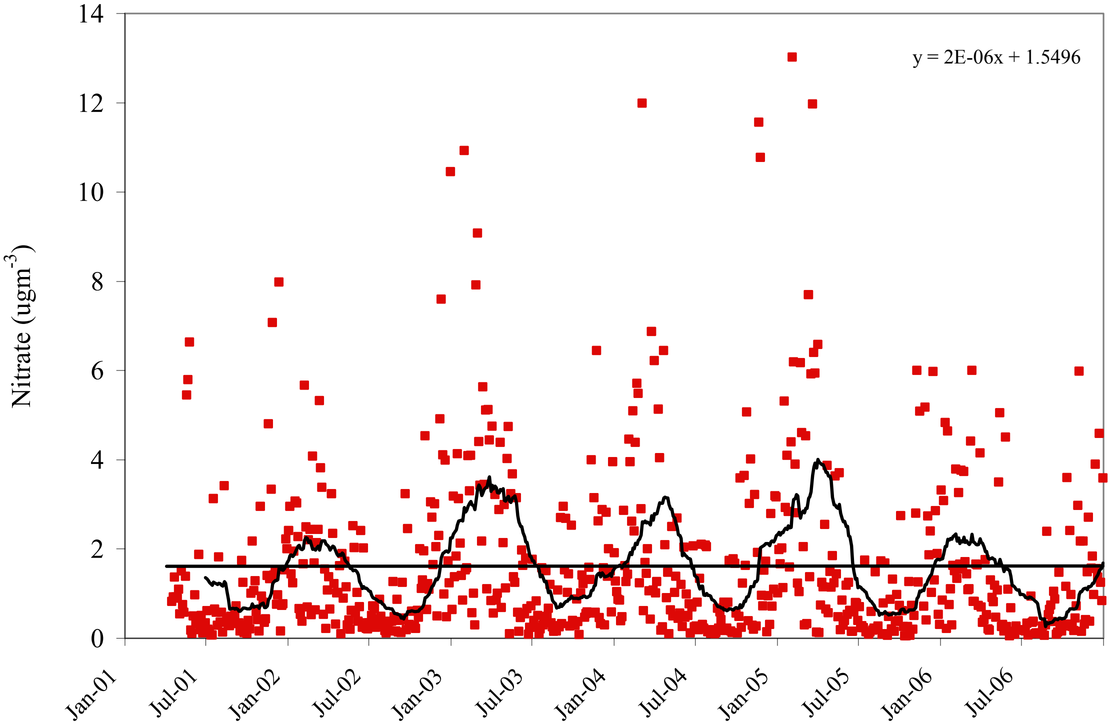


Figure III-13c. Nitrate from the Arendtsville, PA IMPROVE site. Every 3rd day data from 2001-2006. There is no measurable trend in nitrate. A 30 point running mean is also presented.

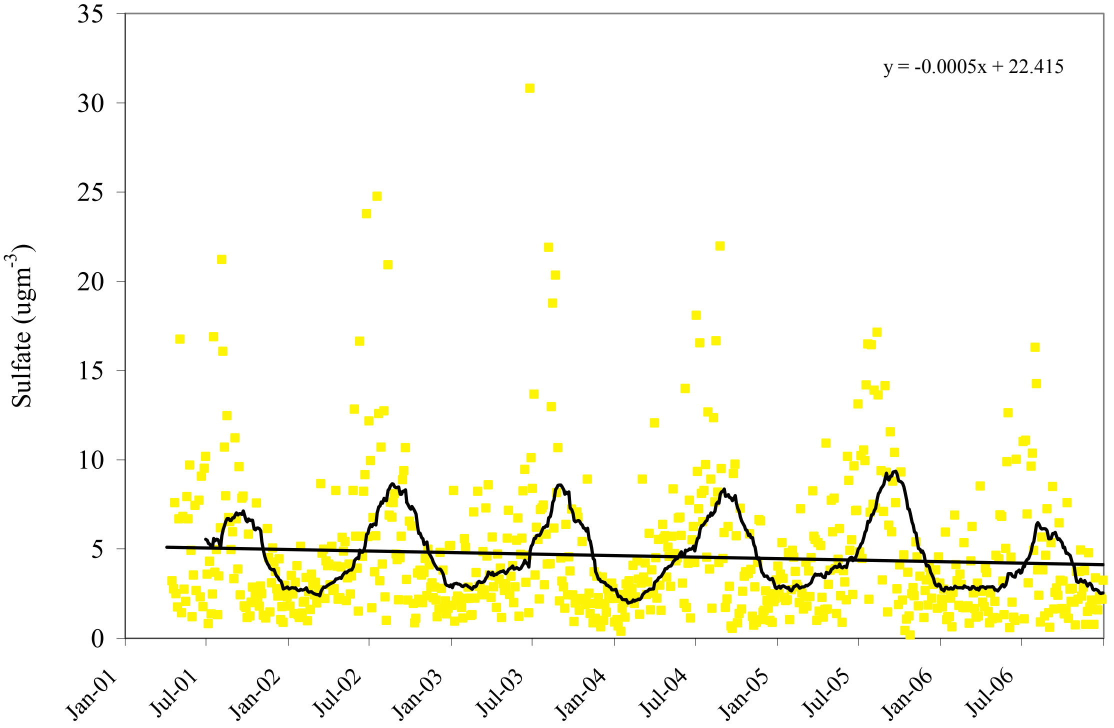


Figure III-13d. Sulfate from the Arendtsville, PA IMPROVE site. Every 3rd day data from 2001-2006. The mean trend in sulfate is -0.194 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0005x + 22.42. A 30 point running mean is also presented.

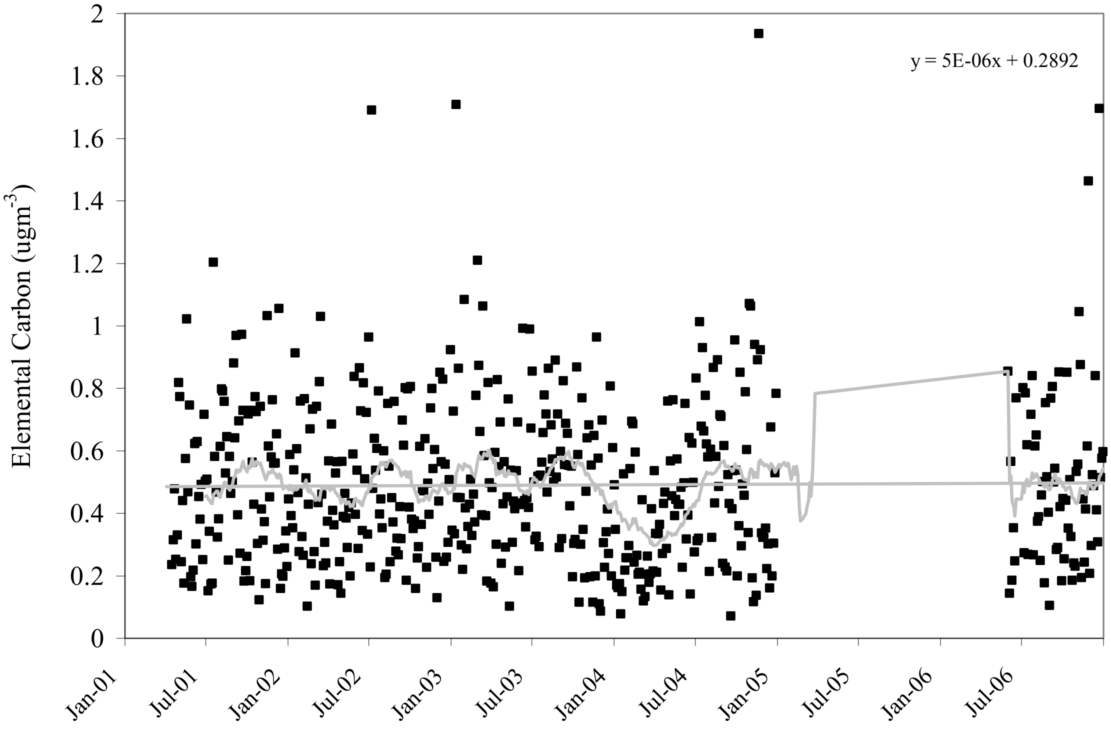


Figure III-13e. Elemental Carbon from the Arendtsville, PA IMPROVE site. Every 3rd day data from 2001-2006. There is no measurable trend in elemental carbon. A 30 point running mean is also presented.

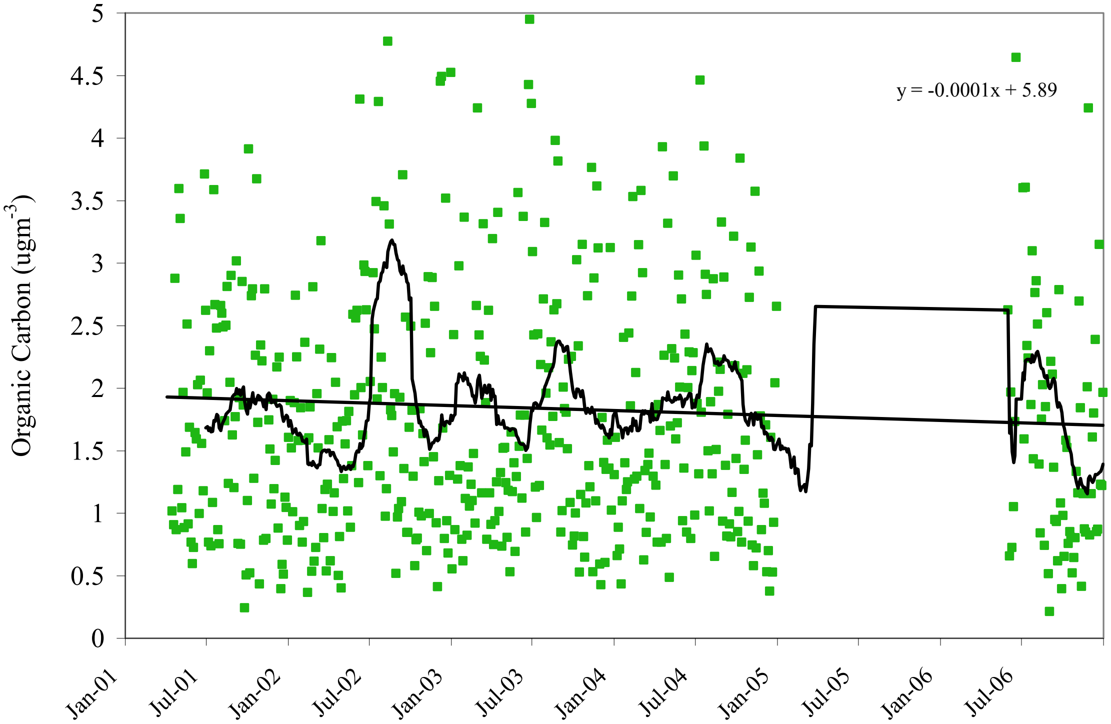


Figure III-13f. Organic Carbon from the Arendtsville, PA IMPROVE site. Every 3rd day data from 2001-2006. The mean trend in organic carbon is -0.194 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0001x + 5.89. A 30 point running mean is also presented.

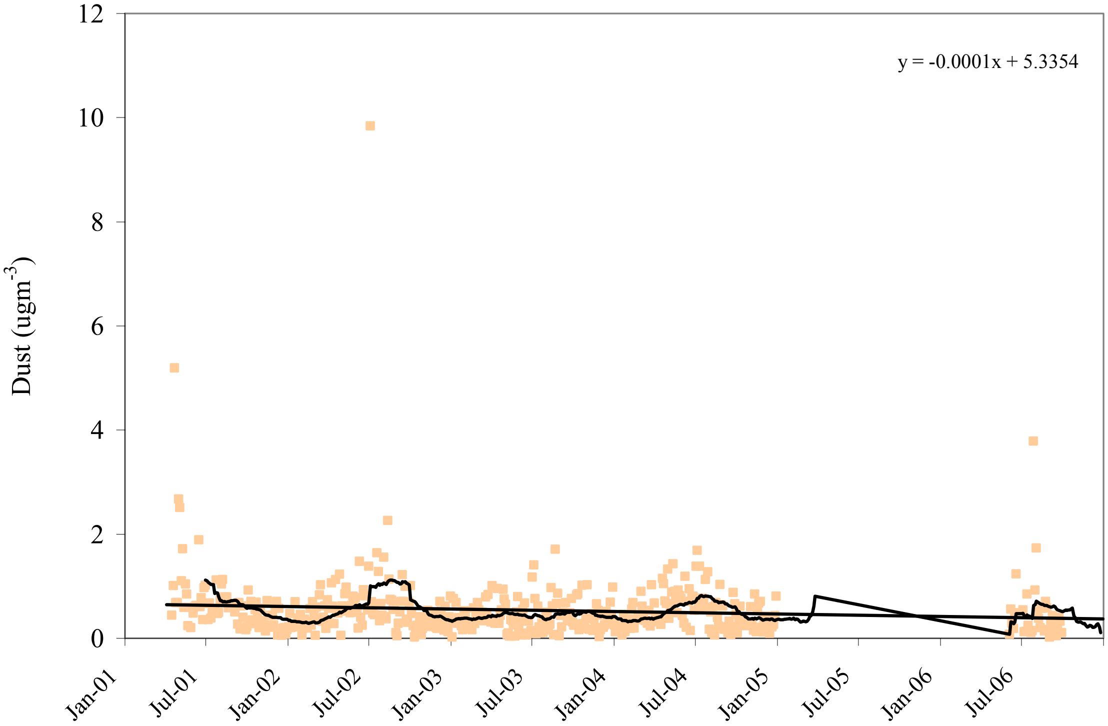


Figure III-13g. Dust from the Arendtsville, PA IMPROVE site. Every 3rd day data from 2001-2006. The mean trend in dust is -0.056 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -0.0001x + 5.33. A 30 point running mean is also presented.

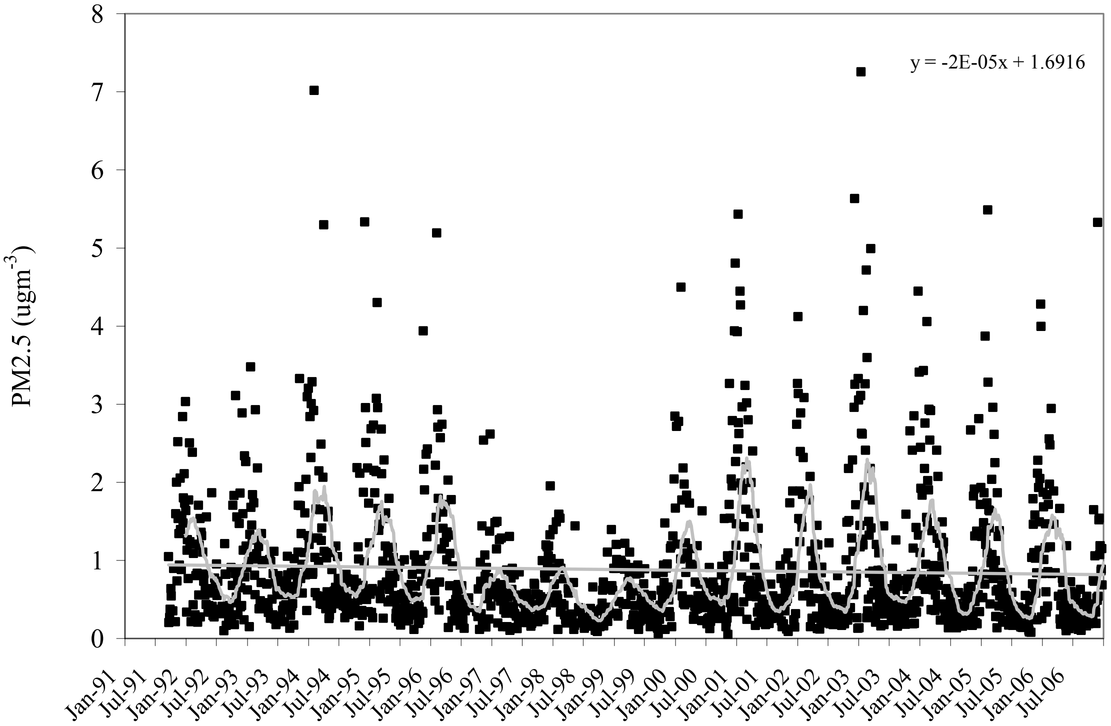


Figure III-14a. PM2.5 from the Brigantine, NJ IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in PM2.5 is -0.167 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -2E-05x + 1.69. A 30 point running mean is also presented. The data contaminated with smoke from forest fires in Quebec have been omitted.

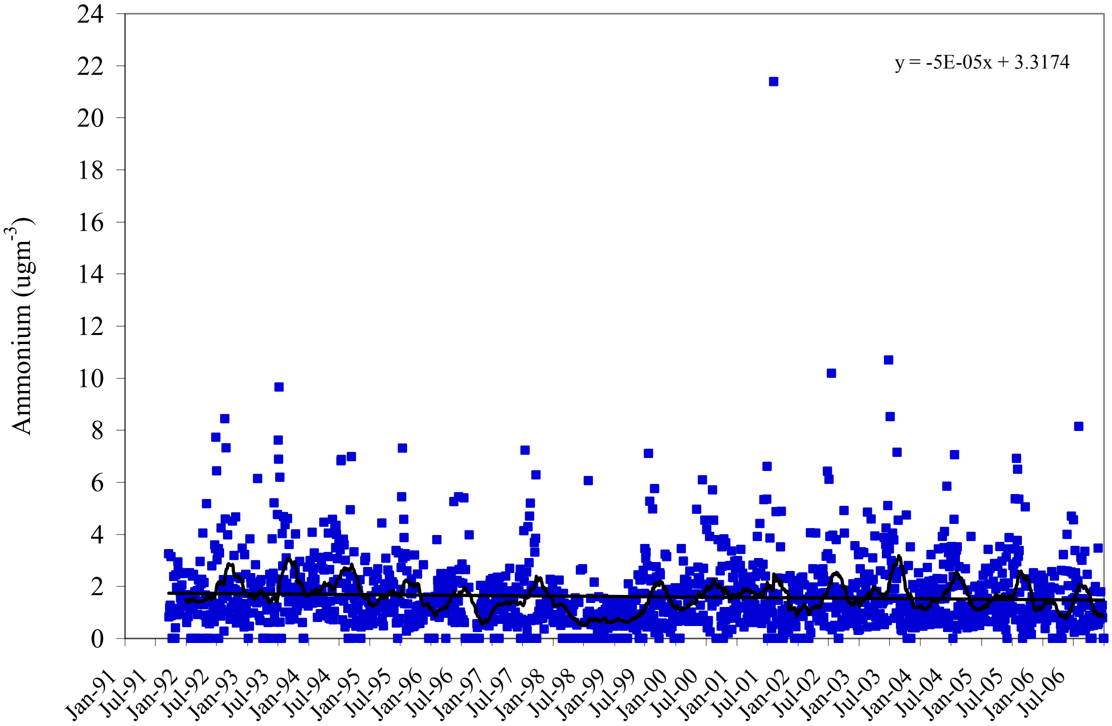


Figure III-14b. Ammonium from the Brigantine, NJ IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in ammonium is -0.018 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -7E-05x + 3.31. A 30 point running mean is also presented.

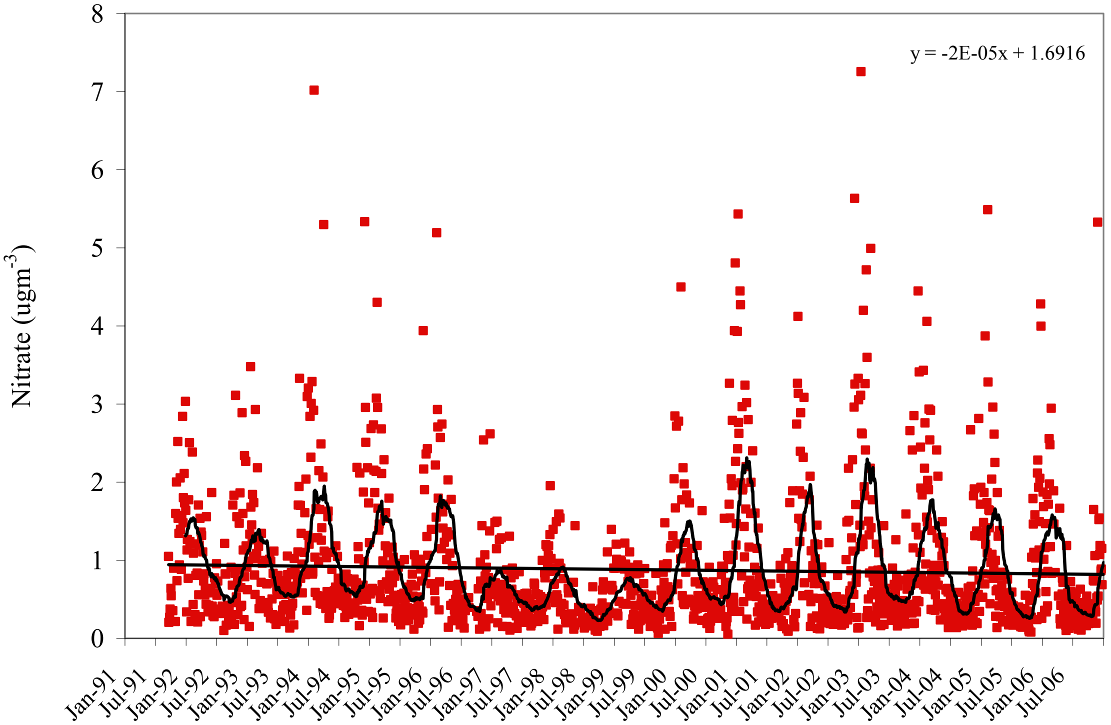


Figure III-14c. Nitrate from the Brigantine, NJ IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in nitrate is -0.013 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -2E-05x + 1.69. A 30 point running mean is also presented.

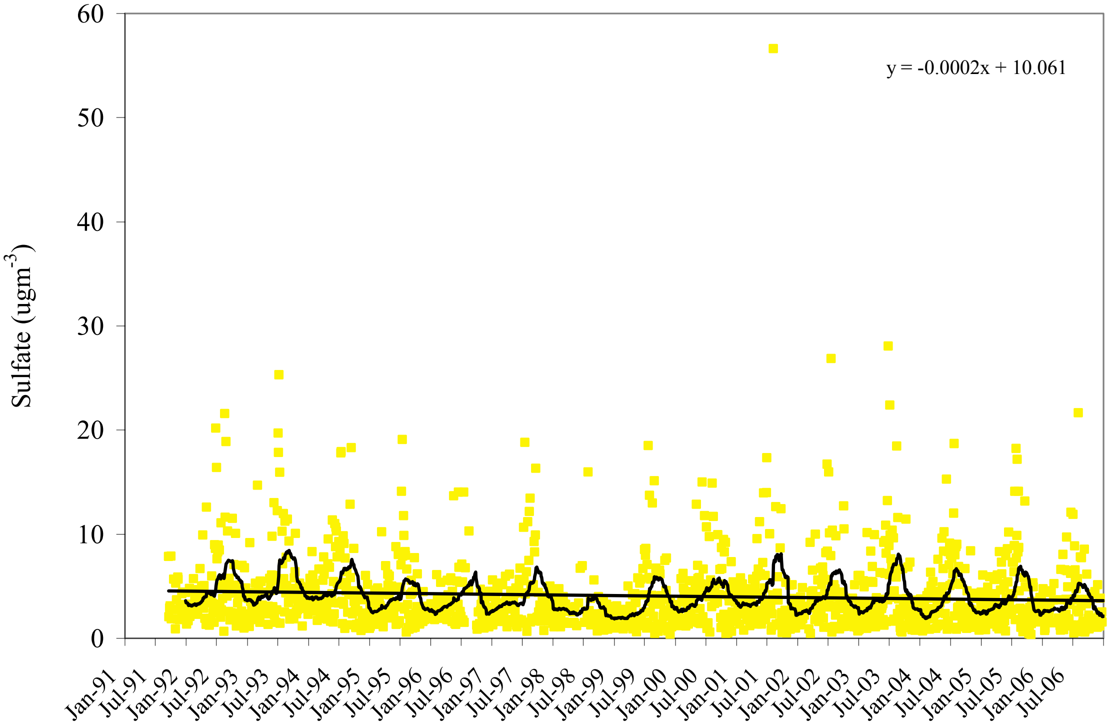


Figure III-14d. Sulfate from the Brigantine, NJ IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in sulfate is -0.013 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -0.0002x + 10.06. A 30 point running mean is also presented.

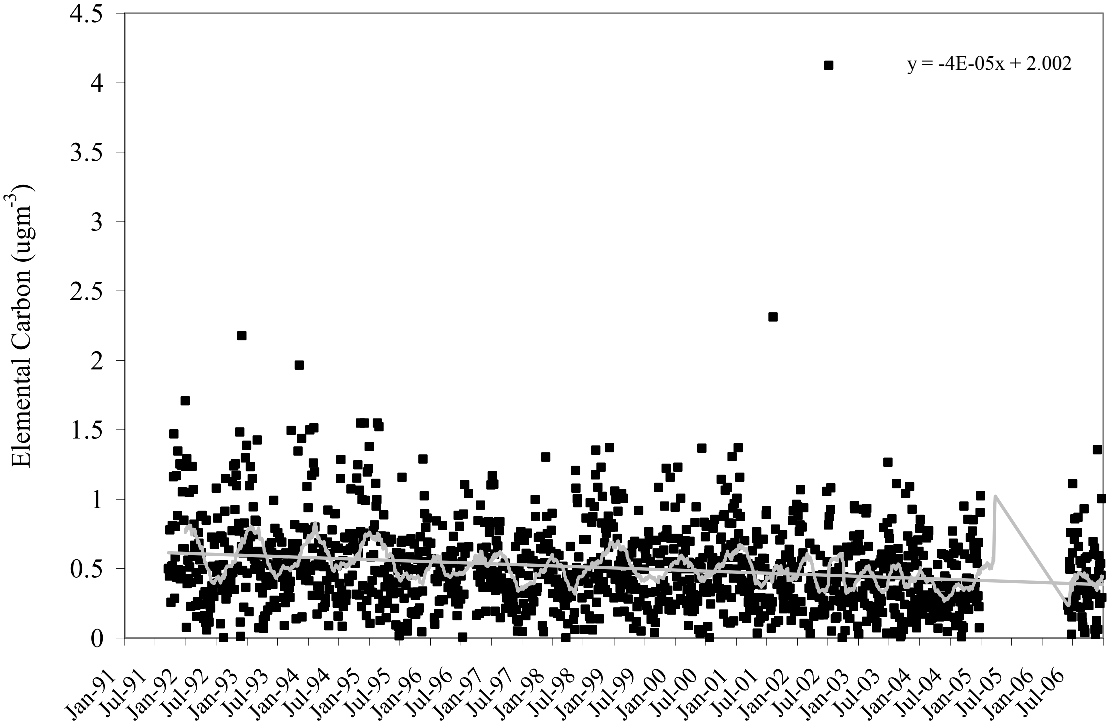


Figure III-14e. Elemental Carbon from the Brigantine, NJ IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in elemental carbon is -0.015 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -4E-05x + 2.00. A 30 point running mean is also presented.

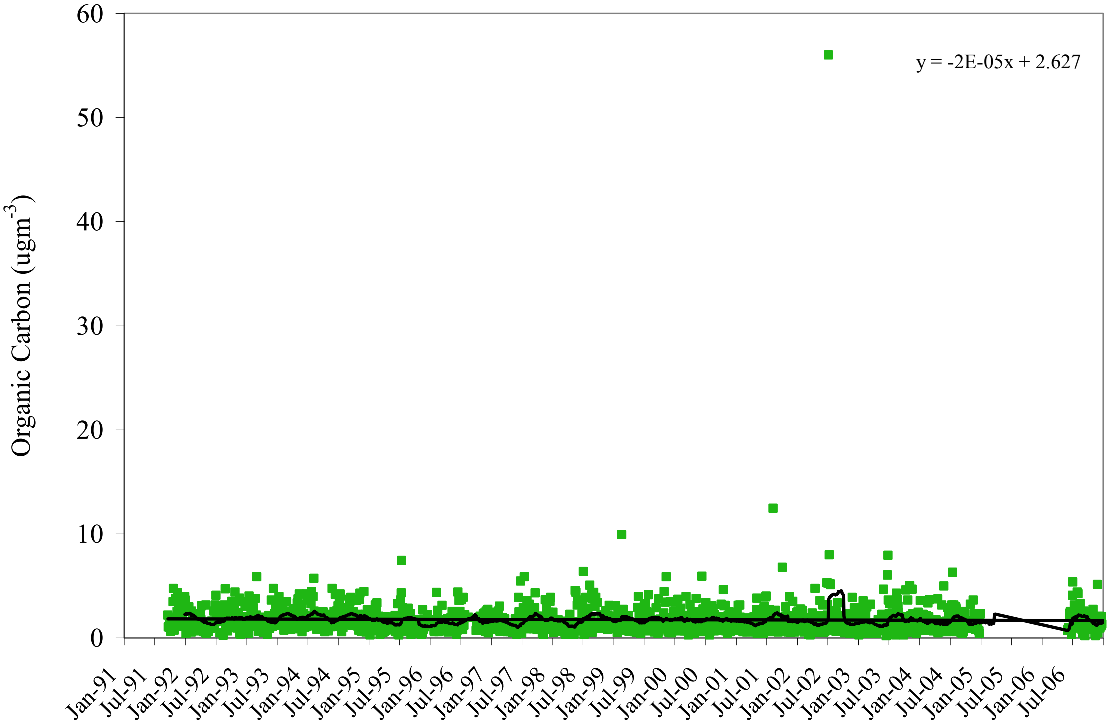


Figure III-14f. Organic Carbon from the Brigantine, NJ IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in organic carbon is -0.011 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is $y = -4E-05x + 2.00$. A 30 point running mean is also presented.

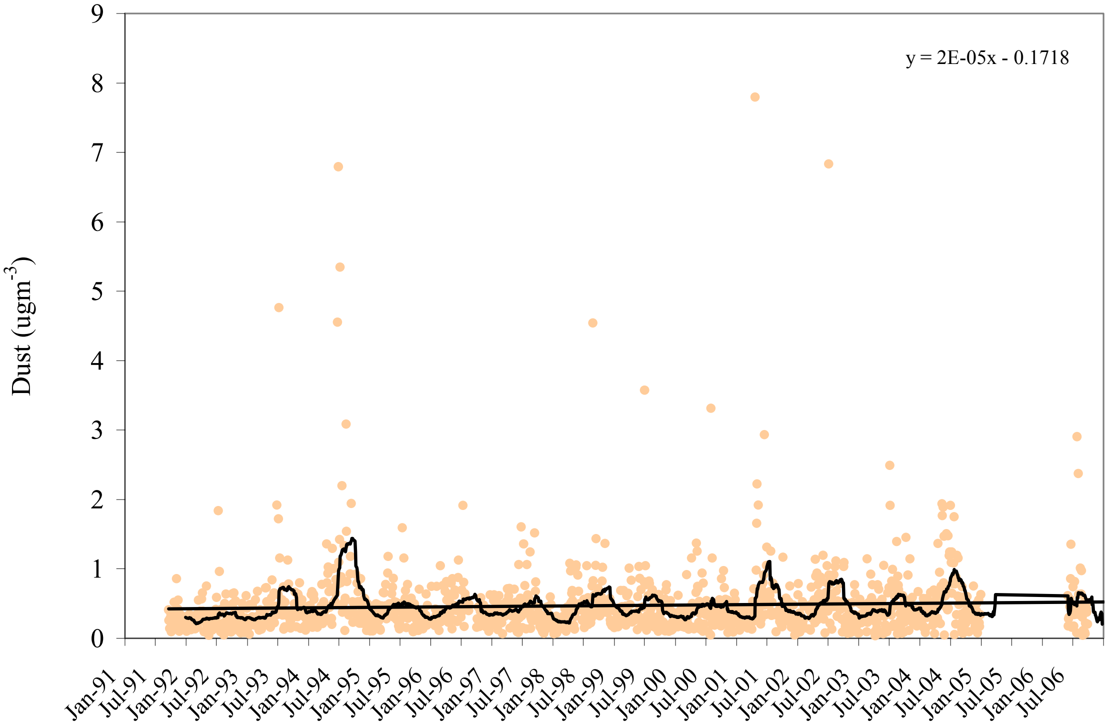


Figure III-14g. Dust from the Brigantine, NJ IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in dust is -0.011 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = 2E-05x - 0.172. A 30 point running mean is also presented.

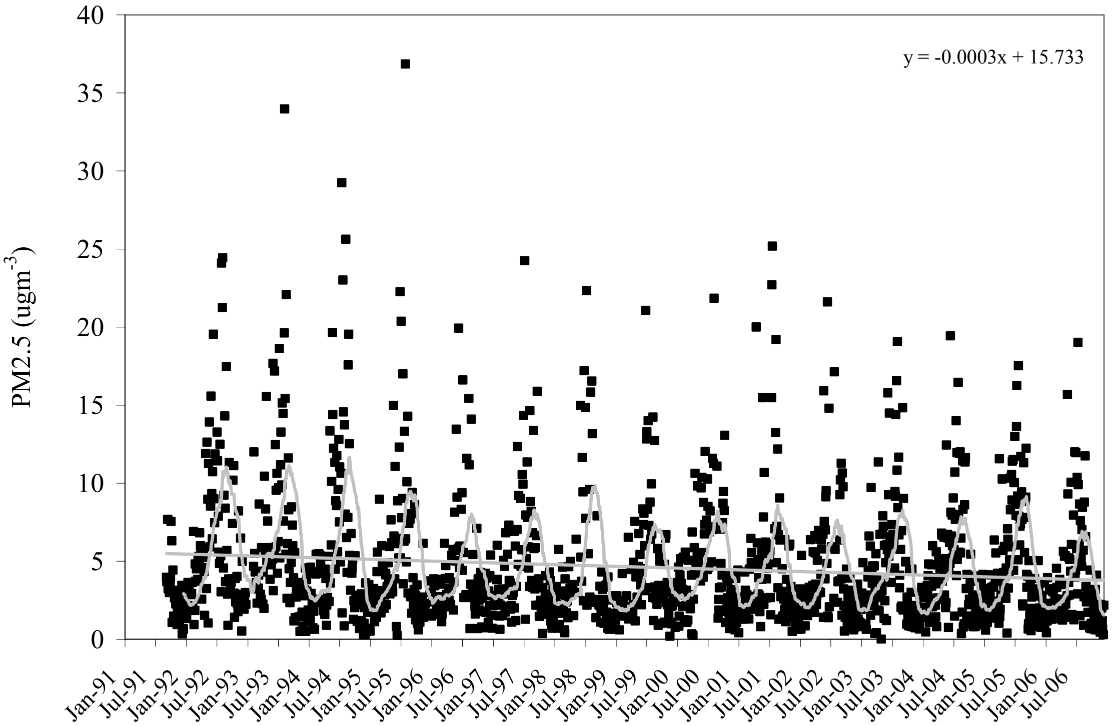


Figure III-15a. PM2.5 from the Dolly Sods, WV IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in PM2.5 is -0.117 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0003x + 15.73. A 30 point running mean is also presented.

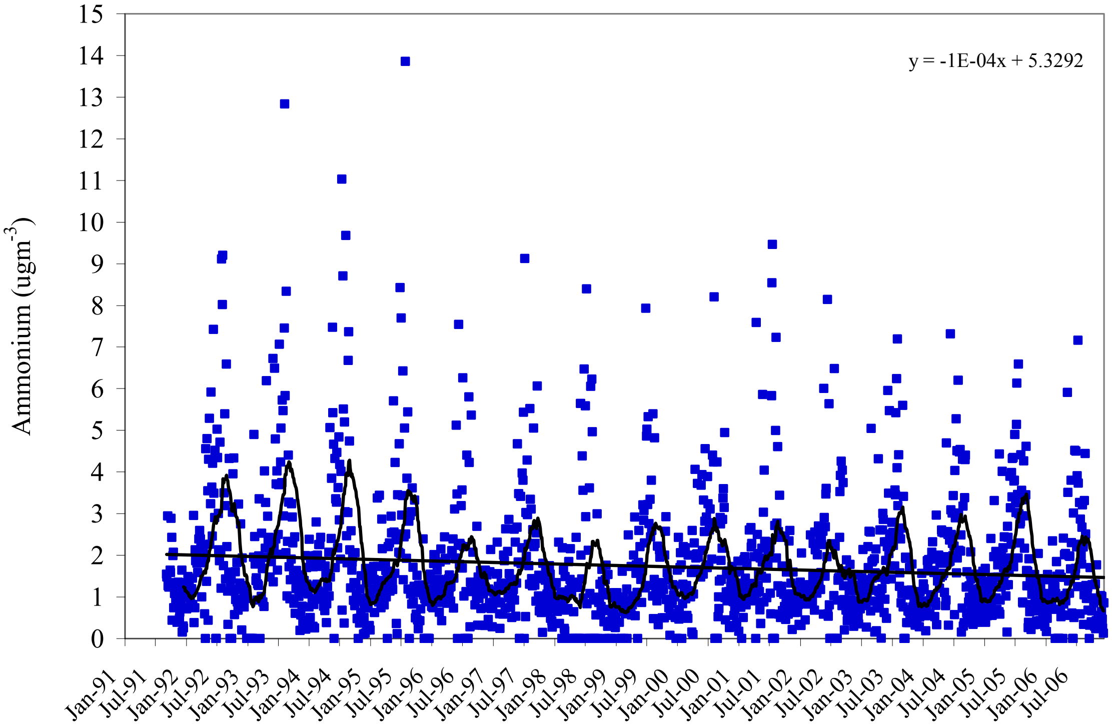


Figure III-15b. Ammonium (inferred) from the Dolly Sods, WV IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in ammonium is -0.048 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -1E-04x + 5.2616. A 30 point running mean is also presented.

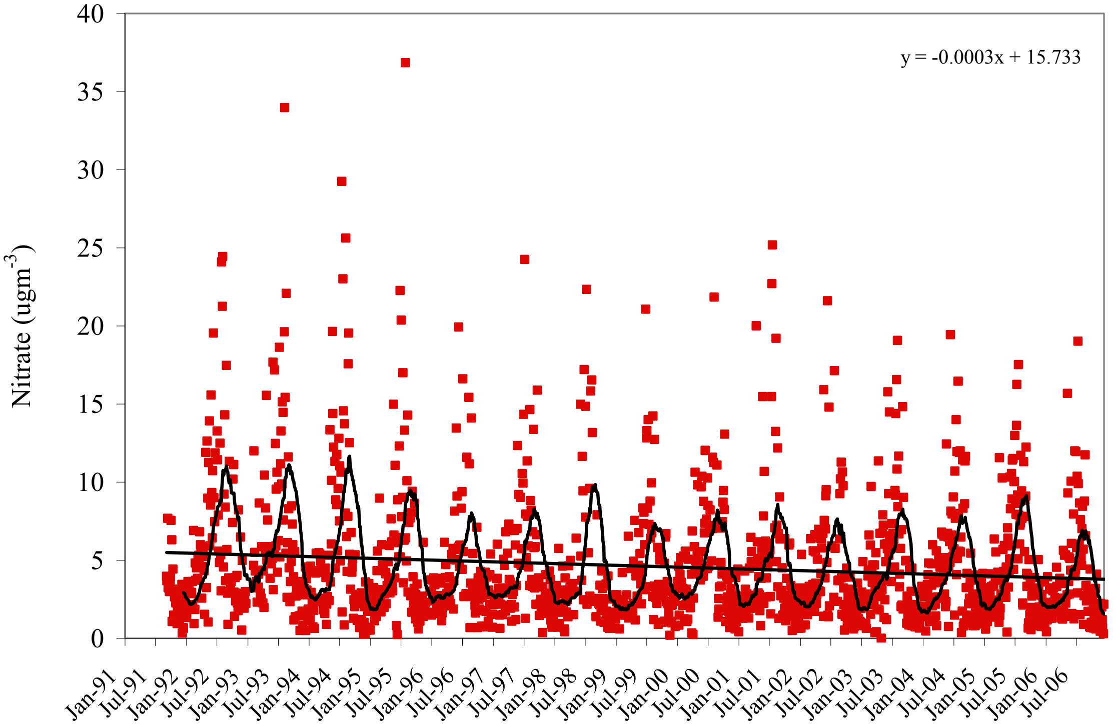


Figure III-15c. Nitrate from the Dolly Sods, WV IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in nitrate is -0.04 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -1E-05x + 0.918. A 30 point running mean is also presented.

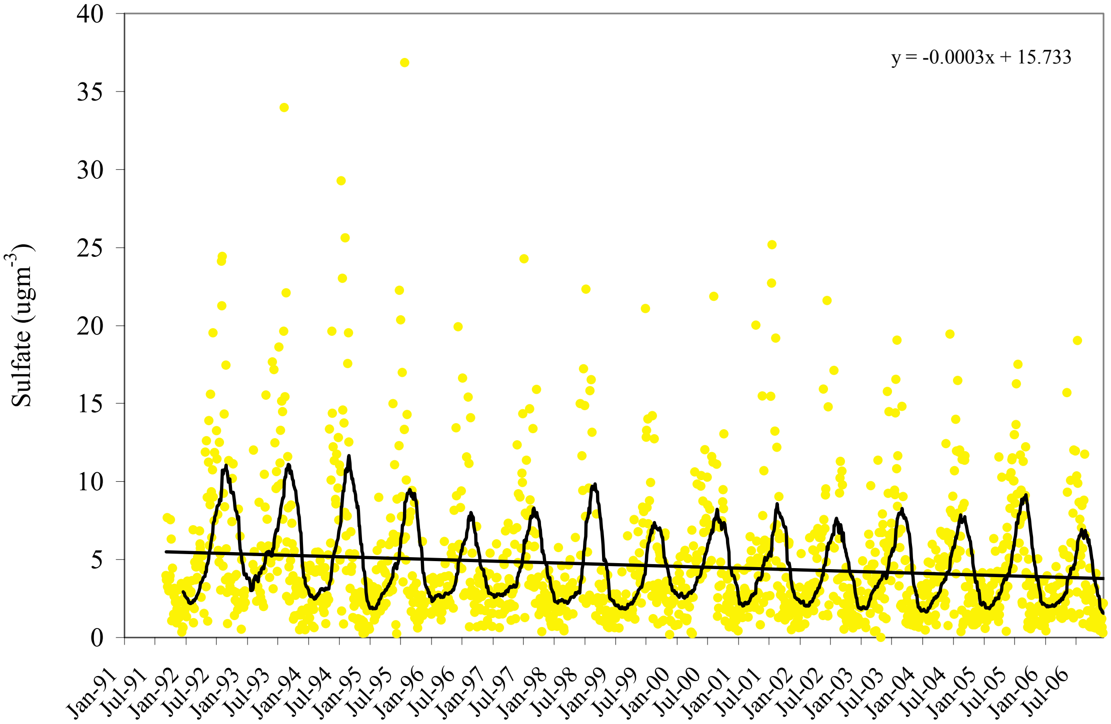


Figure III-15d. Sulfate from the Dolly Sods, WV IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in sulfate is -0.110 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is $y = -0.0003x + 15.73$. A 30 point running mean is also presented.

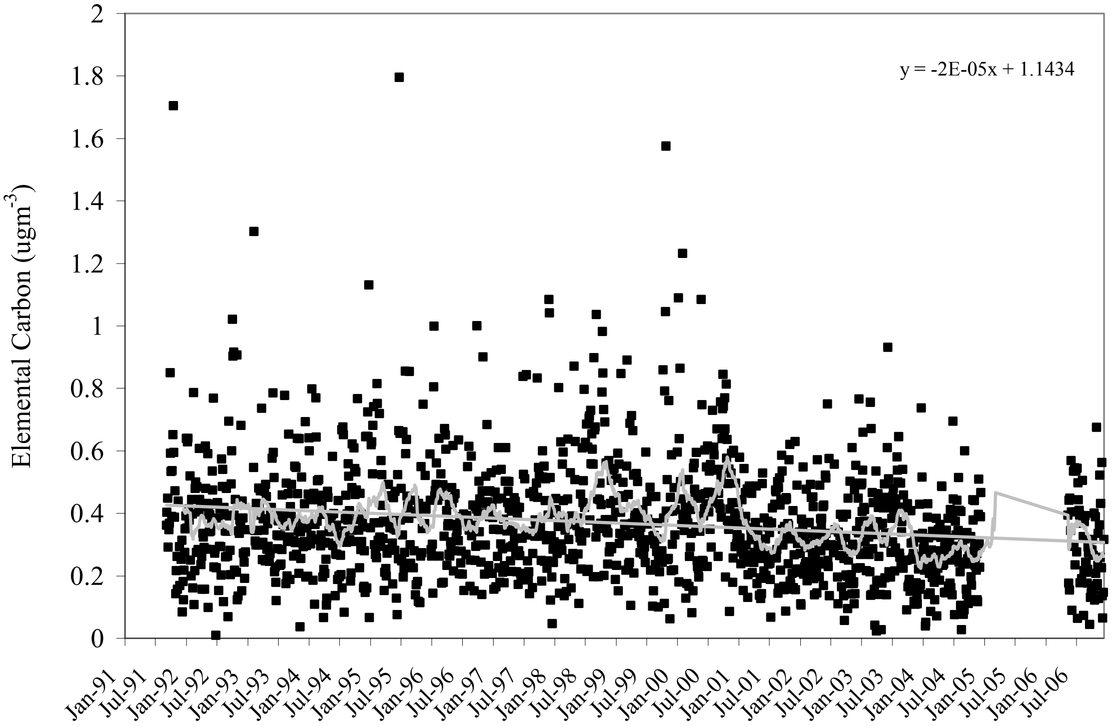


Figure III-15e. Elemental Carbon from the Dolly Sods, WV IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in elemental carbon is -0.067 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -2E-05x + 1.143. A 30 point running mean is also presented.

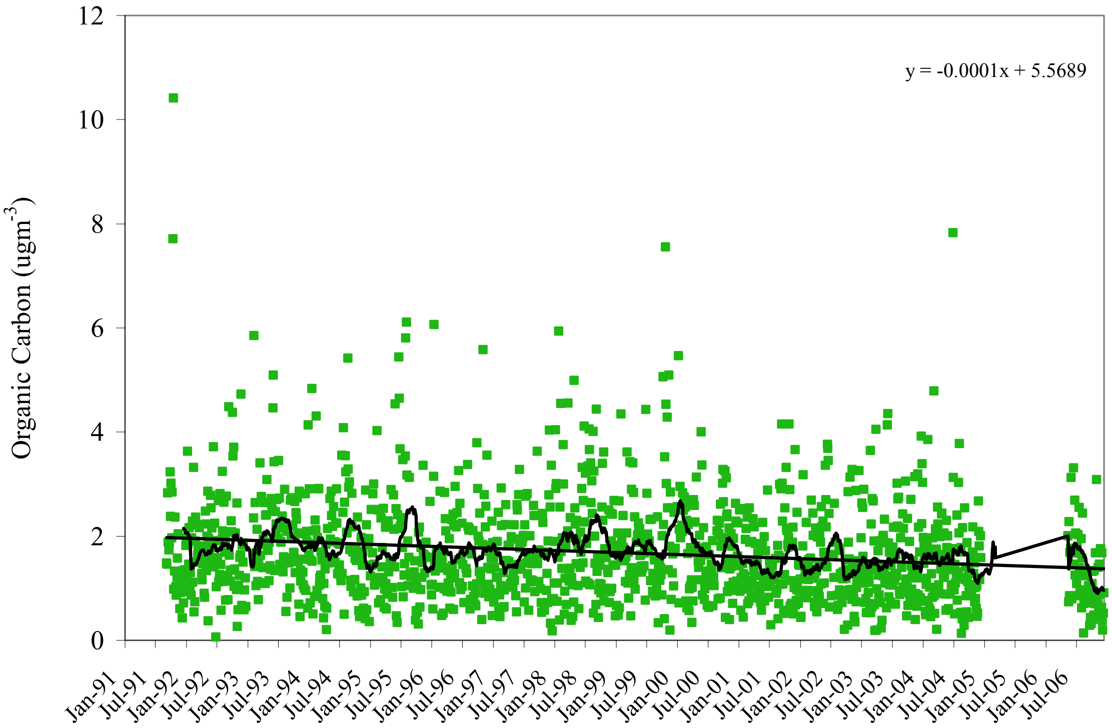


Figure III-15f. Organic Carbon from the Dolly Sods, WV IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in elemental carbon is -0.037 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0001x + 5.567. A 30 point running mean is also presented.

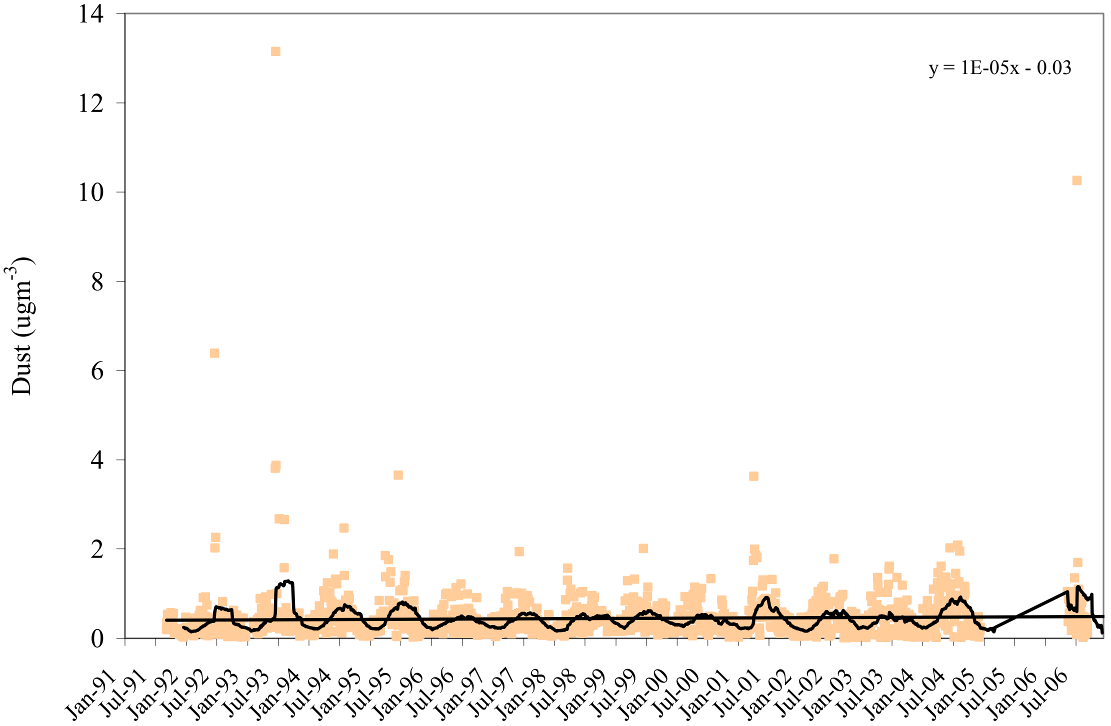


Figure III-15g. Dust from the Dolly Sods, WV IMPROVE site. Every 3rd day data from 1991-2006. The mean trend in dust is 0.06 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = 1E-05x - 0.03. A 30 point running mean is also presented.

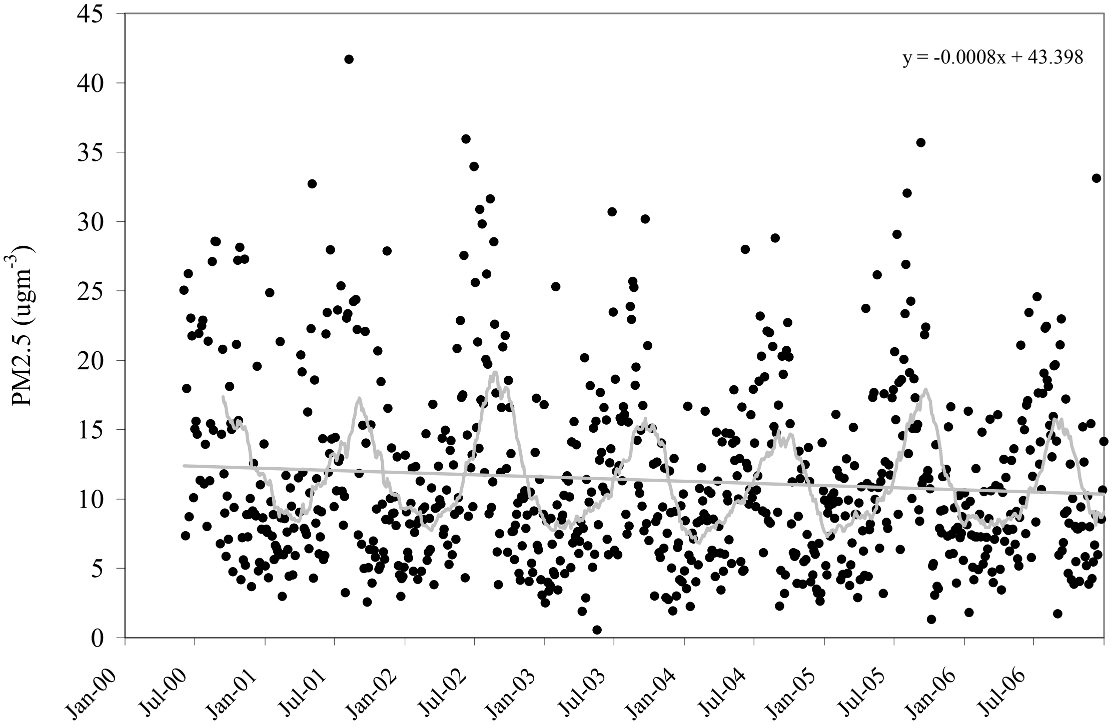


Figure III-16a. PM2.5 from the James River, VA IMPROVE site. Every 3rd day data from 2000-2006. The mean trend in PM2.5 is -0.30 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0008x + 43.40. A 30 point running mean is also presented.

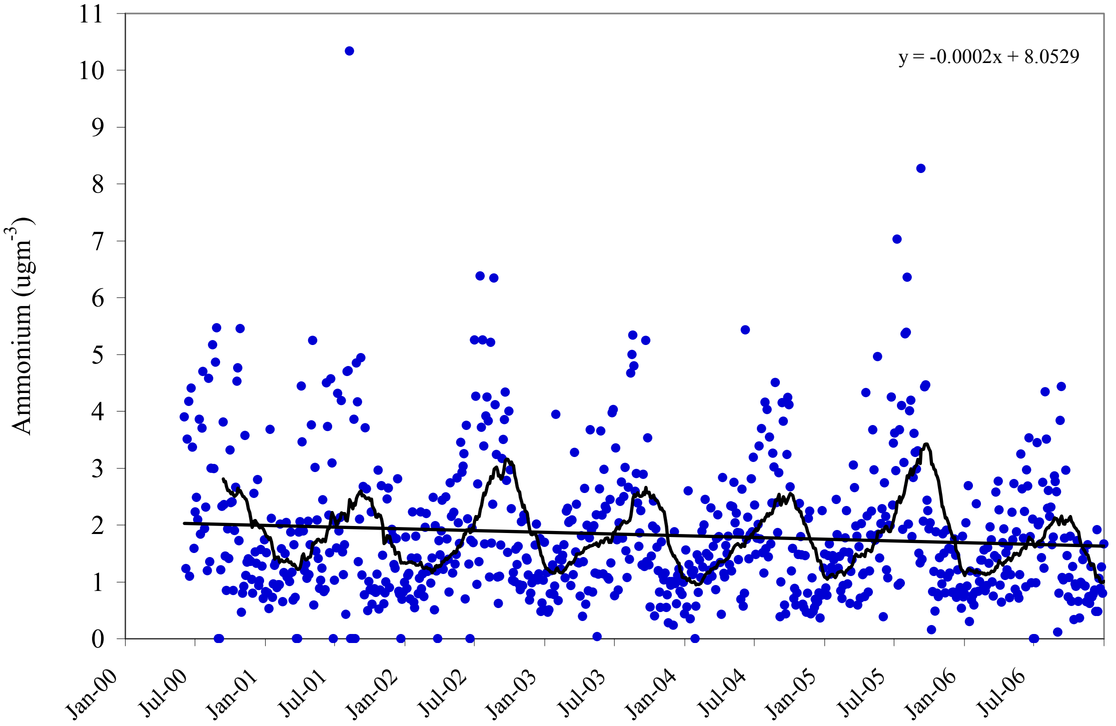


Figure III-16b. Ammonium from the James River, VA IMPROVE site. Every 3rd day data from 2000-2006. The mean trend in ammonium is -0.047 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0002x + 8.05. A 30 point running mean is also presented.

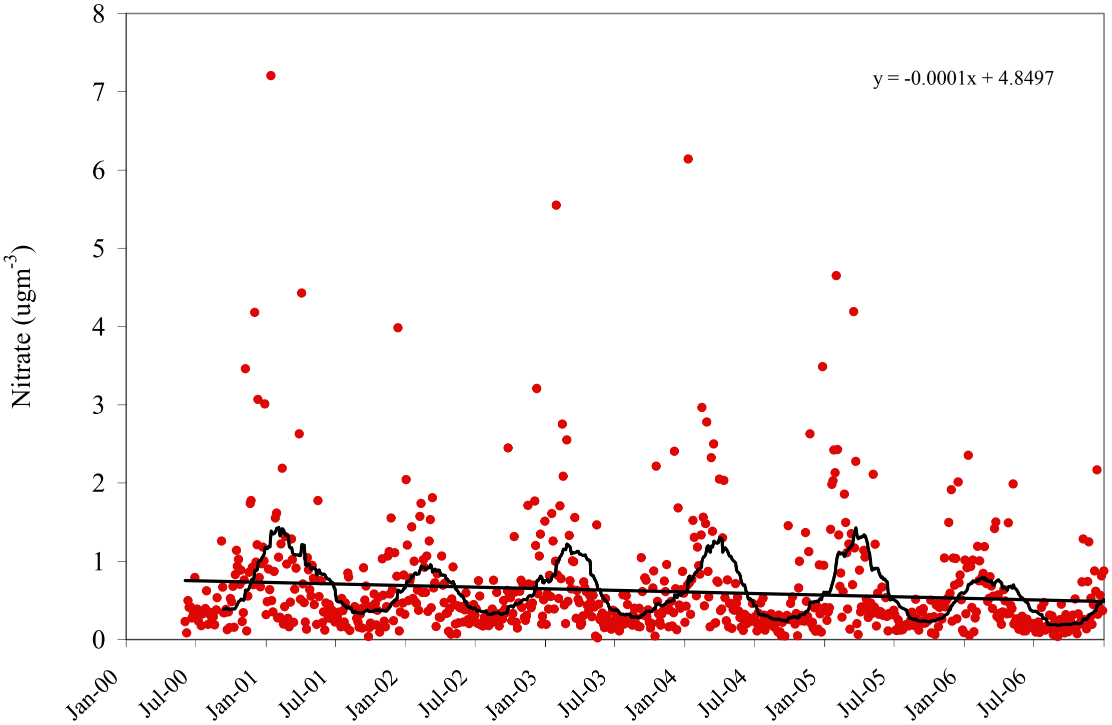


Figure III-16c. Nitrate from the James River, VA IMPROVE site. Every 3rd day data from 2000-2006. The mean trend in nitrate is -0.043 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0001x + 4.85. A 30 point running mean is also presented.

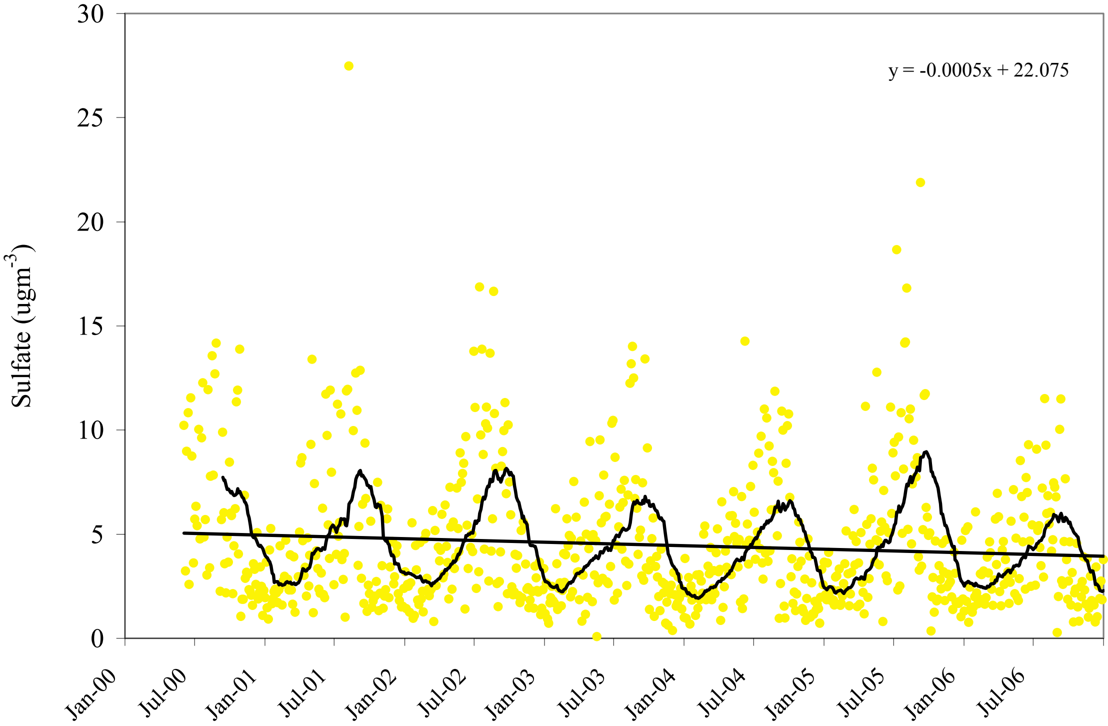


Figure III-16d. Sulfate from the James River, VA IMPROVE site. Every 3rd day data from 2000-2006. The mean trend in sulfate is -0.183 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0005x + 22.08. A 30 point running mean is also presented.

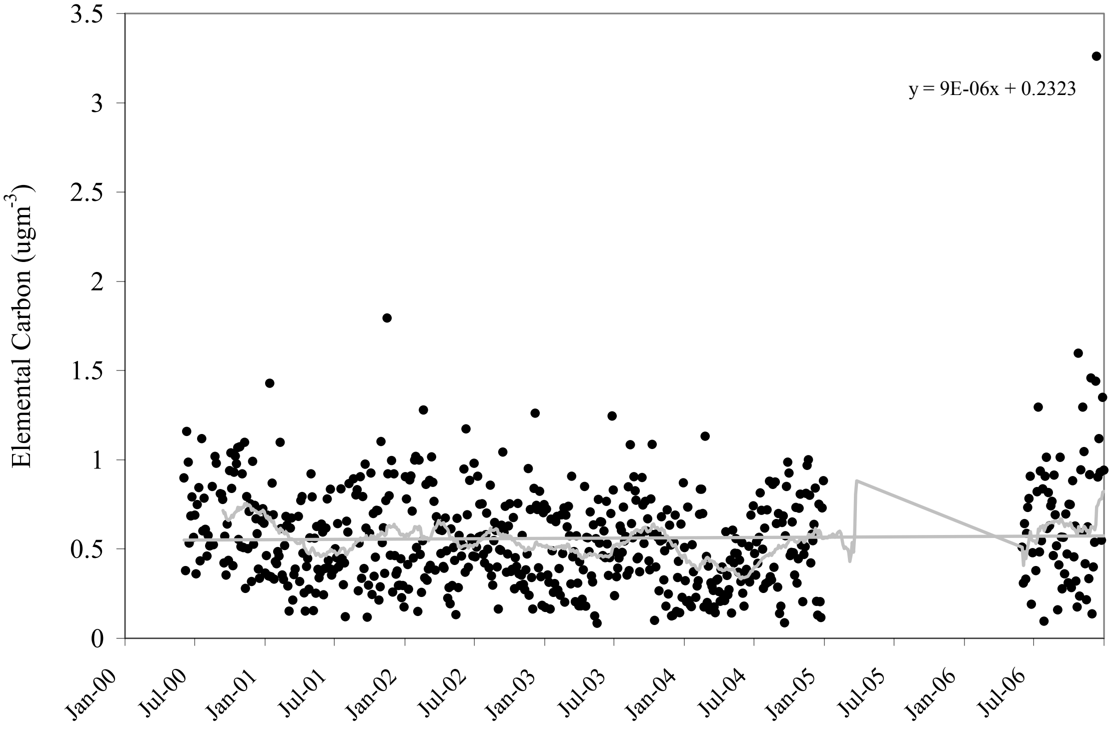


Figure III-16e. Elemental Carbon from the James River, VA IMPROVE site. Every 3rd day data from 2000-2006. The mean trend in elemental carbon is 0.003 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = 9E-06x + 0.232. A 30 point running mean is also presented.

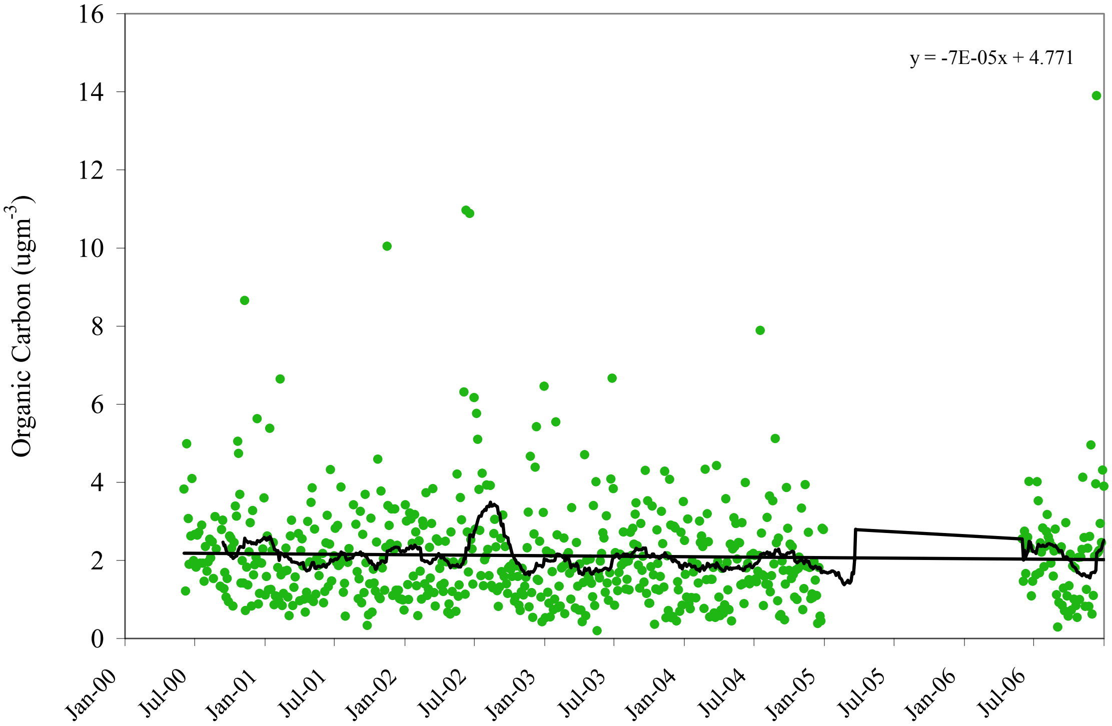


Figure III-16f. Organic Carbon from the James River, VA IMPROVE site. Every 3rd day data from 2000-2006. The mean trend in organic carbon is -0.025 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -7E-05x + 4.77. A 30 point running mean is also presented.

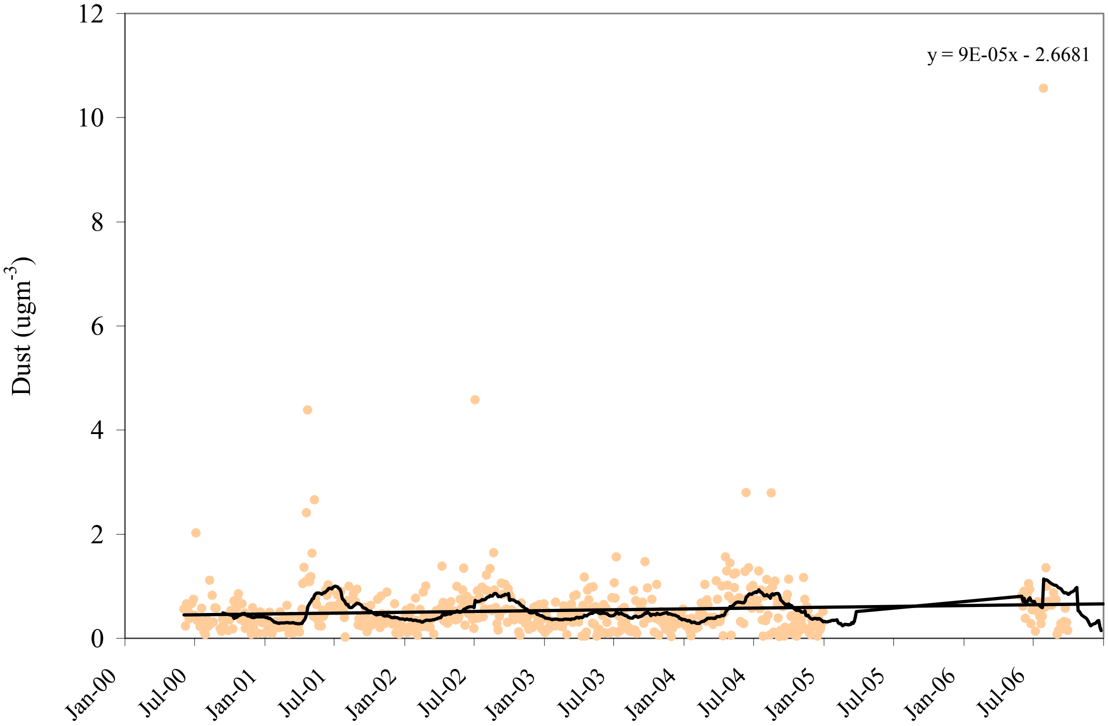


Figure III-16g. Dust from the James River, VA IMPROVE site. Every 3rd day data from 2000-2006. The mean trend in dust is 0.033 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = 9E-05x - 2.67. A 30 point running mean is also presented.

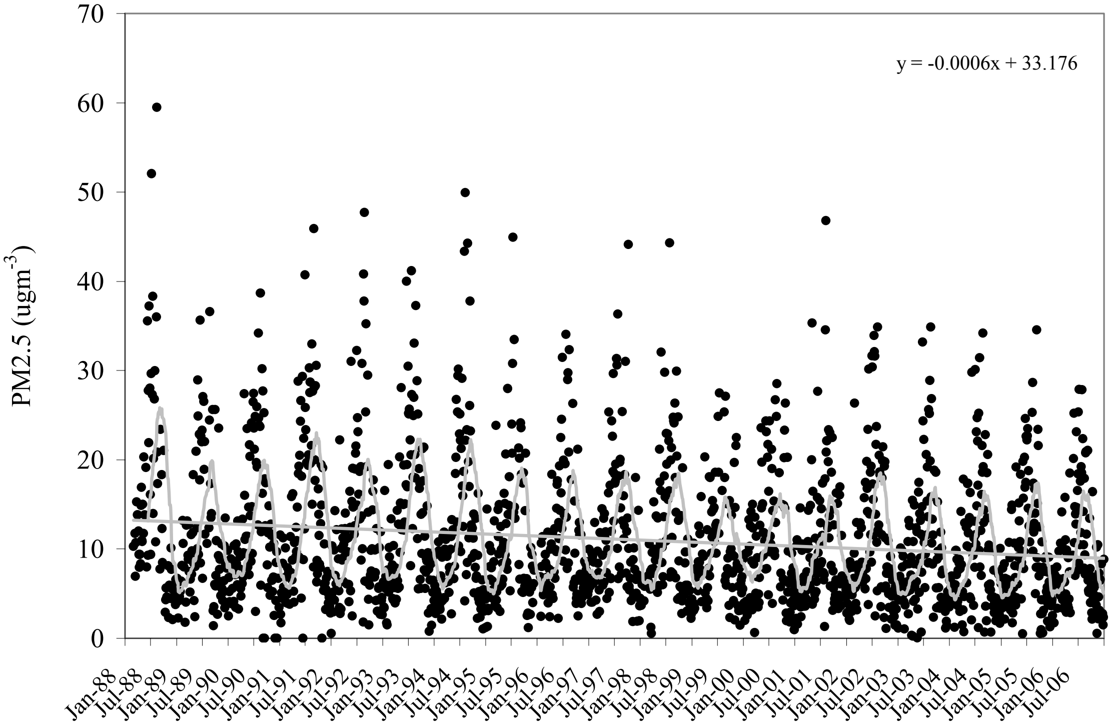


Figure III-17a. PM2.5 from the Shenandoah River, VA IMPROVE site. Every 3rd day data from 1988-2006. The mean trend in PM2.5 is -0.210 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is $y = -0.0006x + 33.18$. A 30 point running mean is also presented.

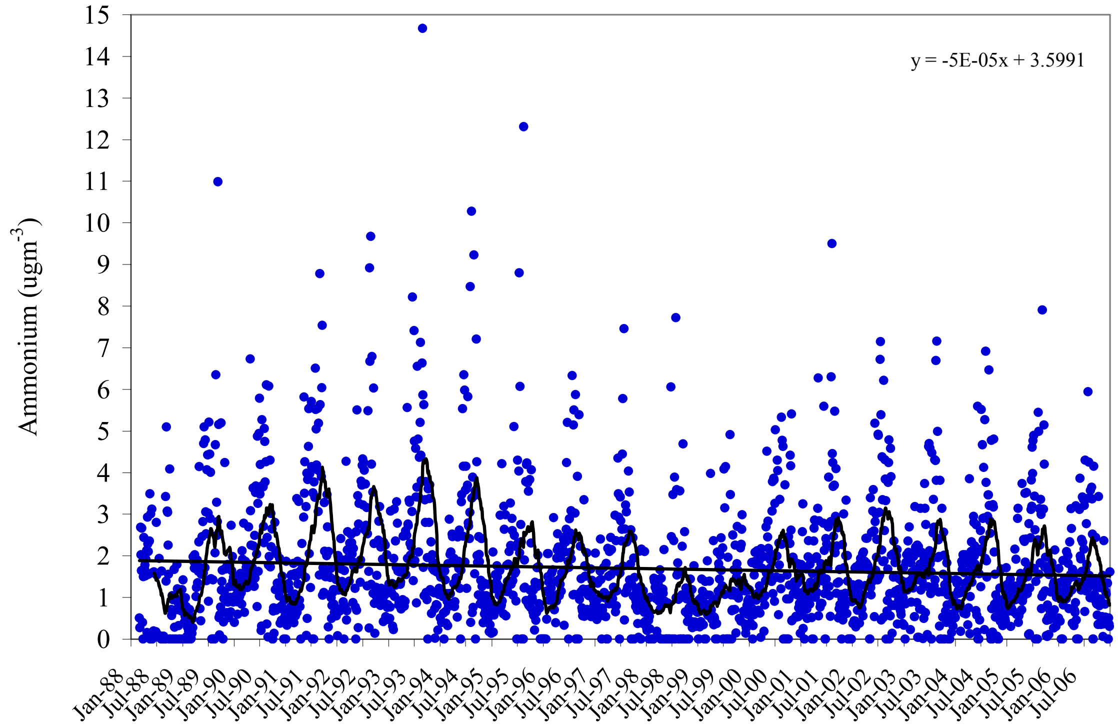


Figure III-17b. Ammonium from the Shenandoah River, VA IMPROVE site. Every 3rd day data from 1988-2006. The mean trend in ammonium is -0.018 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -5E-05x + 3.60. A 30 point running mean is also presented.

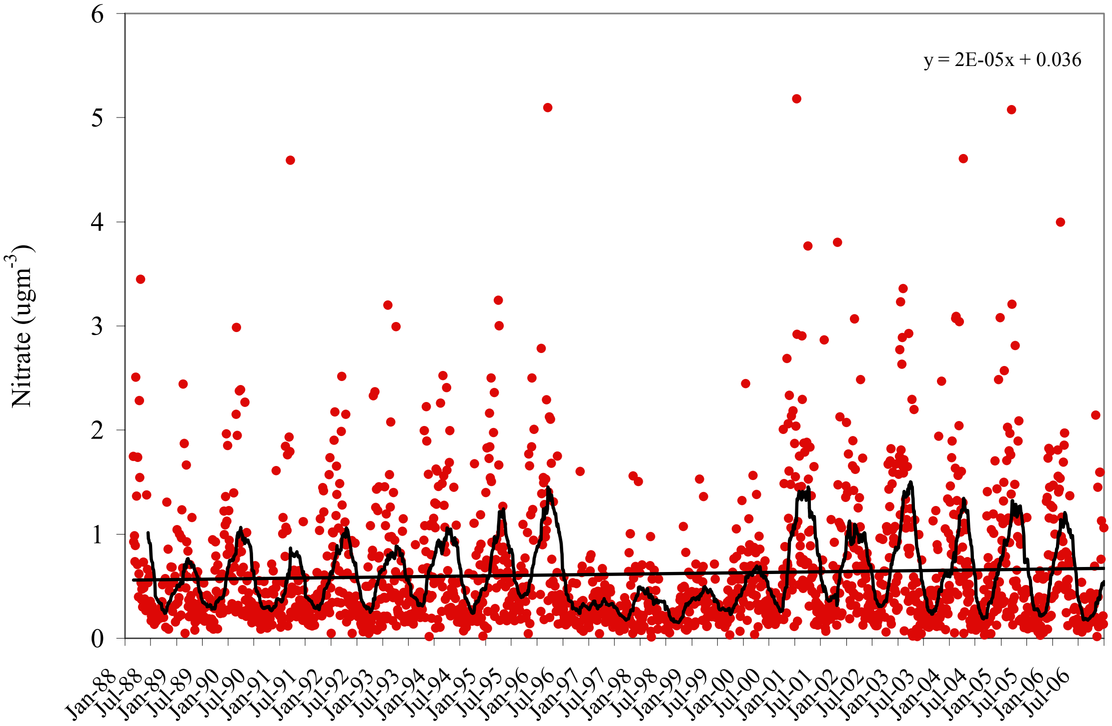


Figure III-17c. Nitrate from the Shenandoah River, VA IMPROVE site. Every 3rd day data from 1988-2006. The mean trend in nitrate is 0.006 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = 2E-05x + 0.036. A 30 point running mean is also presented.

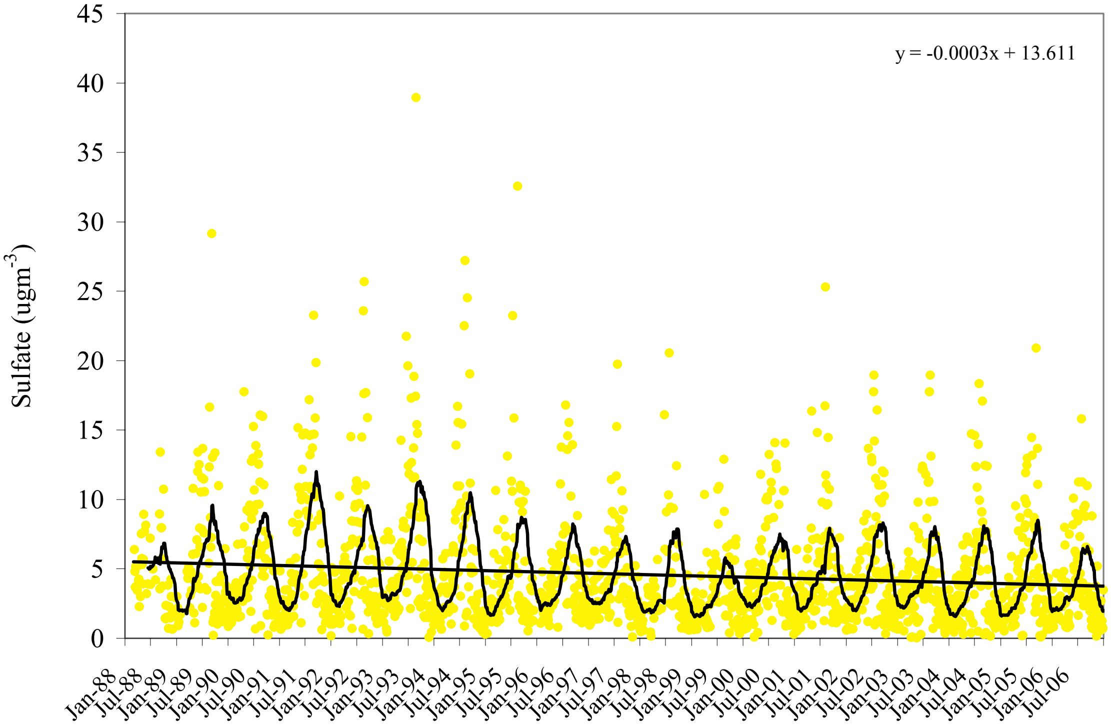


Figure III-17d. Sulfate from the Shenandoah River, VA IMPROVE site. Every 3rd day data from 1988-2006. The mean trend in sulfate is -0.094 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0003x + 13.61. A 30 point running mean is also presented.

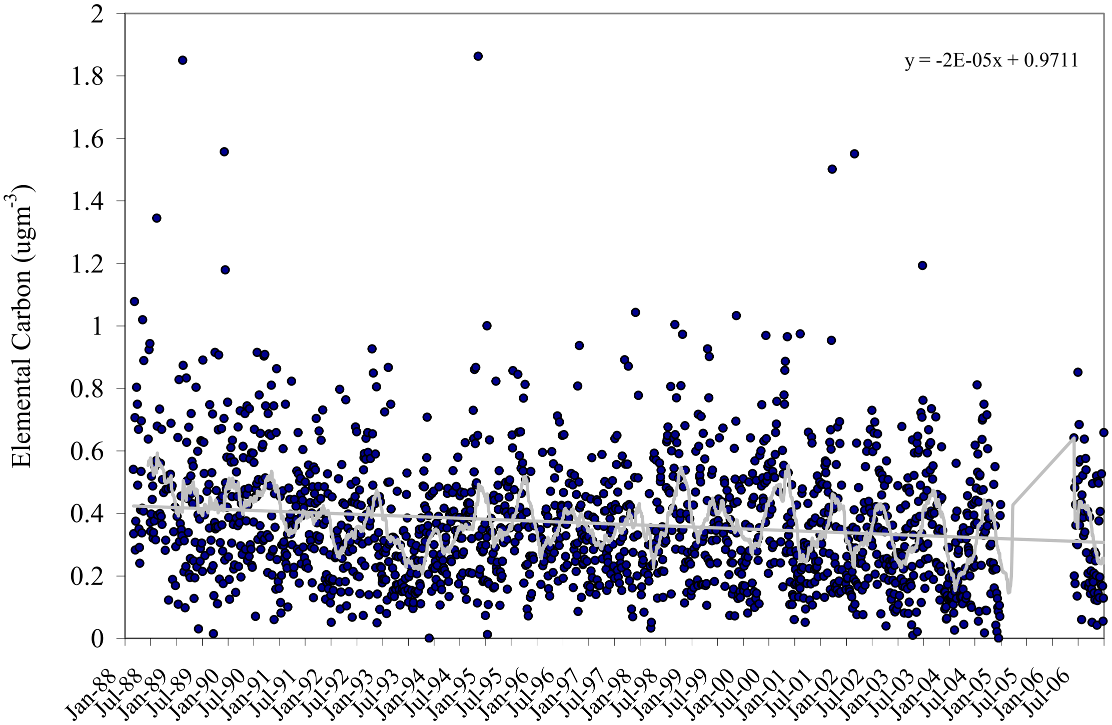


Figure III-17e. Elemental Carbon from the Shenandoah River, VA IMPROVE site. Every 3rd day data from 1988-2006. The mean trend in elemental carbon is -0.006 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -2E-05x + 0.971. A 30 point running mean is also presented.

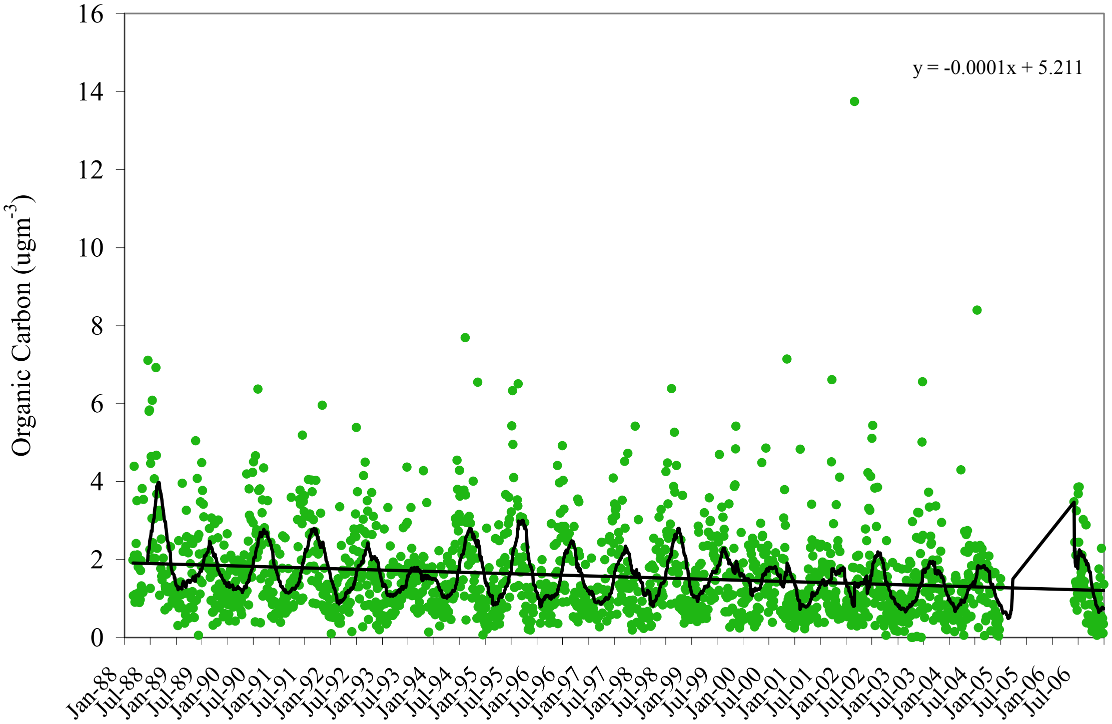


Figure III-17f. Organic Carbon from the Shenandoah River, VA IMPROVE site. Every 3rd day data from 1988-2006. The mean trend in organic carbon is -0.041 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -0.0001x + 5.21. A 30 point running mean is also presented.

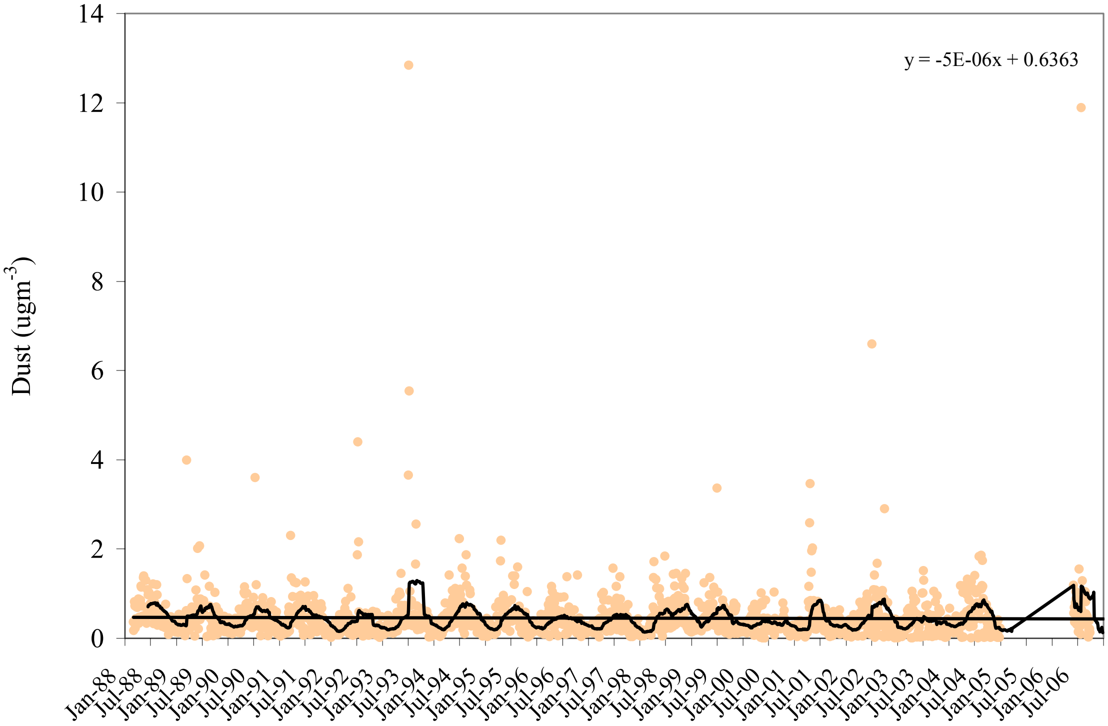


Figure III-17g. Dust from the Shenandoah River, VA IMPROVE site. Every 3rd day data from 1988-2006. The mean trend in dust is -0.0017 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -5E-06x + 0.64. A 30 point running mean is also presented.

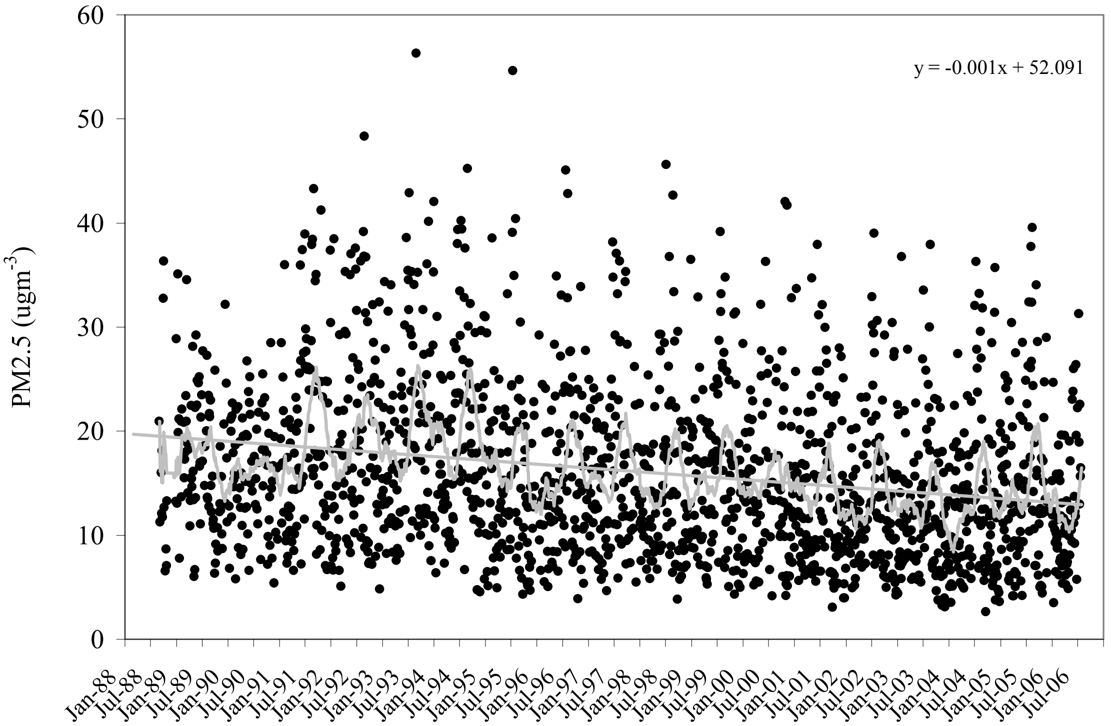


Figure III-18a. PM2.5 from the Hains Point (located in Washington DC) IMPROVE site. Every 3rd day data from 1989-2006. The mean trend in PM2.5 is -0.344 $\mu gm^{-3} yr^{-1}$. The equation for the linear fit is y = -0.001x + 52.091. A 30 point running mean is also presented.

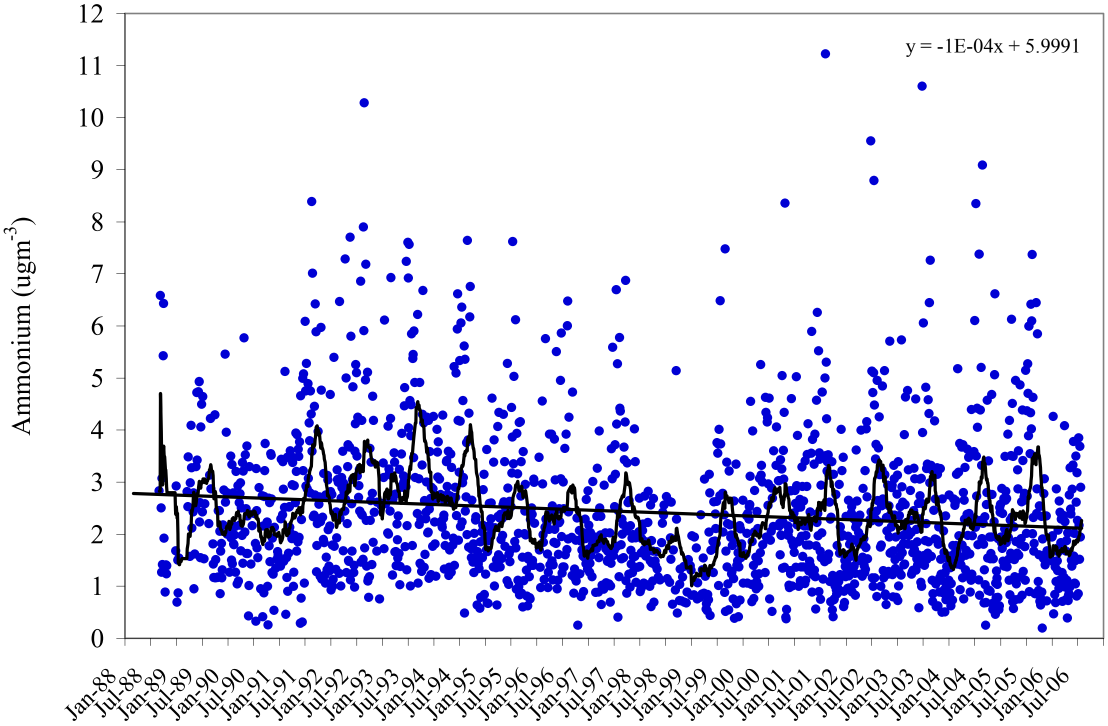


Figure III-18b. Ammonium from the Hains Point (located in Washington, DC) IMPROVE site. Every 3rd day data from 1989-2006. The mean trend in Ammonium is -0.017 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -1E-04x + 5.9991. A 30 point running mean is also presented.

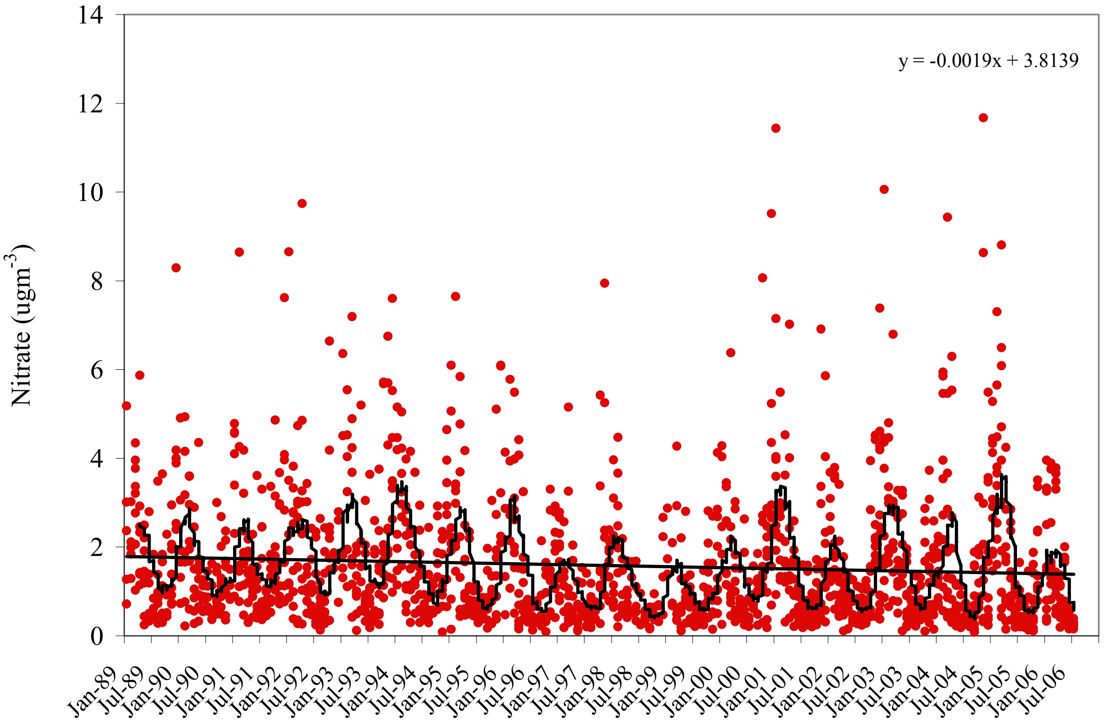


Figure III-18c. Nitrate from the Hains Point (located in Washington DC) IMPROVE site. Every 3rd day data from 1989-2006. The mean trend in nitrate is -0.022 $\mu gm^{-3}yr^{-1}$. The equation for the linear fit is y = -0.0019x + 3.81. A 30 point running mean is also presented.

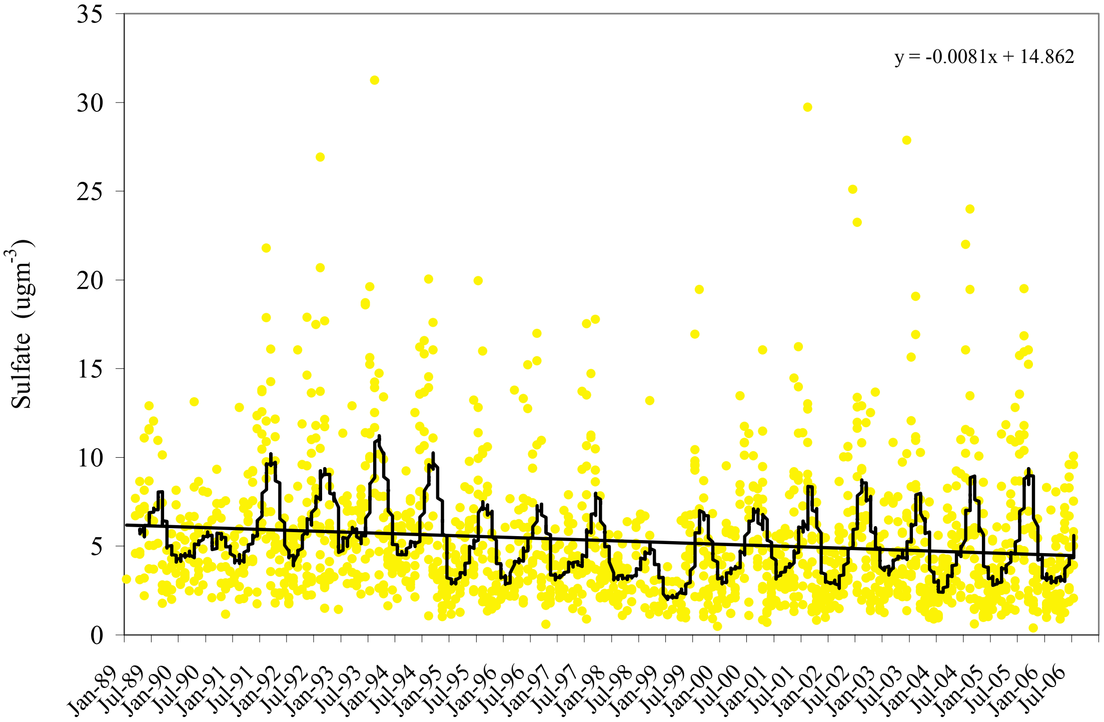


Figure III-18d. Sulfate from the Hains Point (located in Washington DC) IMPROVE site. Every 3rd day data from 1989-2006. The mean trend in sulfate is -0.022 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0081x + 14.86. A 30 point running mean is also presented.

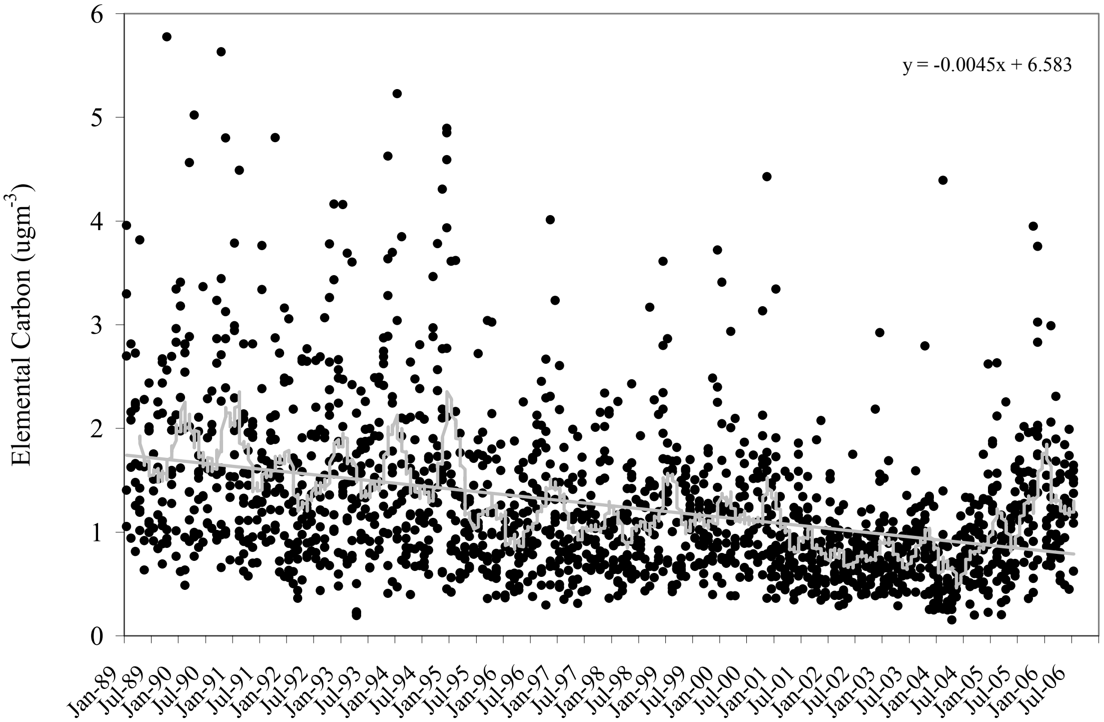


Figure III-18e. Elemental Carbon from the Hains Point (located in Washington DC) IMPROVE site. Every 3rd day data from 1989-2006. The mean trend in elemental carbon is -0.053 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0045x + 6.58. A 30 point running mean is also presented.

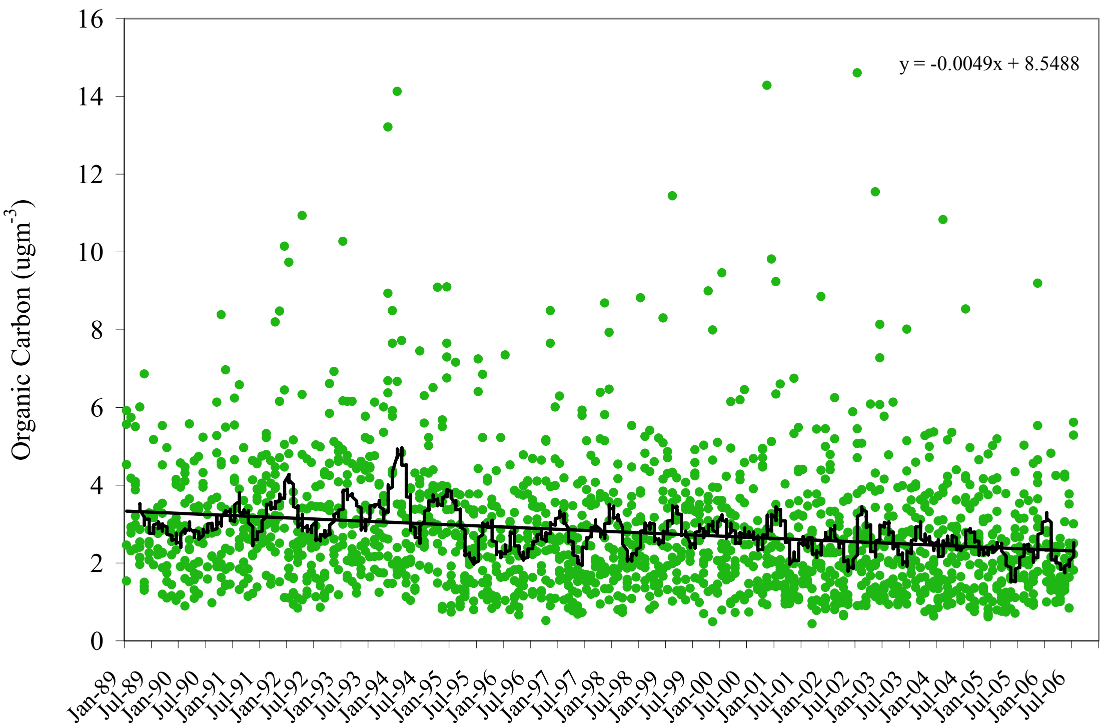


Figure III-18f. Organic Carbon from the Hains Point (located in Washington, DC) IMPROVE site. Every 3rd day data from 1989-2006. The mean trend in OC is -0.067 μgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0049x + 8.549. A 30 point running mean is also presented.

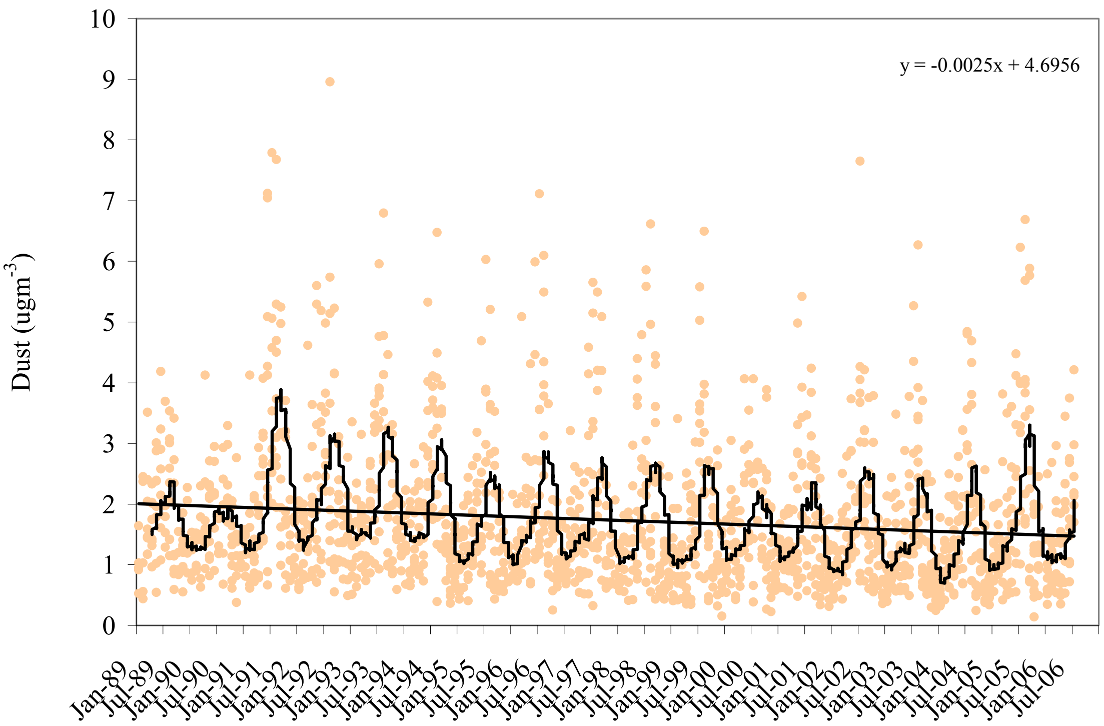


Figure III-18g. Dust from the Hains Point (located in Washington DC) IMPROVE site.. Every 3rd day data from 1989-2006. The mean trend in organic carbon is -0.031 µgm$^{-3}$yr$^{-1}$. The equation for the linear fit is y = -0.0025x + 4.696. A 30 point running mean is also presented.

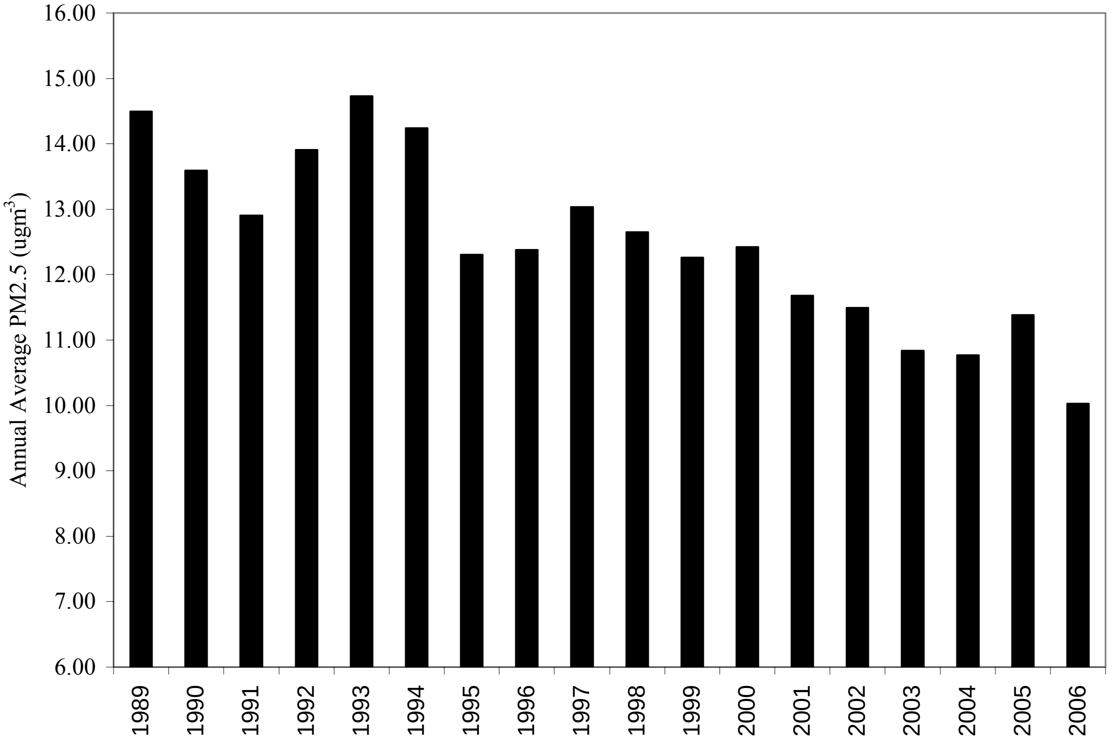


Figure III-19. Annual average PM2.5 plot for all the available monitors in the area (Arendtsville, Baltimore, Brigantine, Dolly Sods, Frostburg, James River, Shenandoah, Washington, DC) regardless of duration. See Table III-1 for a list of monitors and their sampling period. The linear trend is -0.225 $\mu gm^{-3}yr^{-1}$, correlation coefficient r is 0.9, and is statistically significant, $p < 0.01$ levels

### d. Conclusions

The results from this analysis demonstrated that, on a regional scale, average PM2.5 mass concentrations (from monitors with a record of at least 5 years) are decreasing at an average of 0.25 $\mu g\ m^{-3}\ yr^{-1}$, and this trend is statistically significant at the $p = 0.05$ level or stronger for each site. Figure III-19 shows the annual values for averages of all the IMPROVE sites (regardless of duration of measurements) – a clear decline is apparent significant at the $p < 0.01$ level. At all locations investigated in this analysis the PM2.5 species that contributed the most to the decrease in PM2.5 was sulfate which is responsible for ~50% of the PM2.5 decrease on average. Similarly, organic carbon accounts for ~25% of the decrease and ammonium ~15%. Reductions in dust and EC concentrations contribute a small amount to the PM2.5 decrease.

The homogeneity in the decreasing trend of PM2.5 and in PM2.5 species suggests all monitors studied share a common regional "load" of PM2.5 which may account for roughly 60-75% of the total observed PM2.5. Inspection of seasonal cycles suggests the regional contribution may increase during parts of the summer season. Recently implemented regional control strategies, which target sulfur and nitrogen emissions, should combine with current trends to further reduce PM2.5 concentrations on the worst air quality days in Maryland.

The long-term monitoring looked at in this analysis indicates a steady decrease in sulfate, nitrate, organic matter, black carbon, and total PM2.5. This overall trend suggests that the emphasis on regional controls of sulfur dioxide, oxides of nitrogen, black carbon and volatile organic compounds emissions has led to a reduction in PM2.5 that will result in Maryland attaining compliance with the 24-hour and annual average PM2.5 NAAQS by 2009.

### References

Sickles, J., and D. S. Shadwick (2007), Changes in air quality and atmospheric deposition in the eastern United States: 1990-2004, *Journal of Geophysical Research-Atmospheres*, *112*.

# Section IV

## PM2.5 Composition as it Relates to Effectiveness of Controls

Patricia Castellanos

Department of Chemical and Biomolecular Engineering
University of Maryland
College Park, MD

January 28, 2008

1. **Why is this section important?**

   This analysis discusses emissions reductions in Maryland and the MANE-VU region with respect to effectiveness in reducing PM2.5. It shows that the emissions reductions projected for 2009 target the correct species and sources to affect future PM2.5 concentrations.

2. **What questions are answered in this section?**

   - What types of emissions reductions are necessary to reduce PM2.5?
   - Do the emissions reductions projected for 2009 target the right species and emissions sources needed to reduce PM2.5?

3. **What are the key take-away messages of this section?**

   Measurements have shown that $SO_2$ and VOC emissions from point and mobile sources frequently contribute to the formation of PM2.5 in Maryland, and that reductions in emissions of these species will in fact reduce total PM2.5. Likewise, the emissions controls projected for 2009 in Maryland and the MANE-VU region emphasize reductions in $SO_2$ emissions from power plants and VOC emissions from automobiles.

4. **What conclusions are reached in this section with respect to Maryland's attainment demonstration?**

   The emissions reductions projected for 2009 in $SO_2$, VOC, and $NO_x$ in Maryland and MANE-VU will lead to a decline in PM2.5 in Maryland in the future.

## Abstract

Several source apportionment and highly time resolved analyses of PM2.5 episodes in Maryland have revealed that in many instances $SO_2$ from electric utilities and VOC from mobile sources are responsible for the sulfate and organic portion of PM2.5. Other studies have shown that in Maryland and the Northeast region, sulfate is the largest contributor to PM2.5, and that sulfate and nitrate respond positively to reductions in $SO_2$ and $NO_x$ emissions. An analysis of the 2002 NEI and the 2009 projected emissions inventory for Maryland and MANE-VU demonstrates that the emissions controls that will go into place in and surrounding Maryland are geared towards reducing $SO_2$, $NO_x$, and VOC emissions from electric utility and mobile sources. Given the historical trend of decreasing emissions of $SO_2$, $NO_x$, and VOC's coupled with decreases in sulfate, nitrate, organic matter, and PM2.5, it can be expected that PM2.5 in Maryland will decline substantially in the future.

### a. Introduction

Several studies that have analyzed the composition of PM2.5 in the Baltimore area and the Northeast region using various methodologies suggest that sulfate originating from the transformation of regional $SO_2$ emissions is the dominant contributor to PM2.5 mass in Maryland (Section I). Consequently, ammonium, the neutralizing cation that often accompanies sulfate, is a small component of fine particles that is most significant in the winter (Section V). Due to the variability in PM2.5 (Section II) in some instances nitrate, carbonaceous species, and crustal material are present in significant quantities. Recent research conducted by *Robinson et al.* (2007) suggests that secondary organic aerosols that form as a result of oxidation of low vapor pressure organic molecules contribute more to PM2.5 than has been modeled or previously measured. It is reasonable to assume that by controlling the different constituents of PM2.5 you can decrease the mass as a whole. In fact, Likens et al. (2005) show direct correlations between $SO_2$ and sulfate and $NO_x$ and nitrate. Therefore, a combination of $SO_2$, $NO_x$, VOC, and primary PM2.5 emissions controls in Maryland and the surrounding region are key to reducing PM2.5.

### b. Future Year Emissions Reductions

According to 2002 National Emissions Inventory (NEI) and Mid-Atlantic/Northeast Visibility Union (MANE-VU) future year estimates (Figure IV-1 & IV-2), in the MANE-VU region total emissions of oxides of nitrogen ($NO_x$), volatile organic compounds (VOC), and $SO_2$, drop by 35%, 22%, and 53% respectively between 2002 and 2009. Primary PM2.5 emissions show a slight decrease, while $NH_3$ emissions increase by 18% (it should be noted that inventories for $NH_3$ are highly uncertain). In Maryland alone, the emissions show the same trends and relative changes, except $SO_2$ emissions decrease by 63% and PM2.5 emissions increase by 4%. Additional emissions reductions are expected in 2012.

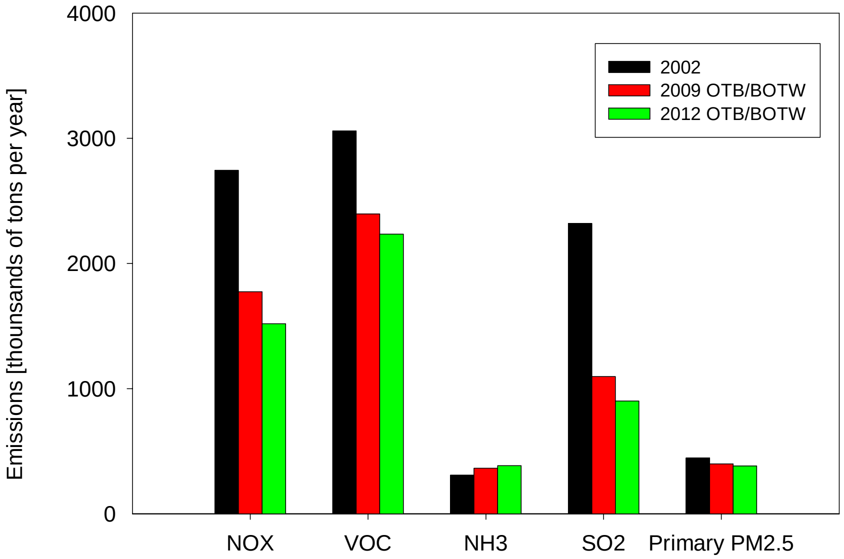


Figure IV-1. MANE-VU 2002 National Emissions Inventory emissions in thousands of tons per year, and MANE-VU 2009 & 2012 emissions projections including on-the-books/beyond-on-the-way (OTB/BOTW) controls.

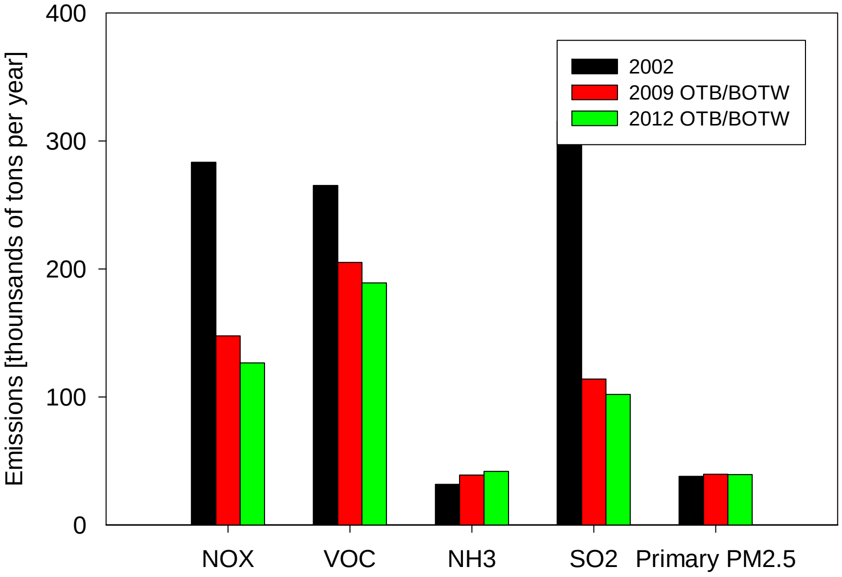


Figure IV-2. Maryland 2002 National Emissions Inventory emissions in thousand of tons per year, and Maryland 2009 & 2012 emissions projections including on-the-books/beyond-on-the-way (OTB/BOTW) controls.

### c. Sources and Source Apportionment

Source apportionment studies and highly time resolved episode analyses by *Ogulei et al.* (2006), *Park et al.* (2006), *Chen et al.* (2002) at the Baltimore Supersite and Fort Meade, MD (Section I Figure I-1, Table I-1) begin to identify a source fingerprint for PM2.5. The results of these analyses give guidance as to where emissions controls should be directed in addition to reducing emissions from PM2.5 components across the board in order to target the root of the problem. A number of PM2.5 local and regional sources were identified at the two sites by various analyses and include the following: power plant, vehicle, roadway dust, steel plant, incinerator, wood smoke, local stationary source, and organic vapor emissions. Reductions targeted at emissions from these sources are illustrated below.

A breakdown of the NEI (Figure IV-3) shows that the MANE-VU region and Maryland have a very similar category distribution of emissions sources implying that corresponding processes create pollution both in Maryland and the MANE-VU region. Point and area sources are the primary contributors to $SO_2$ and PM2.5 emissions respectively. Although biogenic emissions alone make up half of VOC emissions, the anthropogenic portion is mostly due to area and on-road mobile sources. Similarly, over 90% of $NH_3$ emissions come from area and on-road mobile sources. $NO_x$ emissions have significant contributions from all three emissions sectors.

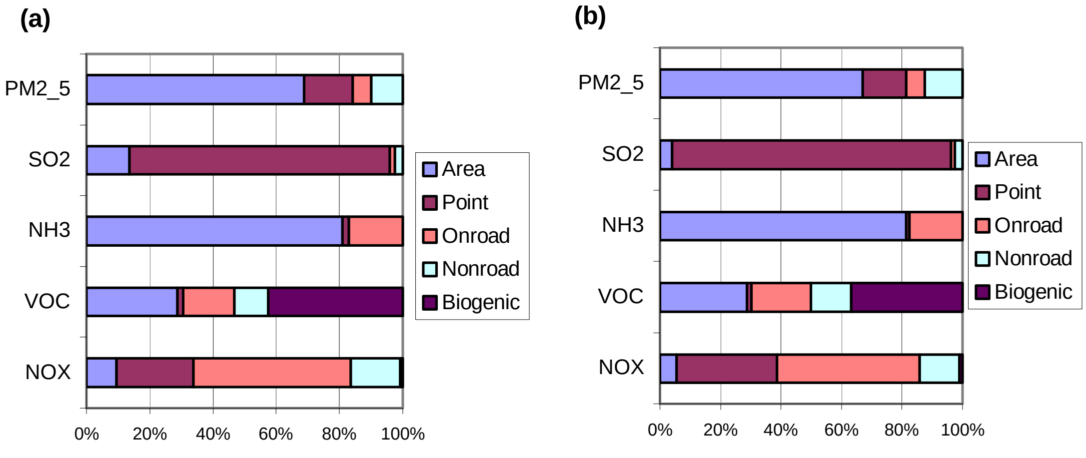


Figure IV-3. (a) 2002 MANE-VU, (b) 2002 Maryland source category contributions to emissions.

From 2002 to 2009, a decrease in PM2.5 area source emissions and a substantial decrease in $SO_2$ point source emissions are scheduled to occur in Maryland and the MANE-VU region (Figure IV-4 & IV-5). A further break down of point source $SO_2$ emissions (Figure IV-6) shows that the largest reductions from 2002 to 2009 are applied to electrical utilities. This source category is mentioned as the contributing factor in several major Baltimore episodes analyzed by *Park et al.* (2006) in 2002. This indicates that the appropriate controls are being applied in order to reduce these PM2.5 contributions in Baltimore.

Reductions in VOC emissions from on-road mobile sources (Figure IV-4 & IV-5), which generate a considerable fraction of the organic matter in fine particles, are also on target to reduce PM2.5. Furthermore, the effects of on-road mobile source controls are seen in reductions of $NO_x$ emissions. Although contributions to $NO_x$ from point sources only decrease slightly in the MANE-VU region, in Maryland the reductions are significant. Furthermore, though not plotted here, point source emissions in the Midwest, a source region that is often upwind of Maryland, are also projected to decrease significantly by 2009.

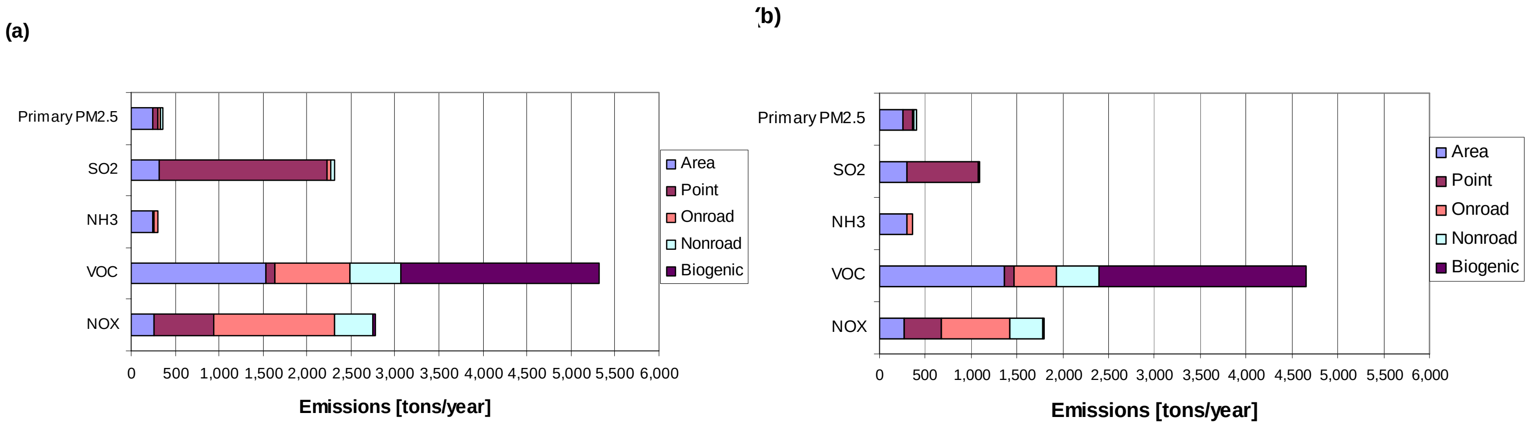


Figure IV-4. (a) 2002 MANE-VU emissions by sector. (b) 2009 MANE-VU emissions by sector.

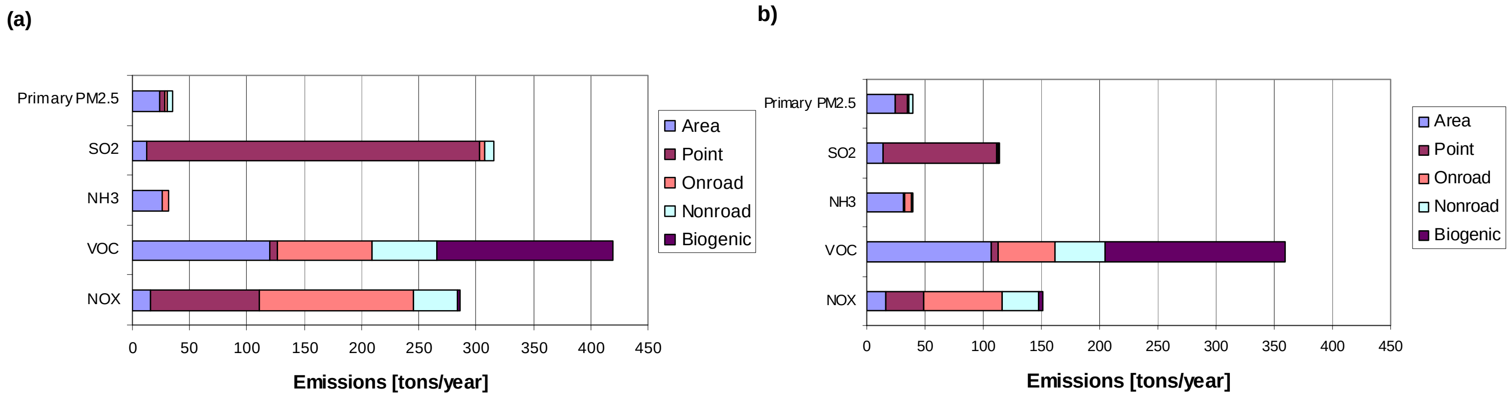


Figure IV-5. (a) 2002 Maryland emissions by sector. (b) 2009 Maryland Emissions by sector.

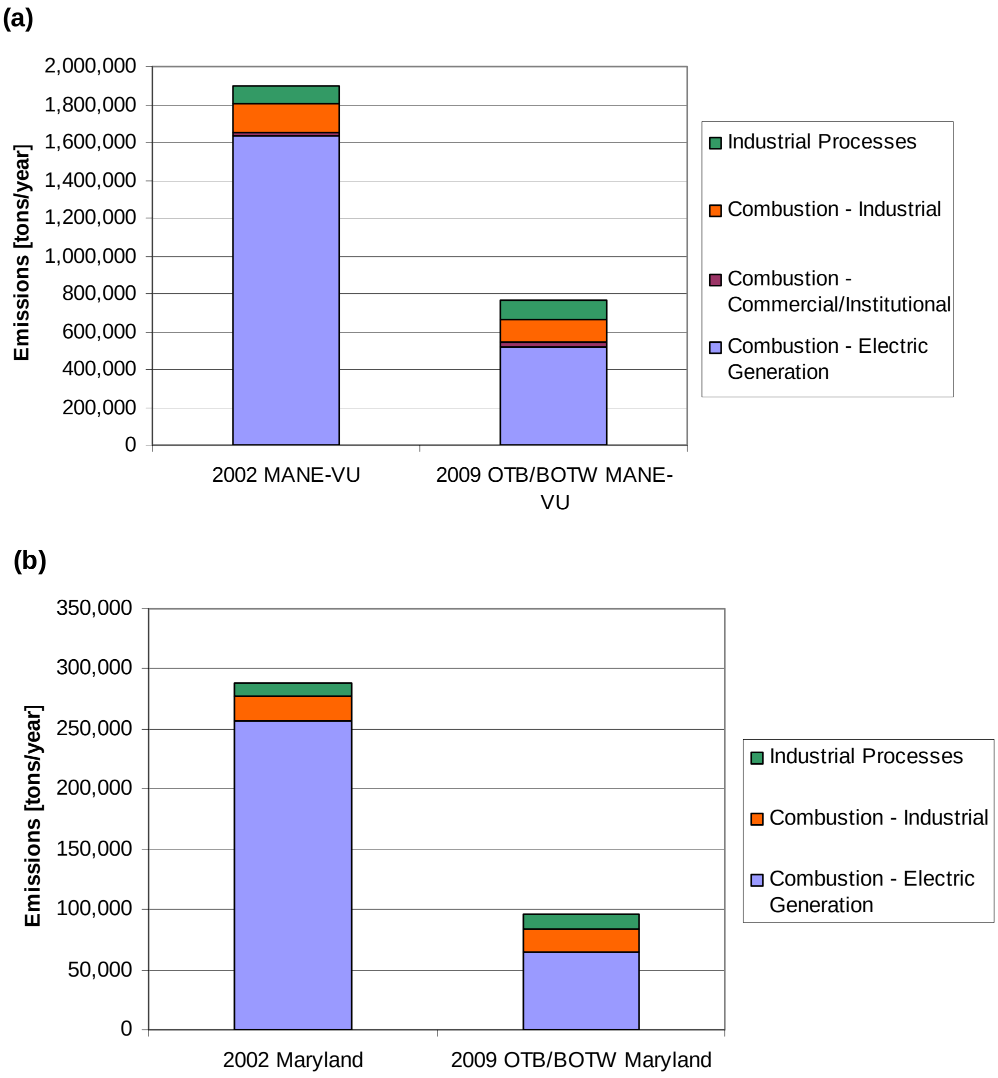
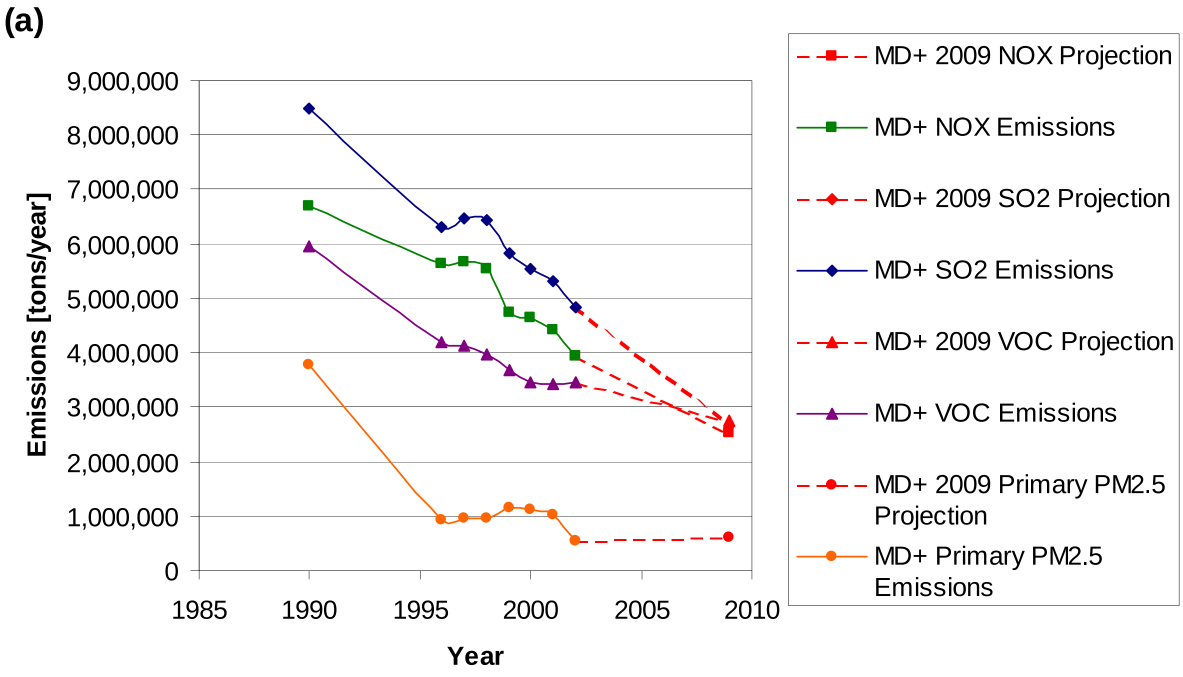


Figure IV-6. 2002 and 2009 emissions inventory process contributions to point source $SO_2$ emissions in (a) MANE-VU and (b) Maryland.

### d. Trends vs. Emissions

Over the long term, we have seen that in Maryland PM2.5, sulfate, nitrate, and organic carbon have been decreasing along with emissions (Sections III & V). Correspondingly, over 1990-2002 according to NEI estimates, annual emissions in Maryland and the surrounding states including Connecticut, District of Columbia, Delaware, Kentucky, New Jersey, New York, Ohio, Pennsylvania, Rhode Island, Virginia, and West Virginia have decreased respectively by 108,000 tons and 3,659,000 tons for $SO_2$, 129,800 tons and 2,746,500 tons for $NO_x$, 96,700 and 2,488,000 for VOC, and 23,800 tons and 3,247,00 tons for primary PM2.5 (Figure IV-7). Given this long-term decreasing glide path in emissions, sulfate, nitrate, organic matter, and PM2.5, and positively correlated responses in sulfate and nitrate to $SO_2$ and $NO_x$ emissions shown in past studies, it is expected that the decreasing trend in PM2.5 will continue into 2009.



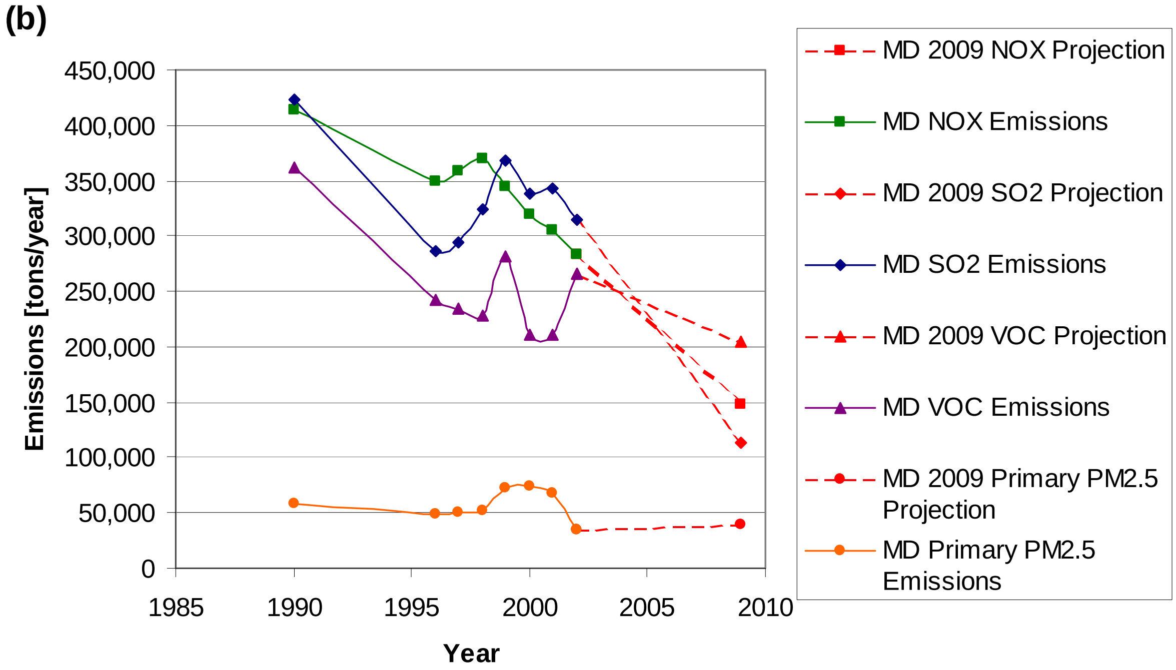


Figure IV-7. (a) 1990-2009 NEI MD+ = CT, DE, DC, MD, KY, NJ, NY, OH, PA, RI, VA, WV $NO_x$, $SO_2$, VOC, and primary PM2.5 emissions. (b) 1990-2009 NEI Maryland $NO_x$, $SO_2$, VOC, and primary PM2.5 emissions.

## References

Chen, L. W. A., et al. (2002), Origins of fine aerosol mass in the Baltimore-Washington corridor: Implications from observation, factor analysis, and ensemble air parcel back trajectories. *Atmospheric Environment***,** *36*, 4541-4554.

Likens, G. E., et al. (2005), Long-term relationships between SO2 and NOx emissions and SO42- and NO3- concentration in bulk deposition at the Hubbard Brook Experimental Forest, NH, *Journal of Environmental Monitoring*, *7*, 964-968.

Ogulei, D., et al. (2005), Receptor modeling for multiple time resolved species: The Baltimore, supersite. *Atmospheric Environment***,** *39*, 3751-3762.

Park, S. S., et al. (2006), Characteristics of PM2.5 episodes revealed by semi-continuous measurements at the Baltimore Supersite at Ponca St., *Aerosol Science And Technology***,** *40*, 845-860.

Robinson, A. L., et al. (2007), Rethinking organic aerosols: Semivolatile emissions and photochemical aging, *Science*, *315*, 1259-1262.

# Section V

## Monitoring Data from Surface-Based Speciation Sites

Dr. Russell R. Dickerson
Department of Atmospheric and Oceanic Science
The University of Maryland
Patricia Castellanos, Dr. Sheryl Ehrman
Department of Chemical Engineering
The University of Maryland

January 30, 2008

## Key Questions

### 1. Why is this section important?

This analysis shows that at numerous sites in and around Maryland the concentration of PM2.5 and its individual constituents have been monitored with sufficient accuracy and for a sufficient period of time to form general conclusions regarding the origins, transport, transformations, and temporal trends of aerosols in the Maryland area.

### 2. What questions are answered in this section?

What are the origins, properties, and statistical distributions of PM as measured at the surface sites in and around Maryland? How are PM transported to and from Maryland? What are the trends in PM?

### 3. What are the key take-away messages of this analysis?

Based on a side-by-side comparison of FRM and CSN filter-based 24-hr average PM2.5 measurements, PM2.5 or its major constituents can be taken with 95% confidence limit to be within about 30% of the actual value. Precision is substantially better than absolute accuracy, and long-term averages are accurate to better than 20%. Meteorology plays a vital role in the occurrence of severe haze episodes. Increases in PM concentration and reduction in visibility resulted from rapid sulfate accumulation under a humid ambient condition.

### 4. What conclusions are reached in this section with respect to Maryland's attainment demonstration?

Examination of ambient concentrations of aerosols and their precursors suggests that the uncertainty in the measurements is now quantified. Basic conclusions regarding the dominant components of PM2.5 can be made with a reasonable degree of confidence, with the inference that the major sources of PM2.5 are known with the same confidence.

## Abstract

The concentrations of PM2.5 and its speciated components have been monitored at several sites in and around Maryland. The overall accuracy of the instruments used in these analyses has been assessed. Daily measurement of PM2.5 (based on a side-by-side comparison of FRM and CSN filter-based 24-hr average) or its major constituents can be taken with 95% confidence limit within about 30% of the actual value. Precision is substantially better than absolute accuracy, and long-term averages are accurate to better than 20%. Chemically speciated fine particulate matter and associated trace gases (including $NH_3$, $HNO_3$, CO, $SO_2$, and NOy) reflect both local and regional sources. Day-to-day and seasonal variations in the PM2.5 chemical composition reflect changes in the weather and changes in the contribution from the various sources.

### a. Introduction

At numerous sites in and around Maryland (Figure V-1) the concentration of PM2.5 and its individual constituents have been monitored with sufficient accuracy and for a sufficient period of time to form general conclusions regarding the origins, transport, transformations, and trends of aerosols in the Maryland area.

### b. Fort Meade

The surface site at Fort Meade, located between Baltimore and Washington, D.C. (39.10°N, 76.74°W; elevation 46 m MSL), has provided several valuable data sets that shed light into the origins and properties of PM in this region [*Chen, et al.*, 2001; *Chen, et al.*, 2003; *Chen, et al.*, 2002; *Hains, et al.*, 2007].

Chen et al. (2001) measured 24-hr average BC (also called elemental carbon or EC) aerosol concentration during July 1999, October 1999, January 2000, April 2000 and July 2000. Higher temporal resolution measurements of carbon monoxide (CO) and sulfur dioxide ($SO_2$) were also conducted over the period. Tight correlation between EC and CO in every month suggests common or proximate sources, likely traffic emissions. The EC versus CO slope was higher in the warmest months, suggesting that summertime emissions are greater. By using the well established emission inventory for CO, and EC/CO ratio found in this study, they estimated EC emissions over North America of $0.31 \pm 0.12$ Tg $yr^{-1}$, on the low end but in reasonable agreement with prior inventories based on emission factors and fuel consumption. The policy implication is that continued improvements in BC emissions from mobile sources will be reflected in continued reductions in the BC component of ambient PM.

Chen et al (2002) chemically speciated fine particulate matter and trace gases (including $NH_3$, $HNO_3$, CO, $SO_2$, and NOy) sampled at Fort Meade reflect both local and regional sources. Measurements over a two-year period included eight seasonally representative months. The PM2.5 showed an annual mean of 13 $\mu g\ m^{-3}$ and primarily consists of sulfate, nitrate, ammonium, and carbonaceous material. Day-to-day and seasonal variations in the PM2.5 chemical composition reflect both meteorological variables and changes in the contribution from various pollutant sources. UNMIX, an innovative receptor model, was used to retrieve potential sources of the PM2.5. A six-factor model, including secondary sulfate, local sulfate, wood smoke, metal processing industry, mobile, and secondary nitrate, was constructed and compared to reported source emission profiles. The six factors were also studied with an ensemble back trajectory method to identify possible source locations. Factors associated with mobile sources were more local in nature. Secondary sulfate and wood smoke are more regional and associated with westerly and southerly transport, respectively. This study suggests that the local contribution to PM2.5 mass can vary from < 30% in summer to > 60% in winter.

Chen et al., (2003) observed PM2.5 mass, PM2.5 chemical composition, light extinction, and meteorology in the urban Baltimore-Washington corridor during July 1999 and July 2000. Chen et al., (2003) studied summertime haze formation in the Mid-Atlantic region, and found that the mass fraction of ammoniated sulfate and carbonaceous material in PM2.5 were each ~ 50% for cleaner air (PM2.5 < 10 $\mu g\ m^{-3}$) but changed to ~ 60% and ~ 20%, respectively for more polluted air (PM2.5 > 30 $\mu g\ m^{-3}$). This shows the central role of sulfate in haze formation, especially on the most polluted days. Comparisons of data from this study with the IMPROVE network suggest that sulfate is more regional than carbonaceous material and likely originates predominantly from the upwind source regions. The value of light extinction coefficient (the sum of absorption and scattering) was well correlated with PM2.5 mass plus water associated with inorganic salts. The most serious haze episode (7/16 – 7/19, 1999) was characterized by a slow westerly transport and stable subsidence that prevented quick removal of pollutants. At the peak of this haze episode, 1-hr PM2.5 concentration reached ~ 45 $\mu g\ m^{-3}$, visual range dropped to ~ 5 km, and water likely contributed to > 40% of the light extinction coefficient.

The primary policy implications from this article are that increases in PM concentration and reduction in visibility resulted from rapid sulfate accumulation under a humid ambient condition. Sulfate spread over a regional scale and with it, haze. Further analyses based on continuous monitoring and thermodynamic model suggest that meteorology plays a vital role in the occurrence of severe haze episodes.

Hains et al. (2007) conducted side-by-side comparisons of different PM sampling and analysis techniques to investigate the reliability and uncertainty of the methods. Two samplers from the USEPA Speciation Trends Network: Met One Speciation Air Sampling System – $STN_S$ and Thermo Scientific Reference Ambient Air Sampler – $STN_R$, two Desert Research Institute Sequential Filter Samplers – $DRI_F$, and a continuous TEOM monitor ( R&P Tapered Element Oscillating Microbalance) were operated in parallel. These monitors differ in both sampling configuration and in protocol-specific sample analysis procedures. Measurements of PM2.5 mass and major contributing species were well correlated among the different methods with r-values > 0.8. Despite the good correlations, daily concentrations of PM2.5 mass and major contributing species were significantly different at the 95% confidence level from 5 to 100% of the time. Larger values of PM2.5 mass and individual species were generally reported from $STN_R$ and $STN_S$. The January $STN_R$ average PM2.5 mass (8.8 $\mu g/m^3$) was 1.5 $\mu g\ m^{-3}$ larger than the $DRI_F$ average mass. The July $STN_S$ average PM2.5 mass (27.8 $\mu g/m^3$) was 3.8 $\mu g\ m^{-3}$ larger than the $DRI_F$ average mass. These differences can only be partially accounted for by known random errors. Variations in flow control, face velocity, and sampling artifacts likely influence the measurement of PM2.5 speciation and mass closure. Statistical tests indicate that the current uncertainty estimates used in the STN network may underestimate the actual uncertainty. The policy implication from comparison of daily FRM and CSN measurements is that any given daily gravimetric measurement of PM2.5 or its major constituents can be taken, with 95% confidence, as within about 30% of the actual value. Precision is substantially better than absolute accuracy, and long-term averages may be accurate to ± 20% with 95% confidence.

### c. The Wye River

[*Stehr, et al.*, 2000] investigated the measurements of CO, $NO_y$, and $SO_2$ at a site on the Wye River on Maryland's eastern shore in order to evaluate emissions inventories. By comparing ratios of ambient concentrations they were able to distinguish NOx from stationary sources (co-emitted with $SO_2$) and $NO_x$ from mobile sources (co-emitted with CO). The analysis showed that the emissions inventories, at least in the relative sense, were in agreement with observed atmospheric levels. The policy implication of these results is that we have identified the major NOx sources and reductions of emissions at power plants and from vehicles will be effective at both reducing both the nitrate component of PM and the possibly the oxidants that contribute to the low-volatility sulfate and SOA.

### d. Essex

Ryan (see attached report) investigated total PM2.5 mass and its constituent components for the urban Essex site located at 39.31° N, 76.47° W, or approximately 15 km E of Baltimore's Inner Harbor. He concluded that aerosols at this site reflect the regional signature of PM, with ammonium sulfate and bisulfate dominant throughout the year, and even more so on the haziest days. Sulfate concentrations were highest in the summer (JJA) and accounted for nearly 50% of the PM2.5 mass. OC shows a bimodal distribution with a dual peak in summer and winter, while EC has little seasonal cycle. These observations point to greater summer EC emission (as observed by Chen at al. 2001) as well as greater summer OC emission or *in situ* formation, because dilution is stronger in the summer due to greater boundary layer depths and mixing. Biogenic VOC's such as terpenes and isoprene that can form SOA's peak in the summer, thus the winter OC maximum is probably due to anthropogenic sources such as vehicles and home heating. $NO_3^-$ is highest in the winter months, but accounts for a small fraction of the total, about 12%. In the cold months, PM2.5 was dominated by OC and $NH_4^+$ and appears to be driven by local emissions. In winter, the correlation between OC and EC (0.77) is higher than in the summer months (0.26) reflecting the greater contribution of local, vehicular emissions.

Analysis (Appendix WFR) of monitored data (2001-2003) did not progress long enough to demonstrate interannual variability or long term trends, but examination of the entire data set for the years of 2001-2006 yields a discernable trend. The total mass of PM fell at a rate of about 0.27 $\mu g\ m^{-3}\ yr^{-1}$ in parallel with a decline in sulfate of about 0.20 $\mu g\ m^{-3}\ yr^{-1}$ and a smaller decrease in OM.

The weather patterns associated with summertime high PM2.5 events are similar to high ozone events. A strong upper level ridge of high pressure is typically located over or west of the mid-Atlantic in both PM2.5 and ozone cases, leading to consistent westerly transport of pollutants into the region. As also indicated by analysis of local smog and haze events [*Kondragunta*, 1997] ozone and PM2.5 peaks often coincide. The main factors that limit peak ozone in summer – cloud cover and convection – have less impact on daily mean PM2.5 concentrations. In the winter, high PM2.5 cases are also associated with a strong upper level ridge and westerly transport aloft. Winter season PM2.5 cases, however, are more frequently characterized by stagnation near the surface and a stable boundary layer – snow cover can exacerbate stability. In these cold, stagnant events OC can dominate PM mass.

### e. Data Compiled by MARAMA

The Mid-Atlantic Regional Air Management Association (MARAMA) compiled and analyzed data from eleven sites in the Maryland airshed (Figure V-2). Monitors in Delaware, the District of Columbia, Maryland, New Jersey, North Carolina, Virginia, and Pennsylvania were chosen to represent the range of rural and urban locations. The report is provided as Appendix MARAMA; here we outline a number of major findings [*Gillespie and Davis,* 2006].

The speciation monitoring network provides data helpful for assessing the impacts of emissions reduction programs such as CAIR. The interannual variability of the data is great, but long-term trends can be useful. Organic matter and sulfate were the largest contributors to PM2.5 mass at all sites for the period from September 10, 2001 to October 12, 2003. Estimates of the OM/OC ratio used to convert direct measurements of organic carbon into estimates of the mass of organic aerosol have risen in recent years as research scientists improve the measurement of organic aerosols in the atmosphere. These higher OM/OC ratios increase the amount of mass attributed to organic species. When an OM/OC ratio of 1.6 is used, organic matter was the largest contributor to PM2.5 mass at seven of the eleven sites analyzed. Sulfate was the largest average contributor to PM2.5 mass at the other four sites. When the mass of ammonium is added to the sulfate, ammonium sulfate or ammonium bisulfate dominates the mass at all sites. Sulfate concentrations reached highest levels in the summer, were often episodic in nature, and correlated well with ammonium concentrations. The regional average sulfate concentration, 2001-2003 was 5.11 $\mu g\ m^{-3}$. Annual average sulfate values ranged from a high of 6.12 $\mu g\ m^{-3}$ in Arendtsville, PA to a low of 4.11 $\mu g\ m^{-3}$ in Kinston, NC.

The organic carbon mass concentration, averaged regionally over 2001-

2003 was 5.41 µg $m^{-3}$. Average organic material levels ranged from a high of 6.93 µg $m^{-3}$ in Elizabeth, NJ to a low of 3.63 µg $m^{-3}$ in Dover, DE. At most sites, organic carbon mass concentrations were highest in summer and lowest in the spring. More needs to be known about organic aerosols, since they constitute a large part of total PM2.5 mass in the MARAMA Region. It remains to be shown whether the organic aerosols result from anthropogenic or biogenic emissions, and what constituents and processes are important to secondary organic aerosol formation.

Over the entire region, nitrate species made a much smaller contribution to PM2.5 mass than organic carbon or sulfate. The regional average nitrate concentration for the period 2001-2003 was 1.76 µg $m^{-3}$, ranging from a high of 2.48 µg $m^{-3}$ in Wilmington, DE to a low of 0.94 µg $m^{-3}$ in Charlotte, NC. As was seen in the prior analysis, nitrate concentrations peaked in the winter due to the thermodynamics of ammonium nitrate formation. The southern part of the MARAMA Region showed lower average nitrate concentrations and higher average nitrate concentrations occurred in northern areas.

Ammonium makes a small, but nontrivial contribution to PM2.5 mass. The regional average ammonium concentration over 2001-2003 was 2.01 µg $m^{-3}$ and fairly uniform across the MARAMA Region, ranging from a high of 2.36 µg $m^{-3}$ in Arendtsville, PA to a low of 1.51 µg $m^{-3}$ in Kinston, NC. In several cases, urban sites showed higher ammonium concentrations than rural sites.

Elemental carbon concentrations, generally small relative to other PM2.5 mass constituents, are none-the-less important from a human health perspective because of the toxic or mutagenic nature of EC. The regional average elemental carbon concentration over 2001-2003 was 0.75 µg $m^{-3}$, ranging from a high of 1.82 µg $m^{-3}$ in Elizabeth, NJ to a low of 0.36 µg $m^{-3}$ in Kinston, NC. Higher EC concentrations occurred in urban sites and lower concentrations in rural areas.

Back trajectories analyses yielded results similar to those shown in Appendix WFR – on days when PM2.5 concentrations were low air originated in relatively “clean” areas in western or central Canada and showed reflected high wind speeds. Back trajectories associated with high PM2.5 concentrations, reflected air masses that spent the last five days over the continental U.S., often showing air circulating or re-circulating through air pollution source regions in the Midwest, Mid-Atlantic, Northeast South, but especially the Ohio River Valley. MARAMA also concluded that speciation data can be used to characterize air quality at a particular site and identify exceptional events such as forest fires. The speciated data generally confirm the regional nature of most haze events.

### f. Evaluation of the Observations

#### i. Comparison of Reconstructed Mass and Gravimetric Mass

The difference between the sum of the masses of the individually measured components and the directly measured mass gives an indication of the uncertainty in the measurements. Using observations from Fort Meade, *Hains et al.* (2007) compared reconstructed mass (the sum of individual species) to the gravimetrically measured total mass for two PM2.5 measurement methods (see also *Hains*, 2007). To reconstruct the PM2.5 mass, the crustal mass, organic mass and mass of all other species are added together. The crustal mass is approximated as the sum of silicon, calcium, iron and titanium multiplied by factors to account for oxygen associated with them as shown below:

$$\text{Crustal mass} = 3.73 \times \text{silicon} + 1.63 \times \text{calcium} + 2.42 \times \text{iron} + 1.94 \times \text{titanium}$$

There is debate over what factor should be used to determine the oxygen, nitrogen and hydrogen associated with organic carbon, and this factor can range from 1.2 to 2.5 (See Appendix Hains, 2007, and references therein). Hains et al. multiplied the organic carbon by a factor of 1.8 [*Rees, et al.*, 2004], because the area is highly influenced by regional sources. Both front and backup filter nitrate were included in the $DRI_F$ reconstructed mass.

Good positive correlations were obtained for the reconstructed mass from the $DRI_F$ samplers in both January and July (r = 0.94 to 0.99; see Appendix Hains, 2007, Table 6), and a good correlation was also found for $STN_S$. For July, the $DRI_F$ reconstructed PM2.5 mass overestimated the gravimetric mass by 6% while the $STN_S$ reconstructed mass underestimated the gravimetric mass by 3%. For January, using the

$STN_R$ the average measured and reconstructed mass differ by less 2%, although their correlation is not as good (r = 0.80). In January, the $DRI_F$ residuals are shifted negatively from the normal distribution, with a mode at -1 µg $m^{-3}$ or about 14%. The $STN_R$ residuals have a mode at zero and an apparent outlier, which explains the poorer correlation. There is better overlap between the $DRI_F$ and $STN_S$ residuals in July, but the $DRI_F$ residuals are still less than $STN_S$ residuals.

The policy implications of this closure study are that the measured species can account for at least 85 % of the observed PM2.5 mass, and that decreasing those major components (sulfate, organic matter, etc.) will decrease significantly the mass of PM2.5.

### ii. Statistics of Concentrations

Concentrations of pollutants in the atmosphere often follow a log-normal distribution to a reasonable approximation. If such relatively simple mathematical function can be used to describe the aerosol concentrations then some predictive properties can be expected. Fit to a log-normal distribution is also an indication of a robust data sets where few of the points lie below the detection limit (there can be no negative concentrations). Figure V-3 shows the distributions of total PM2.5 mass, sulfate, and organic matte for the Essex, MD site for the years 2001-2006.

**Table V-1.** Statistics of measurements at Fort Meade over an eight months sampling period [*Chen et al.*, 2002]. AU represents analytical uncertainty, so the last column represents the number of samples in which the concentration exceeded twice the analytical uncertainty.

| Species | Mean ± 1σ ($\mu g\ m^{-3}$) | # of samples | # of samples > 2 × AU |
|---|---|---|---|
| ***Mass*** | 13.03 ± 7.74 | 266 | 266 |
| $SO_4^{2-}$ | 4.59 ± 3.28 | 266 | 266 |
| $NO_3^-$ | 1.04 ± 1.51 | 266 | 257 |
| $NH_4^+$ | 1.75 ± 1.16 | 266 | 266 |
| EC | 1.06 ± 0.57 | 266 | 266 |
| OC | 3.11 ± 1.41 | 266 | 265 |

## Figures

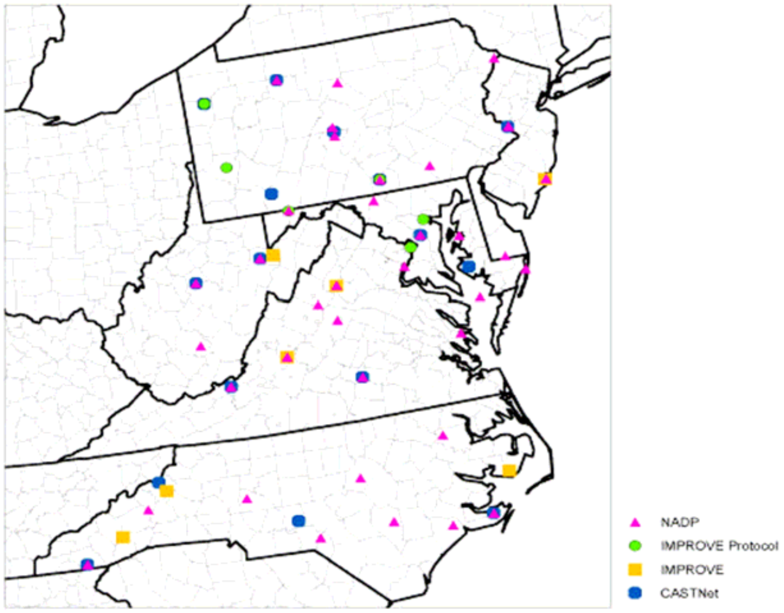


Figure V-1. Location of PM sites under IMPROVE, CASTNET, and NADP Monitoring Sites in the mid-Atlantic region.

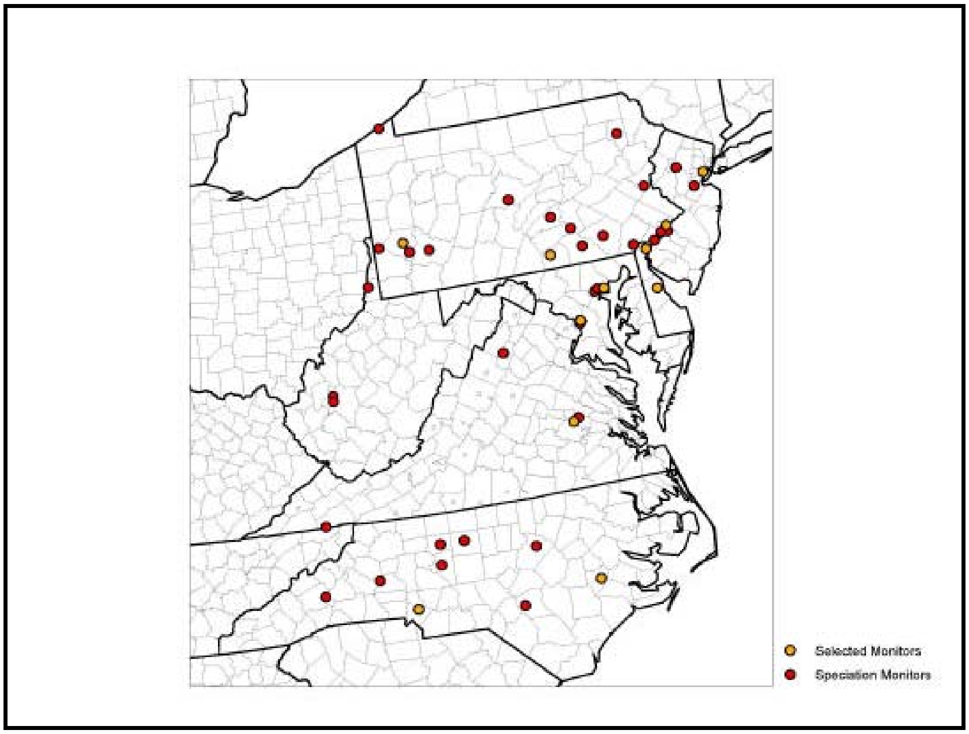


Figure V-2. State air quality operated CSN sites [*Gillespie and Davis*, 2006]; data from those marked in orange were employed in the MARAMA study.

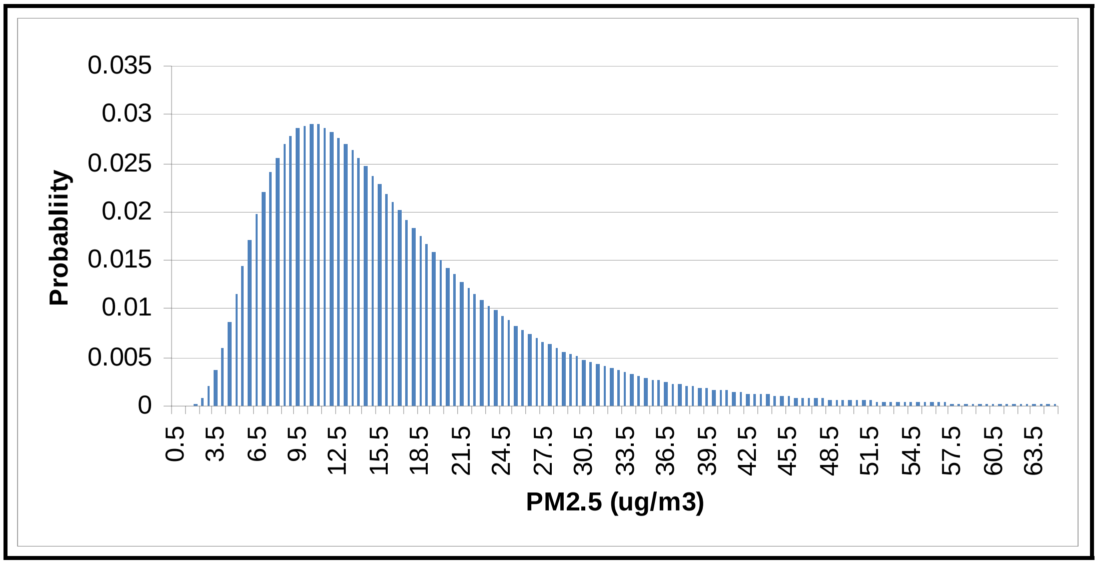


Figure V3a. Histogram of concentrations of PM2.5 measured at Essex, MD showing the log-normal distribution.

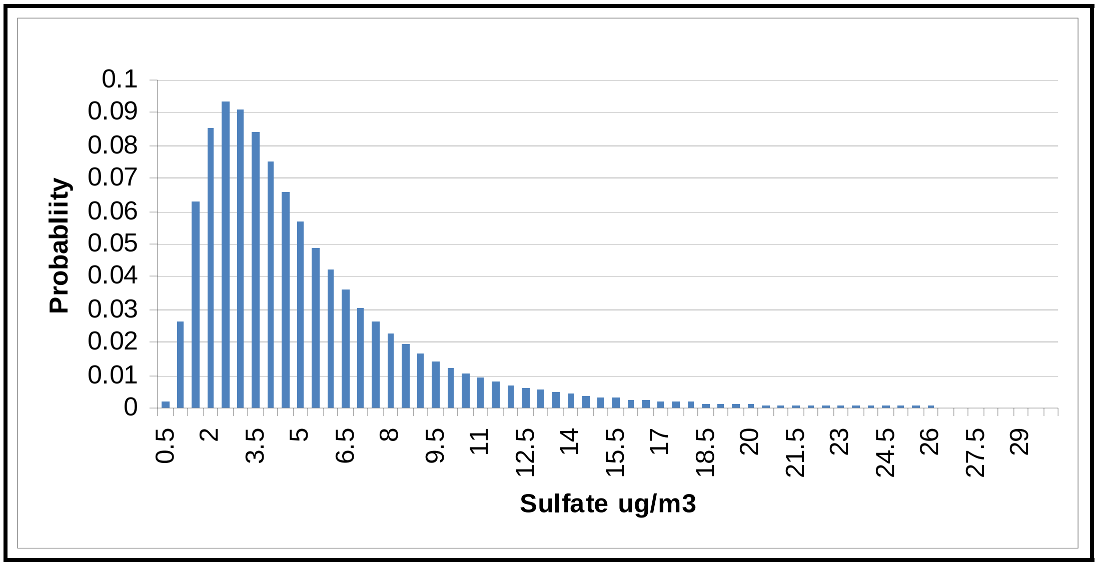


Figure V-3b. Histogram of concentrations of sulfate measured at Essex, MD showing the log-normal distribution.

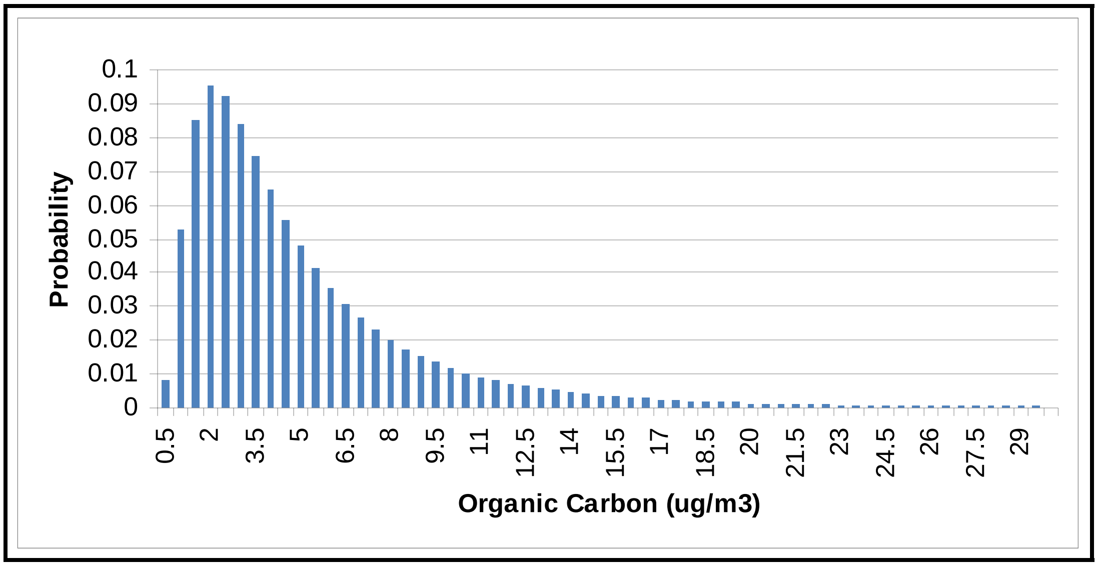


Figure V-3c. Histogram of concentrations of particulate organic carbon measured at Essex, MD showing the log-normal distribution.

## References

Chen, L.-W. A., et al. (2001), Seasonal variations in elemental carbon aerosol, carbon monoxide, and sulfur dioxide: Implications for sources, *Geophys. Res. Lett., 28*, 1711-1714.

Chen, L. W. A., et al. (2003), Analysis of a summertim PM2.5 and haze episode in the mid-Atlantic region, *Journal of the Air & Waste Management Association*, *53,* 946-956.

Chen, L. W. A., et al. (2002), Origins of fine aerosol mass in the Baltimore-Washington corridor: Implications from observation, factor analysis, and ensemble air parcel back trajectories, *Atmospheric Environment, 36*, 4541-4554.

Gillespie, W. G., and P. Davis (2006), An Analysis of Speciated PM2.5 Data in the MARAMA Region, 254 pp, Mid-Atlantic Regional Air Management Association.

Hains, J. C., et al. (2007), A Side-by-Side comparison of Filter-Based PM2.5 Measurements at a Suburban Site: A Closure Study, *Atmos. Environ.*

Kondragunta, S. (1997), The impact of aerosols on urban photochemical smog production, 245 pp, University of Maryland, College Park, College Park.

Rees, S. L., et al. (2004), Mass balance closure and the federal reference method for PM2.5 in Pittsburgh, Pennsylvania, *Atmospheric Environment*, *38,* 3305-3318.

Stehr, J. W., et al. (2000), Observations of NOy, CO, and SO2 and the origin of reactive nitrogen in the eastern United States*, J. Geophy. Res.*, *105*, 3553-3563.

## Section VI

# CMAQ PM2.5 Modeling

Dr. Dale Allen[1], Dr. Jeffrey W. Stehr[1], Patricia Castellanos[2], and Dr. Sheryl Ehrman[2]

Department of Atmospheric and Oceanic Science[1]
Department of Chemical and Biomolecular Engineering[2]
University of Maryland
College Park, MD

January 30, 2008

### 1. Why is this section important?

This analysis examines how well CMAQ simulates PM2.5 air quality over the Mid-Atlantic region. Both strengths and weaknesses of CMAQ are shown. This analysis demonstrates attainment of the PM2.5 NAAQS standard in 2009 and predicts continued decreasing PM2.5 concentrations past 2009.

### 2. What questions are answered in this section?

This analysis will answer the following questions:

a. How well are PM2.5 and its various components simulated by CMAQ?
b. What are the underlying reasons for CMAQ's shortcomings in simulating PM2.5?
c. Will future predictions of PM2.5 from CMAQ be accurate?
d. Will Maryland be in compliance with NAAQS for PM2.5 in 2009?
e. Would Maryland still be in compliance if NAAQS standards were tightened in the future?

### 3. What are the key take-away messages of this section?

The OTB/OTW (On The Books/On The Way) CMAQ modeling predicts that decreasing sulfate, volatile organic carbon, and reactive odd nitrogen emissions will bring Maryland into compliance with all applicable PM2.5 NAAQS by 2009.

### 4. What conclusions are reached in this section with respect to Maryland's attainment demonstration?

Maryland should easily be in attainment of the 2009 NAAQS for PM2.5. The highest Maryland monitor is calculated to continue to be the Old Town monitor in downtown Baltimore, but even the Old Town monitor is predicted to have a 2009 design value range of 14.0-14.4 $\mu g\ m^{-3}$, a range that is just below the lower threshold of the weight of evidence range (14.5 – 15.5 $\mu g\ m^{-3}$). In the future, it appears that Maryland will continue to make steady progress in reducing PM2.5 concentrations after the 2009 attainment deadline. Should the annual PM2.5 standard be tightened in the future, Maryland will be well positioned for continued attainment of the PM2.5 NAAQS.

## Abstract

The performance of CMAQ was examined and found to be acceptable for use in Maryland's PM2.5 attainment demonstration. This analysis will discuss and quantify all biases that are identified in the CMAQ model. In particular, for Maryland, the largest changes in any PM2.5 species are projected to occur in sulfate, and this is the one species where CMAQ's performance is at its best. Most other species show relatively more modest improvements in fine particle concentrations. CMAQ's performance is poorest for soil/crustal material and organic matter. The poor performance for soil/crustal material is only a minor concern since soil/crustal material only comprises 3-6% of PM2.5 in the Mid-Atlantic region. The underestimation of summertime organic matter concentrations by CMAQ is of more concern since organic matter is an important part of the PM2.5 budget at some Mid-Atlantic sites. Much of the bias is likely due to an underestimation of secondary organic aerosols, most of which have a biogenic source. Since changes in biogenic emissions are expected to be small over the next decade, CMAQ-calculated response factors for this term are not crucial. In addition following EPA guidance, the impact of this bias is minimized by normalizing model predicted changes in organic matter by observed PM2.5 partitioning. Therefore CMAQ's PM2.5 modeling performance is acceptable for this modeling demonstration. Biases in CMAQ and the Beyond OTB/OTW inventory used in the model are such that the calculated future design values are somewhat higher than they would likely be in reality. These calculations are therefore conservative with regard to Maryland's PM2.5 attainment or nonattainment status. PM2.5 concentrations were calculated for all Maryland monitors. Based on these calculations, Maryland will be in attainment for all applicable PM2.5 NAAQS by 2009. The highest Maryland monitor is calculated to continue to be the Old Town monitor in downtown Baltimore. This monitor is predicted to have a 2009 design value range of 14.0-14.4 µg $m^{-3}$, a range that is just below the lower threshold of the weight of evidence (WOE) range (14.5 – 15.5 µg $m^{-3}$). In the future, it appears that Maryland will continue to make steady progress in reducing PM2.5 concentrations after the 2009 attainment deadline. Should the annual PM2.5 standard be tightened in the future, Maryland will be well positioned for continued attainment of the PM2.5 NAAQS.

### a. Introduction

The Baltimore MSA (Metropolitan Statistical Area) is in violation of the annual average PM2.5 NAAQS of 15 µg/m$^3$and thus the State of Maryland is required to demonstrate attainment of the PM2.5 standard using photochemical modeling and weight of evidence analyses. The objective of this photochemical modeling study is to enable the Maryland Department of the Environment (MDE) to analyze the efficacy of various emissions control strategies, and to demonstrate that the measures adopted as part of the State Implementation Plan (SIP) will result in attainment of the PM2.5 standard in future years. The modeling exercise begins with 2002 base case emissions inventory and then emissions are grown and various emissions control measures are applied to predict future year 2009 and 2018 PM2.5 concentrations.

Under an agreement by the member States, the Ozone Transport Commission (OTC) performed the photochemical modeling study necessary to demonstrate compliance with the 8-hour ozone NAAQS and the annual PM2.5 NAAQS. The photochemical model selected for the attainment modeling demonstration was the EPA (U.S. Environmental Protection Agency) Community Multi-scale Air Quality (CMAQ) modeling system, version 4.5.1, which is a “one-atmosphere” photochemical grid model capable of addressing PM2.5 at a regional scale. The modeling analyses set forth in this report have been conducted in accordance with EPA Guidance [*EPA*, 2007].

The lead agency for coordinating the running of the CMAQ model and performing the modeling runs for the OTC was the New York State Department of Environmental Conservation (NYSDEC). Modeling centers for the OTC included NYSDEC, the University of Maryland at College Park (UMD), the Northeast States for Coordinated Air Use Management (NESCAUM), the New Jersey Department of Environmental Protection (NJDEP), and the Virginia Department of Environmental Quality (VADEQ). The lead modeling agency for coordinating CMAQ model runs for the OTC and performing the modeling runs was NYSDEC, but member states of the OTC, within the frame-work of the OTC, managed the modeling project jointly. All additional modeling for the Baltimore Non-Attainment Area (NAA) was directed by MDE and performed by UMD under contract with the MDE.

### b. Model Description

Version 3.6 of MM5 with a modified Blackadar planetary boundary layer (PBL) scheme [*Zhang and Zheng*, 2004] was used to simulate the 2002 meteorology [*Zhang and Zhang*, 2005]. The modeling domain covered the Eastern United States (U.S.), including the northeastern, central and southeastern U.S. as well as Southeastern Canada. The final SIP modeling analysis utilized this modeling domain. The OTC platform provided the basic platform for the Baltimore Nonattainment Area (NAA) modeling analysis and utilized a coarse grid continental U.S. domain with a 36 km horizontal grid resolution. The CMAQ domain is nested in the MM5 domain. A larger MM5 domain was selected for the MM5 simulations to provide a buffer of several grid cells around each boundary of the CMAQ 36 km domain. This was designed to eliminate any errors in the meteorology from boundary effects in the MM5 simulation at the interface of the MM5 model. A 12 km inner domain was selected to better characterize air quality in the Ozone Transport Region (OTR, all the states from Northern Virginia [Washington, D.C] northeast through Maine) and surrounding Regional Planning Organization (RPO) regions. The vertical grid used in the CMAQ modeling was primarily defined by the MM5 vertical structure. It consisted of 22 layers with 16 layers below ~3 km. The lowest layer was ~20 meters thick. The MM5 model employed a terrain following vertical coordinate system defined by sigma coordinates. The layer-averaging scheme adopted for CMAQ is designed to reduce the computational cost of the CMAQ simulations. Only the uppermost layers of the CMAQ domain were coalesced. All layers in the planetary boundary layer (PBL) were left undisturbed in moving from the MM5 to the CMAQ simulation. This ensures that the near-surface processes that affect air pollution the most are faithfully represented in CMAQ, while the meteorological systems that are driven by upper level winds are allowed to develop properly in MM5.

### c. Initial and Boundary Conditions

The objective of a photochemical grid model is to estimate the air quality, given a set of meteorological and pollutant emissions conditions. When initializing a model simulation, the exact concentration fields are not known in every grid cell. Therefore, typically photochemical grid models are started with clean conditions within the domain and allowed to stabilize before the period of interest is simulated. In practice, this is accomplished by starting the model several days, called spin-up time, prior to the period of interest. For this simulation, the spin-up time was 17 days. The PM2.5 simulation began December 15, 2001 and was run through December 31, 2002. The winds move pollutants into, out of, and within the domain. The model handles the movement of pollutants within the domain and out of the domain. An estimate of the concentration of pollutants at the edge of the domain, the boundary conditions, and therefore the quantity of pollutants moving into the domain is needed. The 172x172 grid point 12 km grid boundary conditions were extracted from the 149x129 grid point 36 km CMAQ simulation. To estimate the boundary conditions for the modeling study, boundary conditions for the outer 36 km domain were derived every three hours from an annual model run performed by researchers at Harvard University using the GEOS-CHEM global chemical transport model [*Baker*, 2005; *Moon and Byun*, 2004]. The influence of initial conditions was minimized by using a 17-day spin-up period, which is sufficient to establish pollutant levels that are encountered in the eastern U.S.

### d. Emissions Processing

Version 2.1 of The Sparse Matrix Operator Kernel Emissions (SMOKE) Emissions Processing System and version 3.12 of the Biogenic Emission Inventory System (BEIS) were selected for the OTC modeling analysis. SMOKE is principally an emissions processing system, and not a true emissions inventory preparation system in which emissions estimates are simulated from first principles. This means that, with the exception of mobile and biogenic sources, its purpose is to provide an efficient, modern tool for converting emissions inventory data into the formatted, hourly, mapped emissions files required for a photochemical air quality model.

All OTC modeling inventories were developed, updated, and shared among the modeling centers and were provided by the Mid-Atlantic Northeast Visibility Union (MANE-VU). Inside the OTR, the emission inventories prepared for the modeling analyses were developed through a coordinated effort between the OTR states and MARAMA. The 2002 emissions for non-OTR areas within the modeling domain were obtained from other RPOs for their corresponding areas. These RPOs included the Visibility Improvement State and Tribal Association of the Southeast (VISTAS), the Midwest Regional Planning Organization (MRPO) and the Central Regional Air Planning Association (CENRAP). These emissions were then processed by the NYSDEC using the SMOKE processor to provide inputs for the photochemical model.

### e. CMAQ Chemistry

Gas phase chemistry was simulated using the CBM-IV mechanism. Aerosol chemistry was calculated using AE3/ISORROPIA. Secondary aerosol formation was calculated using the Secondary Organic Aerosol Model (SORGAM). RADM-type aqueous chemistry was used.

PM2.5 from the CMAQ model is obtained by summing CMAQ-calculated sulfate ($SO_4$), nitrate ($NO_3$); ammonium ($NH_4$); elemental carbon (EC); other inorganic primary PM2.5 (OPP) also called crustal material (SOIL); and organic matter (OM).

$PM_{2.5}$ =

$(SO_{4i} + SO_{4j}) + (NO_{3i} + NO_{3j}) + (NH_{4i} + NH_{4j}) + (EC_i + EC_j) + (SOIL_i + SOIL_j) + OM$,

Where j and I refer to the accumulation and nucleation modes, respectively. Organic matter consists of anthropogenic secondary organic aerosols (aorga), biogenic secondary organic aerosols (aorgb), and primary organic matter (aorgp). Mathematically,

$$OM = (aorga_i + aorga_j) + (aorgb_i + aorgb_j) + 1.167 * (aorgpa_i + aorgpa_j).$$

The constant 1.167 is the ratio between the molecular weight of $CH_2$ and C and is used because the molecular weight of most primary organic matter has the form $C_nH_{2n}$.

### f. Comparison of 2002 Base Case to Ground-Based Observations

Canadian forest fires impacted northeast U.S. air quality during the July 6 – 9, 2002 time frame. Since these fires were unusual and particulate matter emissions from these files were not included in the CMAQ simulation, this comparison does not include the July 6-9 time period. In addition, the EPA has determined that ozone and PM2.5 measurements from this period should not be used when calculating baseline design values.

Mean concentrations of CMAQ-calculated and observed PM2.5 are compared in Figure VI- 1. When averaged over the year, CMAQ displays a high bias of 1-5 $\mu g\ m^{-3}$ over the eastern portion of its domain and a low bias of comparable magnitude over the western portion of its domain. The biases shown in Figure VI- 1c should not be over interpreted. FRM (Federal

Reference Method) monitors are not randomly distributed throughout the domain. They are usually placed in locations where high PM2.5 concentrations are a concern. Because of this placement-bias, spatial maps created by interpolating values at these locations are likely to overestimate the spatial extent of any PM2.5 problem. Figure VI- 1d shows CMAQ-calculated PM2.5 before interpolating to the location of monitors. PM2.5 concentrations over much of Virginia, central and western Pennsylvania, and upstate New York are much lower than in Figure VI- 1b, which was created after interpolating to the monitor sites.

Figure VI-2 a-d show that the bias has a very strong seasonal component. During the winter, CMAQ overestimates PM2.5 concentrations throughout the eastern part of the OTR+ (the OTR plus all of Virginia). In spring, 1-5 $\mu g\ m^{-3}$ eastern-domain high biases are "balanced" by western-domain low biases of similar magnitude. In summer, a low bias is seen throughout the domain approaching -15 $\mu g\ m^{-3}$ over portions of West Virginia. High biases return over the eastern part of the domain in fall.

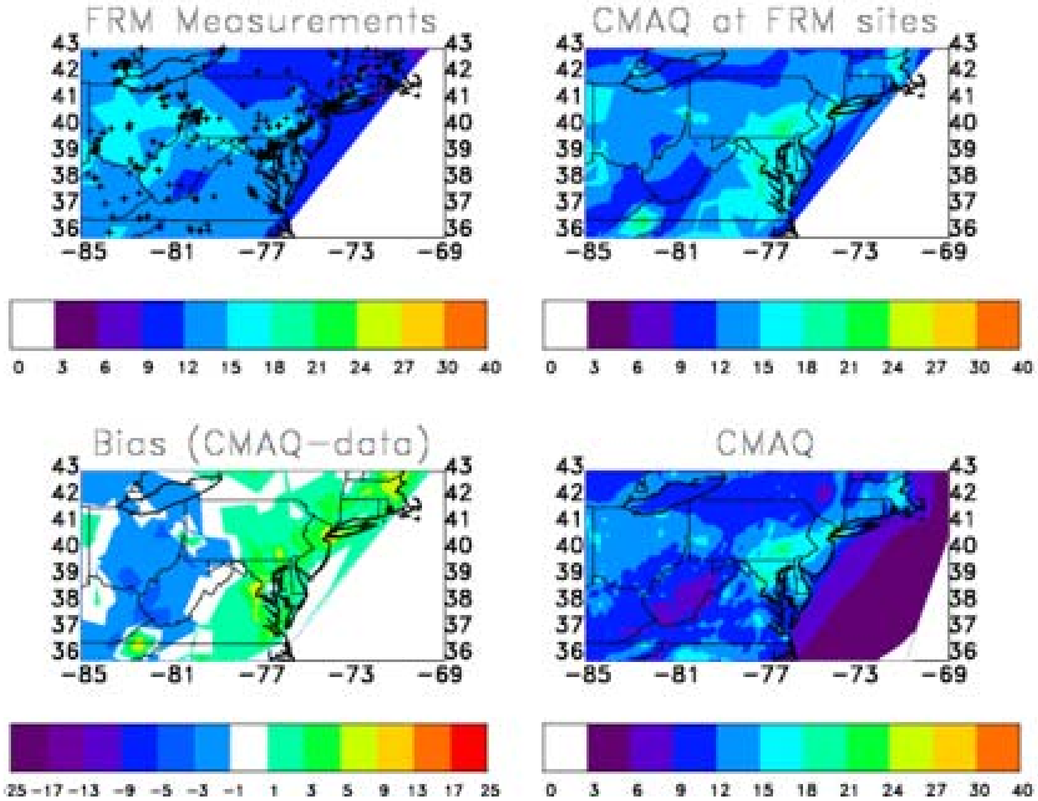


**Figure VI- 1.** Mean PM2.5 fields (µg m$^{-3}$) for January – December 2002: (a) mean of FRM monitors, (b) mean of CMAQ at the locations of FRM monitors on days when measurements are available, (c) bias between CMAQ model and FRM monitors, and (d) mean of CMAQ averaging over all grid boxes and dates. Locations of FRM monitors are shown with '+'s. July 6-9 not included in annual average.

The strong seasonal component of this bias is also evident in Figures VI-3 a-b, which compare monthly-average CMAQ-calculated and measured PM2.5 concentrations over the OTR+ region and Maryland, respectively. Measurements show a bimodal distribution with a strong summertime peak, especially over Maryland and a weaker wintertime peak. CMAQ overestimates the wintertime peak by ~6 µg m$^{-3}$ over the OTR+ region and 10 µg m$^{-3}$ over Maryland. CMAQ hints at a summertime peak over Maryland but shows no sign of a summertime peak when averages are taken over the OTR+ region.

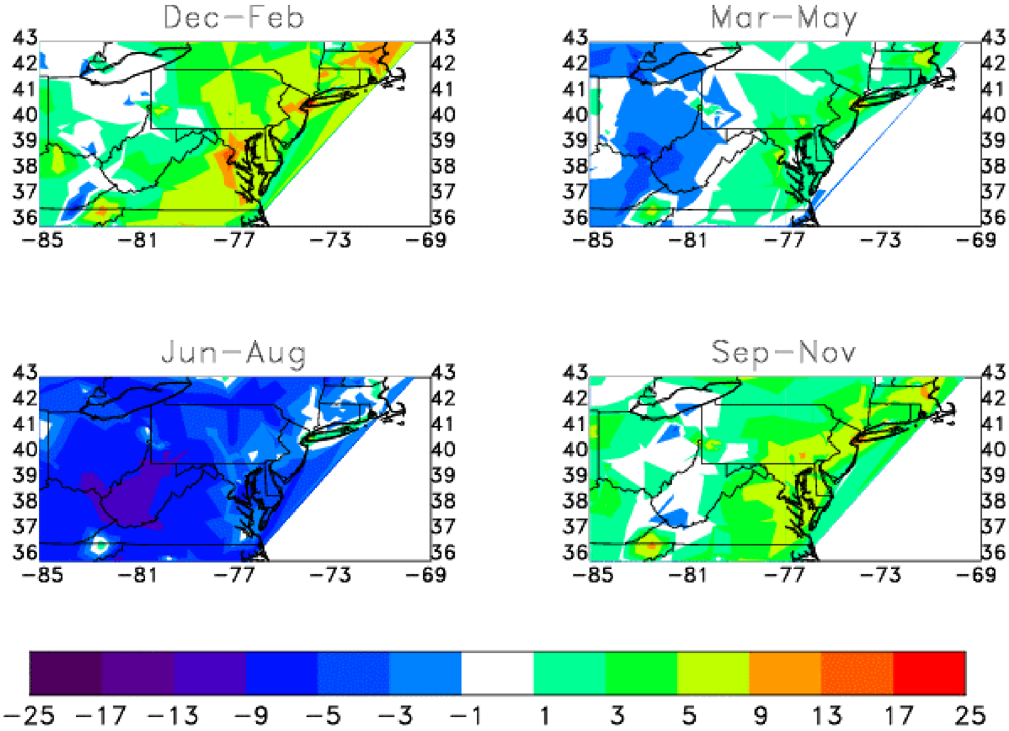


Figure VI- 2. Mean PM2.5 bias (μg $m^{-3}$). Positive (negative) values indicate that CMAQ has a high- (low-) bias: (a) December – February, (b) March-May, (c) June-August, (d) September-November.

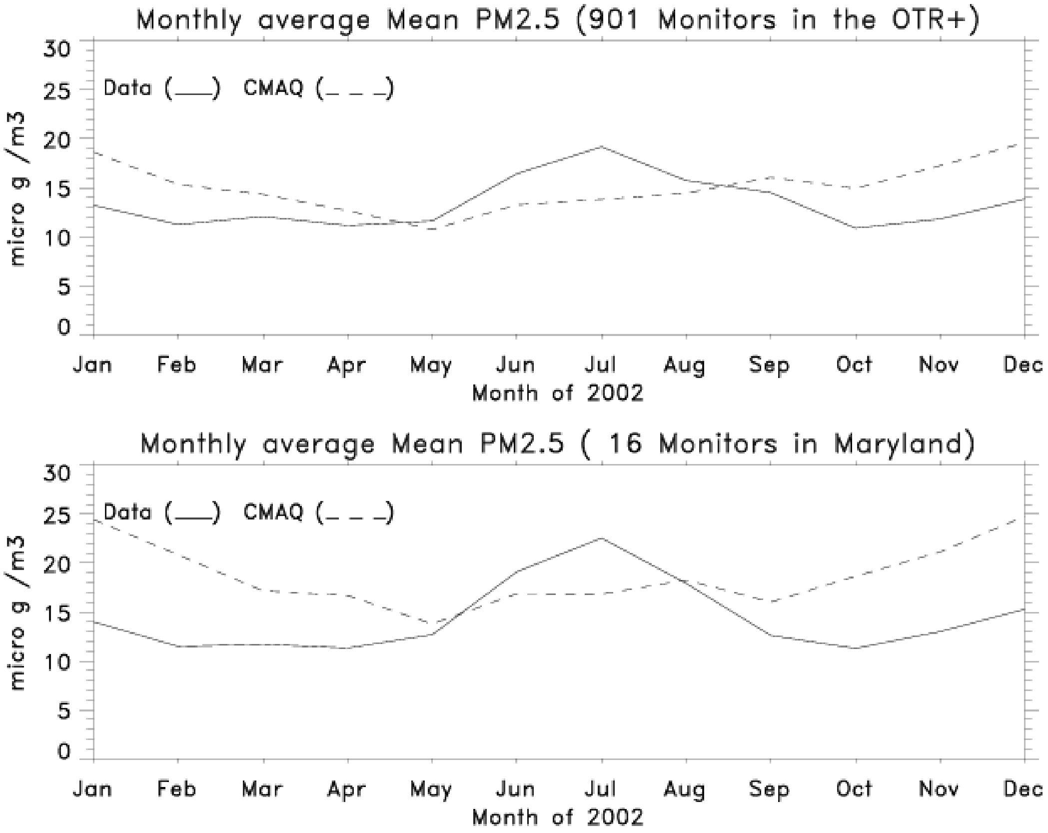


**Figure VI- 3.** Comparison of CMAQ-calculated and observed mean monthly PM2.5 (μg $m^{-3}$). Mean observed values are obtained by averaging available observations. Mean CMAQ-calculated values are obtained by sampling the model at the times and locations when measurements are available and averaging those values. Measurements are shown with a solid line, model output with a dashed line. (a) Mean of 901 monitors in the OTR+ region, (b) Mean of the 16 Maryland monitors with sufficient data to be used in the SIP analysis (Davidsonville, Ft. Meade, Glen Burnie, Riviera Beach, Edgewood, Essex, Cockeysvile/Padonia, FMC-Fairfield, Northeast Police Station, Southeast Police Station, Northwest Police Station, Old Town, and Westport, Hagerstown, Fair Hill, and Rockville).

The contribution of various PM2.5 components to the seasonal cycle in PM2.5 at OTR+ sites (all those in the OTR+ region) and at Maryland+ (McMillan Reservoir [site ID 1100100435], Washington, D.C.; Fort Meade, MD [site IDs 2400300195 and 2400300196]; and Essex, MD [site IDs 2400530015 and 2400530016]) sites can be seen in Figure VI- 4 and Figure VI- 5, respectively. Measurements indicate that sulfate and organic matter are the most important components, with a sizeable contribution from ammonium (~2 μg $m^{-3}$) throughout the year and nitrate (2-4 μg $m^{-3}$) during the winter. Sulfate is very well simulated by the model. The seasonal cycle is captured and biases in monthly average PM2.5 are usually less than 1 μg $m^{-3}$. Organic matter (OM) measurements at OTR+ sites and at Maryland+ sites show a peak of 6-7 $\mu g\ m^{-3}$ during the summer and a smaller peak of 4-6 $\mu g\ m^{-3}$ during the winter. The summertime peak in observed OM is usually attributed to secondary organic aerosols. CMAQ misses the summertime peak in organic matter at OTR+ and Maryland+ sites. CMAQ captures the smaller wintertime peak, although that peak is overestimated at the Maryland+ sites. Nitrate measurements at OTR+ sites and at Maryland+ sites show wintertime peaks and summertime minima, as expected from nitrate's thermal decomposition at high temperatures. CMAQ captures the seasonal nitrate cycle but overestimates its amplitude. CMAQ-calculated nitrate concentrations are 1-2 $\mu g\ m^{-3}$ too high during the winter season. CMAQ-calculated ammonium concentrations are reasonably well simulated throughout the year, differing from measurements by less than 1 $\mu g\ m^{-3}$, although the model misses a weak summertime peak. CMAQ-calculated elemental carbon (EC) concentrations show a high bias of ~1 $\mu g\ m^{-3}$ throughout the year. CMAQ-calculated concentrations of soil/crustal material are too high throughout the year, but especially in the winter when biases of 3 $\mu g\ m^{-3}$ are typical.

Day-to-day variations in PM2.5 are moderately well simulated throughout the OTR+ region and at Maryland locations (Figure VI- 6). Averaged over the year, CMAQ has a high bias of 1.9 $\mu g\ m^{-3}$, a root mean square error after correcting for the bias (RMSc) of 4.4 $\mu g\ m^{-3}$, and a correlation coefficient of 0.61 at OTR+ locations, and a high bias of 4.7 $\mu g\ m^{-3}$, a RMSc of 7.3 $\mu g\ m^{-3}$, and a correlation coefficient of 0.65 at all Maryland locations.

Figure VI- 7a-d compare CMAQ-calculated and measured PM2.5 at the 16 Maryland sites used in the SIP analysis for the January – March (a), April – June (b), July – September (c), and October – December (d) quarters. Encouragingly, day-to-day variations in $PM_{2.5}$ within quarters are reasonably well captured by the models, with correlation coefficients of 0.68 – 0.82 between measurements and model predictions.

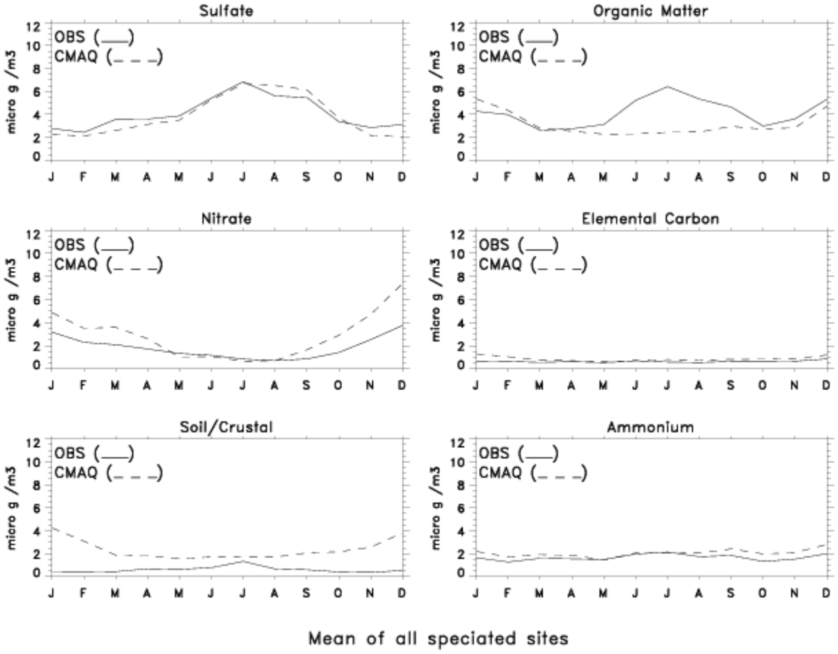


**Figure VI- 4.** PM2.5 speciation as a function of month after averaging over speciated PM2.5 monitoring locations within the OTR+ region. Observations are shown with a solid line. Model output is shown with a dashed line. Clockwise from top left: sulfate, organic matter, elemental carbon, ammonium, soil/crustal, and nitrate.

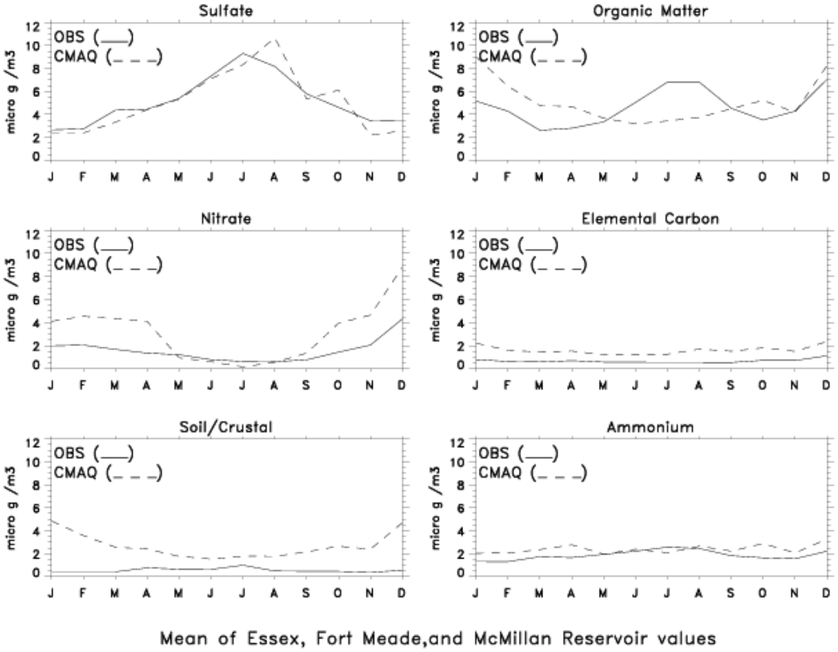


**Figure VI- 5.** Same as Figure VI- 4 but using the mean of Essex, Fort Meade, and McMillan Reservoir.

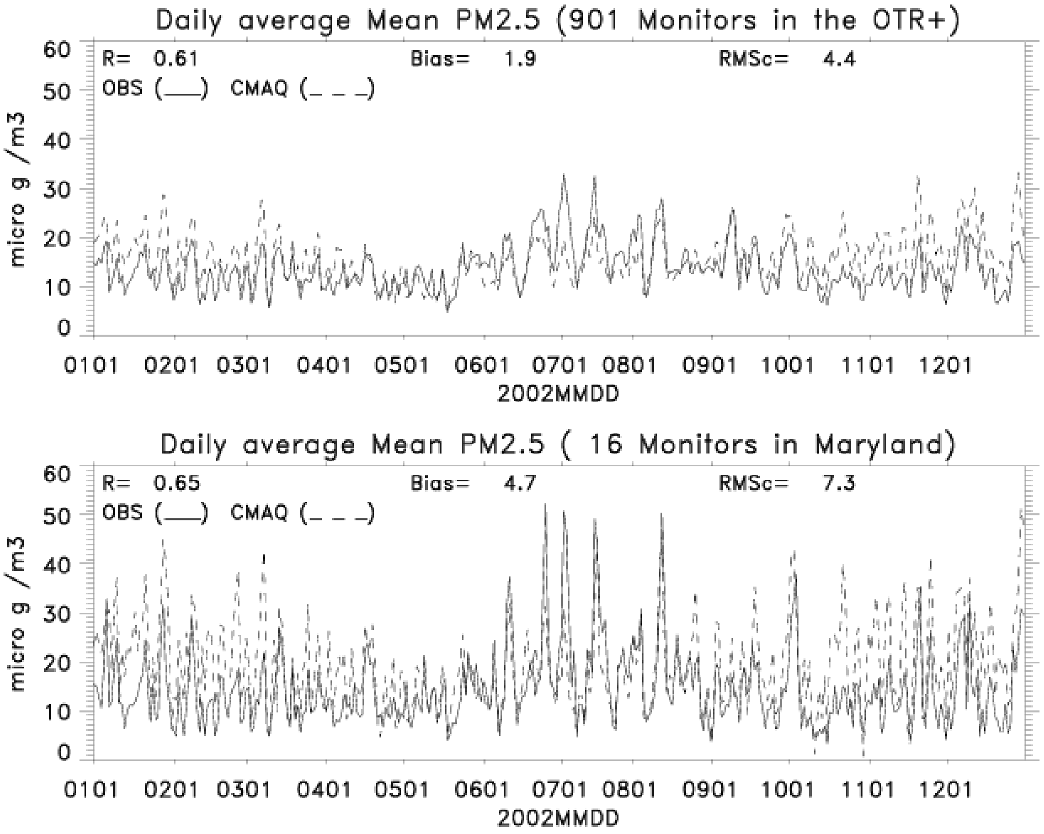


**Figure VI- 6.** Same as Figure VI-3 but for 24-hr average PM2.5 (μg $m^{-3}$). The correlation coefficient (R), bias (model – data), and the root mean square error after correcting for the bias (RMSc) are also shown. (a) Mean of all sites within the OTR+ region. (b) Mean of the 16 Maryland monitors.

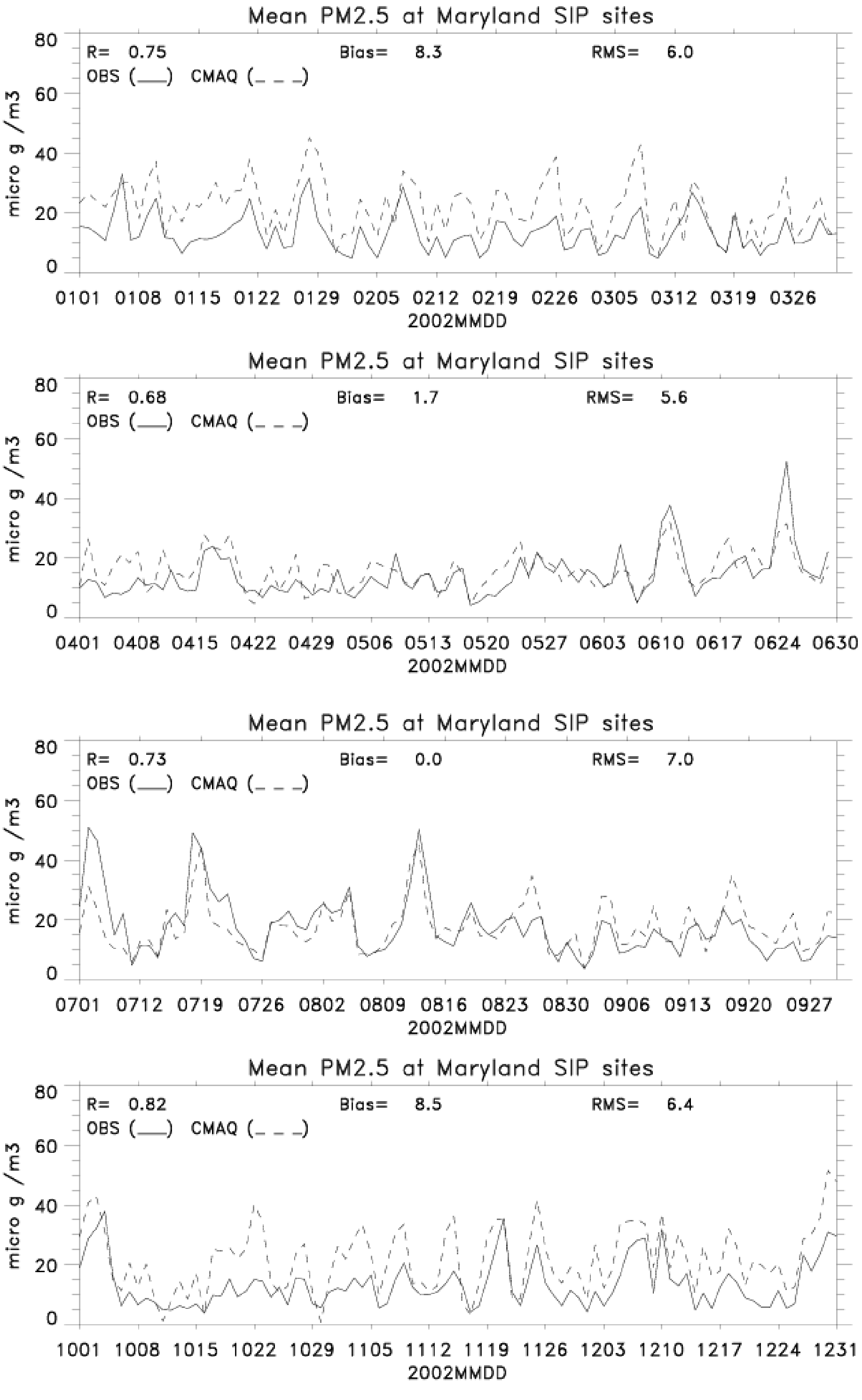


**Figure VI- 7.** Comparisons between CMAQ-calculated (dashed lines) and observed (solid lines) 24-hour average PM2.5 (μg $m^{-3}$) at the Maryland sites. (a) January – March, (b) April – June, (c) July – September (July 6-9 not included), and (d) October – December.

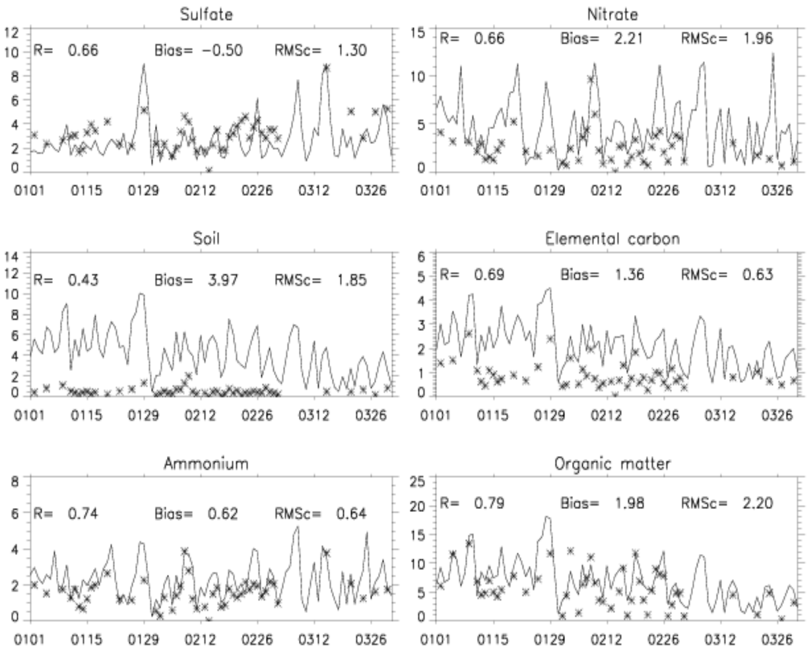


**Figure VI- 8.** Comparisons between CMAQ-calculated and observed concentrations of PM2.5 components for January 1 – March 31, 2002. Solid lines show CMAQ concentrations. Asterisks indicate measurements. Clockwise from top left: sulfate, nitrate, elemental carbon, organic matter, ammonium, and soil/crustal.

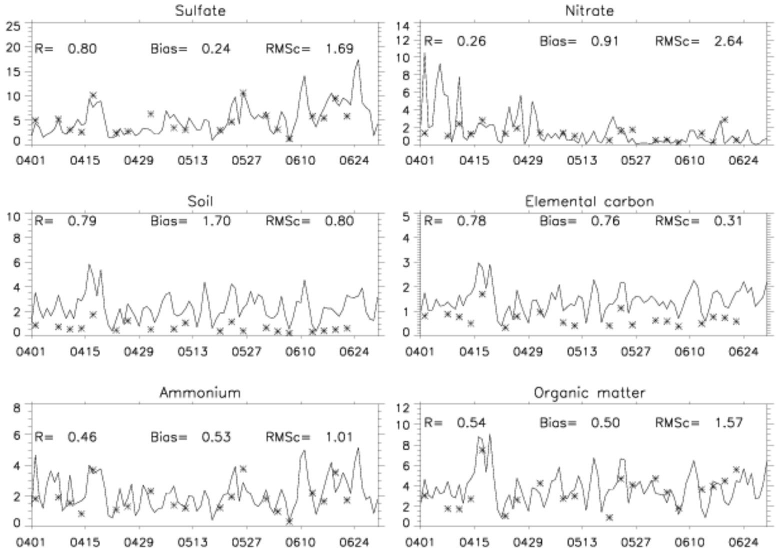


**Figure VI- 9.** Same as Figure VI- 8 but for April 1–June 30, 2002.

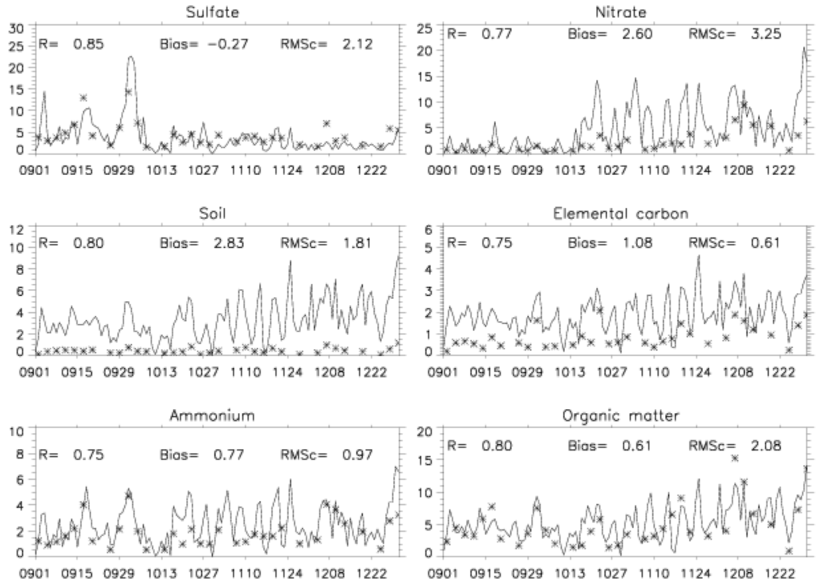


**Figure VI- 10.** Same as Figure VI- 8 but for July 1–September 30, 2002 (July 6-9 excluded).

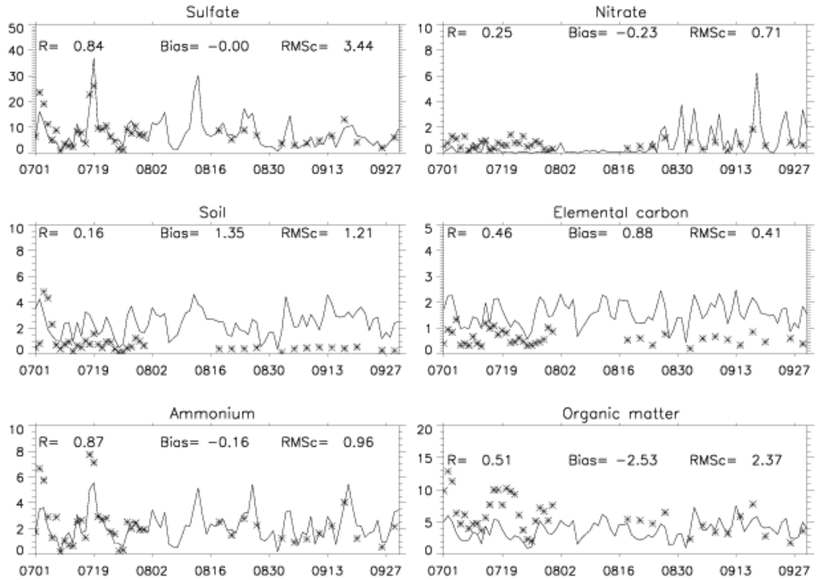


**Figure VI- 11.** Same as Figure VI- 8 but for October 1 – December 31, 2002.

Figure VI- 8 through Figure VI- 11 compare CMAQ-calculated and measured PM2.5 component time series at Essex, Maryland for each of the individual quarters. Sulfate is well simulated with quarterly correlation coefficients of 0.66 to 0.89 and quarterly biases of less than 0.5 µg $m^{-3}$. Ammonium is also well simulated by the model. With the exception of the April-June time period when measurements were scarce, correlations of 0.74 – 0.87 are seen. Biases do not exceed 0.77 μg $m^{-3}$. Day-to-day fluctuations in nitrate are fairly well captured by CMAQ during the winter when nitrate is plentiful. Correlation coefficients of 0.66 and 0.72 are seen for January-March and October-December, respectively. Although CMAQ does a poor job of simulating the seasonal cycle of organic matter, the summertime peak in particular, temporal fluctuations in organic matter within quarters are reasonably well captured with correlations ranging from 0.51 to 0.79. Elemental carbon fluctuations are moderately well simulated by CMAQ. Correlation coefficients range from 0.46 to 0.78. Temporal fluctuations in soil/crustal material are poorly simulated by CMAQ. Quarterly correlation coefficients vary from 0.16 to 0.81; however, the amplitude of daily fluctuations is greatly overestimated by CMAQ even in periods when the correlation coefficient is good (e.g., October – December).

### g. Comparisons with satellite data

*Levy* [2007] developed an improved algorithm for the calculation of optical depth ($\tau$) from the MODerate Imaging Spectrometer (MODIS). As part of his evaluation, he calculated $\tau$ from CMAQ output and compared it to MODIS-derived $\tau$. He calculated $\tau$ by integrating the extinction coefficient ($\beta_{ext}$) for each CMAQ layer over the depth of the model. CMAQ-calculated and MODIS-derived optical depth ($\tau$) on July 16, 2002 are compared in Figure VI- 12 (top panel of Figure 8.9 from *Levy* [2007]). On this fairly typical summer day, CMAQ does a good job of capturing the spatial distribution of $\tau$. Both CMAQ and MODIS show a peak in $\tau$ over Kentucky. The relative magnitude of the pollution plume is also reasonable, as $\tau$ from CMAQ is only ~20% less than $\tau$ from MODIS. Figure VI- 13 (Figure 8.10a of *Levy* [2007]) compares CMAQ-calculated $\tau$ (after averaging over a 60 km by 60 km region) with $\tau$ calculated during spirals by the UMD aircraft during the 2002 Regional Atmospheric Measurement, Modeling and Prediction Program (RAMMPP) aircraft campaign [*Taubman*, 2004; *Taubman et al.*, 2004]. When the six profiles affected by the July 6-9 Quebec forest fire episode were excluded, the slope was 0.37, with a correlation coefficient (R) of 0.45. Overall, CMAQ-calculated $\tau$ for the aircraft spirals was only ~40% of the magnitude of retrieved $\tau$.

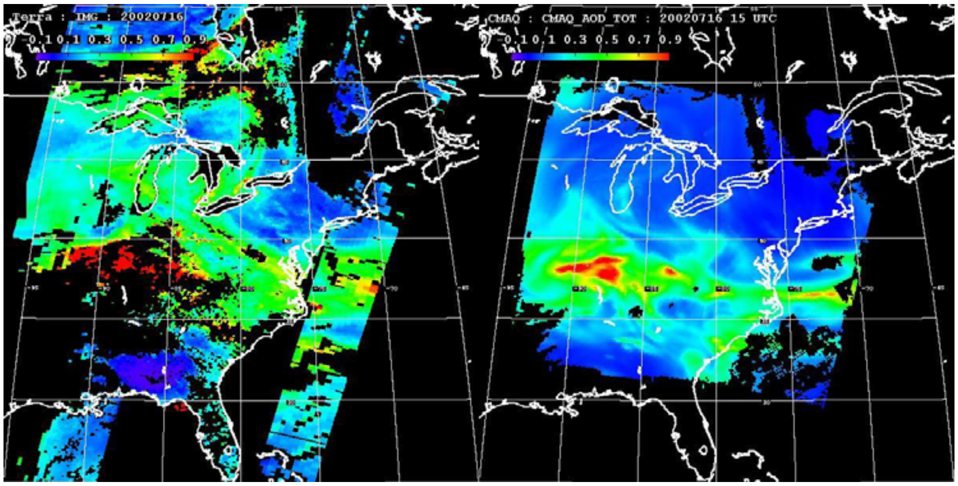


**Figure VI- 12.** Comparison of CMAQ-calculated and MODIS-retrieved τ at 0.55 μm on July 16, 2002.

### h. Implications of CMAQ Uncertainties for Model Predictions of Future Air Quality

Biases between CMAQ-calculated and measured sulfate, ammonium, and elemental carbon are small. The CMAQ model will likely represent the impact of sulfate, ammonium, and/or elemental carbon reduction programs fairly accurately.

The underestimation of summertime organic matter by CMAQ is not surprising. [*Zhang et al.*, 2007] found that version 4.4 of CMAQ underestimated summer 2001 organic carbon (the predominant component of organic matter) by 35% at eastern United States Interagency Monitoring of Protected Visual Environments (IMPROVE) sites. The organic matter low bias in this 2002 CMAQ simulation was 40-50% at OTR+ sites and 50-60% at Maryland+ sites. This low bias is not confined to CMAQ. Quoting Zhang et al., "Current regional and global air quality models tend to underestimate ambient organic matter (OM) presumably owing to incomplete treatments of SOA [Secondary Organic Aerosol] formation as well as uncertainties in the emissions of primary OM (and their atmospheric transformation) and gaseous precursors of SOA".

*Zhang et al.* [2007] reduced the CMAQ low bias by adding isoprene SOA formation to a research version of CMAQ. Zhang et al. [2007] also looked at the sensitivity of SOA formation to precursor emissions and to the SOA yield from various SOA precursors. Underestimation of SOA precursor emissions and/or yield could contribute to model-calculated low biases in organic matter.

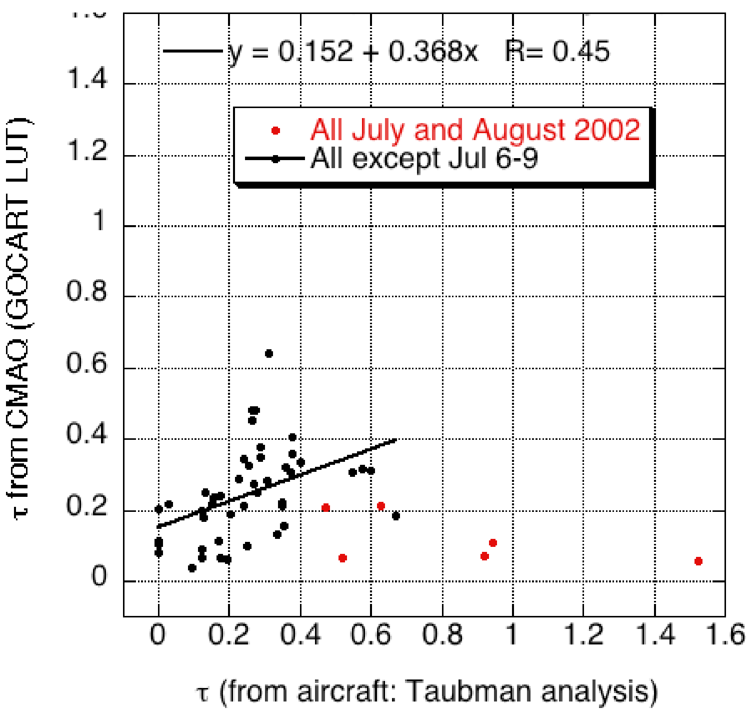


**Figure VI- 13.** Comparison of CMAQ-calculated and aircraft-derived τ from aircraft profiles. The red points are for all profiles during July-August 2002, whereas the black points (with least squares best-fit line) exclude the smoke event of July 6-9, 2002.

Improved representation of SOA formation is a challenging research topic that is beyond the scope of this discussion. The important question is: What does this CMAQ shortcoming mean for CMAQ predictions of future air quality?

CMAQ-calculated organic matter is comprised of three components. These components are primary organic matter, anthropogenic SOA, and biogenic SOA. Figure VI- 14 shows the seasonal cycle of these terms at the 16 Maryland PM2.5 sites. In contrast with OC measurements, CMAQ-calculated OM has a peak in the winter (~8 μg m$^{-3}$) and a broad minimum in the summer (~4 μg m$^{-3}$). Secondary organic aerosols account for ~10% of CMAQ-calculated OM during the winter and ~30% of CMAQ-calculated OM during the summer. Biogenic SOA is the predominant component of CMAQ-calculated SOA, especially during the summer and early fall. CMAQ-calculated summertime concentrations of anthropogenic SOA are predicted to decrease by ~20% between 2002 and 2009. CMAQ-calculated concentrations of wintertime primary organic matter are predicted to decrease by 10%. Biogenic SOA is not predicted to change significantly between 2002 and 2009. SOA formation occurs when anthropogenic and/or biogenic VOCs undergo atmospheric transformations to form oxidation products. Therefore if CMAQ, as expected, underestimates the contribution of anthropogenic SOA to total OM, it will also underestimate the benefit of VOC reduction programs on OM. The overall impact of this CMAQ shortcoming is not expected to be large but it does make CMAQ-estimates of future air quality a bit more conservative than they should be.

Observed concentrations of soil/crustal material were poorly simulated by CMAQ, making CMAQ a questionable choice for the evaluation of programs aimed at reducing soil/crustal emissions. In addition, future-year soil/crustal emissions in the Midwest RPO were grown from a different inventory than the baseline inventory. Because of this inconsistency, future-year emissions of soil/crustal material exceed baseline emissions of soil/crustal material over the Midwest portion of the CMAQ domain. Resulting 2009 concentrations of soil/crustal material exceed 2002 concentrations over a substantial portion of the CMAQ domain.

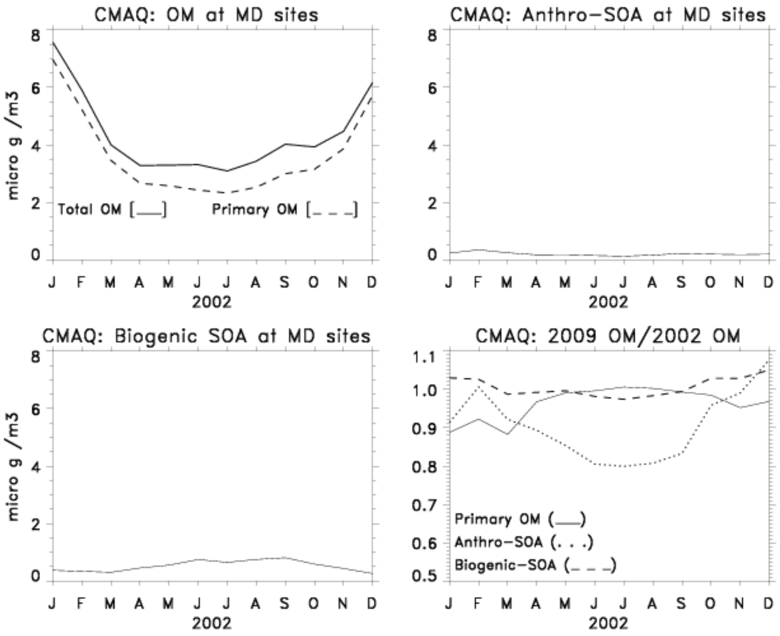


**Figure VI- 14.** Time series showing monthly variations in CMAQ-calculated organic matter at the 16 Maryland PM2.5 monitors. (a) Total organic matter (solid line) and primary OM (dashed line). Difference between solid and dashed lines gives SOA contribution to total OM, (b) anthropogenic SOA, (c) biogenic SOA, (d) relative response factors (ratio of 2009 to 2002 simulation) for organic matter components.

### i. Evaluation of 2009 Air Quality Using Results From the 2002 and 2009 CMAQ Simulations and PM2.5 Measurements

Figure VI- 15 shows the contributions of various PM2.5 species to CMAQ-calculated total PM2.5 for January 1 – December 31, 2002. Sulfate concentrations exceed 3.5 µg $m^{-3}$ over most of the domain. Peak sulfate concentrations exceed 5 µg $m^{-3}$ over portions of southwestern and southeastern Pennsylvania. Nitrate concentrations are highest over northern Ohio, southeastern Pennsylvania, northeastern Maryland, Delaware, and New Jersey. Peak nitrate concentrations exceed 5 µg $m^{-3}$ in portions of western Ohio and southeastern Pennsylvania. Organic matter and elemental carbon concentrations are highest in a corridor extending from northern Virginia to eastern Massachusetts. Organic matter concentrations peak in northern Virginia, where they exceed 5 µg $m^{-3}$. Elemental carbon concentrations are much lower, rarely exceeding 1.5 µg $m^{-3}$. Typical CMAQ-calculated concentrations for crustal material and ammonium are 1-3 µg $m^{-3}$, although ammonium concentrations approaching 3.5 µg $m^{-3}$ can be seen over portions of southeastern Pennsylvania.

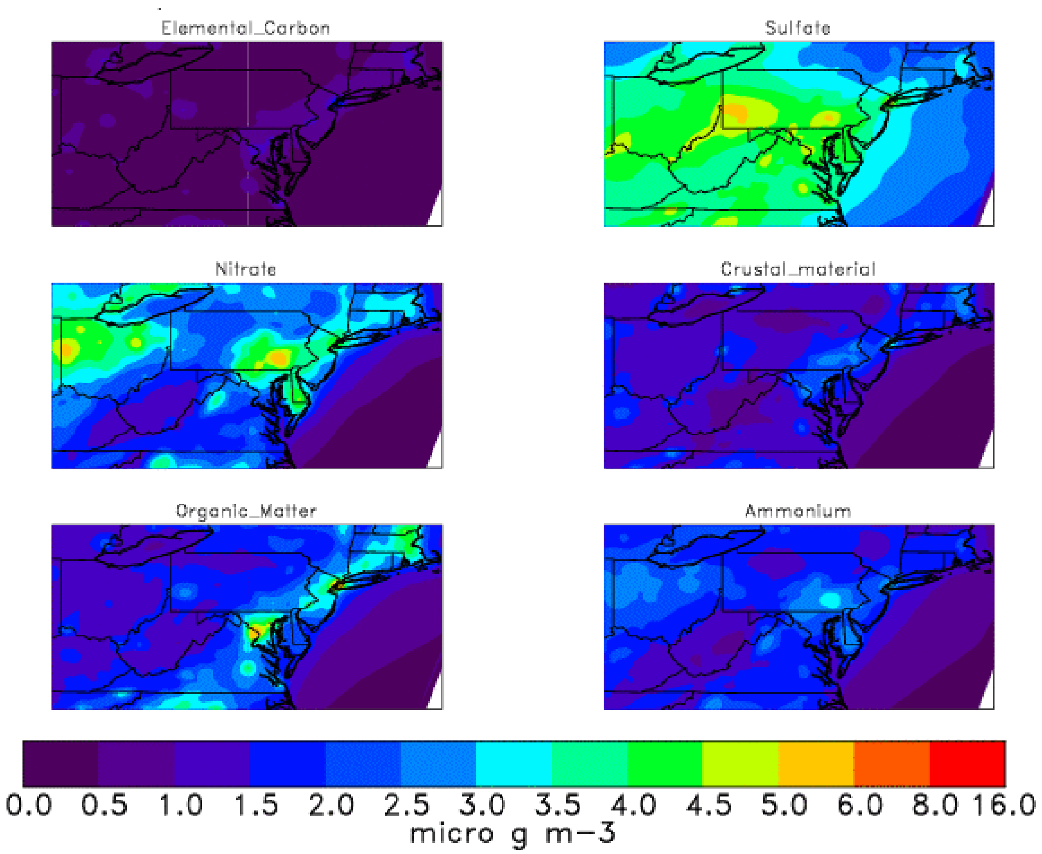


**Figure VI- 15.** CMAQ-calculated mean PM2.5 from the Base B1 simulation for January 1 – December 31, 2002 (µg $m^{-3}$) by PM2.5 species. Counterclockwise from the upper left: Elemental carbon, sulfate, crustal material, ammonium, organic matter, and nitrate.

The fractional contribution of various PM2.5 components to CMAQ-calculated total PM2.5 is shown in Figure VI- 16. Outside of New England, sulfate is the most important PM2.5 component. Its contribution approaches 50% over West Virginia and is 25-40% over much of the domain. Nitrate contributions are most important over Ohio, central Pennsylvania, and the Delmarva Peninsula. Organic matter is particularly important over Virginia, central Maryland, New Jersey, and New England. Crustal matter (5-15%) and ammonium (10-20%) contributions are relatively uniform over the domain. Elemental carbon's contribution to total PM2.5 is less than 10% throughout the domain.

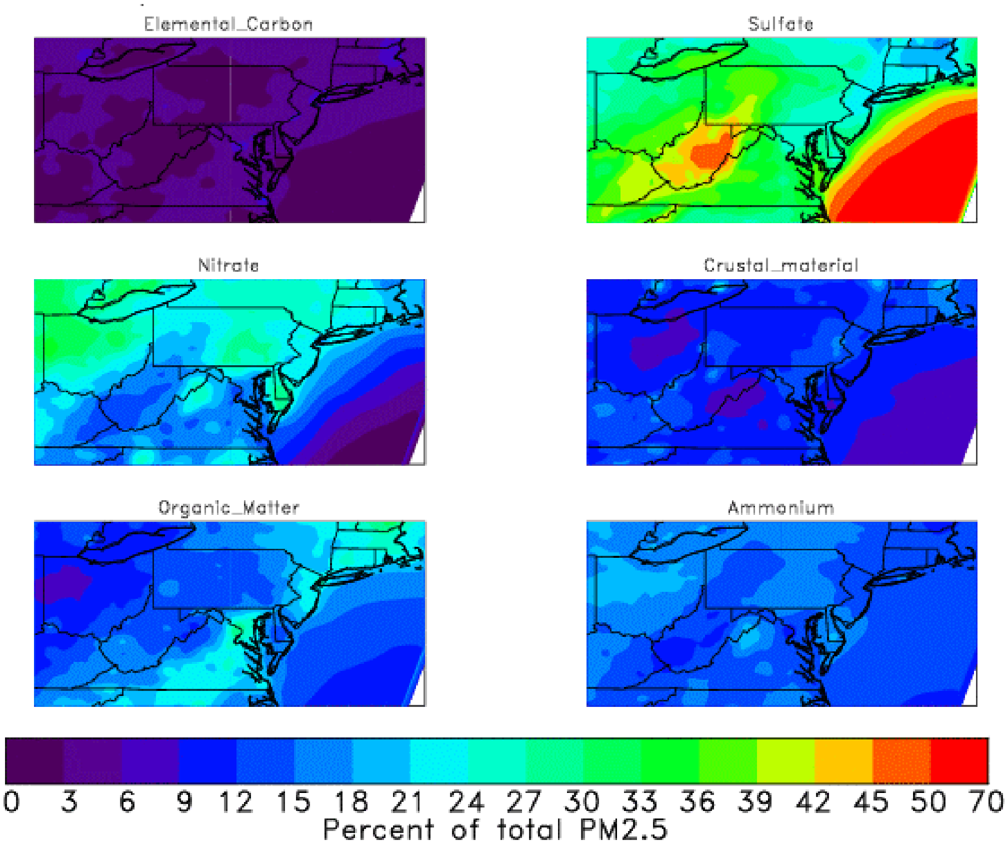


**Figure VI- 16.** CMAQ-calculated mean PM2.5 from the Base B1 simulation for January 1 – December 31, 2002 (Percent from each component). Counterclockwise from the upper left: elemental carbon, sulfate, crustal material, ammonium, organic matter, and nitrate.

The mean predicted change in PM2.5 components between 2002 and 2009 is shown in Figure VI- 17. Substantial decreases in sulfate concentrations are seen throughout the domain. As expected, decreases are largest over areas where 2002 PM2.5 concentrations were highest (compare with Figure VI- 15). Decreases of 1-2 μg $m^{-3}$ are seen at all locations outside of upstate New York and New England. Substantial decreases in nitrate, organic matter, and ammonium are also seen but only over hotspots located in northern Virginia for organic matter, western Ohio, southeastern Pennsylvania, and Delaware for nitrate, and southeastern Pennsylvania for ammonium. Predicted future values of PM2.5 are not always lower than baseline values. Organic matter concentrations increase by 0 – 0.2 μg $m^{-3}$ over Ohio, northwestern Pennsylvania, and northwestern New York. Crustal matter concentrations increase over much of the northern part of the domain with increases of 0.2-0.4 μg $m^{-3}$ common throughout Ohio, Pennsylvania, New Jersey, and northeastern Maryland.

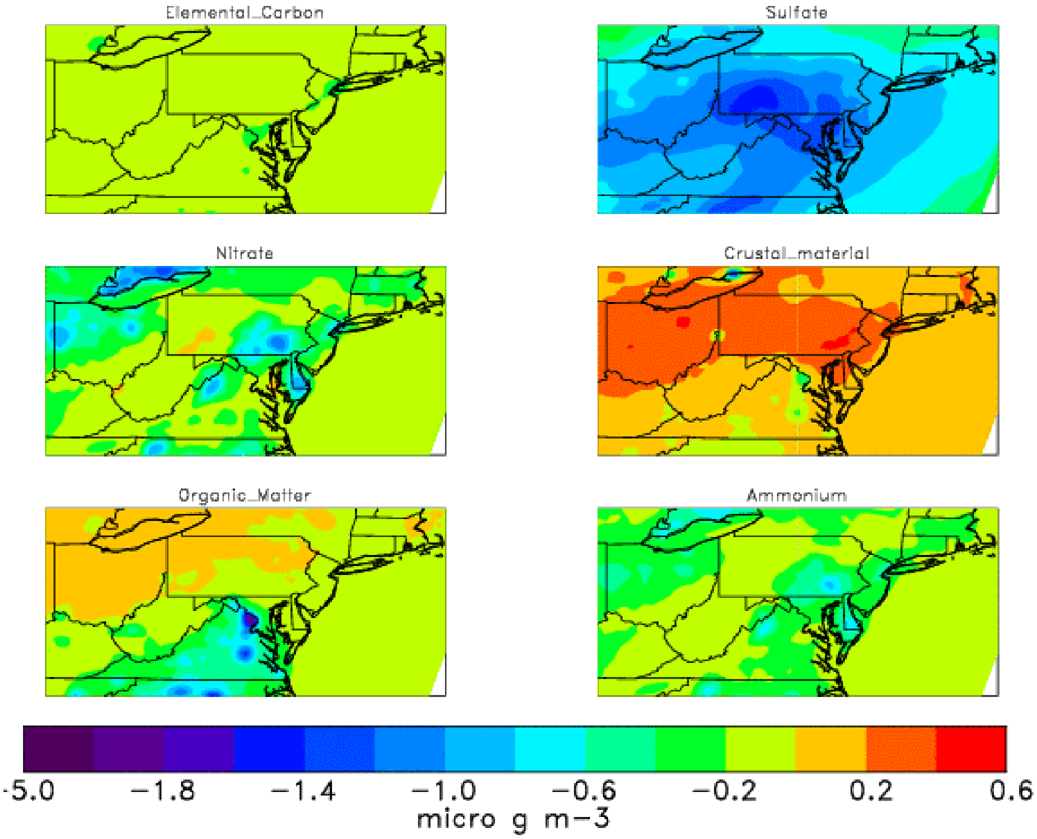


**Figure VI- 17.** CMAQ-calculated mean change in PM2.5 (Beyond On The Way (BOTW)-Base B1) [µg $m^{-3}$]. Counterclockwise from the upper left: Elemental carbon, sulfate, crustal material, ammonium, organic matter, and nitrate.

Are these calculated changes in PM2.5 sufficient to bring Maryland into compliance with the PM2.5 annual NAAQS? In order to determine this, quarterly relative response factors (RRFs) were calculated for each PM2.5 component. The quarters are 1: January – March, 2: April-June, 3: July-September, and 4: October-December. The RRFs were calculated by dividing quarterly mean PM2.5 component concentrations from a future run (2009 or 2018 in this SIP) by quarterly mean PM2.5 component concentrations from a base run (the 2002 Base B1 in this SIP). In accordance with EPA guidance, to minimize noise, a three-point north-south and east-west spatial smoother (a “Tic-Tac-Toe smoother”) was applied to model output before calculating the RRFs or to state it another way, the grid cell containing the monitor and all its nearest neighbors were averaged together before the RRFs were calculated.

Figure VI- 18 through Figure VI-24 show the spatial distribution of quarterly RRFs for total PM2.5, sulfate, nitrate, elemental carbon, organic carbon, ammonium and soil/crustal material, respectively. The predicted improvement in air quality between 2002 and 2009 has a strong seasonal component (Figure VI- 18). July-September PM2.5 concentrations decrease by 20-25% over the southern three-quarters of the domain. Springtime improvements of 10-15% are typical, although larger improvements are seen over portions of Virginia, Maryland, Pennsylvania, and Delaware. Wintertime improvements are confined to the southern portion of the domain (Virginia and portions of West Virginia and Maryland). Wintertime PM2.5 concentrations are predicted to increase slightly at some northern locations. Relative response factors for elemental carbon (Figure VI-19) show decreases throughout the domain during each quarter. Elemental carbon decreases are most pronounced during the winter season over Virginia. The overall contribution of this decrease to air quality is small, however, as elemental carbon is a relatively small fraction of total annual PM2.5 mass. Predicted decreases in sulfate between 2002 and 2009 are substantial during the summer season (Figure VI-20); July-September RRFs of 0.6-0.7 are common over much of the domain. Nitrate RRFs (Figure VI-21) have much more spatial variability than sulfate RRFs. Percent decreases in nitrate are large during the summer season when nitrate concentrations are small. Percent changes in nitrate during the winter season are slightly negative (reductions in nitrate) over the southeastern portion of the domain, but positive over much of the Ohio River Valley. Predicted changes in crustal material (Figure VI-22) are positive over most of the domain. The largest increases are predicted in the summertime over the northwestern portion of the modeling domain. Predicted changes in organic matter (Figure VI-23) also show substantial seasonal and geographic variability. Organic matter concentrations decrease over eastern Kentucky, West Virginia, and Virginia throughout the year, with the largest decreases during the winter season; Decreases of 30-45% are common over this region during the January-March quarter. Organic matter concentrations over the northern portion of the domain increase by 0-15% throughout much of the year. Substantial decreases (20-35%) in summertime ammonium are predicted during the summer season outside of the Ohio River Valley (Figure VI-24). Predicted wintertime ammonium changes are small over much of the domain, with increases over the Ohio River Valley and decreases over the southeastern portion of the domain.

Table VI- 1 and Table VI- 2 shows CMAQ-calculated 2009/2002 RRFs at FRM monitor locations within the Baltimore, MD and Washington, D.C.NAAs, respectively. CMAQ-calculated 2009/2002 RRFs at Maryland locations within the Hagerstown, MD/Martinsburg NAA WV and at Maryland's Fair Hill monitor are shown in Table VI- 3 and Table VI- 4, respectively. Overall, both the Baltimore and Washington, D.C. NAAs are predicted to show a decrease in PM2.5 concentrations. When comparing both the Baltimore and Washington, D.C. PM2.5 concentrations, the most striking difference occurs during January – March when the mean PM2.5 RRF for the Baltimore NAA is 0.94 and the Washington, D.C. RRF is 0.83. Differences in predicted elemental carbon and soil contribute to this difference but the main reason is large differences in predicted organic matter changes (0.69 RRF for Washington, D.C. and 0.91 RRF for Baltimore). Predicted changes in sulfate (30-40% decrease during the summer and 10-17% decrease in winter), nitrate (15-20% decrease during the summer and 3-5% decrease during the winter), and ammonium (20-25% decrease during the summer and ~5% decrease during the winter) do not vary much between the Baltimore and Washington, D.C. NAAs.

Relative response factors are also needed for particle bound water (PBW). PBW is a measure of the mass of water bound to hygroscopic PM2.5 components such as ammonium, sulfate, and nitrate. PBW was not calculated by CMAQ so it is not possible to determine its RRF by taking ratios between future and current CMAQ-calculated PBW concentrations. In this analysis, the RRF for PBW is assumed to have a lower bound equal to the measurement mass weighted mean of the quarterly RRFs for sulfate, nitrate, and ammonium and an upper bound of 1.

Relative response factors for soil/crustal material are greater than one over much of the domain. This counterintuitive result is likely an artifact of the fact that future year soil emissions in the Midwest RPO were grown from a different inventory than the baseline inventory. Since there is little reason to expect future concentrations of soil/crustal material to differ from present-day concentrations, the RRF for crustal material was set to one when calculating future design values.

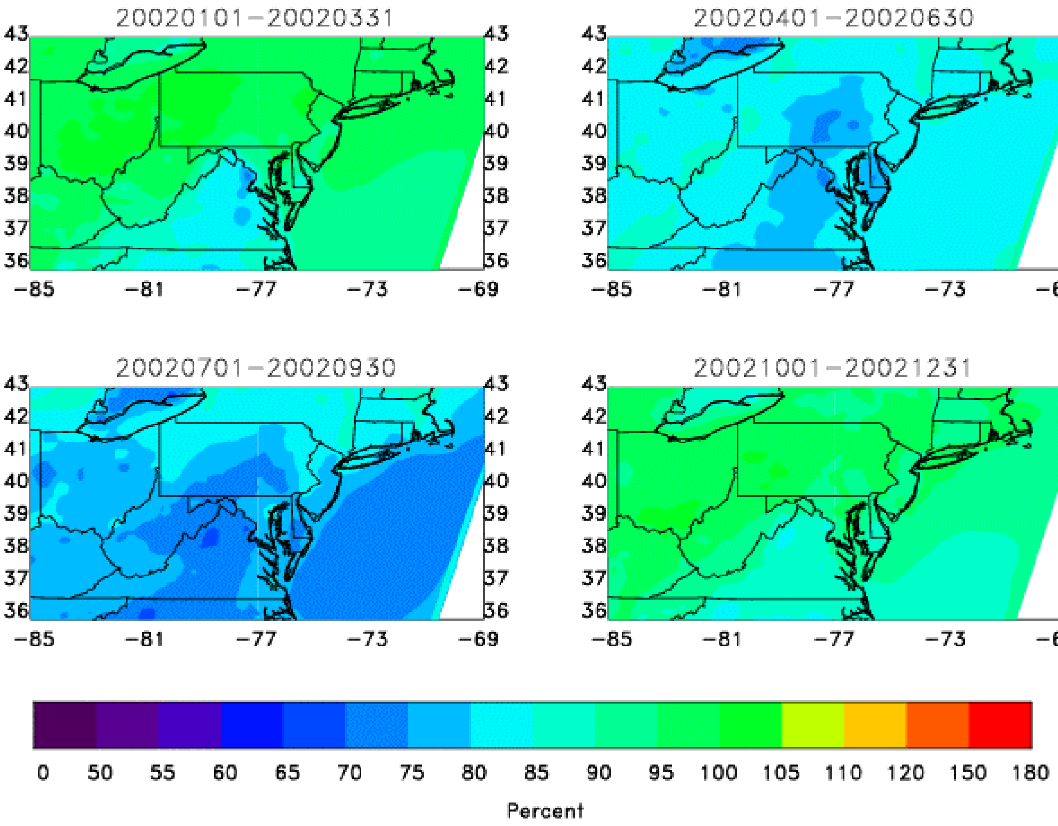


**Figure VI- 18.** Seasonal variation of CMAQ-calculated Relative Response Factor (RRF) for PM2.5. The RRF is calculated by dividing the mean PM2.5 concentration from the BOTW simulation by the mean $PM_{2.5}$ concentration from the Base B1 simulation and multiplying by 100.

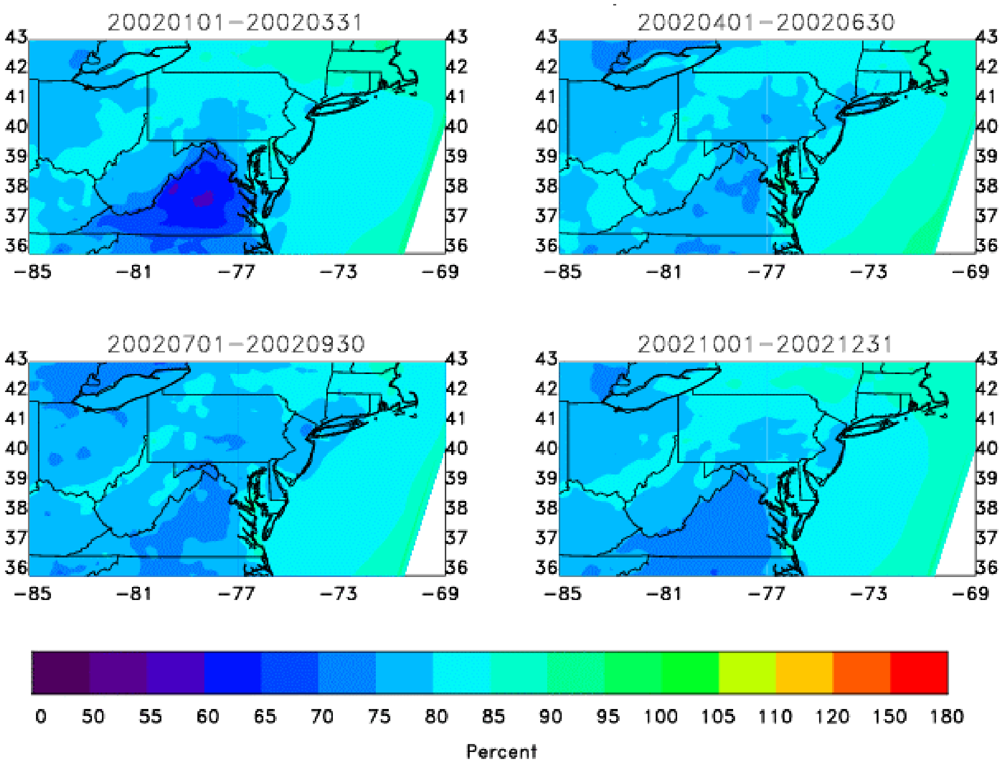


Figure VI- 19**.** Same as Figure VI- 18 but for elemental carbon.

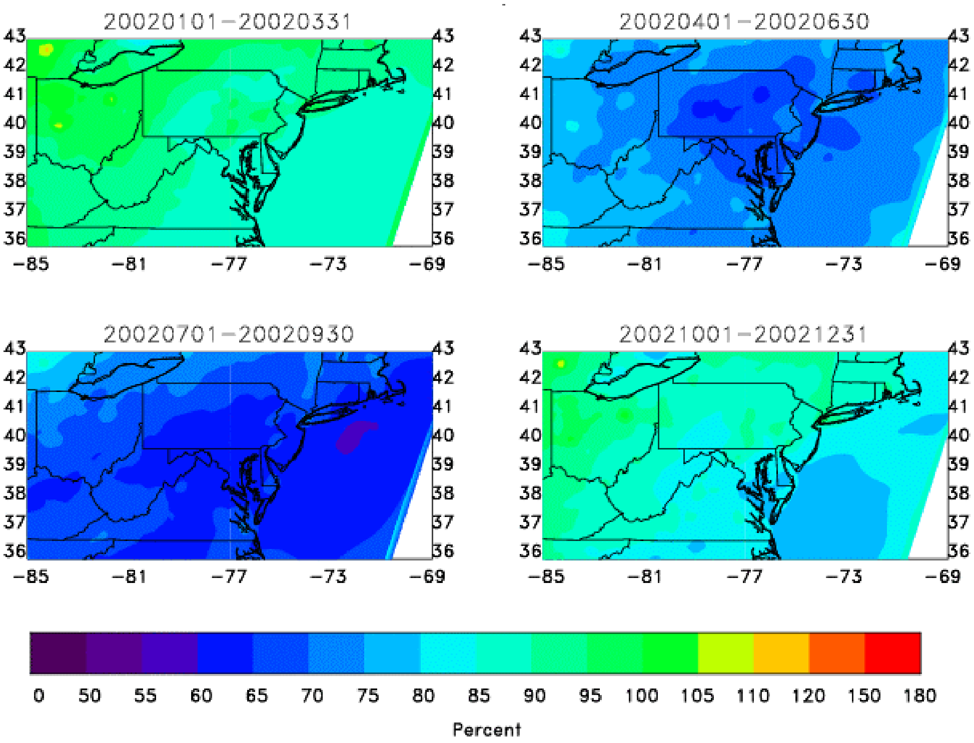


Figure VI- 20**.** Same as Figure VI- 18 but for sulfate.

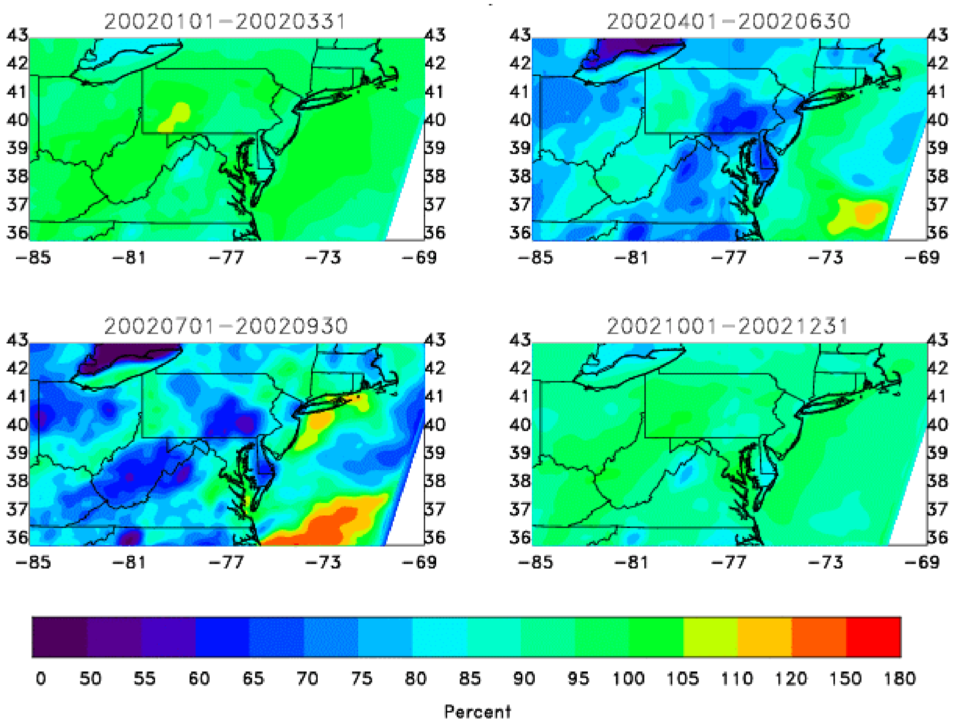


Figure VI- 21**.** Same as Figure VI- 18 but for nitrate.

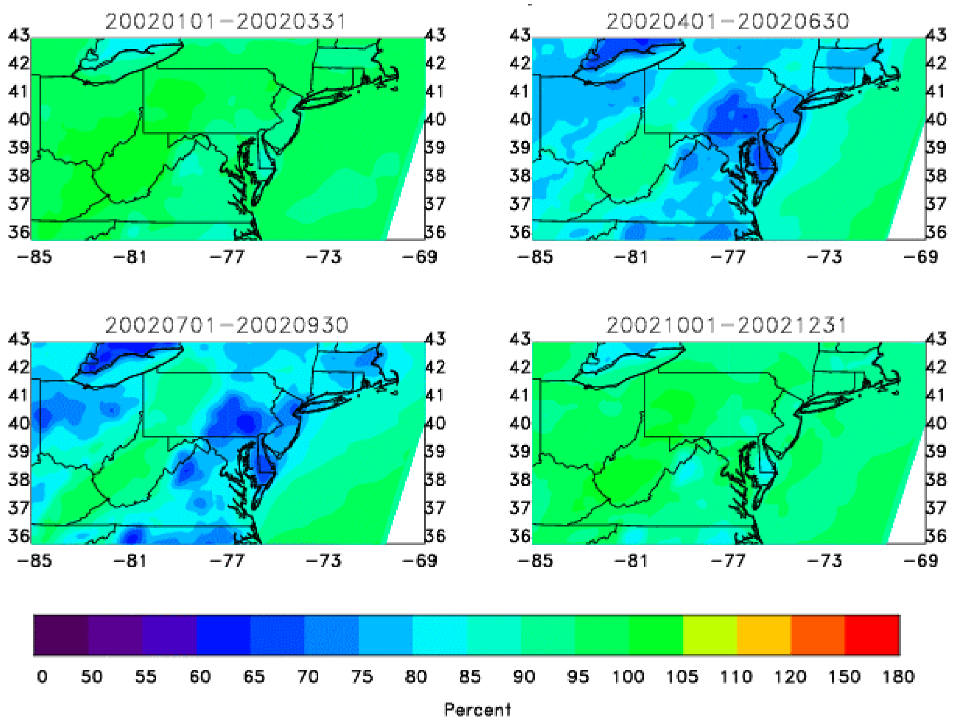


Figure VI- 22**.** Same as Figure VI- 18 but for soil/crustal material (OPP).

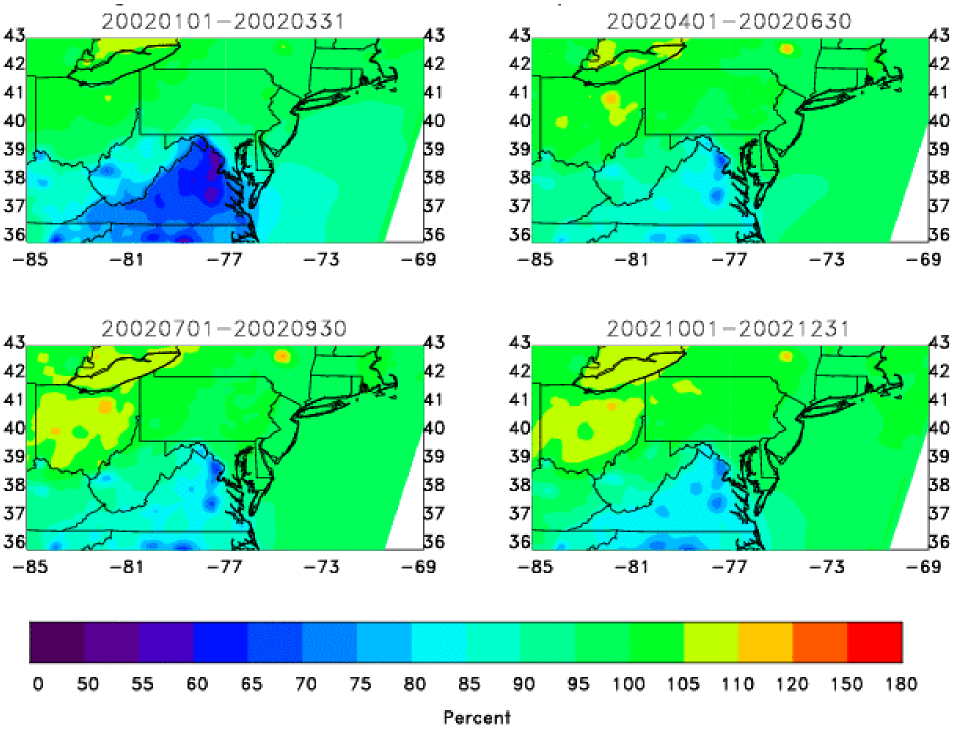


Figure VI- 23. Same as Figure VI- 18 but for organic carbon (matter).

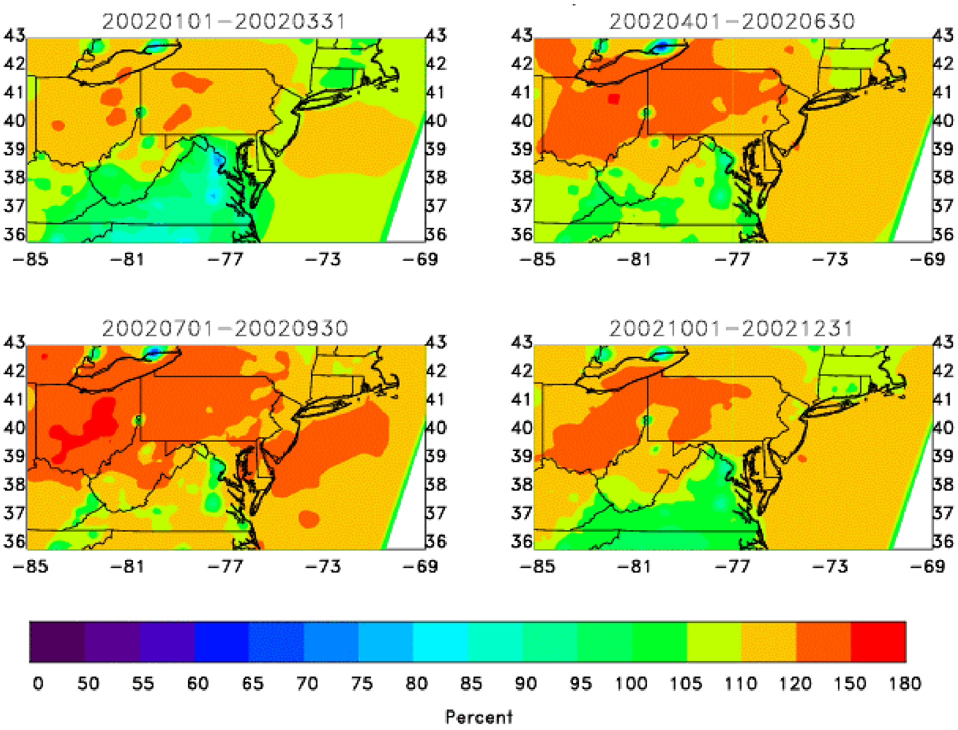


Figure VI- 24. Same as Figure VI- 18 but for ammonium.

**Table VI- 1.** Quarterly CMAQ-calculated 2009/2002 relative response factors (RRFs) for PM2.5 components at PM2.5 FRM monitors within the Baltimore Nonattainment Area (NAA).

| Site Name | Quarter | PM2.5 | EC | $SO_4$ | $NO_3$ | SOIL | OM | $NH_4$ | PBW | NAA |
|---|---|---|---|---|---|---|---|---|---|---|
| Davidsonville | JFM | 0.93 | 0.79 | 0.88 | 0.98 | 1.02 | 0.88 | 0.95 | 0.92 | Balt. |
| 240030014 | AMJ | 0.82 | 0.79 | 0.67 | 0.80 | 1.12 | 0.97 | 0.76 | 0.69 | |
| | JAS | 0.80 | 0.78 | 0.62 | 0.91 | 1.18 | 0.98 | 0.80 | 0.64 | |
| | OND | 0.95 | 0.80 | 0.81 | 0.99 | 1.10 | 0.97 | 0.96 | 0.88 | |
| Fort Meade | JFM | 0.92 | 0.78 | 0.89 | 0.96 | 1.02 | 0.89 | 0.94 | 0.91 | Balt. |
| 240030019 | AMJ | 0.82 | 0.78 | 0.68 | 0.78 | 1.12 | 0.97 | 0.75 | 0.69 | |
| | JAS | 0.80 | 0.77 | 0.62 | 0.87 | 1.17 | 0.98 | 0.78 | 0.64 | |
| | OND | 0.95 | 0.79 | 0.82 | 0.96 | 1.10 | 0.97 | 0.95 | 0.88 | |
| Glen Burnie | JFM | 0.94 | 0.80 | 0.90 | 0.96 | 1.04 | 0.91 | 0.95 | 0.92 | Balt. |
| 240031003 | AMJ | 0.83 | 0.79 | 0.69 | 0.81 | 1.11 | 0.98 | 0.77 | 0.70 | |
| | JAS | 0.81 | 0.78 | 0.62 | 0.90 | 1.15 | 0.99 | 0.80 | 0.65 | |
| | OND | 0.96 | 0.80 | 0.83 | 0.97 | 1.10 | 0.98 | 0.96 | 0.89 | |
| Riviera Beach | JFM | 0.95 | 0.81 | 0.89 | 0.98 | 1.05 | 0.91 | 0.96 | 0.93 | Balt. |
| 240032002 | AMJ | 0.84 | 0.82 | 0.69 | 0.83 | 1.11 | 0.98 | 0.77 | 0.71 | |
| | JAS | 0.81 | 0.81 | 0.63 | 0.92 | 1.15 | 0.99 | 0.81 | 0.65 | |
| | OND | 0.96 | 0.82 | 0.82 | 0.99 | 1.10 | 0.98 | 0.97 | 0.89 | |
| Edgewood | JFM | 0.96 | 0.85 | 0.89 | 0.98 | 1.08 | 0.93 | 0.96 | 0.92 | Balt. |
| 240251001 | AMJ | 0.84 | 0.85 | 0.69 | 0.78 | 1.17 | 1.00 | 0.76 | 0.70 | |
| | JAS | 0.80 | 0.84 | 0.62 | 0.80 | 1.22 | 1.02 | 0.80 | 0.65 | |
| | SON | 0.97 | 0.85 | 0.83 | 0.96 | 1.13 | 1.00 | 0.96 | 0.89 | |
| Essex | JFM | 0.96 | 0.84 | 0.90 | 0.97 | 1.06 | 0.93 | 0.96 | 0.93 | Balt. |
| 240053001 | AMJ | 0.84 | 0.84 | 0.70 | 0.80 | 1.12 | 0.99 | 0.78 | 0.71 | |
| | JAS | 0.81 | 0.83 | 0.63 | 0.85 | 1.15 | 1.00 | 0.81 | 0.65 | |
| | OND | 0.96 | 0.84 | 0.84 | 0.96 | 1.10 | 0.99 | 0.96 | 0.89 | |
| Padonia | JFM | 0.95 | 0.80 | 0.89 | 0.97 | 1.05 | 0.91 | 0.95 | 0.92 | Balt. |
| 240051007 | AMJ | 0.82 | 0.81 | 0.68 | 0.76 | 1.16 | 0.99 | 0.75 | 0.70 | |
| | JAS | 0.79 | 0.80 | 0.62 | 0.85 | 1.20 | 0.99 | 0.78 | 0.64 | |
| | OND | 0.96 | 0.82 | 0.84 | 0.94 | 1.12 | 0.98 | 0.95 | 0.89 | |
| FMC-Fairfield | JFM | 0.94 | 0.81 | 0.90 | 0.96 | 1.05 | 0.92 | 0.95 | 0.93 | Balt. |
| 245100035 | AMJ | 0.84 | 0.81 | 0.69 | 0.80 | 1.11 | 0.98 | 0.77 | 0.71 | |
| | JAS | 0.81 | 0.80 | 0.63 | 0.88 | 1.15 | 0.99 | 0.80 | 0.65 | |
| | OND | 0.96 | 0.82 | 0.84 | 0.96 | 1.10 | 0.98 | 0.96 | 0.89 | |

**Table VI- 1** (Cont.) 2009/2002 RRF for PM2.5 monitors in the Baltimore NAA

| | Quarter | PM2.5 | EC | $SO_4$ | $NO_3$ | SOIL | OM | $NH_4$ | PBW | NAA |
|---|---|---|---|---|---|---|---|---|---|---|
| NE Police St. | JFM | 0.95 | 0.82 | 0.90 | 0.96 | 1.05 | 0.92 | 0.95 | 0.93 | Balt. |
| 245100006 | AMJ | 0.84 | 0.81 | 0.70 | 0.79 | 1.12 | 0.99 | 0.77 | 0.71 | |
| | JAS | 0.81 | 0.81 | 0.63 | 0.86 | 1.15 | 0.99 | 0.79 | 0.65 | |
| | OND | 0.96 | 0.82 | 0.84 | 0.95 | 1.10 | 0.98 | 0.96 | 0.89 | |
| NW Police St. | JFM | 0.94 | 0.79 | 0.90 | 0.96 | 1.05 | 0.91 | 0.95 | 0.92 | Balt. |
| 245100007 | AMJ | 0.83 | 0.79 | 0.69 | 0.77 | 1.14 | 0.98 | 0.76 | 0.70 | |
| | JAS | 0.80 | 0.78 | 0.62 | 0.86 | 1.18 | 0.99 | 0.79 | 0.65 | |
| | OND | 0.95 | 0.80 | 0.84 | 0.94 | 1.11 | 0.98 | 0.95 | 0.88 | |
| SE Police St. | JFM | 0.94 | 0.81 | 0.90 | 0.96 | 1.05 | 0.92 | 0.95 | 0.93 | Balt. |
| 245100008 | AMJ | 0.84 | 0.81 | 0.69 | 0.80 | 1.11 | 0.98 | 0.77 | 0.71 | |
| | JAS | 0.81 | 0.80 | 0.63 | 0.88 | 1.15 | 0.99 | 0.80 | 0.65 | |
| | OND | 0.96 | 0.82 | 0.84 | 0.96 | 1.10 | 0.98 | 0.96 | 0.89 | |
| Old Town | JFM | 0.94 | 0.81 | 0.90 | 0.96 | 1.05 | 0.92 | 0.95 | 0.93 | Balt. |
| 245100040 | AMJ | 0.84 | 0.81 | 0.69 | 0.80 | 1.11 | 0.98 | 0.77 | 0.71 | |
| | JAS | 0.81 | 0.80 | 0.63 | 0.88 | 1.15 | 0.99 | 0.80 | 0.65 | |
| | OND | 0.96 | 0.82 | 0.84 | 0.96 | 1.10 | 0.98 | 0.96 | 0.89 | |
| Westport | JFM | 0.94 | 0.81 | 0.90 | 0.96 | 1.05 | 0.92 | 0.95 | 0.93 | Balt. |
| 245100049 | AMJ | 0.84 | 0.81 | 0.69 | 0.80 | 1.11 | 0.98 | 0.77 | 0.71 | |
| | JAS | 0.81 | 0.80 | 0.63 | 0.88 | 1.15 | 0.99 | 0.80 | 0.65 | |
| | OND | 0.96 | 0.82 | 0.84 | 0.96 | 1.10 | 0.98 | 0.96 | 0.89 | |
| Average | JFM | 0.94 | 0.81 | 0.90 | 0.97 | 1.05 | 0.91 | 0.95 | 0.92 | Balt. |
| N/A | AMJ | 0.83 | 0.81 | 0.69 | 0.79 | 1.12 | 0.98 | 0.77 | 0.70 | |
| | JAS | 0.80 | 0.80 | 0.62 | 0.87 | 1.16 | 0.99 | 0.80 | 0.65 | |
| | OND | 0.96 | 0.82 | 0.83 | 0.96 | 1.10 | 0.98 | 0.96 | 0.89 | |

**Table VI- 2.** CMAQ-calculated 2009 / 2002 relative response factors for PM2.5 components at PM2.5 FRM monitors within the Washington, D.C. NAA.

| Site Name | Quarter | PM2.5 | EC | $SO_4$ | $NO_3$ | Soil | OM | $NH_4$ | PBW | NAA |
|---|---|---|---|---|---|---|---|---|---|---|
| Rockville | JFM | 0.90 | 0.76 | 0.89 | 0.96 | 0.98 | 0.85 | 0.94 | 0.92 | D.C. |
| 240313001 | AMJ | 0.82 | 0.77 | 0.68 | 0.79 | 1.09 | 0.96 | 0.76 | 0.70 | |
| | JAS | 0.80 | 0.76 | 0.62 | 0.86 | 1.14 | 0.98 | 0.78 | 0.64 | |
| | OND | 0.95 | 0.78 | 0.83 | 0.96 | 1.08 | 0.96 | 0.96 | 0.89 | |
| River Terrace | JFM | 0.87 | 0.75 | 0.89 | 0.95 | 0.92 | 0.78 | 0.94 | 0.91 | D.C. |
| 110010041 | AMJ | 0.80 | 0.77 | 0.69 | 0.79 | 1.03 | 0.90 | 0.77 | 0.70 | |
| | JAS | 0.78 | 0.76 | 0.63 | 0.86 | 1.08 | 0.90 | 0.79 | 0.65 | |
| | OND | 0.92 | 0.78 | 0.83 | 0.96 | 1.03 | 0.90 | 0.95 | 0.88 | |
| Hains Point | JFM | 0.87 | 0.75 | 0.89 | 0.95 | 0.92 | 0.78 | 0.94 | 0.91 | D.C. |
| 110010042 | AMJ | 0.80 | 0.77 | 0.69 | 0.79 | 1.03 | 0.90 | 0.77 | 0.70 | |
| | JAS | 0.78 | 0.76 | 0.63 | 0.86 | 1.08 | 0.90 | 0.79 | 0.65 | |
| | OND | 0.92 | 0.78 | 0.83 | 0.96 | 1.03 | 0.90 | 0.95 | 0.88 | |
| McMillan | JFM | 0.87 | 0.75 | 0.89 | 0.95 | 0.92 | 0.78 | 0.94 | 0.91 | D.C. |
| 110010043 | AMJ | 0.80 | 0.77 | 0.69 | 0.79 | 1.03 | 0.90 | 0.77 | 0.70 | |
| | JAS | 0.78 | 0.76 | 0.63 | 0.86 | 1.08 | 0.90 | 0.79 | 0.65 | |
| | OND | 0.92 | 0.78 | 0.83 | 0.96 | 1.03 | 0.90 | 0.95 | 0.88 | |
| Aurora Hills | JFM | 0.82 | 0.73 | 0.89 | 0.95 | 0.86 | 0.70 | 0.94 | 0.91 | D.C. |
| 510130020 | AMJ | 0.79 | 0.77 | 0.69 | 0.79 | 0.99 | 0.83 | 0.78 | 0.71 | |
| | JAS | 0.76 | 0.76 | 0.63 | 0.85 | 1.03 | 0.84 | 0.79 | 0.66 | |
| | OND | 0.90 | 0.77 | 0.83 | 0.95 | 0.99 | 0.84 | 0.95 | 0.88 | |
| Franconia | JFM | 0.79 | 0.72 | 0.89 | 0.96 | 0.81 | 0.64 | 0.94 | 0.91 | D.C. |
| 510590030 | AMJ | 0.76 | 0.77 | 0.69 | 0.80 | 0.95 | 0.77 | 0.79 | 0.71 | |
| | JAS | 0.74 | 0.76 | 0.63 | 0.86 | 0.98 | 0.77 | 0.80 | 0.66 | |
| | OND | 0.87 | 0.77 | 0.83 | 0.96 | 0.94 | 0.79 | 0.95 | 0.88 | |
| Annandale | JFM | 0.79 | 0.72 | 0.89 | 0.96 | 0.81 | 0.64 | 0.94 | 0.91 | D.C. |
| 510591005 | AMJ | 0.76 | 0.77 | 0.69 | 0.80 | 0.95 | 0.77 | 0.79 | 0.71 | |
| | JAS | 0.74 | 0.76 | 0.63 | 0.86 | 0.98 | 0.77 | 0.80 | 0.66 | |
| | OND | 0.87 | 0.77 | 0.83 | 0.96 | 0.94 | 0.79 | 0.95 | 0.88 | |
| McLean | JFM | 0.76 | 0.71 | 0.89 | 0.95 | 0.78 | 0.60 | 0.94 | 0.91 | D.C. |
| 510595001 | AMJ | 0.76 | 0.76 | 0.69 | 0.80 | 0.94 | 0.74 | 0.78 | 0.71 | |
| | JAS | 0.73 | 0.76 | 0.63 | 0.85 | 0.97 | 0.74 | 0.79 | 0.65 | |
| | OND | 0.87 | 0.77 | 0.83 | 0.96 | 0.94 | 0.76 | 0.95 | 0.88 | |
| Ashburn | JFM | 0.76 | 0.69 | 0.87 | 0,95 | 0.79 | 0.54 | 0.93 | 0.90 | D.C. |
| 511071005 | AMJ | 0.74 | 0.77 | 0.68 | 0.79 | 0.95 | 0.71 | 0.77 | 0.70 | |
| | JAS | 0.71 | 0.77 | 0.62 | 0.86 | 0.98 | 0.70 | 0.79 | 0.65 | |
| | OND | 0.87 | 0.77 | 0.83 | 0.95 | 0.96 | 0.73 | 0.95 | 0.88 | |
| Average | JFM | 0.83 | 0.73 | 0.89 | 0.95 | 0.87 | 0.69 | 0.94 | 0.91 | |
| | AMJ | 0.78 | 0.77 | 0.69 | 0.79 | 1.00 | 0.83 | 0.77 | 0.71 | |
| | JAS | 0.76 | 0.76 | 0.63 | 0.85 | 1.04 | 0.83 | 0.79 | 0.65 | |
| | OND | 0.90 | 0.77 | 0.83 | 0.96 | 1.00 | 0.84 | 0.95 | 0.88 | |

**Table VI- 3.** CMAQ-calculated 2009 / 2002 relative response factors (RRF) for PM2.5 components at the Hagerstown - Martinsburg, MD-WV NAA monitor.

| Site Name | Quarter | PM2.5 | EC | $SO_4$ | $NO_3$ | SOIL | OM | $NH_4$ | PBW | NAA |
|---|---|---|---|---|---|---|---|---|---|---|
| Hagerstown | JFM | 0.88 | 0.74 | 0.92 | 0.93 | 0.98 | 0.73 | 0.94 | 0.93 | Hagerstown-Martinsburg, MD-WV |
| 240430009 | AMJ | 0.77 | 0.77 | 0.69 | 0.69 | 1.10 | 0.88 | 0.72 | 0.69 | |
| | JAS | 0.75 | 0.76 | 0.63 | 0.72 | 1.13 | 0.90 | 0.74 | 0.65 | |
| | OND | 0.93 | 0.78 | 0.88 | 0.92 | 1.09 | 0.89 | 0.94 | 0.90 | |
| Martinsburg | JFM | 0.85 | 0.70 | 0.90 | 0.94 | 0.93 | 0.64 | 0.95 | 0.92 | |
| 540030003 | AMJ | 0.77 | 0.75 | 0.69 | 0.75 | 1.06 | 0.81 | 0.76 | 0.70 | |
| | JAS | 0.74 | 0.74 | 0.63 | 0.76 | 1.08 | 0.81 | 0.78 | 0.65 | |
| | OND | 0.92 | 0.75 | 0.86 | 0.94 | 1.05 | 0.82 | 0.96 | 0.90 | |

**Table VI- 4.** CMAQ-calculated 2009 / 2002 relative response factors for PM2.5 components at the Fair Hill, MD Monitor

| Site Name | Quarter | PM2.5 | EC | $SO_4$ | $NO_3$ | SOIL | OM | $NH_4$ | PBW |
|---|---|---|---|---|---|---|---|---|---|
| Fair Hill | JFM | 0.96 | 0.84 | 0.89 | 0.94 | 1.10 | 0.97 | 0.93 | 0.91 |
| 240150003 | AMJ | 0.80 | 0.79 | 0.68 | 0.73 | 1.18 | 0.99 | 0.72 | 0.69 |
| | JAS | 0.77 | 0.78 | 0.62 | 0.73 | 1.22 | 1.00 | 0.73 | 0.64 |
| | OND | 0.94 | 0.80 | 0.85 | 0.91 | 1.15 | 0.99 | 0.92 | 0.88 |

In order to minimize the impact of biases in the fractional composition of model-calculated PM2.5 on predicted future design values for PM2.5, RRFs at the location of FRM monitors are applied to the observed quarterly baseline concentrations of each PM2.5 component. Table VI-5 through Table VI-8 show these baseline design values at sites within the Baltimore NAA; Washington, D.C. NAA; Hagerstown, MD – Martinsburg, WV NAA; and the Fair Hill monitor, respectively. Where possible, these baseline design values were calculated by taking the average of the design values for the three three-year periods that straddle the baseline inventory year. Mathematically:

DV2002 = (2000QM + 2001QM + 2002QM)/3

DV2003 = (2001QM + 2002QM + 2003QM)/3

DV2004 = (2002QM + 2003QM + 2004QM)/3

DVbase = (DV2002 + DV2003 + DV2004) / 3,

Where YYYYQM is the quarterly mean concentration of PM2.5 for year YYYY and YYYY equals 2000, 2001, 2002, 2003, or 2004. DVYYYY is the design value for year YYYY and ideally is the mean of year YYYY and the two years preceding that year.

DVbase is the baseline design value that is obtained by averaging DV2002, DV2003, and DV2004.

This formula must be modified if PM2.5 data are missing for one or more quarters.

The following formula is used for quarters when 2000 data are missing.

DV2002 = (2001QM + 2002QM)/2

DV2003 = (2001QM + 2002QM + 2003QM)/3

DV2004 = (2002QM + 2003QM + 2004QM)/3

DVbase = (DV2002 + DV2003 + DV2004) / 3.

The above formula is used for Davidsonville Quarter 1 (Q1), McLean Q3, and Southeast Police Station Q2-Q4.

The following formula is used for quarters when 2001 data are missing.

DV2002 = (2000QM + 2002QM)/2.

DV2003 = (2002QM + 2003QM)/2.

DV2004 = (2002QM + 2003QM + 2004QM)/3.

DVbase = (DV2002 + DV2003 + DV2004) / 3.

The above formula is used for Franconia Q3.

The following formula is used for quarters when 2000-2001 data are missing.

DV2002 = 2002QM

DV2003 = (2002QM + 2003QM)/2.

DV2004 = (2002QM + 2003QM + 2004QM)/3.

DVbase = (DV2002 + DV2003 + DV2004) / 3.

The above formula is used at Southeast Police Station Q1 and Annandale Q2-Q4.

The following approach is used for quarters when 2000-2002 data are missing.

DV2002 = 2003QM

DV2003 = (2003QM + 2004QM)/2.

DVbase = (DV2002 + DV2003) / 2.

Fortunately, this formula is only needed at Annandale Q1.

The quarterly concentrations at FRM sites contain contributions from organic carbon (OC), elemental carbon (EC), sulfate ($SO_4$), nitrate ($NO_3$), ammonium ($NH_4$), particle bound water (PBW), other primary inorganic PM2.5 (OPP or SOIL), and a blank correction (assumed to equal 0.5 µg $m^{-3}$). Mathematically,

$$PM2.5 = OC + EC + SO_4 + NO_3 + NH_4 + PBW + OPP + 0.5$$

In order to calculate a future design value, it is necessary to calculate the contribution of each PM2.5 component to total PM2.5 at each of the air quality sites. Unfortunately, speciated data are generally not available at the locations of most FRM monitors. Within the Baltimore NAA, speciated data are available at Fort Meade and Essex. Within the Washington, D.C. NAA, speciated data are available at McMillan Reservoir. It was decided to use concurrent speciated data at Essex to estimate species concentrations at FRM monitors within the Baltimore NAA, Washington, D.C. NAA, Hagerstown– Martinsburg NAA, and at the Fair Hill monitor. The reason speciated data at Essex was used is because it is plentiful and representative of the type of location (urban) where Maryland PM2.5 air quality is worst (Old Town and Southeast Police Station are both located in Baltimore City). When averaged over a season, the fractional composition of PM2.5 at Essex should contain a larger contribution from organic carbon and elemental carbon and a smaller contribution from sulfate, nitrate, and ammonium than a more rural site. Since the largest reductions are in sulfate, this procedure makes the calculation more conservative.

**Table VI- 5.** Quarterly baseline design values (DVbase) for PM2.5 monitors within the Baltimore NAA.

| Site Name | Site ID | Quarter 1 | Quarter 2 | Quarter 3 | Quarter 4 |
|---|---|---|---|---|---|
| Davidsonville | 240030014 | 9.66 | 13.70 | 15.82 | 9.92 |
| Fort Meade | 240030019 | 10.89 | 14.54 | 16.88 | 10.65 |
| Glen Burnie | 240031003 | 14.41 | 15.58 | 17.61 | 13.93 |
| Riviera Beach | 240032002 | 12.96 | 14.89 | 16.58 | 12.49 |
| Edgewood | 240251001 | 11.91 | 13.81 | 15.32 | 11.03 |
| Essex | 240053001 | 14.63 | 14.87 | 17.02 | 13.61 |
| Padonia | 240051007 | 13.29 | 14.57 | 16.71 | 12.20 |
| FMC-Fairfield | 245100035 | 15.97 | 15.77 | 17.85 | 14.56 |
| NE Police Station | 245100006 | 13.59 | 14.83 | 16.73 | 12.33 |
| NW Police Station | 245100007 | 14.21 | 15.68 | 17.61 | 12.67 |
| SE Police Station | 245100008 | 14.63 | 17.52 | 17.83 | 14.26 |
| Old Town | 245100040 | 16.64 | 16.38 | 18.50 | 15.05 |
| Westport | 245100049 | 13.76 | 16.38 | 17.52 | 13.70 |

**Table VI- 6.** Quarterly baseline design values (DVbase) for PM2.5 monitors within the Washington, D.C. NAA.

| Site Name | Site ID | Quarter 1 | Quarter 2 | Quarter 3 | Quarter 4 |
|---|---|---|---|---|---|
| Rockville | 240313001 | 11.23 | 13.64 | 16.01 | 10.43 |
| River Terrace | 110010041 | 14.85 | 14.91 | 18.76 | 14.16 |
| Hains Point | 110010042 | 13.43 | 15.49 | 17.33 | 12.98 |
| McMillan Reservoir | 110010043 | 13.65 | 15.28 | 18.10 | 13.55 |
| Aurora Hills | 510130020 | 13.27 | 14.88 | 17.27 | 13.05 |
| Franconia | 510590030 | 11.59 | 14.01 | 16.95 | 12.02 |
| Annandale | 510591005 | 12.58 | 14.20 | 17.25 | 11.37 |
| McLean | 510595001 | 12.63 | 14.05 | 17.80 | 12.37 |
| Ashburn | 511071005 | 11.38 | 14.14 | 17.32 | 11.71 |

**Table VI- 7.** Quarterly baseline design values (DVbase) for Maryland PM2.5 monitors within the Hagerstown, MD/Martinsburg, WV NAA.

| Site Name | Site ID | Quarter 1 | Quarter 2 | Quarter 3 | Quarter 4 |
|---|---|---|---|---|---|
| Hagerstown | 240430009 | 13.08 | 14.80 | 17.16 | 12.00 |
| Martinsburg | 540030003 | 14.67 | 16.29 | 19.33 | 14.65 |

**Table VI- 8.** Quarterly baseline design values (DVbase) for the Fair Hill, MD PM2.5 monitor.

| Site Name | Site ID | Quarter 1 | Quarter 2 | Quarter 3 | Quarter 4 |
|---|---|---|---|---|---|
| Fair Hill | 240150003 | 11.10 | 14.14 | 15.74 | 11.32 |

Table VI- 9 through Table VI-11 show the observed contribution of various PM2.5 components to total PM2.5 at Essex, Fort Meade, and McMillan Reservoir, respectively. At Essex, sulfate contributes at least ~30% to total PM2.5 throughout the year and ~50% during the growing season (April-September). Organic carbon's (OC's) observed contribution to PM2.5 ranges from 18% during April-June to 30% during October-December. The substantial increase from the spring to summer is probably due to a seasonal increase in biogenic SOA. Nitrate contributes 12-15% to total PM2.5 during the winter season, but is insignificant during the summer season. Ammonium and PBW contribute 9-11% and 7-11%, respectively, throughout the year. Contributions from other primary PM2.5 (OPP) and EC are minor (< ~5% for each throughout the year). The seasonal cycle of PM2.5 partitioning at Fort Meade is similar to Essex with the following important exceptions. The relative importance of sulfate is larger and the relative importance of organic carbon is smaller. The contrast is greatest during the late summer and fall. Organic carbon's contribution to total PM2.5 is largest at McMillan Reservoir. The contribution of OC and sulfate to total PM2.5 at McMillan Reservoir are comparable when averaged over the year, although the contribution of sulfate is largest during the summer, the time period when emission reductions are the largest.

Future quarterly design values for each PM component are obtained by multiplying the baseline design value for each site (after subtracting out 0.5 $\mu g\ m^{-3}$ [the assumed contribution from passively collected mass]) by the sum over PM2.5 components of the relative reduction factor for each component multiplied by an estimate of the fractional contribution of each PM2.5 component to the PM2.5 mass at that site. The future annual design values are obtained by averaging the quarterly design values and adding back in the blank mass. Mathematically,

$$\mathrm{DVfuture} = [(\mathrm{DVbase} - 0.5) * \{\sum_{i=1}^{N} \mathrm{RRF}_i * \mathrm{fraction}_i\}] + 0.5.$$

Values for DVbase are given in Table VI-5 through Table VI-8. PM2.5 component specific values for RRF are given in Table VI-1 through Table VI-4. Component specific values for "$\mathrm{fraction}_i$" are given in Table VI-9 through VI-11.

**Table VI- 9.** Quarterly species fractions (as percentages) at Essex, Maryland.

| Species | Quarter 1 | Quarter 2 | Quarter 3 | Quarter 4 |
|---|---|---|---|---|
| Ammonium | 10.40 | 10.96 | 8.76 | 10.73 |
| Elemental carbon | 4.25 | 3.45 | 2.47 | 5.08 |
| Nitrate | 15.45 | 1.86 | 0.00 | 11.79 |
| Organic carbon | 26.19 | 17.87 | 28.30 | 29.80 |
| Sulfate | 34.00 | 51.10 | 48.70 | 29.86 |
| Other primary PM2.5 | 2.64 | 4.22 | 3.04 | 3.64 |
| Particulate bound water | 7.06 | 10.53 | 8.72 | 9.10 |

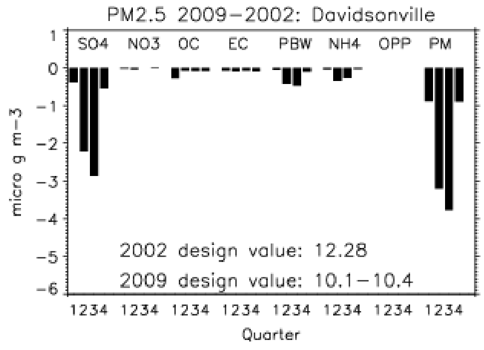
**Table VI- 10.** Quarterly species fractions (as percentages) at Ft. Meade, Maryland.

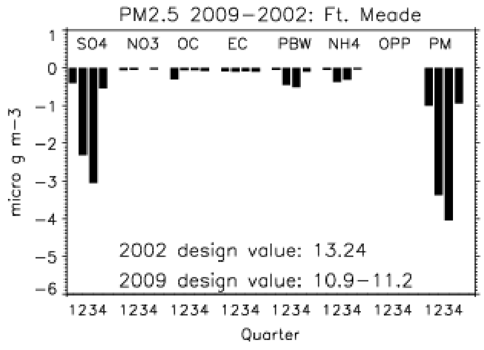
| Species | Quarter 1 | Quarter 2 | Quarter 3 | Quarter 4 |
|---|---|---|---|---|
| Ammonium | 12.28 | 10.65 | 9.45 | 9.11 |
| Elemental carbon | 3.92 | 3.05 | 2.46 | 4.59 |
| Nitrate | 18.67 | 3.26 | 0 | 8.76 |
| Organic carbon | 13.55 | 18.86 | 20.66 | 23.30 |
| Sulfate | 39.90 | 51.97 | 56.07 | 43.39 |
| Other primary PM2.5 | 3.15 | 3.12 | 2.08 | 2.99 |
| Particulate bound water | 8.53 | 9.09 | 9.29 | 7.86 |

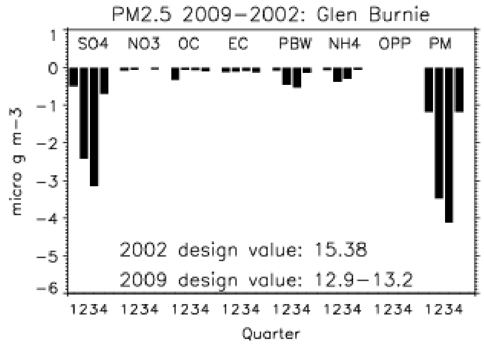
**Table VI-11.** Quarterly species fractions (as percentages) at McMillan Reservoir.

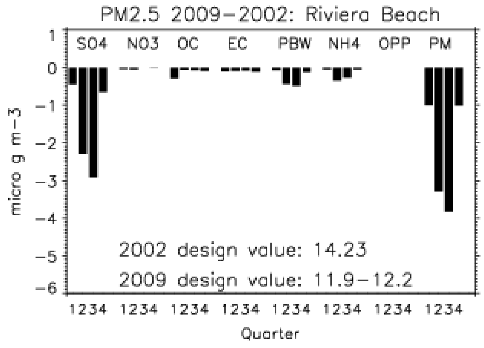
| Species | Quarter 1 | Quarter 2 | Quarter 3 | Quarter 4 |
|---|---|---|---|---|
| Ammonium | 10.40 | 12.52 | 11.46 | 12.81 |
| Elemental carbon | 5.12 | 4.16 | 3.07 | 6.17 |
| Nitrate | 6.55 | 0.07 | 0.05 | 9.91 |
| Organic carbon | 40.55 | 25.25 | 28.93 | 25.63 |
| Sulfate | 25.21 | 39.55 | 40.23 | 31.37 |
| Other primary PM2.5 | 4.06 | 5.60 | 5.31 | 4.76 |
| Particulate bound water | 8.11 | 12.84 | 10.95 | 9.35 |

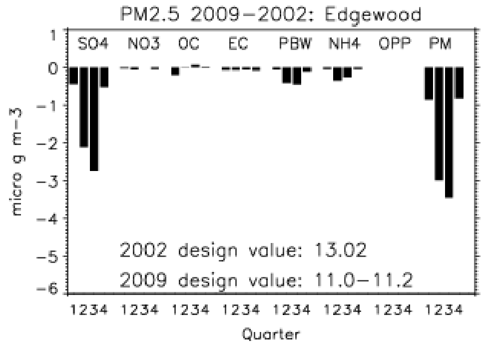
Predicted change in quarterly PM2.5 component concentrations after application of component specific RRFs to observed air quality for sites within the Baltimore; Washington, D.C.; Hagerstown-Martinsburg, MD-WV NAAs; and the Fair Hill, MD monitor are shown in Figure VI- 25 through Figure VI- 28, respectively. Within the Baltimore NAA, changes in predicted sulfate are the predominant cause of decreased PM2.5 concentrations between 2002 and 2009. Within the Washington, D.C. NAA, sulfate continues to be important but changes in organic carbon are also important at some of the sites.

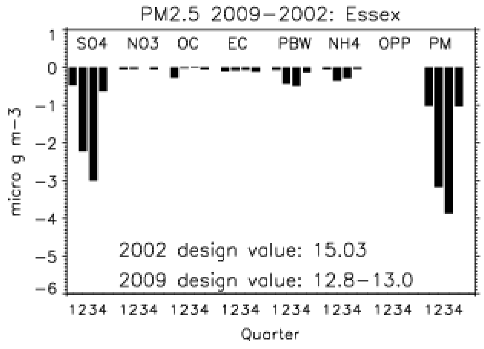

PM2.5 2009−2002: Davidsonville
SO4 NO3 OC EC PBW NH4 OPP PM
micro g m−3
1 0 −1 −2 −3 −4 −5 −6
2002 design value: 12.28
2009 design value: 10.1−10.4
1234 1234 1234 1234 1234 1234 1234 1234
Quarter

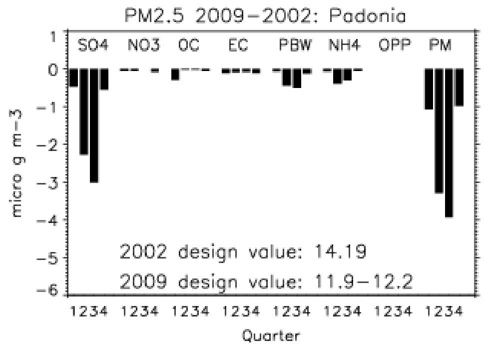

PM2.5 2009−2002: Ft. Meade
SO4 NO3 OC EC PBW NH4 OPP PM
micro g m−3
1 0 −1 −2 −3 −4 −5 −6
2002 design value: 13.24
2009 design value: 10.9−11.2
1234 1234 1234 1234 1234 1234 1234 1234
Quarter

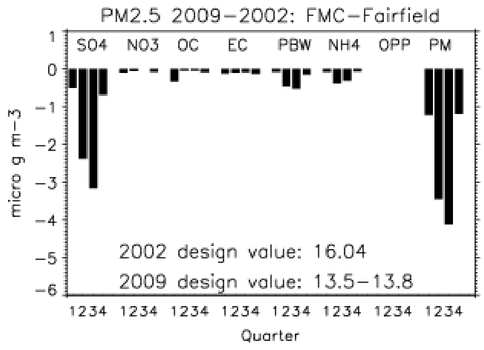

PM2.5 2009−2002: Glen Burnie
SO4 NO3 OC EC PBW NH4 OPP PM
micro g m−3
1 0 −1 −2 −3 −4 −5 −6
2002 design value: 15.38
2009 design value: 12.9−13.2
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: Riviera Beach
SO4 NO3 OC EC PBW NH4 OPP PM
micro g m−3
1 0 −1 −2 −3 −4 −5 −6
2002 design value: 14.23
2009 design value: 11.9−12.2
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: Edgewood
SO4 NO3 OC EC PBW NH4 OPP PM
micro g m−3
1 0 −1 −2 −3 −4 −5 −6
2002 design value: 13.02
2009 design value: 11.0−11.2
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: Essex
SO4 NO3 OC EC PBW NH4 OPP PM
micro g m−3
1 0 −1 −2 −3 −4 −5 −6
2002 design value: 15.03
2009 design value: 12.8−13.0
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: Padonia
SO4 NO3 OC EC PBW NH4 OPP PM
micro g m−3
1 0 −1 −2 −3 −4 −5 −6
2002 design value: 14.19
2009 design value: 11.9−12.2
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: FMC−Fairfield
SO4 NO3 OC EC PBW NH4 OPP PM
micro g m−3
1 0 −1 −2 −3 −4 −5 −6
2002 design value: 16.04
2009 design value: 13.5−13.8
1234 1234 1234 1234 1234 1234 1234 1234
Quarter

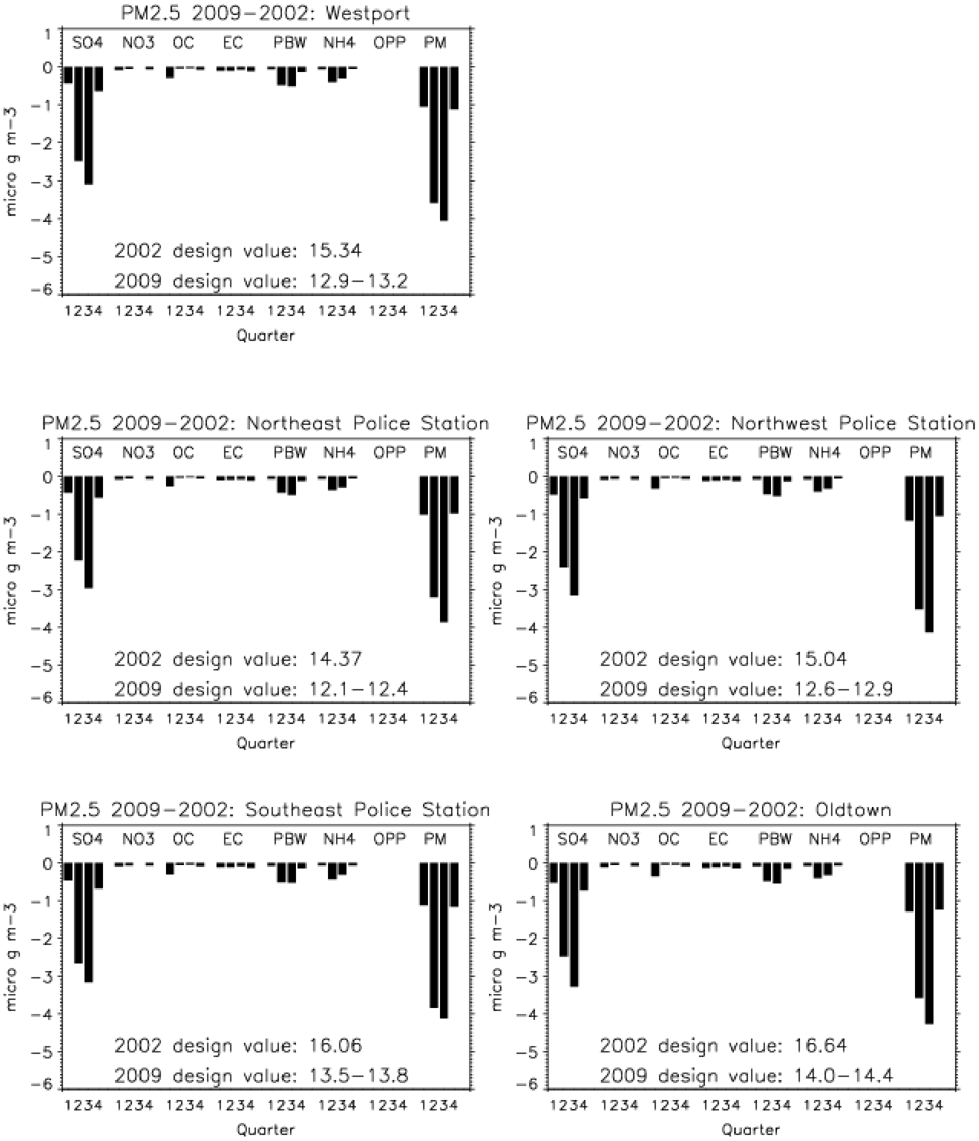
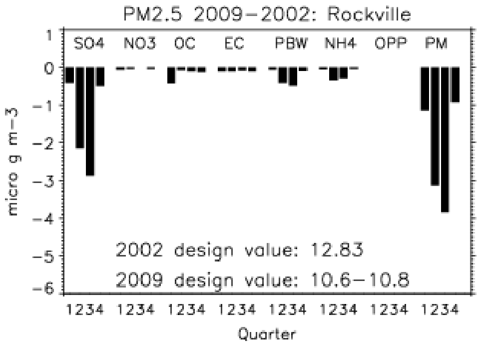
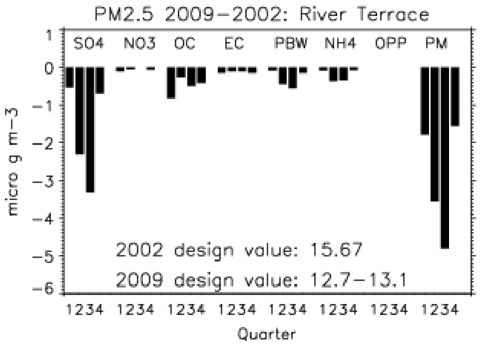
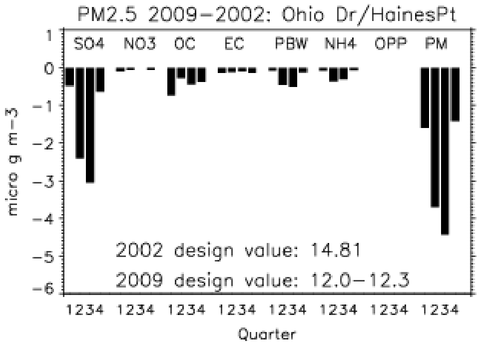
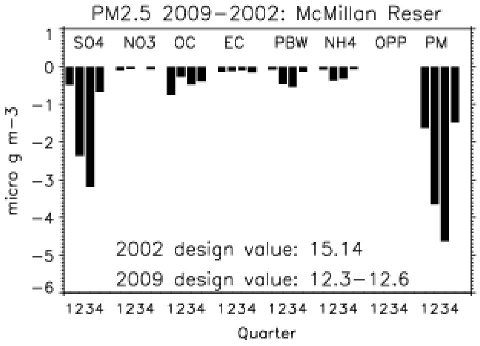


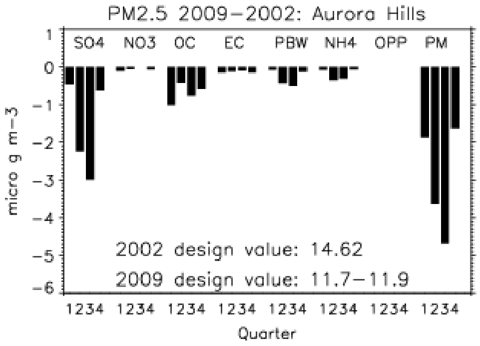
**Figure VI- 25.** Predicted change in PM2.5 concentrations after application of component-specific RRFs to observed air quality. 2002-2009 changes at sites within the Baltimore NAA are shown as a function of PM species and quarter. (a) Davidsonville, (b) Fort Meade, (c) Glen Burnie, (d) Riviera Beach, (e) Edgewood, (f) Essex, (g) Padonia, (h) FMC-Fairfield, (i) Westport, (j) Northeast Police Station, (k) Northwest Police Station, (l) Southeast Police Station, and (m) Old Town.

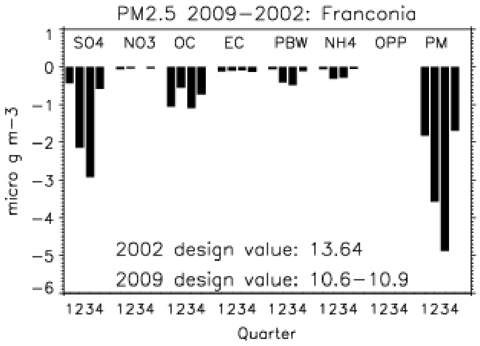

PM2.5 2009−2002: Rockville
SO4
NO3
OC
EC
PBW
NH4
OPP
PM
micro g m−3
1
0
−1
−2
−3
−4
−5
−6
2002 design value: 12.83
2009 design value: 10.6−10.8
1234 1234 1234 1234 1234 1234 1234 1234
Quarter

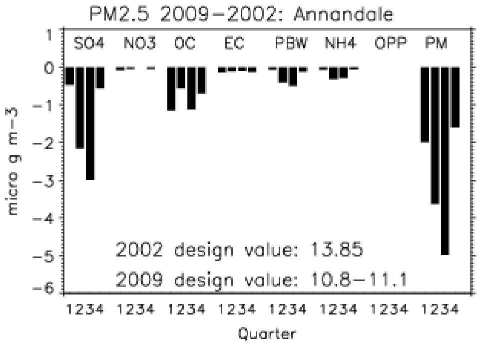

PM2.5 2009−2002: River Terrace
SO4
NO3
OC
EC
PBW
NH4
OPP
PM
micro g m−3
1
0
−1
−2
−3
−4
−5
−6
2002 design value: 15.67
2009 design value: 12.7−13.1
1234 1234 1234 1234 1234 1234 1234 1234
Quarter

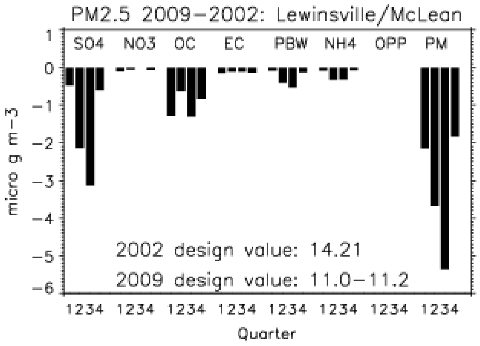

PM2.5 2009−2002: Ohio Dr/HainesPt
SO4
NO3
OC
EC
PBW
NH4
OPP
PM
micro g m−3
1
0
−1
−2
−3
−4
−5
−6
2002 design value: 14.81
2009 design value: 12.0−12.3
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: McMillan Reser
SO4
NO3
OC
EC
PBW
NH4
OPP
PM
micro g m−3
1
0
−1
−2
−3
−4
−5
−6
2002 design value: 15.14
2009 design value: 12.3−12.6
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: Aurora Hills
SO4
NO3
OC
EC
PBW
NH4
OPP
PM
micro g m−3
1
0
−1
−2
−3
−4
−5
−6
2002 design value: 14.62
2009 design value: 11.7−11.9
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: Franconia
SO4
NO3
OC
EC
PBW
NH4
OPP
PM
micro g m−3
1
0
−1
−2
−3
−4
−5
−6
2002 design value: 13.64
2009 design value: 10.6−10.9
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: Annandale
SO4
NO3
OC
EC
PBW
NH4
OPP
PM
micro g m−3
1
0
−1
−2
−3
−4
−5
−6
2002 design value: 13.85
2009 design value: 10.8−11.1
1234 1234 1234 1234 1234 1234 1234 1234
Quarter


PM2.5 2009−2002: Lewinsville/McLean
SO4
NO3
OC
EC
PBW
NH4
OPP
PM
micro g m−3
1
0
−1
−2
−3
−4
−5
−6
2002 design value: 14.21
2009 design value: 11.0−11.2
1234 1234 1234 1234 1234 1234 1234 1234
Quarter

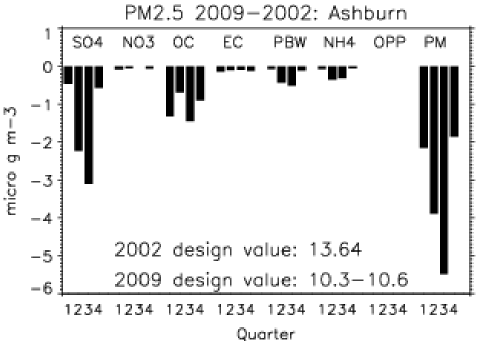


**Figure VI- 26.** Same as Figure VI- 25 but for the Washington, D.C. NAA. (a) Rockville, (b) River Terrace, (c) Ohio Drive/ Hains Point, (d) McMillan Reservoir, (e) Aurora Hills, (f) Franconia, (g) Annandale, (h) Lewinsville/McLean, and (i) Ashburn.

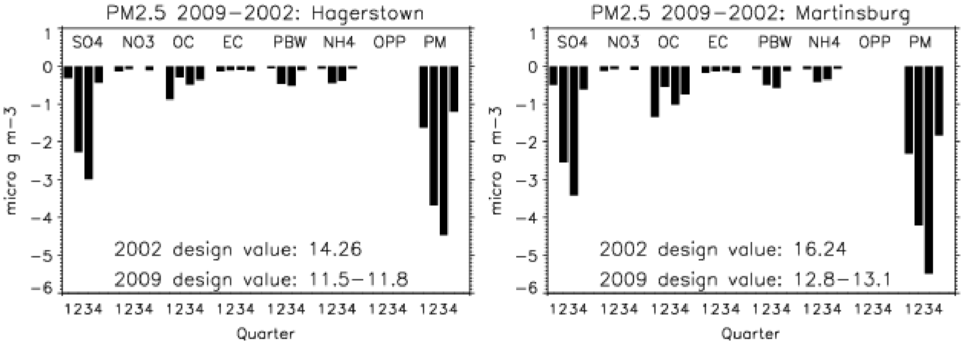


**Figure VI- 27.** Predicted change in PM2.5 concentrations after application of component specific RRFs to observed air quality. 2002-2009 changes at Hagerstown, MD (a) and Martinsburg, WV (b), sites within the Hagerstown, MD/ Martinsburg, WV NAA. Changes are shown as a function of PM species and quarter.

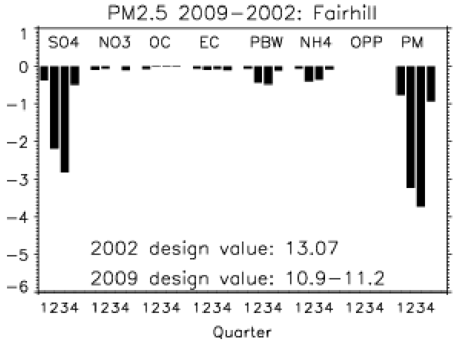


**Figure VI- 28.** Predicted change in PM2.5 concentrations after application of component specific RRFs to observed air quality. 2002-2009 changes at Fair Hill, MD monitor. Changes are shown as a function of PM species and quarter.

The predicted decreases in PM2.5 concentrations between 2002 and 2009 and 2002 and 2018 at sites within the Baltimore; Washington, D.C.; Hagerstown-Martinsburg, MD-WV NAAs; and Fair Hill, MD monitor are shown in Table VI-12 through Table VI-15, respectively. For all sites, speciation data for Essex are used in the determination of $fraction_i$. If the values for Ft. Meade are used for Washington, D.C. area sites, the future year design values are slightly lower (approximately 0.1 μg $m^{-3}$ lower) because sulfate is a slightly higher fraction of total PM2.5 at Fort Meade than at Essex. The Essex percentages were used in the interest of using the most conservative estimate of future year design values.

In 2002, the annual PM2.5 NAAQS (15.0 μg $m^{-3}$) was exceeded at seven monitoring sites within the Baltimore NAA and three sites within the Washington, D.C. NAA. The highest 2002 baseline design values within the Baltimore NAA were found at SE Police Station (16.06), FMC-Fairfield (16.04), and Old Town (16.64). The highest baseline design value in the Washington, D.C. NAA was 15.67 at River Terrace. The highest value in the Hagerstown-Martinsburg, MD-WV NAA was 16.24 at Martinsburg. A range is presented for the 2009 and 2018 design values. The lower end of the range assumes particulate bound water concentrations decrease at the same rate as the weighted mean of sulfate, nitrate, and ammonium concentrations. In other words, the lower bounds assume that water is bound to these PM2.5 components and will decrease as they decrease in concentration. The upper bound assumes that particle bound water concentrations are unchanged between 2002 and 2009 or 2018. Concentrations of OPP (soil/crustal material) are assumed to be unchanged between 2002 and 2009 or 2018. Design values at all sites within the Baltimore and Washington, D.C. NAA are all well under 15.0 μg $m^{-3}$ by 2009. In addition, all monitoring sites are below the weight of evidence concentration of 14.5 μg/$m^3$, which means that only a basic supplemental analyses needs to be completed to confirm the results of the modeled attainment test.

### j. Will Maryland be in compliance with NAAQS if the PM2.5 standard is tightened?

With the health effects of PM2.5 still being studied, some policy makers are suggesting that the annual PM2.5 standard be tightened to 13.0 μg $m^{-3}$ at some future date. Predicted 2018 PM2.5 annual design values at the worst sites within the Baltimore NAA range from 9.2 – 13.5

$\mu g\ m^{-3}$, about 1 $\mu g\ m^{-3}$ less than 2009 design values but slightly above a possible 13.0 $\mu g\ m^{-3}$ NAAQS.

**Table VI- 12.** Baseline design values (2002) and predicted future (2009 and 2018) design value ranges for PM2.5 monitors within the Baltimore NAA.

| Site Name | Site ID | DV2002 | DV2009 | DV2018 |
|---|---|---|---|---|
| Davidsonville | 240030014 | 12.28 | 10.1-10.4 | 9.2-9.6 |
| Fort Meade | 240030019 | 13.24 | 10.9-11.2 | 10.0-10.4 |
| Glen Burnie | 240031003 | 15.38 | 12.9-13.2 | 11.9-12.4 |
| Riviera Beach | 240032002 | 14.23 | 11.9-12.2 | 11.1-11.5 |
| Edgewood | 240251001 | 13.02 | 11.0-11.2 | 10.1-10.4 |
| Essex | 240053001 | 15.03 | 12.8-13.0 | 11.9-12.3 |
| Padonia | 240051007 | 14.19 | 11.9-12.2 | 10.8-11.2 |
| FMC-Fairfield | 245100035 | 16.04 | 13.5-13.8 | 12.6-13.0 |
| NE Police Station | 245100006 | 14.37 | 12.1-12.4 | 11.2-11.6 |
| NW Police Station | 245100007 | 15.04 | 12.6-12.9 | 11.5-11.9 |
| SE Police Station | 245100008 | 16.06 | 13.5-13.8 | 12.5-12.9 |
| Old Town | 245100040 | 16.64 | 14.0-14.4 | 13.0-13.5 |
| Westport | 245100049 | 15.34 | 12.9-13.2 | 11.9-12.4 |

**Table VI- 13.** Baseline design values (2002) and future (2009 and 2018) design value ranges for PM2.5 monitors within the Washington, D.C. NAA.

| Site Name | Site ID | DV2002 | DV2009 | DV2018 |
|---|---|---|---|---|
| Rockville | 240313001 | 12.83 | 10.6-10.8 | 9.7-10.1 |
| River Terrace | 110010041 | 15.67 | 12.7-13.1 | 11.7-12.1 |
| Hains Point | 110010042 | 14.81 | 12.0-12.3 | 11.0-11.4 |
| McMillan Reservoir | 110010043 | 15.14 | 12.3-12.6 | 11.3-11.7 |
| Aurora Hills | 510130020 | 14.62 | 11.7-11.9 | 10.7-11.1 |
| Franconia | 510590030 | 13.64 | 10.6-10.9 | 9.8-10.2 |
| Annandale | 510591005 | 13.85 | 10.8-11.1 | 9.9-10.3 |
| McLean | 510595001 | 14.21 | 11.0-11.2 | 10.1-10.5 |
| Ashburn | 511071005 | 13.64 | 10.3-10.6 | 9.4-9.8 |

**Table VI- 14**. Baseline design values (2002) and future (2009 and 2018) design value ranges for PM2.5 monitors within the Hagerstown – Martinsburg, MD-WV NAA.

| Site Name | Site ID | DV2002 | DV2009 | DV2018 |
|---|---|---|---|---|
| Hagerstown | 240430009 | 14.26 | 11.5-11.8 | 10.3-10.7 |
| Martinsburg | 540030003 | 16.24 | 12.8-13.1 | 11.5-11.9 |

**Table VI- 15.** Baseline design value (2002) and future (2009 and 2018) design value ranges for the Fair Hill, MD PM2.5 monitor.

| Site Name | Site ID | 2002DV | 2009DV | 2018DV |
|---|---|---|---|---|
| Fair Hill | 240150003 | 13.07 | 10.9-11.2 | 9.9-10.3 |

### k. Conclusions

CMAQ’s performance was examined and found to be adequate for the species that will change the most between 2002 and 2009. In particular, for Maryland, the largest changes in any PM2.5 species are projected to occur in sulfate, and this is the one species where CMAQ’s performance is at its best. Most other species have annual RRFs that indicate relatively more modest improvements in fine particle concentrations. CMAQ’s performance is poorest for soil/crustal material and organic matter. The poor performance for soil/crustal material is only a minor concern since soil/crustal material only comprises 3-6% of PM2.5 in the Mid-Atlantic region. The underestimation of summertime organic matter concentrations by CMAQ is of more concern since organic matter is an important part of the PM2.5 budget at some Mid-Atlantic sites. Much of the bias is likely due to an underestimation of secondary organic aerosols, most of which have a biogenic source. Since changes in biogenic emissions are expected to be small over the next decade, the accuracy of CMAQ-calculated RRFs for this term is not crucial. In addition, following EPA guidelines, biases in model predicted changes are minimized through weighting with observed PM2.5 partitioning. Therefore CMAQ’s PM2.5 modeling performance is acceptable for this modeling demonstration. The biases in CMAQ and the inventory used to drive it are such that the calculations here are somewhat higher than they would probably be in reality. These calculations are therefore conservative with regard to PM2.5 attainment or nonattainment.

For all monitors in Maryland, PM2.5 concentrations were calculated to be well in attainment of the PM2.5 NAAQS by 2009. The highest monitor in Maryland is projected to continue to be the Old Town monitor (located in downtown Baltimore City), but even that monitor falls below the weight of evidence range.

## References

Baker, K. (2005), Model Performance for Ozone in the Upper Midwest over 3 Summers, in *2005 AWMA Annual Conference*, edited, Minneapolis, MN.

EPA (2007), Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5, and Regional Haze, 262 pp, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Levy, R. C. (2007), Second Generation Retrieval of Tropospheric Aerosol Properties over Land from Inversion of Visible and Near-Infrared Spectral Reflectance: Application over Maryland, The University of Maryland, College Park.

Moon, N. K., and D. W. Byun (2004), A Simple User's Guide for "geos2cmaq" Code: Linking CMAQ with GEOS-CHEM. Version 1.0 University of Houston, Institute for Multidimensional Air Quality Studies (IMAQS), Houston, Texas.

Taubman, B. F. (2004), Airborne Characterization of Regional Aerosol Origins and Optical Properties, 242 pp, University of Maryland, College Park.

Taubman, B. F., et al. (2004), Airborne characterization of the chemical, optical, and meteorological properties, and origins of a combined ozone-haze episode over the eastern United States, *Journal of the Atmospheric Sciences*, *61*(14), 1781-1793.

Zhang, D.-L., and S. Zhang (2005), Numerical Experimental Analysis Data for the Year of 2002, Report, 6 pp, Ozone Transport Commission, Boston.

Zhang, D. L., and W. Z. Zheng (2004), Diurnal cycles of surface winds and temperatures as simulated by five boundary layer parameterizations, *Journal of Applied Meteorology*, *43*(1), 157-169.

Zhang, Y., et al. (2007), Role of isoprene in secondary organic aerosol formation on a regional scale, *J Geophys Res-Atmos*, *112*(D20).