2.0 FINE PARTICLE POLLUTION

2.1 Definition of Fine Particle Matter

Fine particle ($PM_{2.5}$) matter consists of tiny airborne particles that result from particulate emissions; condensation of sulfates, nitrates, and organics from the gas phase; and coagulation of smaller particles. Unlike $PM_{2.5}$, coarse particles such as dust, pollen, sea salt, and ash are usually produced by mechanical processes including wind and erosion. $PM_{2.5}$ are less than or equal to 2.5 microns across, about 1/30th the average width of a human hair, whereas coarse particles are more than 2.5 microns and may be as large as 10 microns across.

Gas-phase precursors SO_2, NO_x, VOCs, and ammonia undergo chemical reactions in the atmosphere to form secondary PM (see Figure 2-1). Formation of secondary PM depends on numerous factors including the concentrations of precursors; the concentrations of other gaseous reactive species; atmospheric conditions including solar radiation, temperature, and relative humidity (RH); and the interactions of precursors with preexisting particles and with cloud or fog droplets. Several atmospheric aerosol species, such as ammonium nitrate and certain organic compounds, are semi-volatile and are found in both gas and particle phases. Given the complexity of $PM_{2.5}$ formation processes, new information from the scientific community continues to emerge to improve our understanding of the relationship between sources of PM precursors and secondary PM formation.

There are 14 monitors, Federal Reference Monitors or FRMs that sample $PM_{2.5}$ in the Washington region (see Figure 1-1). The purpose of the filter-based FRMs is to determine compliance with the $PM_{2.5}$ NAAQS. FRMs are filter based that measure $PM_{2.5}$ mass by passing a measured volume of air through a preweighed filter. The coarse PM is separated out before air is passed through the filter.

2.2 Health and Environmental Effects

The size of particles is directly linked to their potential for causing health problems. Fine particles less than 2.5 microns in diameter pose the greatest problems because they can lodge deep into the lungs and some may get into the bloodstream. Therefore, exposure to such particles can affect both lungs and heart. Particle pollution may occur all year as opposed to ozone, which occurs during the summer months. Particle pollution exposure is linked to a variety of health problems, including increased respiratory symptoms, such as irritation of the airways, coughing, or difficulty breathing; decreased lung function; aggravated asthma; development of chronic bronchitis; irregular heartbeat; nonfatal heart attacks; and premature death in people with heart or lung disease.

Studies have demonstrated a relationship between increased levels of $PM_{2.5}$ and higher rates of death and complications from cardiovascular disease. Evidence shows that inhalation of particles leads to direct vascular injury and atherosclerosis, or hardening of the arteries. According to the American Lung Association, an estimated 1.0 million people, 25% of the population in the metropolitan Washington area, are at risk for cardiovascular disease.[1] Additional populations at increased risk in the Metropolitan Washington region include 404,135 asthmatics, including 104,161 children and 299,974 adults, and 196,356 residents with other chronic or persistent respiratory diseases, such as chronic bronchitis and emphysema.

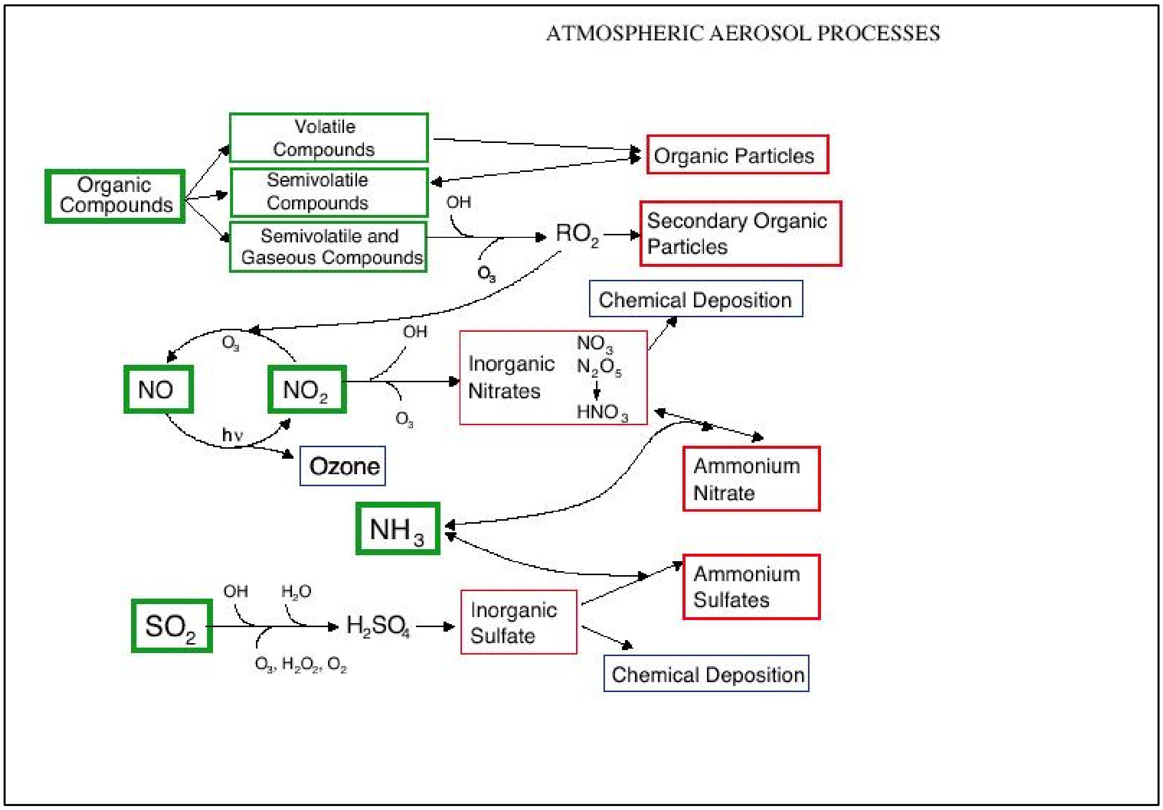

Figure 2-1. Atmospheric chemical reactions that contribute to $PM_{2.5}$, from the North American Strategy for Tropospheric Ozone (NARSTO) Assessment 2004.[1]

Environmental effects of particle pollution include reduced visibility, environmental damage, and aesthetic damage. $PM_{2.5}$ are the major cause of reduced visibility (haze) in parts of the United States, including many of our treasured national parks and wilderness areas. Particles can be carried over long distances by wind and then settle on ground or water. The effects of this settling include making lakes and streams more acidic, changing the nutrient balance in coastal waters and large river basins, depleting the nutrients in soil, damaging sensitive forests and farm crops, and affecting the diversity of ecosystems. Particle pollution can stain and damage stone and other materials, including culturally important objects such as statues and monuments.

When implemented, the measures in this plan will result in levels of particle pollution below the annual standard and close to the new daily standard for fine particles. According to the CASAC, reductions in fine particles should improve the health of all residents in the region and reduce mortality for people at risk for cardiovascular disease.[2]

2.3 Seasonal Variation of $PM_{2.5}$ Concentrations and Constituents

Seasonal variation of $PM_{2.5}$ concentrations (Figure 2-2) depends on the composition and speciation of the particles and the precursors from which the particles form via preferred chemical reactions. Figure 2-1 shows how precursors such as SO_2, NO_x, and organic compounds help produce important components of $PM_{2.5}$, such as ammonium sulfate, ammonium nitrate, and organic particles. These $PM_{2.5}$ components may coagulate to produce $PM_{2.5}$, or these reactions may take place on the surfaces of $PM_{2.5}$ and thus produce secondary particles. Chemical reactions that produce nitrates are favored in the winter, when nitrate concentrations are enhanced and ozone concentrations are lowered. However, organic carbon and sulfates are produced more readily during the summer because warmer temperatures favor chemical reactions involving SO_2 and VOCs.

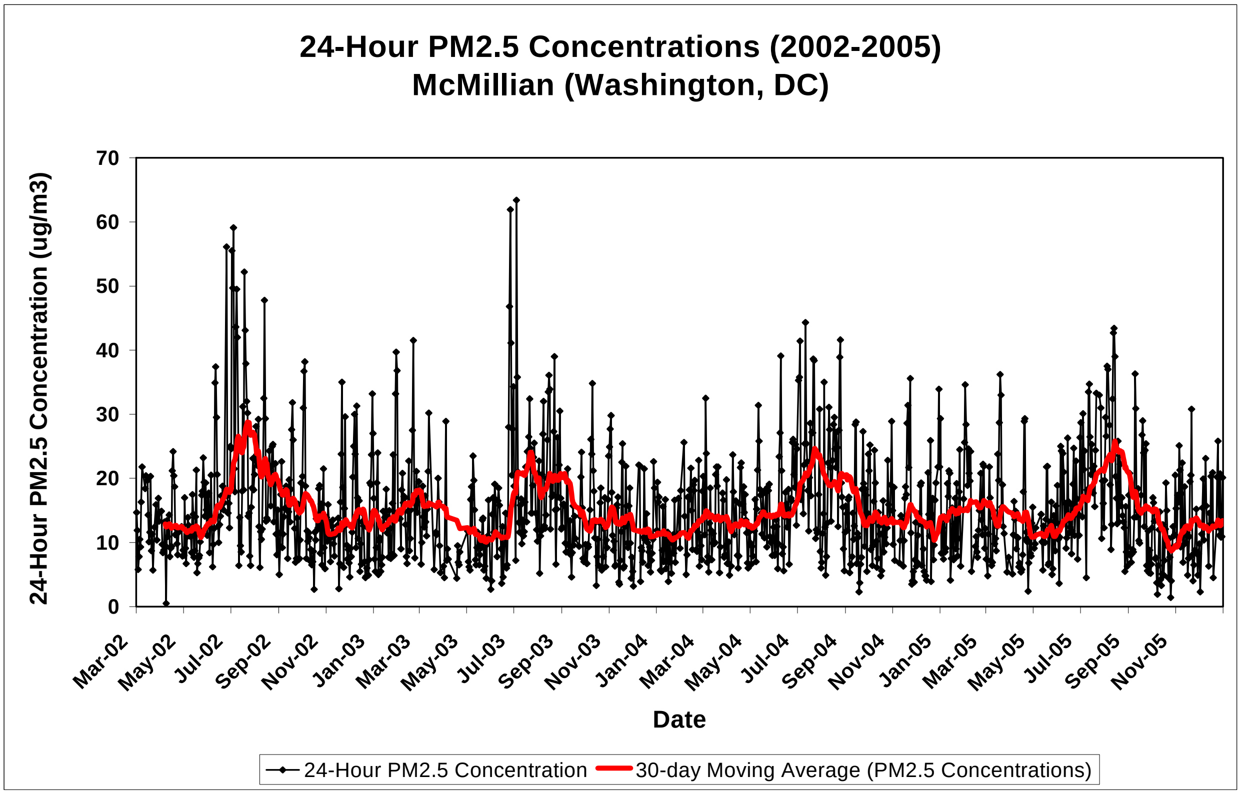

Figure 2-2. Seasonal variation of $PM_{2.5}$ Concentrations during 2002-2005 at the River Terrace monitor (110010041), Washington, DC. Source: 24-Hour PM2.5 Concentrations, AQS.

1) Sulfates

Sulfates, one of the most significant components of $PM_{2.5}$ in the Washington, DC region, generally has higher average concentrations during the spring and summer than during the autumn and winter in the Washington, DC area (Figure 2-3). Sulfates are produced when sulfur dioxide (SO_2) is oxidized; these oxidation reactions occur more frequently during the summer, hence the higher sulfate concentrations occur during the summertime.

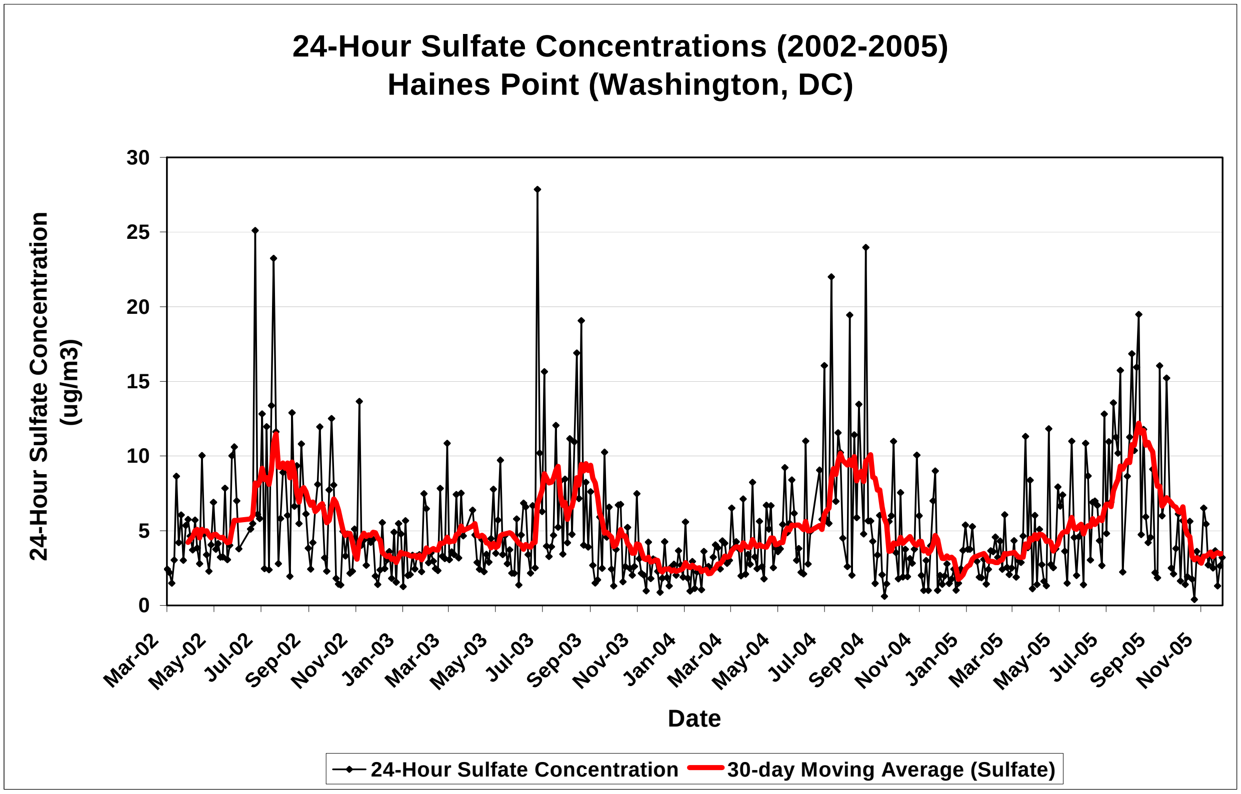

Figure 2-3. Seasonal variation of sulfates during 2002-2005 at the Haines Point monitor (110010042), Washington, DC. Source: 24-Hour Sulfate Concentrations, AQS.

2) Nitrates

Nitrate concentrations increase markedly as seasonal temperatures decrease. Nitrate concentrations are thus heightened during winter and spring (Figure 2-4); thus NO_x typically does not react as readily with VOCs during winter and spring, hence the higher wintertime and spring-time nitrate concentrations. During summer, however, higher air temperatures enable NO_x to react more readily with VOCs and produce ozone. As a result, nitrate concentrations are minimized during the warm season. During winter, heightened nitrate concentrations contribute to slightly elevated $PM_{2.5}$ levels, despite relatively low sulfate concentrations.

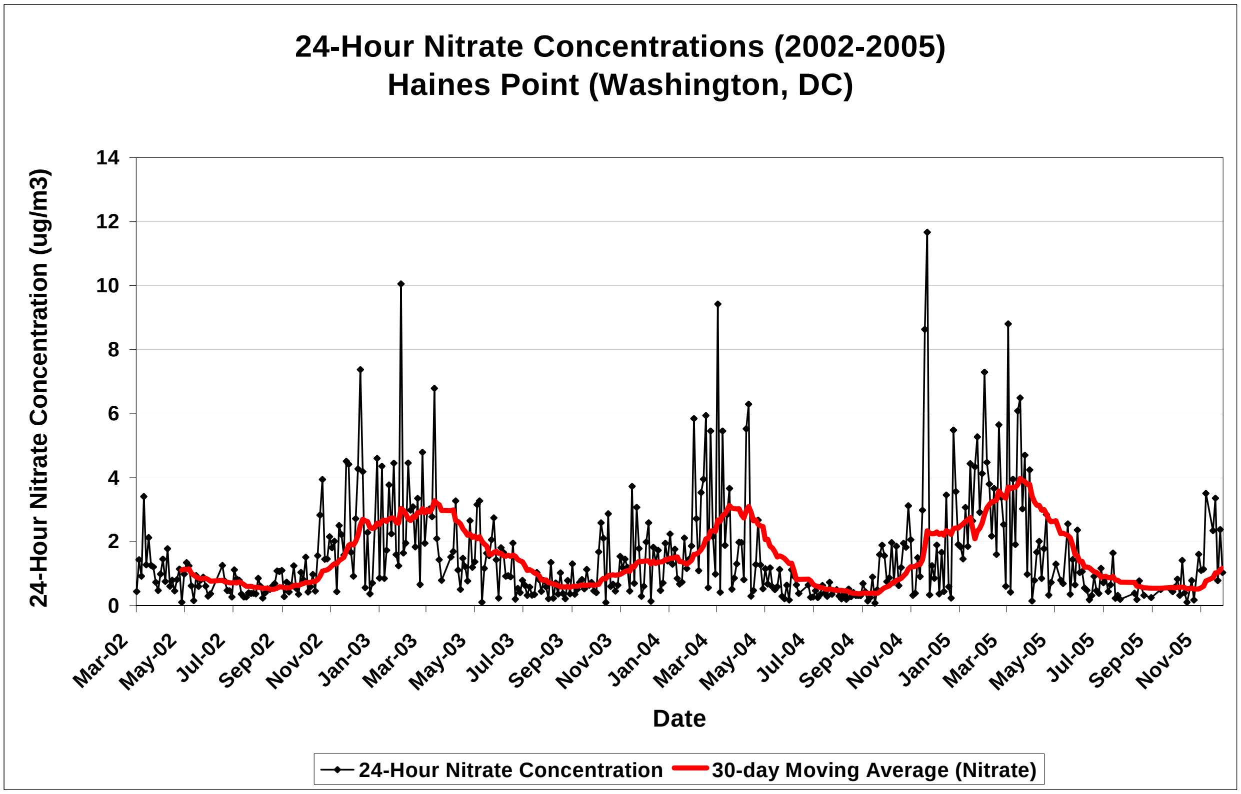

Figure 2-4. Seasonal variation of nitrates during 2002-2005 at the Haines Point monitor (110010042), Washington, DC. Source: 24-Hour Nitrate Concentrations, AQS.

3) Organic and Elemental Carbon

Concentrations of another precursor, organic carbon (Figure 2-5), is quite variable at almost any time of the year, and the highest daily values may originate from forest fires upwind of the region. Another precursor that has high variability throughout the year is elemental carbon. Elemental carbon concentrations are highest during the fall and winter seasons and lowest during the spring and summer seasons.[2]

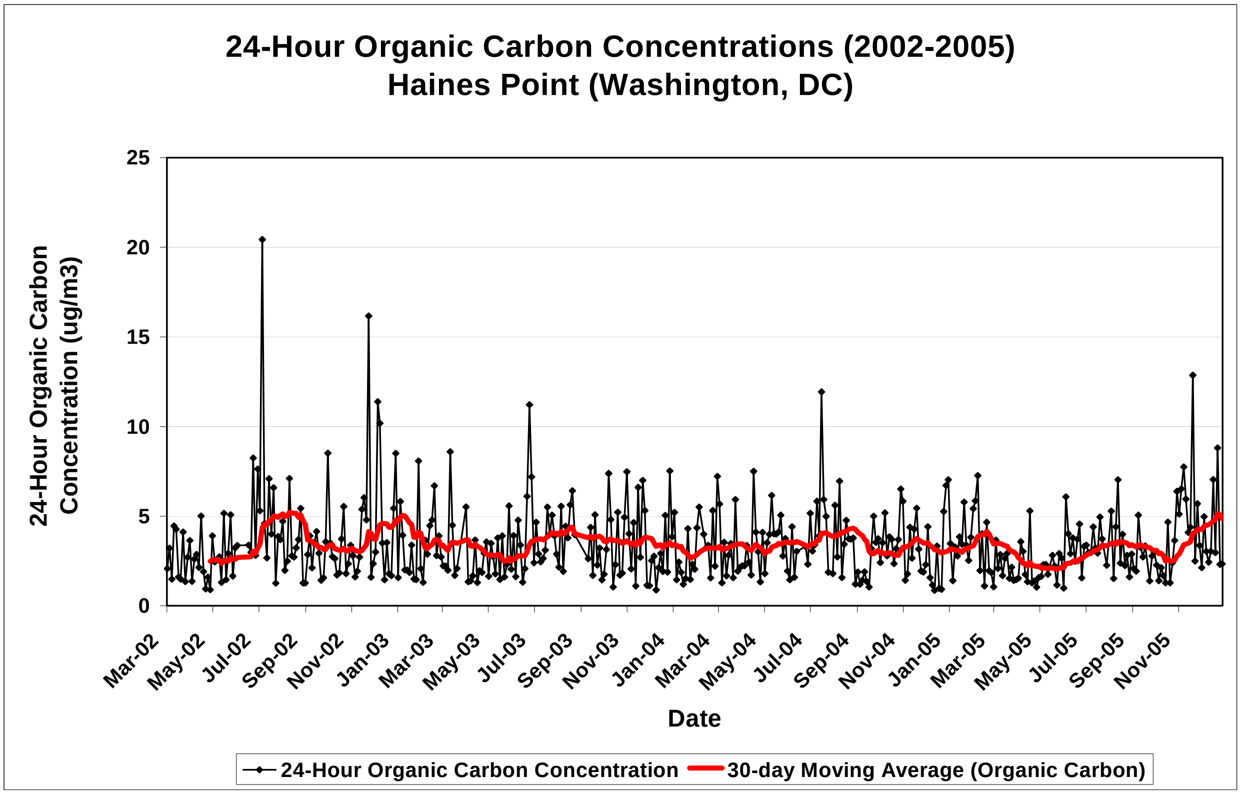

Figure 2-5. Seasonal variation of organic carbon during 2002-2005 at the Haines Point monitor (110010042), Washington, DC. Source: 24-Hour Organic Carbon Concentrations, AQS.

4) Ammonium

Ammonium ions do not exist independently in the atmosphere. They either exist as ammonium sulfate or ammonium nitrate as ammonia reacts with sulfates and nitrates to form these two compounds. Therefore, ammonium concentrations depend on ammonium sulfate or ammonium nitrate concentrations. Concentrations of ammonium sulfate and ammonium nitrate vary seasonally depending on whether sulfates or nitrates have higher concentrations. The chemicals that have higher concentrations are more available for chemical reactions than those with lower concentrations. Since sulfates have much higher concentrations during the summer than other precursors, ammonia will typically react with the sulfates to produce ammonium sulfate, as in Figure 2-1. Hence, ammonium sulfates have higher concentrations in the summer (Figure 2-6), whereas ammonium nitrates have elevated concentrations in the winter due to heightened concentrations of nitrates available for chemical reactions with ammonia.

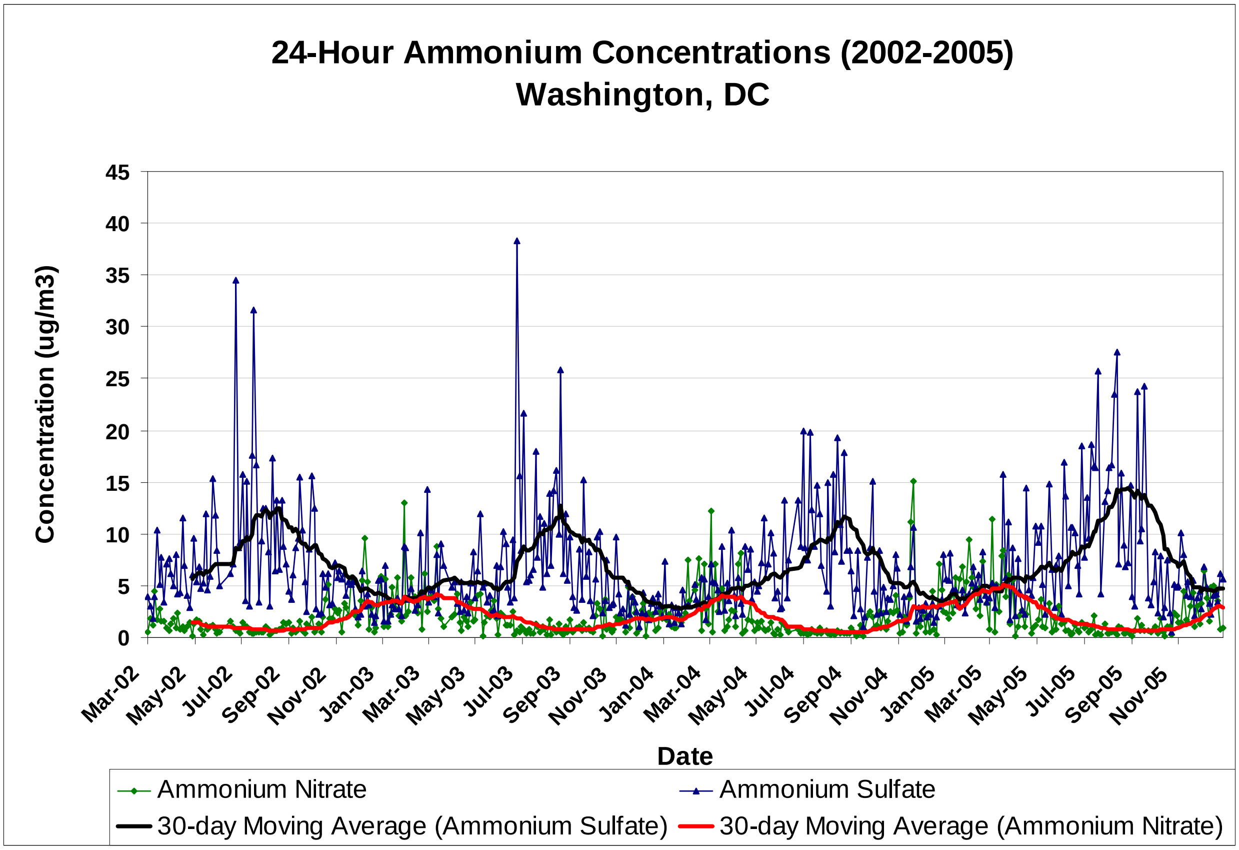

Figure 2-6. Seasonal variation of ammonium during 2002-2005 at the McMillan monitor (110010043), Washington, DC. Source: 24-Hour Ammonium Nitrate & Ammonium Sulfate Concentrations, AQS.

2.4 Diurnal Variation of Fine Particles

$PM_{2.5}$ concentrations not only vary seasonally but also diurnally, as shown in Figure 2-7 using hourly $PM_{2.5}$ data between March 2003 and March 2007. $PM_{2.5}$ concentrations appear to be heightened during the morning and early evening hours, coinciding with peak traffic times for the Washington, DC metropolitan area. A notable minimum in $PM_{2.5}$ concentrations occurs during the late morning to early afternoon hours, presumably due to a diurnal increase in surface winds that help diffuse the particles about and away from the region**.** A lesser minimum also occurs during the overnight hours due to a strong reduction in mobile and industrial activity during sleeping hours.

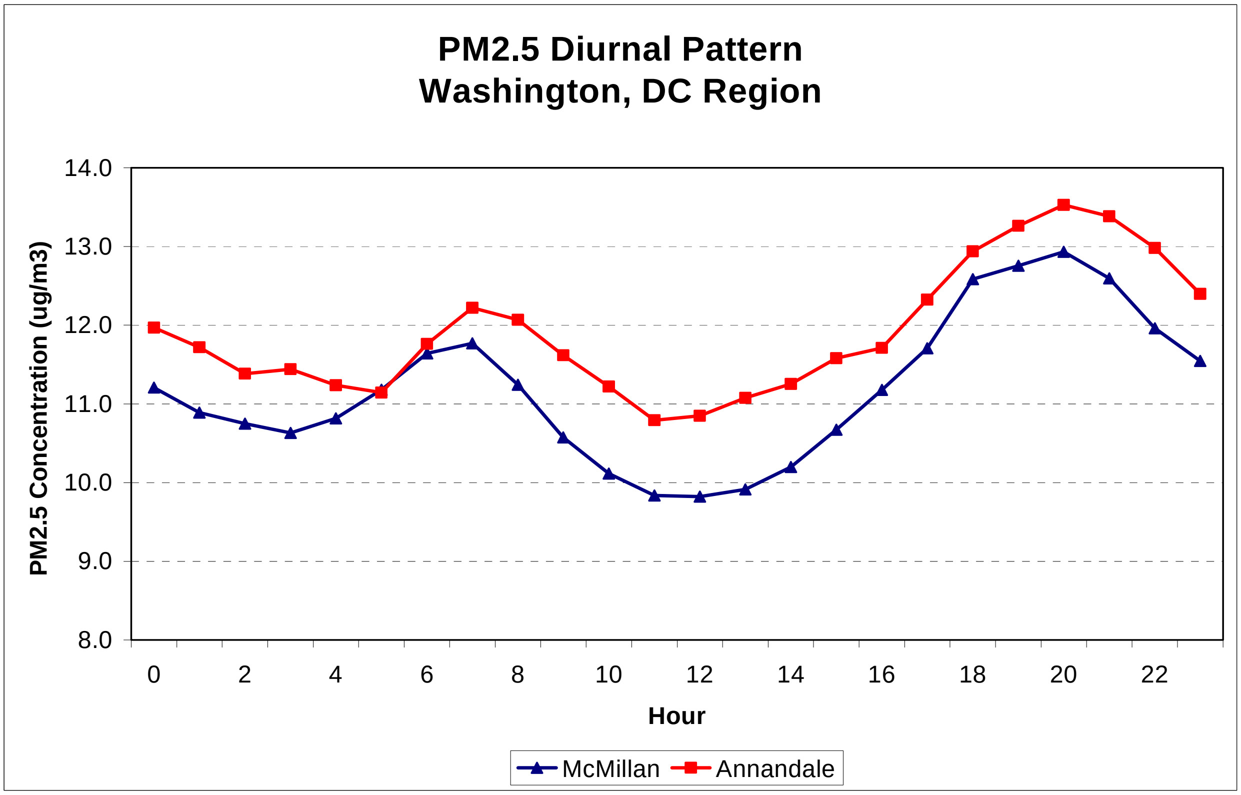

Figure 2-7. Washington $PM_{2.5}$ diurnal pattern based on daily $PM_{2.5}$ data from March 2003 to March 2007. MWCOG, October 2007.

2.5 Trajectories of Fine Particles

$PM_{2.5}$ may originate both locally and remotely. A back trajectory analysis show particles from remote areas are carried by the wind into the region.[1] When high particle concentrations occur upwind, concentrations in the area of interest may also increase as a result. Back trajectories for days with high $PM_{2.5}$ concentrations usually show particle tracks originating over the continental United States (Figure 2-8). Many of these trajectories circulate and track through pollution source regions in the Midwest and Ohio Valley. When winds flow through pollution-heavy

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[1] Back Trajectory is a trace backward in time showing where an air mass has been.

regions, particles are carried downstream by the wind, causing $PM_{2.5}$ concentrations to jump in affected areas. Forest fires, however, are a special case where trajectories need not circulate through the continental United States but may originate from the burning areas that are typically clean and unpolluted, such as eastern Canada on July 7, 2002. Clean days with low particle concentrations typically have trajectories running from distant points in western Canada or looping clockwise from eastern Canada through the Atlantic Ocean into the Washington area.

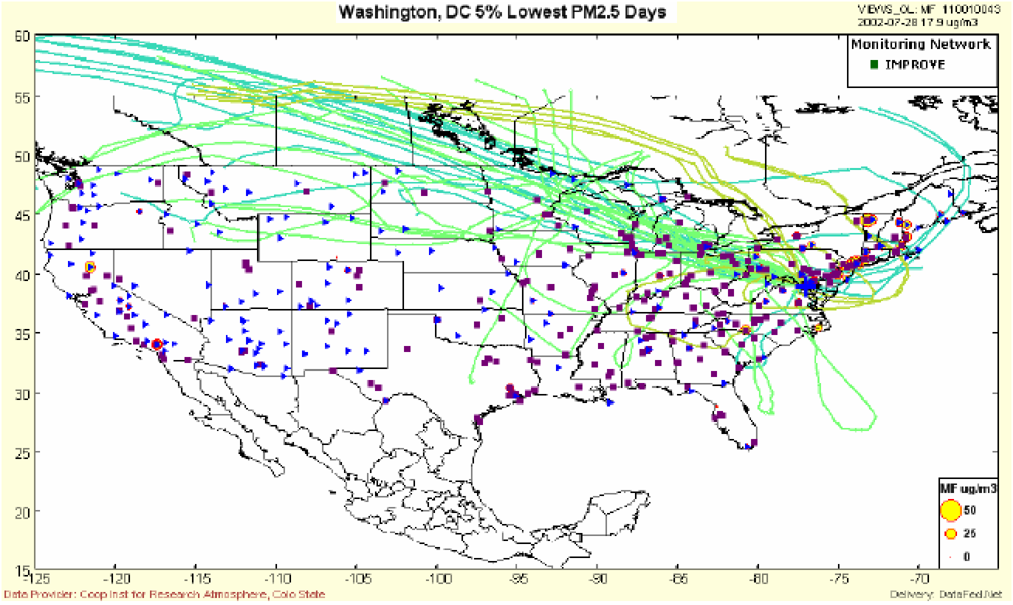


Figure 5-136 Washington, DC, Back Trajectories for the Five Percent Cleanest Days

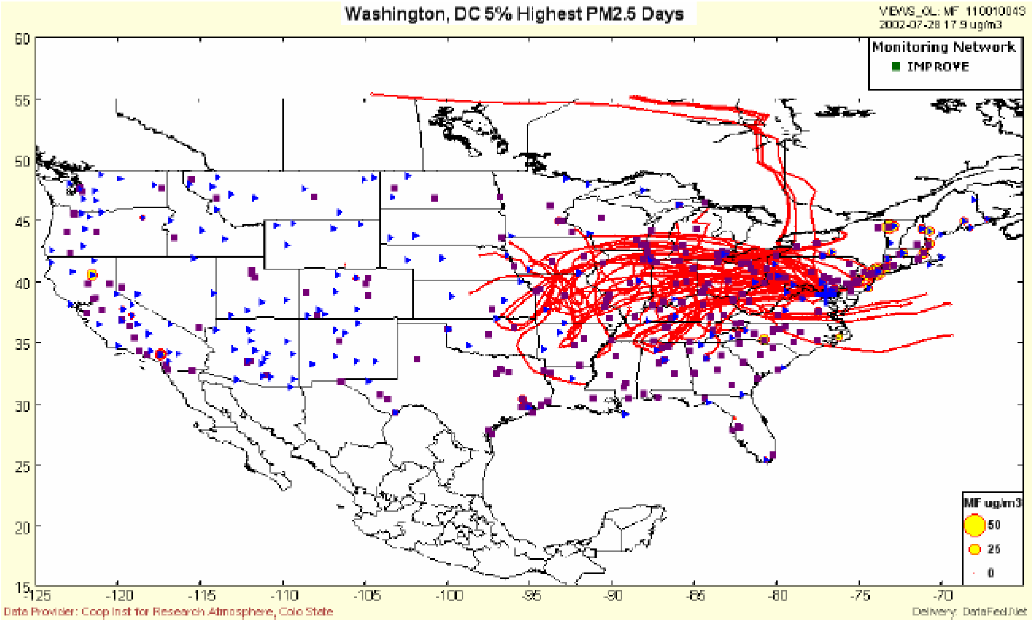


Figure 5-137 Washington, DC, Back Trajectories for the Five Percent Dirtiest Days

Figure 2-8. Fine PM trajectories for Washington, DC based on data from April 2001 to December 2003.[2]

2.6 Major Constituents of $PM_{2.5}$ in the Washington Region

Most observed ambient $PM_{2.5}$ matter originates from precursor gases, SO_2, NO_x, ammonia (NH_3), VOCs, and primary $PM_{2.5}$ emissions and is transferred to the condensed phase through a variety of physiochemical processes, forming major constituents of $PM_{2.5}$. Data from speciation monitors provide information about the relative contribution of the chemical components and the sources of these pollutants.

$PM_{2.5}$ speciation monitors are used to support SIP development by providing information on $PM_{2.5}$ chemical composition. There are two speciation monitors in the Washington nonattainment area, one located at McMillan Station in the District and the other at Annandale, Virginia. The relative concentrations of each $PM_{2.5}$ constituent, annually averaged over 2001-2003, are shown in Figure 2-9, with sulfates being one of the most significant contributors to $PM_{2.5}$ mass concentrations. However, primary aerosol particles have both direct and indirect roles in the formation of secondary particle matter. For example, primary particles can serve as reaction sites for the formation of new PM.

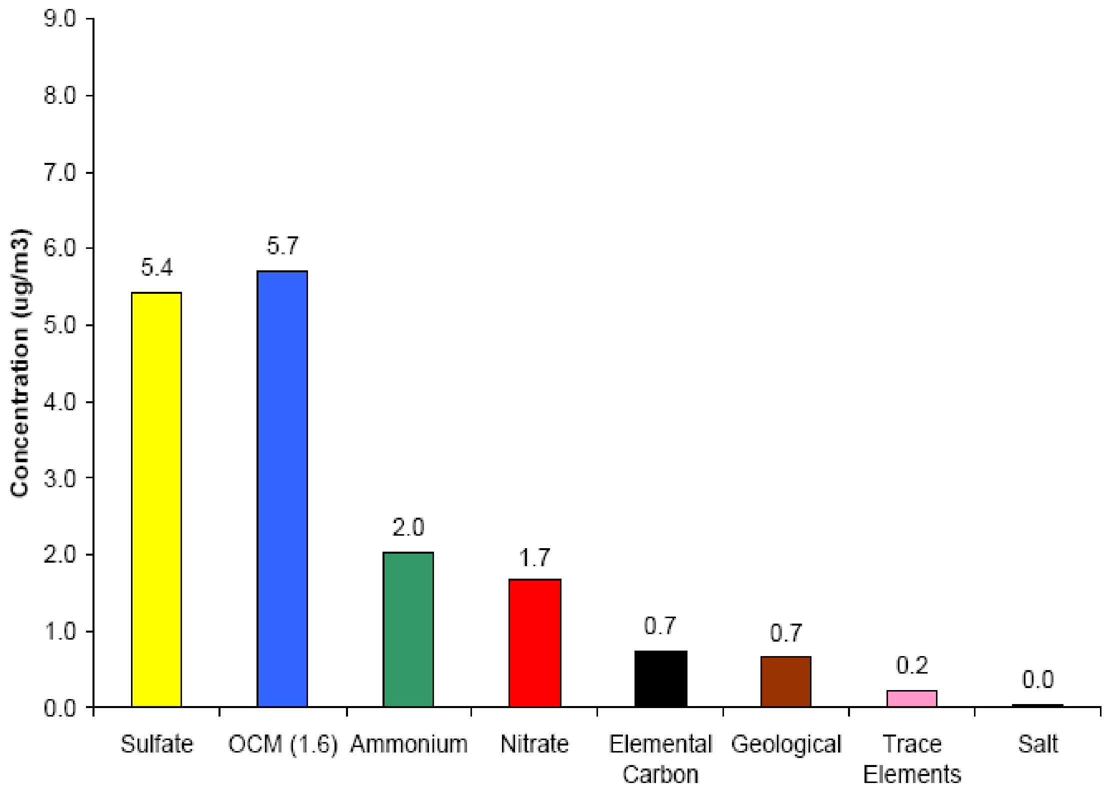


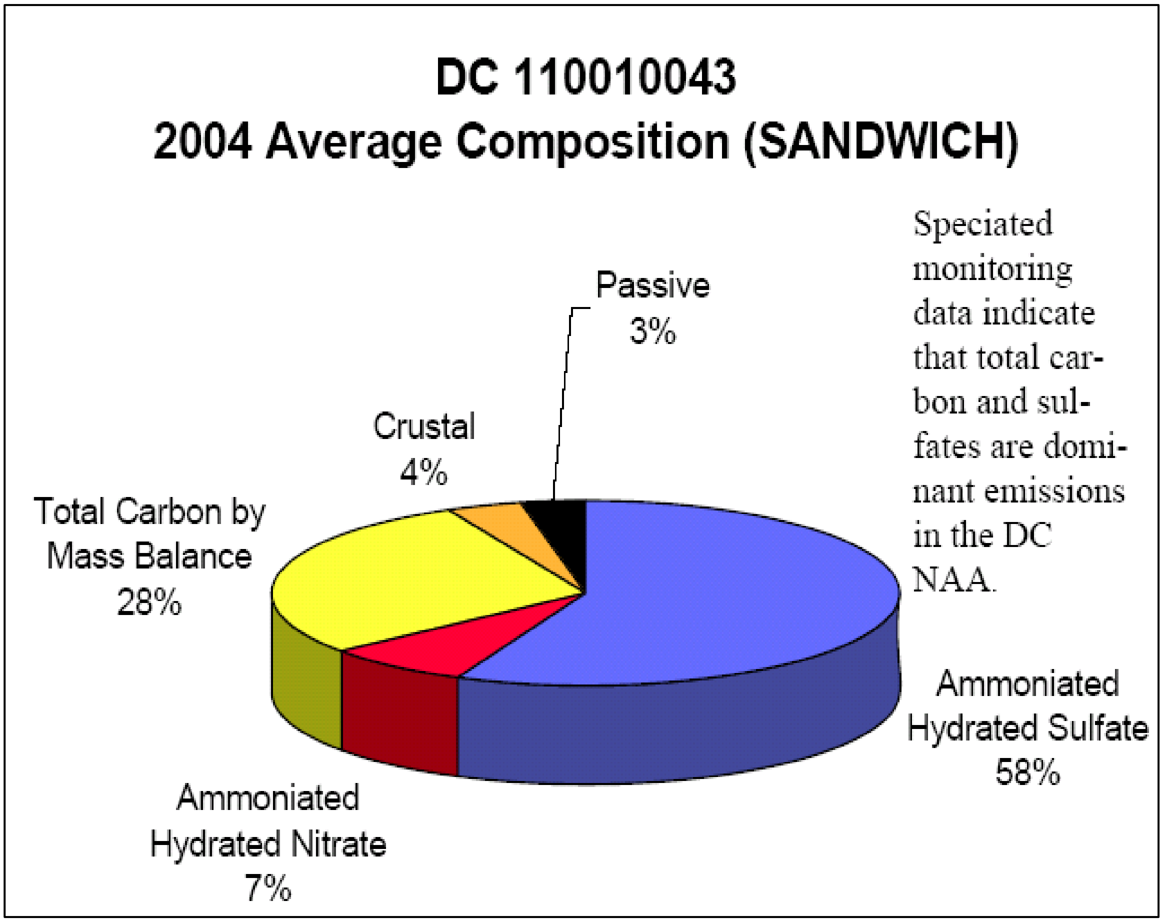
Figure 5-128 Major Constituents of $PM_{2.5}$ Mass, Washington, DC

Figure 2-9. Annually averaged 2001-2003 concentrations of $PM_{2.5}$ constituents for Washington, DC.[3] Source: "$PM_{2.5}$ Area Profiles Mid-Atlantic Region Observations," August 2006. EPA Staff working draft. OCM is Organic Carbon Mass. Organic Mass / Organic Carbon ratio of 1.6.

2.7 Sources of $PM_{2.5}$ and Constituents

Sources of $PM_{2.5}$ include all types of combustion activities including motor vehicle emissions, coal power plants, wood and vegetative burning, and certain industrial processes involving nitrates and sulfates. EPA uses the SANDWICH (Sulfate, Adjusted Nitrate, Derived Water, Inferred Carbon Hybrid material balance) method to chemically characterize ambient $PM_{2.5}$ speciation data. Figure 2-10 shows that a large portion, about 65%, of annual averaged $PM_{2.5}$ composition consists of ammonium sulfate and ammonium nitrate, which are products of reactions of ammonia, sulfates, and nitrates in the atmosphere in summer and winter, respectively.

Ammonia from sources such as fertilizer and animal feed operations contribute to the formation of ammonium sulfates and ammonium nitrates suspended in the atmosphere. The rest originates from sulfates, carbon and organic compounds from vegetative burning, coal power plants, geological dust, oil combustion, motor vehicle emissions, and diesel vehicle emissions. Nitrates usually originate from vehicle emissions and power generation.



DC 110010043
2004 Average Composition (SANDWICH)

Speciated monitoring data indicate that total carbon and sulfates are dominant emissions in the DC NAA.

Figure 2-10. $PM_{2.5}$ Composition (% by mass) data from the McMillan Station in Washington, DC in 2004. "$PM_{2.5}$ Area Profiles Mid-Atlantic Region Observations," August 2006. EPA Staff working draft. NAA is nonattainment area. "Passive" represents other components not shown in the graph.

2.8 Determination of Significance for Precursors

The significance of each precursor for $PM_{2.5}$ has been analyzed and determined by EPA. Based on EPA's advice, $PM_{2.5}$ Direct, SO_2, and NO_x were deemed significant for the Washington, DC nonattainment area, while NH_3 and other precursors were deemed insignificant at this time. According to EPA's $PM_{2.5}$ implementation guidance, sources of direct $PM_{2.5}$ and SO_2 must be evaluated for control measures in all nonattainment areas.[2] Direct $PM_{2.5}$ emissions include organic carbon, elemental carbon, and crustal material. If emissions of a precursor contribute significantly to $PM_{2.5}$ concentrations in the area, then the sources of that precursor will need to be evaluated for reasonable control measures. EPA found sulfates and carbon to be the most significant fractions of $PM_{2.5}$ mass in all nonattainment areas and therefore concluded that the reductions in SO_2 will lead to a significant net reduction in $PM_{2.5}$ concentrations despite a potential slight increase in nitrates.

The contribution of VOC to $PM_{2.5}$ formation is the least understood of all precursors, and the reactions involving VOC are highly complex. In light of these factors, states are not required by EPA to address VOC as a $PM_{2.5}$ attainment plan precursor and evaluate them for control measures, unless the state or EPA makes a finding that VOCs significantly contributes to $PM_{2.5}$ concentrations in the non-attainment area or to other downwind air quality concerns. Due to lack of conclusive information at this time, given the state of science and research on $PM_{2.5}$ precursors, the Washington, DC region decided to follow EPA's advice on VOC for the current Annual $PM_{2.5}$ NAAQS SIP and reevaluate VOCs and their significance in future $PM_{2.5}$ SIPs and revisions.

The role of ammonia in $PM_{2.5}$ is also not as well understood as those of SO_2 and carbon. Although ammonia is a constituent of $PM_{2.5}$ as ammonium sulfate and ammonium nitrate as shown in Figure 2-10, the mass of ammonia takes up only a small fraction of the total mass of $PM_{2.5}$ constituents. Reducing ammonia emissions may marginally reduce $PM_{2.5}$ concentrations, but particle and precipitation acidity may increase as a result. Increased acidity in particles and precipitation is a more adverse side effect of reducing ammonia concentrations, so ammonia is not required by EPA to be evaluated in this implementation plan unless deemed significant by the state or EPA. Due to lack of conclusive information at this time, the states decided to follow EPA's advice on ammonia in the current SIP for Annual $PM_{2.5}$ NAAQS and reevaluate ammonia's significance in future $PM_{2.5}$ SIPs and revisions.

The role of NO_x in the formation of $PM_{2.5}$ is very important. It forms nitrate in significant amounts during winter, favored by the availability of ammonia, low temperatures, and high relative humidity. $PM_{2.5}$ concentrations respond most effectively to NO_x reductions in the winter by reducing the oxidation process and SO_2 formation. Therefore, states are required to address NO_x as a $PM_{2.5}$ attainment plain precursor and evaluate reasonable controls for nitrates in implementation plans, unless the EPA finds that NO_x emissions from sources in the state do not significantly contribute to the $PM_{2.5}$ concentrations in the nonattainment area. The states have determined that NO_x is a significant precursor in the plan for the Metropolitan Washington region.

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[2] EPA, $PM_{2.5}$ Implementation Guidance, *Federal Register*, vol. 72, No. 79m 4/25/07, pp. 20586-20666.

EPA's $PM_{2.5}$ implementation rule requires that state air agencies make a determination of the significance of $PM_{2.5}$ pollutants/precursors for SIP planning purposes, including requirements for motor vehicle emission budgets for use in conformity. The known PM pollutants include $PM_{2.5}$ Direct as well as the precursors NO_x, SO_2, VOCs, and NH_3 (see Table 2-1). $PM_{2.5}$ Direct and the precursors NO_x and SO_2 are deemed significant under the EPA guidance. PM_{10} is required for the base year emission inventory but does not need to be included in the SIP control strategy. For the current annual $PM_{2.5}$ SIP, several precursors are presumed to be insignificant and are not required be included in the SIP control strategy unless the state or EPA makes a finding of significance. Table 2-1 summarizes the federal requirements for each precursor.

Table 2-1. EPA SIP Requirements for PM Pollutants

	$PM_{2.5}$ Direct	NO_x	SO_2	VOC	NH_3	PM_{10}
Base Year Emission Inventory	√	√	√	√	√	√
SIP Controls	√	√	√	-	-	Not required

- = Not required unless precursor deemed significant by states or EPA.

Summary of Significance Determinations for PM Pollutants

Through interagency consultation and consideration of available information, the state air agencies have completed significance determinations for each of the PM precursors. The determination was conducted using a two-step process. Step 1 involved determining whether PM pollutants/precursors are considered significant for SIP planning purposes. Step 2 involved determining whether PM pollutants/precursors identified as significant in Step 1 require Motor Vehicle Emission Budgets (MVEBs) for conformity. Table 2-2 summarizes the determination.

Table 2-2. Summary of Significance Determinations for SIP Controls and Motor Vehicle Emission Budgets

	PM Direct	NO_x	SO_2	VOC	NH_3
Step 1: Determine Significance for SIP Controls	√	√	√	No*	No*
Step 2: Determine Significance for Establishing Motor Vehicle Emission Budgets for Conformity	√	√	No	No*	No*

* = Due to lack of conclusive information at this time, given the state of science and research on $PM_{2.5}$ precursors, the Washington, DC region decided to follow EPA's advice on VOC and NH_3 for the current Annual $PM_{2.5}$ NAAQS SIP and reevaluate their significance in future $PM_{2.5}$ SIPs and revisions.

EPA notes that any significance or insignificance finding made prior to EPA's adequacy finding for budgets in a SIP, or EPA's approval of the SIP, should not be viewed as the ultimate determination of the significance of precursor emissions in a given area. State and local agencies may reconsider significance findings based on information and analyses conducted as part of the SIP development process.

Determine Significance for SIP Controls

The only precursors for which significance determinations are needed for SIP control purposes are VOCs and ammonia. EPA requires that $PM_{2.5}$ Direct, NO_x, and SO_2 controls be evaluated and included in the SIP. A primary factor considered for VOCs and ammonia is that the region's monitors already show compliance with the $PM_{2.5}$ annual NAAQS so no additional controls are needed for attainment purposes. A second factor considered is that EPA guidance allows states to presume that these precursors are insignificant unless modeling or other analysis indicates that the precursor should be considered significant. A summary of the rationale for the significance determinations for VOCs and ammonia is listed in Table 2-3.

Table 2-3. Summary of Rationale for Insignificance Determinations for VOCs and NH_3 for SIP Controls

Criteria	Pollutant	
	VOC	**NH_3**
Are emission controls needed for attainment or maintenance?	No	No
Is there evidence to counter EPA's presumption that the precursor be considered insignificant?	No	No
Will reducing emissions of the precursor have a significant impact on $PM_{2.5}$ concentrations?	No, based on VISTAS modeling	No, based on VISTAS modeling
Are technology options available to control emissions?	Yes	Varies by source
Is the precursor considered significant for Annual $PM_{2.5}$ NAAQS SIP planning purposes?	No	No

*VISTAS is Visibility Improvement State and Tribal Association of the Southeast.

National research is underway to assess the contribution of VOCs to secondary organic aerosol formation. States are following the research and will reconsider the significance determination for both VOC and ammonia when further technical information becomes available for future $PM_{2.5}$ SIPs and revisions.

2.9 Compliance with the $PM_{2.5}$ NAAQS

The Metropolitan Washington region's Federal Reference Monitors (FRMs) (see Figure 1-1) demonstrate compliance with the annual $PM_{2.5}$ National Ambient Air Quality Standard in 2005 and 2006 and with the 24-hour standard throughout the period 2001-2006. The purpose of the filter-based FRMs is to determine compliance with the $PM_{2.5}$ NAAQS. Filter-based FRMs measure $PM_{2.5}$ mass by passing a measured volume of air through a preweighed filter.

Design value trends for the annual and 24-hour $PM_{2.5}$ standards are shown in Figure 2-11 and 2-12 respectively. The data are from EPA's air trends data (www.epa.gov/air/airtrends). In 2005 the design value was 14.6 µg/m^3; in 2006 the design value was 14.5 µg/m^3, again below the annual $PM_{2.5}$ standard of 15.0 µg/m^3.

Figure 2-11. Annual $PM_{2.5}$ Design Values, Washington Region, 2001-2006

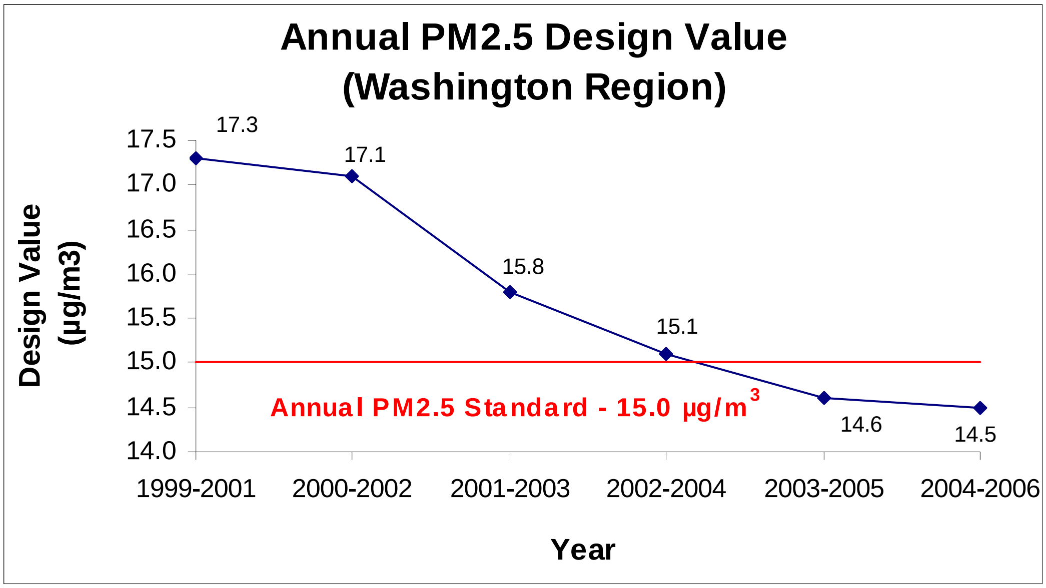
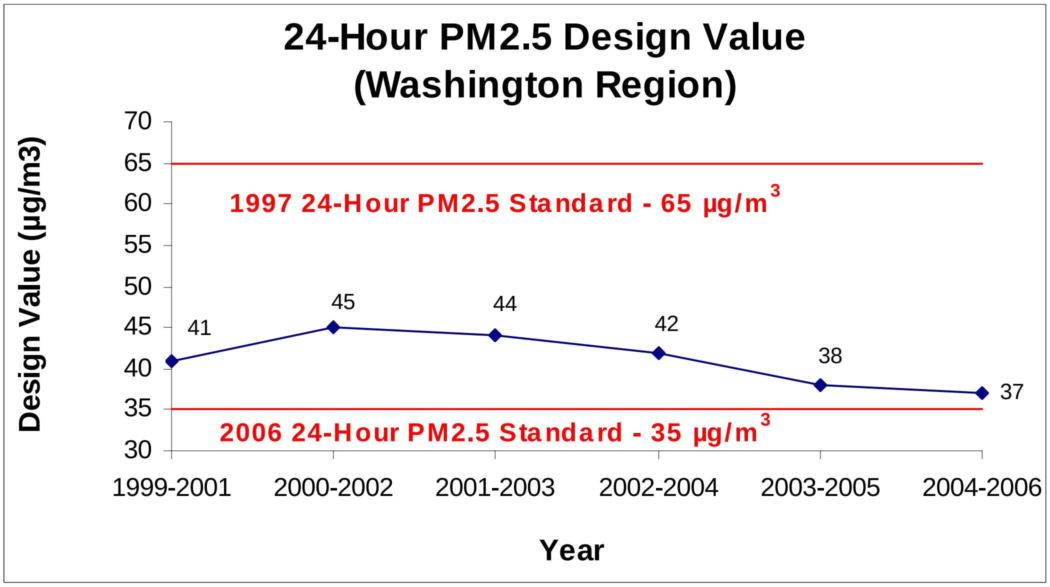


Figure 2-12. 24-Hour $PM_{2.5}$ Design Values, Washington Region, 2001-2006



References

1. American Lung Association, State of the Air Report 2007, www.lungusa.org

2. EPA, Air Quality Criteria Document for PM (October 2004), EPA/600/P-99/002aF

3. NARSTO 2004 PM Assessment for Policy Makers: A NARSTO Assessment. P. McMurry, M. Shepherd and J. Vickery, Cambridge University Press, Cambridge, England ISBN 0-52-1842875.

4. An Analysis of Speciated $PM_{2.5}$ Data in the MARAMA Region," Mid-Atlantic Regional Air Management Association. May 31, 2006, pp. 171-181.

5. "PM2.5 Area Profiles Mid-Atlantic Region Observations," August 2006. EPA Region 3 Staff working draft, pp.103-118.