2.0 FINE PARTICLE POLLUTION

2.1 Definition of Fine Particle Matter

Fine particle 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 fine particles, coarse-mode particles such as dust, pollen, sea salt, and ash, are usually produced by mechanical processes including wind and erosion. Fine particles ($PM_{2.5}$) are less than or equal to 2.5 microns across, about 1/30th the average width of a human hair, while coarse-mode particles are more than 2.5 to around 10 microns across.

Gas-phase precursors SO_2, NO_X, VOC, and ammonia undergo chemical reactions in the atmosphere to form secondary particulate matter. 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 fourteen monitors, Federal Reference Monitors or FRM, that sample fine particles in the Washington region (see Figure 1-1). The purpose of the filter-based FRM monitors is to determine compliance with the PM2.5 NAAQS. FRM monitors are filter-based that measure $PM_{2.5}$ mass by passing a measured volume of air through a pre-weighed 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 your lungs and some may get into your bloodstream. Therefore, exposure to such particles can affect both lungs and heart. 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.

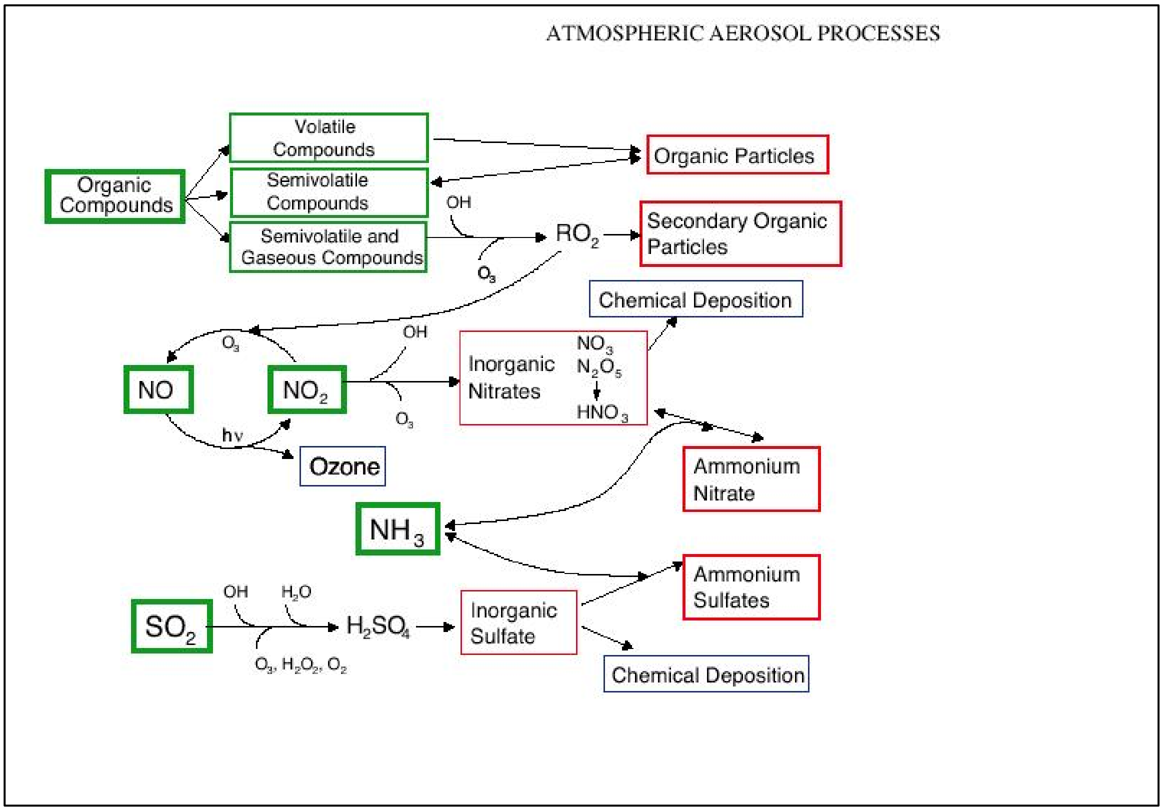


Figure 2-1: **Atmospheric chemical reactions that contribute to PM2.5, from the NARSTO Assessment 2003.**

Studies have demonstrated a relationship between increased levels of fine particles 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.[1]

Environmental effects of particle pollution include reduced visibility, environmental damage, and aesthetic damage. Fine particles ($PM_{2.5}$) 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.

2.3 Seasonal Variation of PM2.5 Constituents

[1] Cardiovascular Risks from Fine Particulate Air Pollution. *Douglas W. Dockery, Sc.D., and Peter H. Stone, M.D.,* New England Journal of Medicine, February 1, 2007, Volume 356:511-513, Number 5

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 1 shows how precursors such as SO_2, NO_x, and organic compounds help produce components of $PM_{2.5}$, including inorganic sulfates and nitrates, ammonium sulfate, ammonium nitrate, and organic particles. These $PM_{2.5}$ components may coagulate to produce fine particles, or these reactions may take place on the surfaces of fine particles 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 VOC.

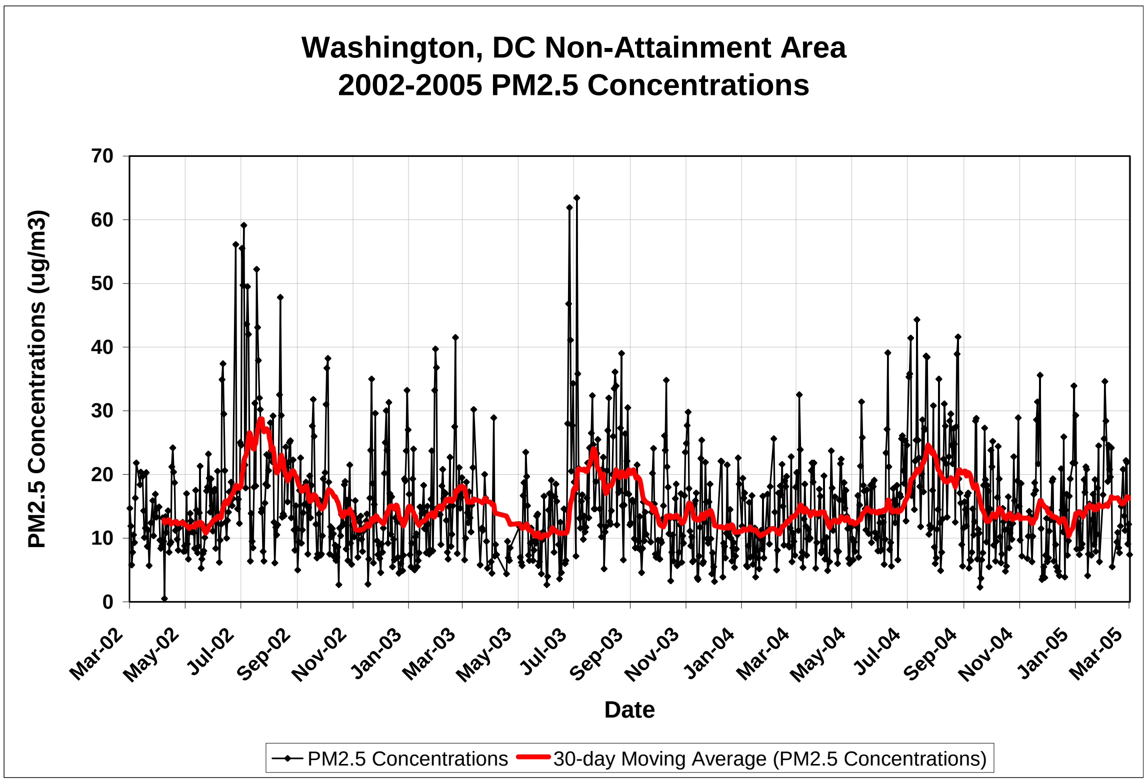


Figure 2-2: Seasonal variation of $PM_{2.5}$ during 2002-2005 in the Washington, DC non-attainment area.

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 3). Sulfates are produced when sulfur dioxide (SO_2) is oxidized, and these oxidation reactions occur more frequently during the summer, hence higher sulfate concentrations during summertime.

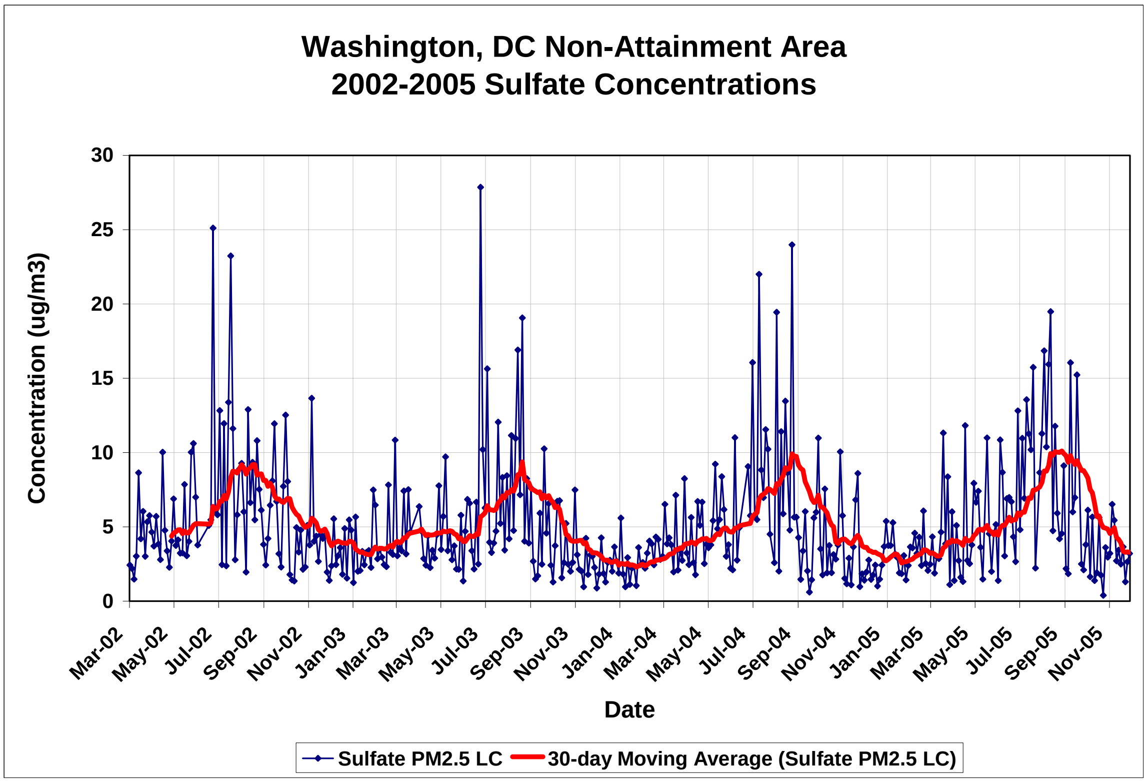


Figure 2-3: Seasonal variation of sulfates during 2002-2005 in the Washington, DC non-attainment area.

2) Nitrates

Nitrate concentrations increase markedly as seasonal temperatures decrease. Nitrate concentrations are thus heightened during winter (Figure 4, thus NO_x typically does not react as readily with VOC during winter, hence higher wintertime nitrate concentrations. During summer, however, higher air temperatures enable NO_x to react more readily with VOC and produce ozone. As a result, nitrate concentrations are minimized during the warm season. During winter, heightened nitrate concentrations contribute to slightly elevated PM2.5 levels, despite relatively low sulfate concentrations.

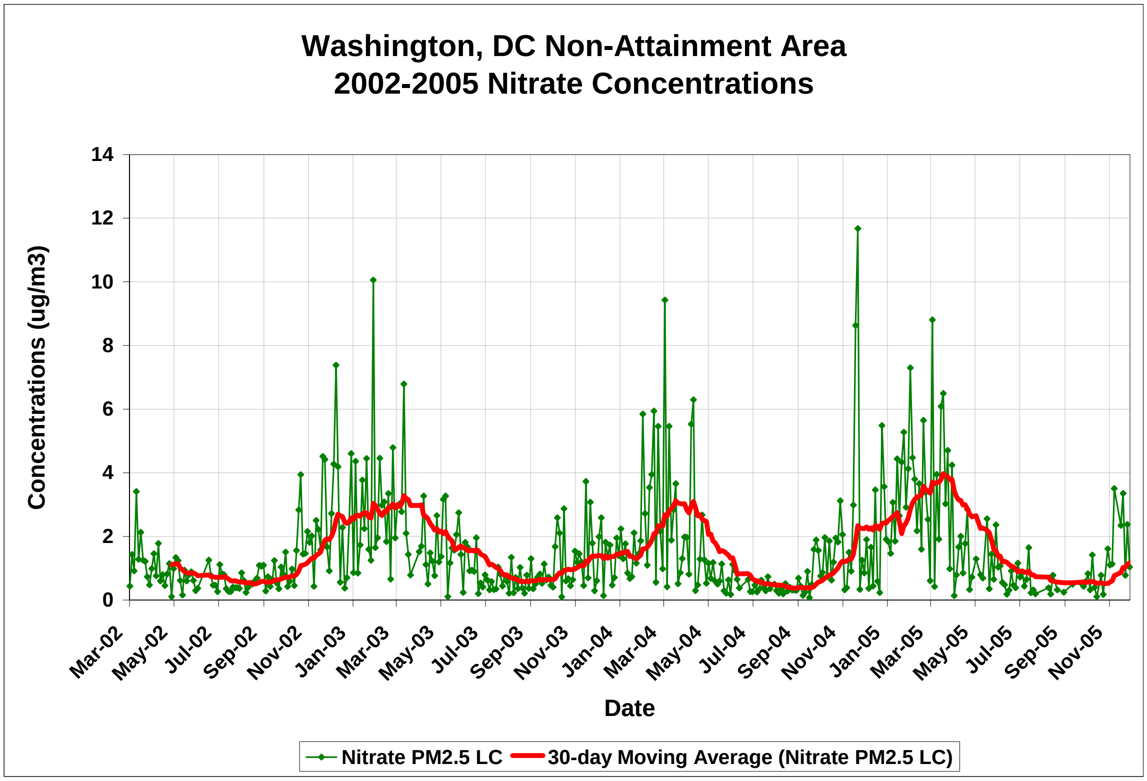


Figure 2-4: Seasonal variation of nitrates during 2002-2005 in the Washington, DC non-attainment area.

3) Organic and Elemental Carbon

Concentrations of another precursor, organic carbon (Figure 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 spring and summer seasons.[1]

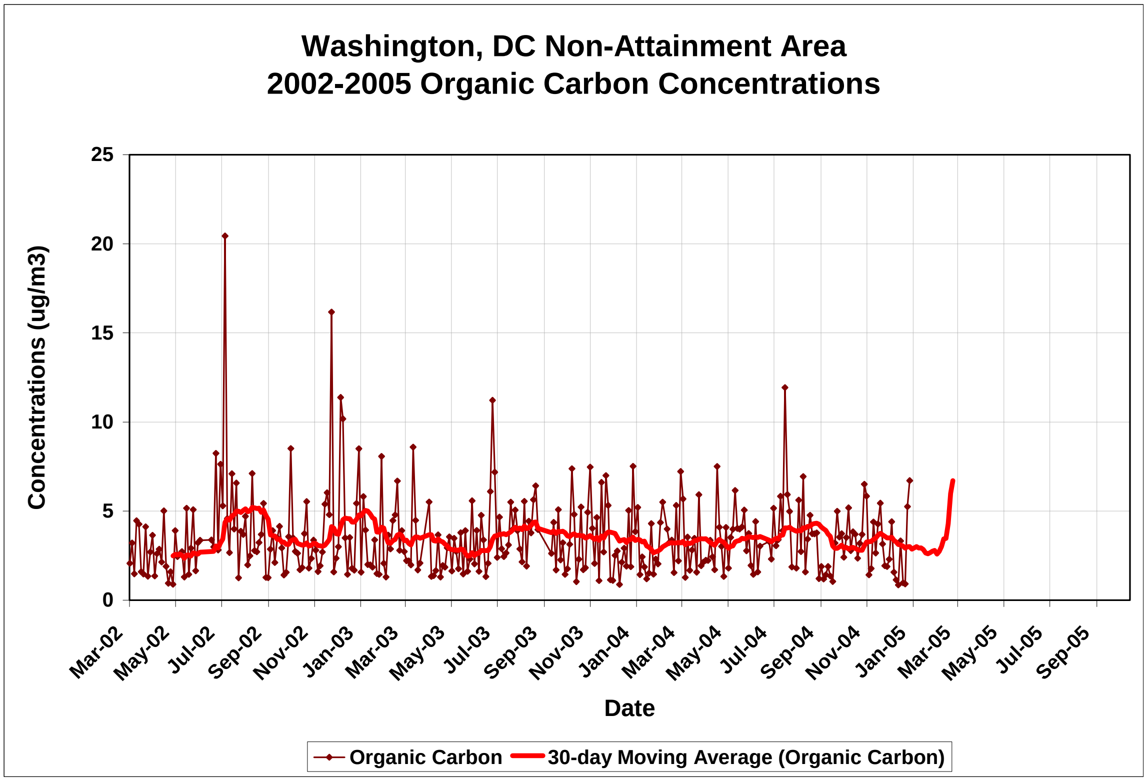


Figure 2-5: Seasonal variation of organic carbon during 2002-2005 in the Washington, DC area.

4) Ammonium

Ammonium concentrations vary seasonally according to whichever has higher concentrations; sulfates or nitrates. The chemicals that have higher concentrations are more available for chemical reactions than those with lower concentrations. Since during the summer, sulfates have much higher concentrations than other precursors, ammonia will typically react with the sulfates to produce ammonium sulfate, as in Figure 1. Hence, ammonium sulfates have higher concentrations in the summer (Figure 6), while ammonium nitrates have elevated concentrations in the winter due to heightened concentrations of nitrates available for chemical reactions with ammonia.

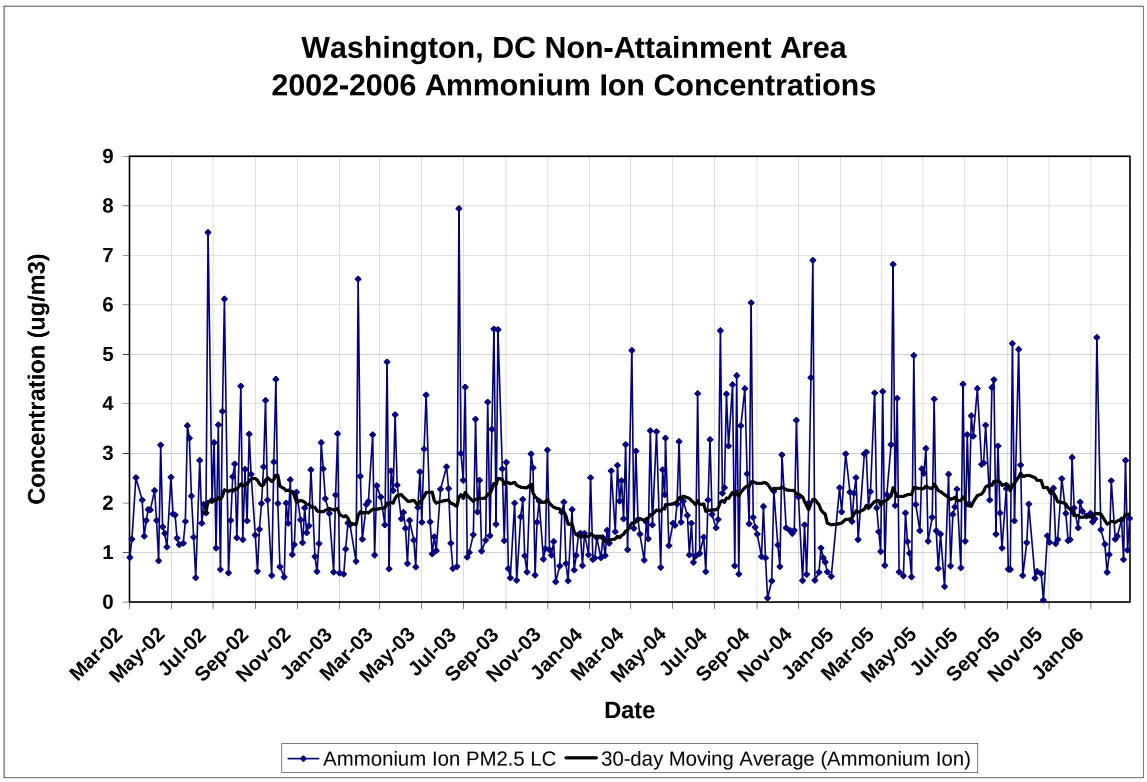


Figure 2-6: Seasonal variation of ammonium during 2002-2005 in the Washington, DC non-attainment area.

2.4 Diurnal Variation of Fine Particles

Fine particle 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. Fine particle 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 fine particle 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.

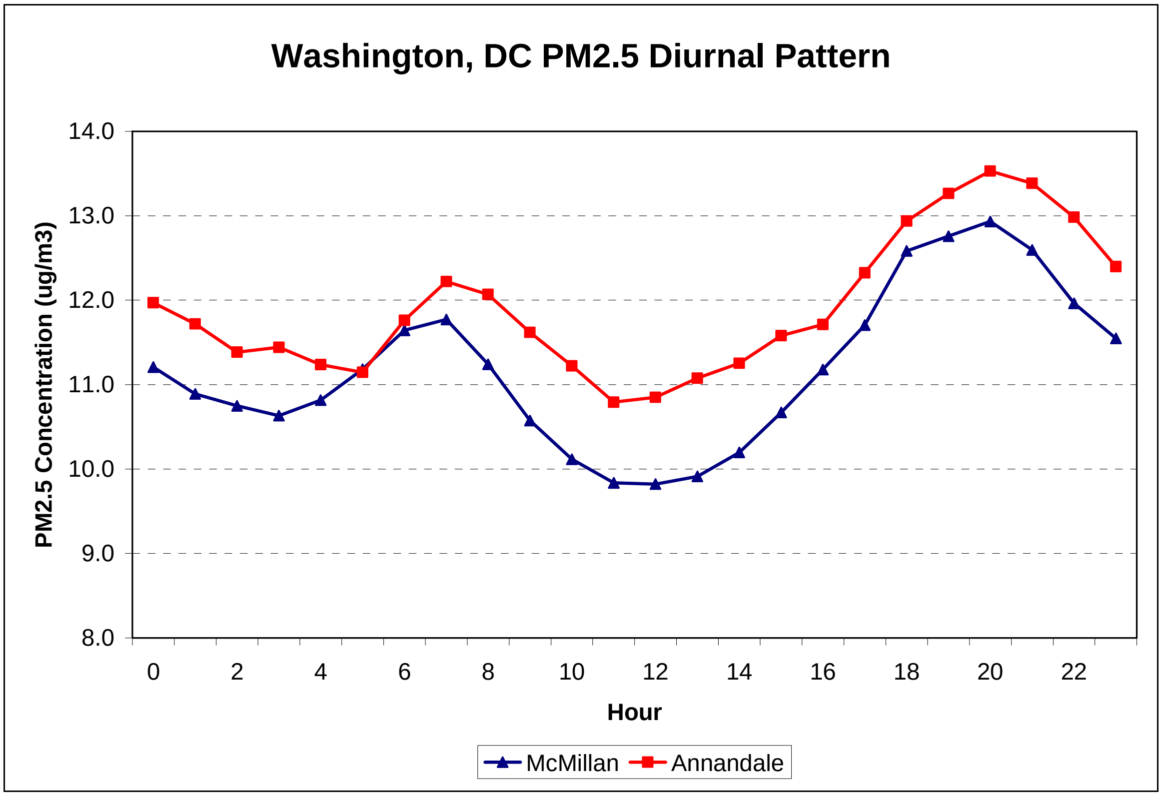


Figure 2-7: Washington $PM_{2.5}$ Diurnal Pattern based on daily $PM_{2.5}$ data from March 2003 to March 2007.

2.5 Trajectories of Fine Particles

Fine particles may originate both locally and remotely. Particles from remote areas are carried by the wind into the region. When high particle concentrations occur upwind, concentrations in the area of interest may also increase as a result. Back trajectories for days with high fine particle concentrations usually show particle tracks originating over the continental U.S (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 regions, particles are carried downstream by the wind, causing fine particle concentrations to jump in affected areas. Forest fires, however, are a special case where trajectories need not circulate through the continental U.S., 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.

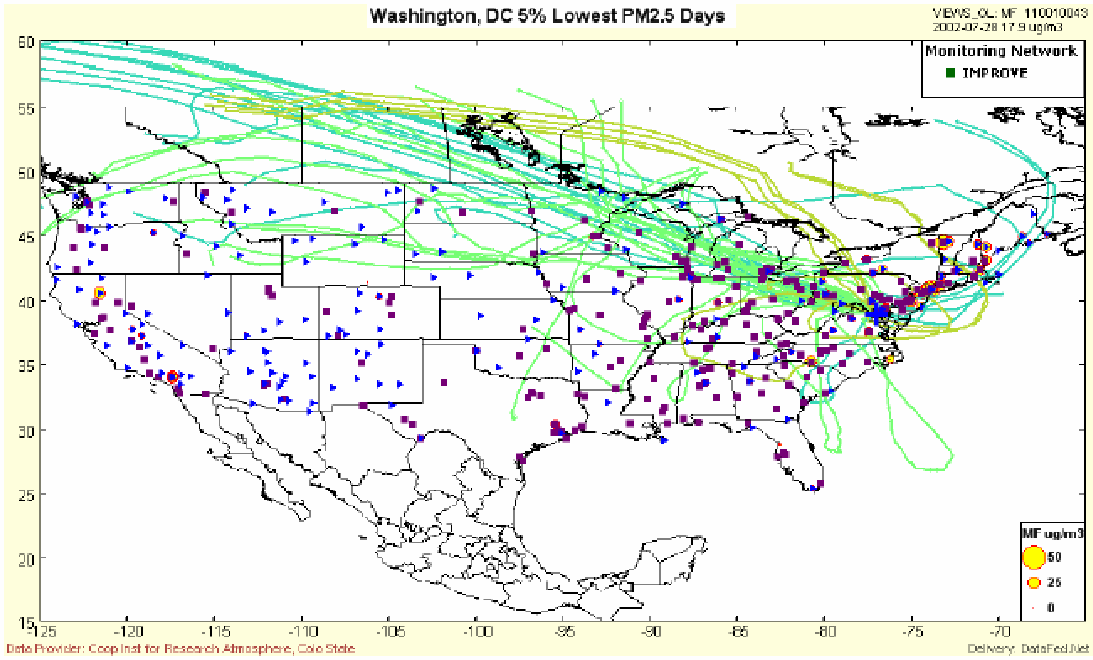


Figure 5-136 Washington, DC, Back Trajectories for the Five Percent Cleanest Days

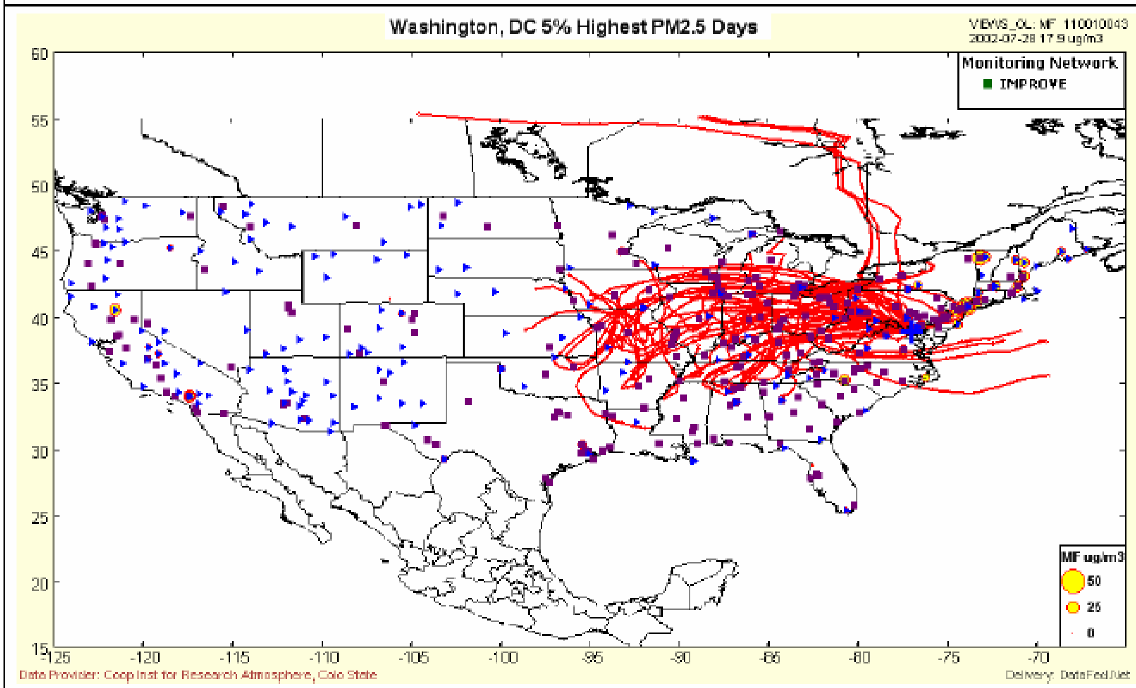


Figure 5-137 Washington, DC, Back Trajectories for the Five Percent Dirtiest Days

Figure 2-8: Fine PM Trajectories for Washington, DC based on data from April 2001 to December 2003[1]

2.6 Major Constituents of PM2.5 and Sources in the Washington Region

Most observed ambient $PM_{2.5}$ originate from precursor gases, sulfur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3), volatile organic compounds (VOC), and primary $PM_{2.5}$ emissions and is transferred to the condensed phase through a variety of physicochemical processes, forming major constituents of $PM_{2.5}$. Data from speciation monitors provides information about the relative contribution of the chemical components and the sources of these pollutants.

$PM_{2.5}$ speciation monitors are used to support State Implementation Plan development by providing information on PM2.5 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 9, with sulfates being one of the most significant contributors to fine particle 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 particulate material.

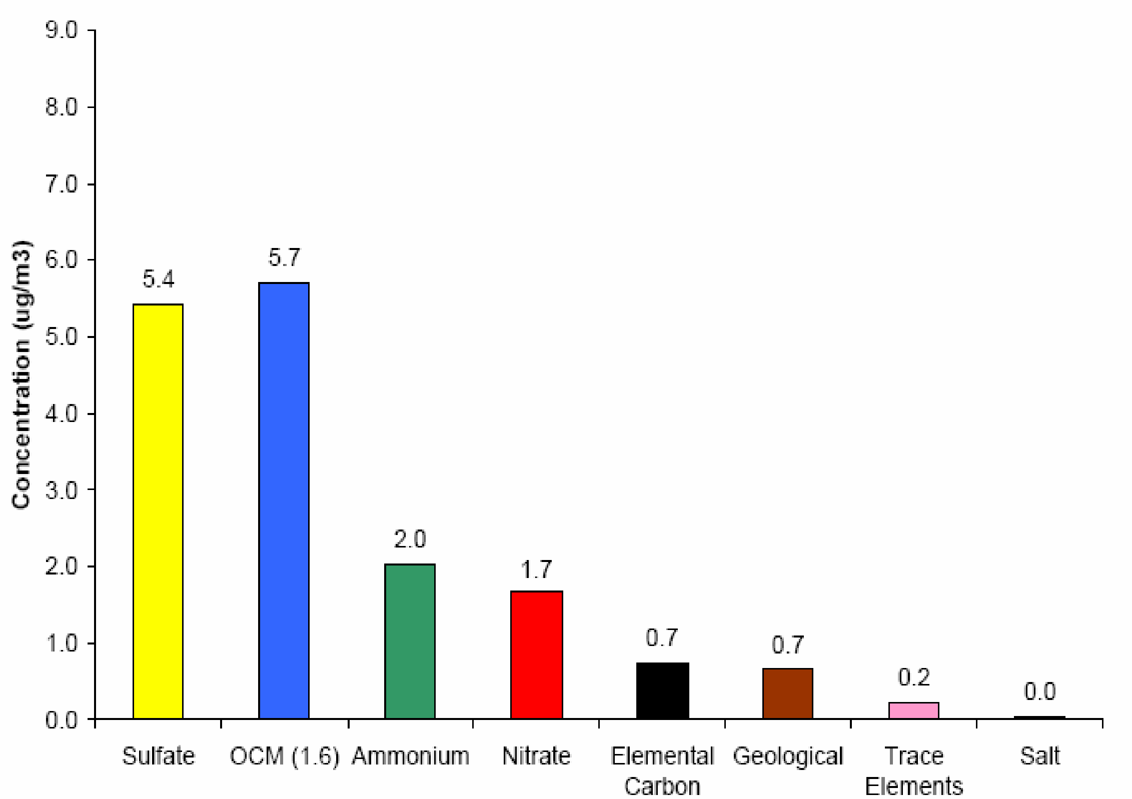


Figure 5-128 Major Constituents of $PM_{2.5}$ Mass, Washington, DC

Figure 2-9: Annually averaged 2001-2003 concentrations of PM2.5 constituents for Washington, DC.[2]

2.7 Sources of Fine Particles and Constitutents

Sources of fine particles 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. Figure 10 shows that a large portion, about 65%, of annual averaged PM2.5 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.

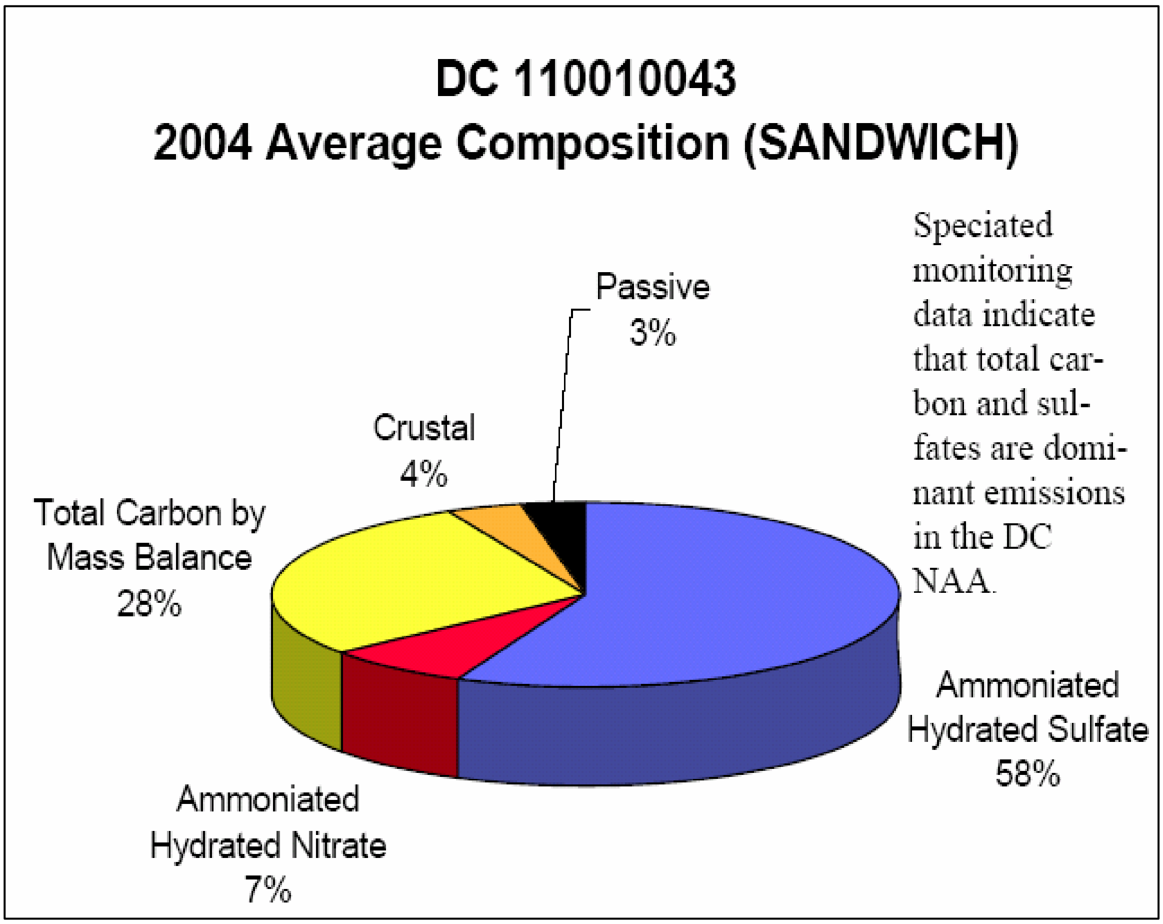


Figure 2-10: PM2.5 Composition data from the McMillan Station in Washington, DC in 2004.

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 NOx were deemed significant for the Washington, DC non-attainment area, while ammonia (NH_3) and other precursors were deemed insignificant at this time. According to EPA, sources of direct $PM_{2.5}$ and SO_2 must be evaluated for control measures in all non-attainment areas. 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 non-attainment 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. Washington, DC region decided to follow EPA's advice on VOC. The role of ammonia in $PM_{2.5}$ is also not as well understood as those of SO_2 and carbon. 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. Washington, DC region decided to follow EPA's advice on ammonia.

The role of NO_x in the formation of $PM_{2.5}$ is very important. It forms nitrate quite significantly during winter, favored by the availability of ammonia, low temperatures, and high relative humidity. $PM_{2.5}$ concentrations will 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 it is found by the EPA that NO_x emissions from sources in the state do not significantly contribute to the $PM_{2.5}$ concentrations in the non-attainment area. The Washington, DC region decided to follow EPA's advice on NO_x.

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, VOC, and ammonia (NH_3) (see Table 4). $PM_{2.5}$ 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. Several precursors are presumed to be insignificant and do not need to 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

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

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 VOC 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 VOC and ammonia is that the region is already showing attainment of 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 VOC and ammonia is listed in Table 2-3.

Table 2-3: Summary of Rationale for Insignificance Determinations for VOC and NH3 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 SIP Planning purposes?	No	No

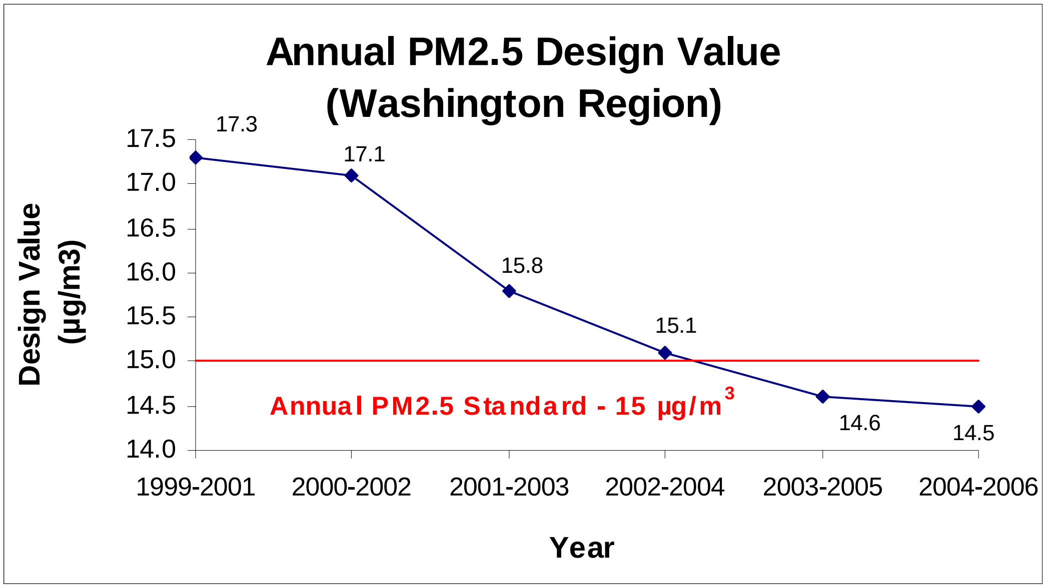
National research is underway to assess the contribution of VOCs to secondary organic aerosol formation. States are following the research and will reconsider the significance determination for VOCs when further technical information becomes available.

2.9 Compliance with the Annual $PM_{2.5}$ NAAQS

The Metropolitan Washington region's Federal Reference Monitors (see Figure 1-2) demonstrate compliance with the annual PM2.5 National Ambient Air Quality Standard in 2005 and 2006. The purpose of the filter-based FRM monitors is to determine compliance with the $PM_{2.5}$ NAAQS. FRM monitors are filter-based that measure PM2.5 mass by passing a measured volume of air through a pre-weighed filter.

The design value trend for the annual PM2.5 standard is shown in the figure below. In 2005 the design value was 14.6 ug/m^3 ; in 2006 the design value was 14.5 ug/m^3, again below the annual $PM_{2.5}$ standard of 15 ug/m^3 .

Figure 2-11. Annual PM2.5 Design Value, Washington Region, 2001-2006



References

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

2. "PM2.5 Area Profiles Mid-Atlantic Region Observations", August 2006. Staff working draft. pp. 106-118.