# Mid-Atlantic Regional Air Management Association



# A Guide to Mid-Atlantic Regional Air Quality



October 2005

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#### About MARAMA

The Mid-Atlantic Regional Air Management Association is a voluntary, non-profit association of ten state and local air pollution control agencies. MARAMA's mission is to strengthen the skills and capabilities of member agencies and to help them work together to prevent and reduce air pollution impacts in the Mid-Atlantic Region.

MARAMA provides cost-effective approaches to regional collaboration by pooling resources to develop and analyze data, share ideas, and train staff to implement common requirements.

The following State and Local governments are MARAMA members: Delaware, the District of Columbia, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia, Philadelphia, and Allegheny County, Pennsylvania.

#### Cover Photos: (clockwise from lower left)

Lidar from the Northeast Oxidant and Particle Study (NE-OPS) in Philadelphia --Photo, Russell Philbrick. (See page 6 for more about this project.)

Research aircraft from the University of Maryland -- Photo, Bruce Doddridge.

Rehoboth Beach, Delaware -- Photo, Alice Lutrey

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### Mid-Atlantic Regional Air Management Association

# Introduction A Guide to Mid-Atlantic Regional Air Quality

Understanding the causes of the Region's air quality problems and taking steps to prevent air pollution are two of the most important duties of state and local air pollution control agencies. The information in this report is intended as a basic resource for explaining and describing air quality issues to air quality managers, officials, and the public. For more in-depth explanations and discussions about topics in the report, please investigate the bibliography.

This report's main focus is on ozone, fine particle pollution, and pollutant interactions. It reviews the current status of air quality, pollution and its sources, and the roles geography and weather play in the Region's air quality. Key points are highlighted in text boxes.

Throughout this report, short "Features" highlight important studies, results, or activities that help understand air quality in the Mid-Atlantic Region. The Features demonstrate much of the new and important work in the air quality arena since the mid-1990s, laying the groundwork for improved air quality management.

In the Mid-Atlantic Region, areas surrounding New York City, Philadelphia, Baltimore, and Washington, D.C. record the highest number of days with unhealthy ozone pollution. The highest concentrations are often found downwind from the central cities and are affected by a combination of local emissions and transport from outside the area. Driving and electricity generation are the major human activities contributing to ozone pollution.

High levels of fine particulate matter are also found in the metropolitan areas between Washington and New York. The greater Pittsburgh region, the Huntington-Ashland region, and several counties in Pennsylvania, West Virginia, and North Carolina also suffer from elevated levels of fine particle pollution. High levels of fine particulate matter may be experienced in industrial, urban, or rural areas due to the diversity of particulate matter sources.

This report explains how weather patterns play a major role in defining the nature and extent of air pollution episodes in the Mid-Atlantic Region. Summertime air pollution episodes are typically hazy, hot, and humid, with light winds and few clouds. Polluted air from outside the region, carrying high concentrations of both ozone and fine particles, nearly always contributes to these episodes. Winter-time air pollution episodes, in contrast, have high levels of particulate matter (not ozone), are typically cool, with light winds, and are more dominated by local stagnation and local emissions. While long-range pollution transport and local pollution stagnation are important throughout the Region, the relevant range of transport is generally shorter in the south than in the north. There are many variations on these themes, giving each pollution episode unique characteristics.

The Region's air pollution problems will not be solved by local controls alone, nor by upwind controls alone; not by controlling only power plants, nor by just reducing emissions from transportation. Effective air pollution control requires a partnership of local, state, and federal authorities as well as private citizens, businesses, and industries, and a commitment in all areas to continuing improvement.

# Setting the Stage

#### An Air Pollution Episode in the Mid-Atlantic Region

The sun rises through a warm haze as the Mid-Atlantic Region begins to dry out from storms that left the area the previous night. The forecast calls for clearing skies and rising temperatures over the next few days and mentions that the Bermuda High is backing in over the area. Forecasters warn that this is the beginning of a heat wave; we are advised to check on the elderly and be sure our pets have plenty of water when they are outside. Tucked into the weather forecast is a "code orange" air quality forecast that many mistake for a heat alert. Light winds wander from one direction to the other and seem only to push the heat around. The sun beats down from a hazy, cloudless sky, baking the ground beneath.

By the second day, the air quality forecast shifts to "code red" and warns the public to stay indoors in the afternoons and evening and limit their driving. Hospitals notice that more people are complaining of the heat and of difficulty breathing. The skies above have given up their natural blue and turned a bright, milky white color. A few



clouds turn up in the late afternoon, but show no inclination to rain and never seem to offer any shade. Power company officials come on the radio and the local news to discuss capacity, over-taxed power lines, and the heat wave. They mention that some home air conditioners have been shut down to conserve energy when power demand peaks. Spotty power outages are reported, but with no storms and no winds, those who return home to find the power off are puzzled. Those lucky



enough to have planned a beach vacation enjoy strong breezes off the ocean during the day. However, air quality monitors, a short distance inland indicate that the air just a few miles away from the ocean is particularly dirty.

Finally, the forecast contains some good news. Relief, promised in the form of showers and thunderstorms, should arrive the next day. Nature explodes in a fury of rain, wind, and cooler air. Weather forecasters announce that a burst of clean, cool Canadian air has entered the Region, and air quality forecasts return to their more normal code green or yellow. Areas in the northern part of the Re-

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gion get the quickest relief from both the heat and the cleansing rain, while areas farther south must be content with the cleansing action of a few thunderstorms. At area hospitals, individuals treated for heat exhaustion disappear from the waiting rooms, while those suffering from respiratory illness continue to come in for a few days.



The Mid-Atlantic Region has just suffered through one of its worst air pollution episodes in years. What causes these episodes? How do they start? Why do they persist? Where does our pollution come from, and why does the weather seem to play such a critical role in producing these events? These are the questions we seek to answer in this document.

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# The Nature of Air Pollutants

This report focuses on outdoor (also called ambient) air quality and the emissions of various substances that cause outdoor air pollution. Indoor air quality is also very important to health, but is beyond the scope of this report. This section introduces terms and concepts, describes the nature of ozone and particulate matter, and explains their relationships. For more information about the health effects of air pollution, see Appendix A. Appendix B summarizes air quality impacts on ecosystems and the environment.

# Introduction to Terms and Concepts

#### Smog

The term "smog," coined in London, refers to the thick, soupy combination of smoke and fog so vividly described in Sir Arthur Conan Doyle's Sherlock Holmes books. The term's use has since broadened to include two varieties: the London-type smog, and the hot-weather Los Angeles-type smog. Los Angeles' smog is created when a mixture of auto exhaust, industrial emissions, and other pollutants react in

sunlight. In general use today, smog refers to the whole mixture of air pollution in an area, and may include ozone, a whole host of other gases, and fine particles and the hazy conditions they cause. Fog is no longer a necessary component of smog, though humidity certainly plays a role, as will be described later.

Smog is a general term referring to the entire mixture of air pollution in an area.

#### Primary and Secondary Pollutants

Scientists distinguish between primary and secondary pollutants. These terms do not refer to their relative importance, but to how pollutants come to exist in the atmosphere. Primary pollutants are compounds such as sulfur dioxide that come directly from their sources. Particles such as soil and soot are also primary pollutants. Secondary pollutants are not emitted directly, but are either formed or modified in the atmosphere. Ozone, for example, is a secondary pollutant that forms as a result of reactions involving primary pollutants. Essentially no ozone is emitted directly into the atmosphere. Sulfate is a

secondary particulate pollutant; it is the product of the transformation of a primary pollutant, sulfur dioxide, in the atmosphere. Ozone and fine particles, two of the most troublesome air pollutants for the Mid-Atlantic Region, are described in more detail in the following sections.

## Ground-Level Ozone

High concentrations of ground-level ozone pose a particularly nettlesome problem for the Mid-Atlantic Region. The western and northern parts of the Region are routinely saddled with a large burden of ozone entering from the industrialized Midwest. In the southern part of the Region, ozone episodes tend to have stronger local influences, so episodes in North Carolina are different from those in Maryland and Pennsylvania. In some areas the burden of transported pollution may be enough to push ozone concentrations above the health standard even before winds have reached the urbanized areas of the Mid-Atlantic Region.

Primary pollutants such as sulfur dioxide are emitted directly from their sources. Secondary pollutants such as ozone are the products of reactions in the atmosphere. In some areas the burden of transported pollution may be enough to push ozone concentrations above the health standard even before winds have reached the urbanized areas of the Mid-Atlantic Region. Ozone is a colorless highly reactive gas, composed of three oxygen atoms instead of the usual, breathable two. The three oxygen atoms are not held very tightly in the molecule, making it very reactive. The smell that is often attributed to ozone is likely not due to the molecule itself, but to the hydrocarbon fragments created when the molecule burns the inside of one's nose.

In any discussion of ozone, it is important to distinguish between

the effects of ozone at the ground and ozone high in the atmosphere, several miles above our heads. An advertisement might use the slogan "good up high, bad nearby," to describe ozone. Regardless of where it is, no one would want to breathe it. However, up high in what's called the ozone layer, ozone is essential to the health of nearly every living thing, since it protects the Earth from harmful ultraviolet



#### Figure 1 Ozone molecule (O<sub>3</sub>)

Unlike the oxygen that we breathe, which has only two atoms of oxygen  $(O_2)$ , ozone has an additional oxygen atom, making it very reactive. This is why ozone is said to burn or irritate the lungs. (UV) light. If not for this natural layer, UV light would sterilize the Earth's surface, and life as we know it would cease to exist. Near the ground, ozone reacts with buildings, plants, animals, and people, and is one of the most irritating, harmful components of smog.

#### **Ozone Precursors and Ozone Formation**

Near the ground, ozone is formed when volatile organic compounds (VOCs) and oxides of nitrogen (NO<sub>x</sub>) react in the presence of sunlight. VOCs are organic compounds that evaporate readily, such as gasoline vapors and paint fumes. NO<sub>x</sub> stands for two compounds, nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). Nitric oxide forms in high temperature burning processes when nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>) each split. The free nitrogen and oxygen atoms largely recombine with themselves to return to N<sub>2</sub> and O<sub>2</sub>, but some link up with each other to form NO. NO<sub>2</sub> forms in subsequent atmospheric processes.

Ozone,  $NO_x$ , and VOCs are all present naturally in the atmosphere, though their concentrations are substantially smaller under normal natural conditions than under smoggy ones.  $NO_x$  is emitted naturally by soil microbes and formed in lightning and forest fires. Nitric oxide is found naturally in the human body, where it is an important neurotransmitter. In developed areas, natural sources have minimal impact; here human activities, such as fuel burning,

Ozone is a highly reactive form of oxygen. High above, in the ozone layer, it protects the health of nearly every living thing on Earth by absorbing harmful ultraviolet light. Near the surface, where it reacts readily with anything it comes into contact with, it is a health hazard and can be harmful to the environment. emit much more NO, than do natural sources.

In contrast to natural  $NO_x$  emissions, which are normally insignificant in urban air pollution, natural VOC emissions are highly significant in smog chemistry. VOCs are naturally emitted by vegetation, soils, and animals. Some of the most reactive VOCs are emitted by trees: terpenes from pine trees and isoprene from oaks and aspens. VOC emissions from trees typically increase with temperature, though extremely high temperatures hinder their release as tree stomata (pores) close to reduce water loss, consequently limiting VOC emissions.

VOCs that come from human activities are called anthropogenic VOCs. Anthropogenic VOCs are important and may dominate the emissions by mass (weight) in an urban area, even though natural sources dominate in the overall region. Some anthropogenic VOCs, such as benzene, are themselves toxic and may increase risks of cancer or lead to other adverse health effects in addition to helping form ozone.

Ozone is generated when volatile organic compounds (VOCs) react with oxides of nitrogen (particularly NO and  $NO_2$ , known together as  $NO_x$ ) in sunlight. VOCs are emitted by trees, plants, animals, soils, and by human activities such as solvent use and driving.  $NO_x$  is mostly formed in high temperature burning processes. Ozone forms as VOCs are broken down into simpler compounds in the presence

VOC emissions are typically measured or estimated by the mass

of the pollutants emitted, but, particularly where ozone production is concerned, not all VOCs are equal. Some VOCs are considerably more reactive in the atmosphere than others. The reactivity of a VOC influences how quickly ozone forms. A compound that reacts in a few minutes to produce ozone will have a much greater impact near its source than one that reacts more slowly. Thus, ozone can form nearer or farther downwind of a VOC source due to faster or slower chemical reactions.

Ozone is formed when a mixture of VOCs and  $NO_x$  is exposed to sunlight. Ozone is merely an undesirable intermediary generated as the Sun's energy gradually breaks down VOCs into water vapor and carbon dioxide. Essentially, the process is a low-temperature VOC burning process. Unlike normal burning, in this process,  $NO_x$  is not produced, but is turned into nitric acid and other compounds, which are ultimately deposited to the Earth's surface.

# Why are the Highest Ozone Levels found Downwind of Cities and Large Industrial Sources?

It is tempting to think of compounds in the atmosphere as sitting in neat little boxes that only interact with a few other compounds through one or two pathways. While such a simple view might make it easier to learn basic atmospheric chemistry, the atmosphere recognizes no such boundaries. This is particularly true when considering VOCs,  $NO_x$ , and ozone. Eventually, VOCs are broken down by the process that produces ozone. However, this big picture masks the intermediate reactions of all three with one another. Certain VOCs react with both  $NO_x$  and ozone, while  $NO_x$  and ozone react readily with each other.

The reaction of  $NO_x$  with ozone, called " $NO_x$  titration," is particularly important in the plume from a city or a large industrial source of highly concentrated  $NO_x$ . This reaction can temporarily eliminate nearly all the ozone in a plume. Later, as the plume disperses and the  $NO_x$  concentration drops, ozone will form in the same plume. Eventually the ozone concentration downwind of the city will be higher than it was when entering the city. Ozone disappears near the city as  $NO_x$  titration takes its toll, and then reappears at even higher concentrations as  $NO_x$  and VOCs react in sunlight downwind. The highest ozone concentrations in the Washington, DC, Baltimore, and Philadelphia metropolitan areas are not in the urban centers, but are downwind of the cities and their suburbs.

VOCs are also necessary for ozone formation, and they are abundant in any city. If VOCs are less abundant, less ozone is formed in the short term. The plume from a coal-fired boiler or power plant represents just such a case. Near the plant, the plume has abundant NO<sub>2</sub> but only low levels of VOCs,

NO<sub>x</sub> titration is just one example of an interaction between cycles and families of compounds. When NO<sub>x</sub> is very abundant, as is the case in the plume from a major city or power plant, it reacts with ozone directly, destroying the molecule, and reducing ozone concentrations. As the plume disperses and more VOCs mix into the plume, conditions become more favorable for ozone production, and ozone will be produced inside the same plume. so little ozone is produced initially. Later, as the plume mixes with its surroundings, VOCs from other sources mix into the plume and more ozone will be produced. The mix of VOCs and  $NO_x$  in the plume will affect how much ozone is produced in the plume and how quickly. Eventually, VOCs will mix into the plume and react with the existing  $NO_x$  to produce ozone.

#### NO<sub>x</sub> Limited and VOC Limited Ozone Production

The concentrations of VOCs and  $NO_x$  are usually not optimal for producing as much ozone as possible. The concentration of one is typically too low when compared with the other. When the concentration of  $NO_x$  is too low, ozone production is  $NO_x$  limited. Additional  $NO_x$  will increase ozone, but additional VOCs will not. Conversely, when the concentration of VOCs is too low, ozone production is VOC limited.

These conditions have implications for ozone control. When ozone

production is VOC limited, VOC controls will be more effective, while  $NO_x$  controls are more effective when conditions are  $NO_x$  limited. This assumes that all sources of  $NO_x$  and VOC can be controlled. Given the abundance of highly reactive natural VOCs, this is often not the case in the Mid-Atlantic Region.

Distinctions between whether an area is  $NO_x$  or VOC limited do not hold for all parts of a Region or even for all parts of a plume. Because cars and other combustion sources produce a large amount of  $NO_x$ , conditions in a city center may well be VOC limited, while conditions downwind, where the  $NO_x$ has aged and fresh natural VOCs are available, are often  $NO_x$  limited. An area may be  $NO_x$  limited

 $NO_x$  limited conditions occur when there is an overabundance of VOCs, and relatively little  $NO_x$ , so reducing  $NO_x$  emissions will reduce ozone concentrations, while changes in VOC emissions will have relatively little impact. When VOCs are scarce, and  $NO_x$  is overabundant, conditions are then VOC limited, and VOC controls will have a greater impact. during some parts of the a day and VOC limited during other times of the day.

## Fine Particles (PM<sub>2.5</sub>)

Gases such as ozone are not the only air pollutants that cause environmental and health problems. Solid and liquid particles can stay in the air and, if small enough, can make their way far into the lungs. Particles come in a wide variety of shapes and sizes, which affect their impacts on the environment and human health. Bigger particles, such as dust, are easier to see and can cause problems, but smaller particles are probably worse for our health.

Fine particles, those 2.5 micrometers ( $\mu m$ ) in diameter or less, called

 $PM_{2.5}$ , can be inhaled deeply into the lungs. A diameter of 2.5 µm corresponds to 1/100<sup>th</sup> of an inch, which is about 40 times smaller than the diameter of a human hair. Three additional terms related to particle size are also useful:  $PM_{10}$ , Total Suspended Particles (TSP), and PM-coarse.  $PM_{10}$  represents the fraction of particles below 10 micrometers. PM-coarse represents all the particles between 2.5 micrometers and 10 micrometers in diameter.  $PM_{10}$  includes both  $PM_{2.5}$  and PM-coarse. Particles below 10 micrometers in diameter can make their way into the lungs, though not as deeply as those below 2.5 micrometers. TSP represents all particles that can stay suspended in the atmosphere, which



Figure 2 Diurnal pattern, PM

This graph shows the average hourly concentrations, giving a diurnal pattern for  $PM_{2.5}$  from January 1, 2003 - April 10, 2003 at the Oldtown monitoring site in Baltimore, Maryland. The hour by hour fluctuations seem to track traffic patterns, which is a reasonable finding for an inner city monitor.

loosely corresponds to those with diameters below roughly 50 micrometers. Particles larger than 50 micrometers will settle quickly out of the atmosphere.

#### The General Composition of Particulate Matter (PM)

Fine particles are treated as though they are a single pollutant, but fine particles come from many different sources and are composed of thousands of different compounds. Fortunately, these com-

pounds fall into a few dominant categories: sulfates, nitrates, ammonium compounds, soil, organic carbon compounds, and elemental carbon. Water is nearly always an important and variable part of PM, and sea salt is often significant near the coast. Specifics of Mid-Atlantic Region particle composition are described later in this document.

An aerosol is a suspension of fine solid or liquid particles in gas.

Given the complex composition of PM, it is no surprise that its chemistry is also complex. Particles may be liquid, dry or wet. An important distinction is between primary and secondary particles. Primary particles are emitted directly into the atmosphere as particles, while secondary particles are produced when gases or other particles coalesce. Many particles are collections of smaller particles that have collided and stuck together, and particles are often collections of both primary and secondary particles.

## Northeast Oxidant and Particle Study (NE-OPS)

This project contributed to the understanding of how pollutant transport in the upper levels of the atmosphere contribute to high levels of air pollution. Located in Philadelphia, the Northeast Oxidant and Particle Study (NE-OPS) conducted intensive air quality measurements in the summers of 1999, 2001, and 2002. Seven universities, three national laboratories, six agencies, and private industry collaborated on the project.



A tethered weather balloon used during NE-OPS research to gather data.

#### **Objectives**

- Investigate the urban polluted environment to find the relationships among conditions leading to concentrations of ozone and fine particles
- Determine the contributions from local and distant pollution sources.
- Examine the role that meteorological properties play in the build-up and distribution of pollutant concentrations over urban and regional scales and interpret these results within the context of past measurement programs to extend the knowledge gained to other applicable locations and atmospheric conditions.

#### Research Conclusions

- Meteorology is the primary driver and leading factor controlling high ozone and particulate matter episodes in the northern U.S.
- Essentially all of the major air pollution events involve regional scale circulations and are associated with transport from the Midwest.
- Vertical mixing of pollutants and precursors from the storage/transport reservoir above the nocturnal boundary layer provide major input to pollution episodes.
- Vertical profiles of atmospheric properties are essential for understanding the processes and evolution of air pollution episodes.
- Successful application of simpler modeling options has been validated using the NE-OPS ground and upper air data. The NE-OPS data base will provide opportunities for critical testing and evaluation of models.

Funding for this project was provided by the U.S. EPA and the state of Pennsylvania. The principal investigator was Russell Philbrick of the Pennsylvania State University.

For more information see: http://lidar1.ee.psu.edu/narsto-neops/index.htm

Primary particles are the simplest. Soil and other crustal materials are fairly straightforward primary particles. When the wind blows hard enough, soil, silt, and sand can be lifted from the surface. Human activities such as mining, construction, plowing, and driving on unpaved roads, also lift particles into the air. Soil particles that are sufficiently small will remain airborne for long periods. Larger particles are not typically transported as far as smaller ones. This was overlooked in many early estimates of the impact of soil emissions, resulting in overestimates of the importance of these particles. The bulk of these particles are either too heavy to stay suspended in the atmosphere or too large to be inhaled deeply into the lungs.





Soot, also referred to as black carbon or elemental carbon, is emitted directly by diesel engines and forest fires, among other sources. When fresh, soot does not take on water. However, as soot ages in the atmosphere, it will take on water and combine with other aerosols.

On an annual basis, sulfates comprise the largest portion of the fine particulate matter in the Mid-Atlantic Region. Sulfate particles are secondary particles, which are almost entirely formed from sulfur dioxide emitted from the combustion of coal and other fossil fuels. Both coal and crude oil naturally contain some (typically a few percent) sulfur, with the exact composition varying dramatically depending on the source. Natural sources of atmospheric sulfur include emissions from volcanoes and a few sulfurous compounds, but these sources are ordinarily insignificant contributors to urban air pollution.

Sulfur dioxide is transformed into sulfate, and thereby sulfuric acid, via numerous pathways, though two are considered dominant. Sulfur dioxide is slowly turned into sulfate as a gas in the air, but a much more rapid reaction takes place in cloud particles to turn sulfur dioxide into sulfate. Sulfate has a very high affinity for Particulate pollutants are characterized by the sizes of the particles. TSP stands for Total Suspended Particles all those particles with diameters less than 50 micrometers. PM<sub>10</sub> and PM<sub>2.5</sub> stand for all particles with diameters less than 10 micrometers and 2.5 micrometers, respectively. Particles smaller than 2.5 micrometers in diameter can be inhaled deeply into the lungs, making them more likely to cause health problems than larger particles.

water—so high that it almost immediately acquires an ensemble of six surrounding water molecules. Sulfate dissolved in such a particle is sulfuric acid, a strong acid, which makes the particle very acidic. The acidity draws in some atmospheric ammonia, making the particle highly attractive to water. These particles then grow rapidly into larger particles that scatter light efficiently, reducing visibility. Seldom is there enough ammonia to fully neutralize the sulfuric acid in these particles, so they end up as a significant component of acid rain.

Nitrate (NO<sub>3</sub>), represents the fate of NO<sub>x</sub> once it has been fully oxidized from NO to NO<sub>2</sub> to NO<sub>3</sub>. Though the formation process is less complex than that of sulfate, nitrates are formed in a process similar to the gas-phase process that forms sulfate. Nitrates also form aerosol particles readily, though

As with gases, fine particles are also classified as primary and secondary. Sulfate particles, most organic particles, and nitrates are secondary particles. not as quickly as sulfate. And once nitrates are incorporated into an aerosol, they too form an acid—nitric acid, a significant component of acid rain. Nitrates are also fertilizers. As such, they contribute to nutrient loading in bodies of water such as the Chesapeake Bay and Pamlico Sound. Roughly a third of the nitrogen entering the Chesapeake Bay comes from the air. For other bodies of water, somewhere between 10 and 45 percent of the nitrogen comes from the air.

In contrast to the two acids just discussed, ammonia is the only significant atmospheric base. As such, it reacts readily with sulfuric acid and nitric acid to form ammonium sulfate and ammonium nitrate. Both of these gases take on water readily to form aerosols. Ammonium sulfate is fairly stable, but ammonium nitrate decomposes promptly as temperatures rise. When ammonia deposits to the ground, it is quickly converted to nitrate by soil microbes, so one is faced with the conundrum of an atmospheric base that increases soil acidity. Ammonia comes from a variety of sources, some of which are not well quantified. Its main sources are thought to be agricultural, particularly from the excreta of livestock. Ammonia emissions from human activities result in elevated ammonia levels in cities as well. Some emission control processes in power plants add ammonia to the stack to remove  $NO_x$ ; the result is considerably less  $NO_y$  with a small amount of ammonia slipping out the stack.

Organic carbon aerosols form when gaseous organic compounds, such as VOCs, condense to form particles. In contrast to elemental carbon, which is a primary particle, a significant fraction of organic carbon particles are secondary pollutants. Organic carbon (OC) aerosols are typically mixtures of a wide variety of compounds. Natural compounds such as terpenes are a significant source of OC. Terpenes come from pine trees, and will swiftly form aerosols, producing some of the famous blue haze of the Blue Ridge Mountains in the southern Mid-Atlantic Region.

#### **Physical Properties**

Particles in different size ranges tend to have different physical properties, so, for example, those particles which most affect visibility may not necessarily be the same as those which most affect human health.

Particles larger than 2.5 micrometers in diameter contribute the majority of particle mass, but the most numerous particles are the very smallest, below 0.1 micrometers. Most of the surface area of particles

Nitrate and sulfate particles tend to be acidic, while ammonia, the only significant atmospheric base tends to neutralize those acids. Both nitrate and sulfate are important components of acid rain. Nitrate has other impacts on the environment, since it is also a fertilizer. Sulfate is the principal component of regional haze. occurs on particles with diameters somewhere between these extremes. Sheer numbers are important for some physical processes, such as cloud formation, while surface area is more important in haze, visibility, and certain processes in atmospheric chemistry.

Particle sizes differ according to how they are emitted, grow, and are removed from the atmosphere. The particles remaining in the atmosphere reflect the result of a balance between growth and removal processes. Aerosols usually come in three size groups, called modes. The names of the modes, and the bound-

aries between the modes, may shift slightly depending on the preference of the author or the nature of regulations in a country, but a loose guide is given here.

The group containing the smallest particles is the Aitken mode, containing ultrafine particles and nuclei—the beginnings of fine particles. These tiny particles occur in the greatest number, though their small size means that they make up only a tiny fraction of the mass. Nuclei may be only a few molecules held together. These particles tend to grow rapidly by coalescing with

Fine particles are composed of thousands of different compounds that can be lumped into a few categories: organic carbon compounds, sulfates, nitrates, elemental carbon or soot, ammonium compounds, soils and crustal materials. Water is generally a significant part of most particles. Sulfates are the largest single category.

other particles and by taking on gases directly from the atmosphere. Certain nuclei are particularly suited to taking on water, giving them the name condensation nuclei. These nuclei are essential to life as we know it, because they start raindrop growth long before it would otherwise start. Without them, the atmosphere would have to absorb considerably more moisture before rainfall would start.

The next larger mode is the accumulation mode. Particles of this size can grow by taking on gases and smaller particles. If they do grow larger, accumulation mode particles are efficiently removed by rain, snow, and other precipitation processes. The result is a mode of very fine particles that tend to remain about the same size, products of the growth of nuclei and the removal of larger particles. Whereas the Aitken mode or nuclei were greatest in number, the accumulation mode is greatest in surface area. A large surface area is important for producing haze and for accommodating reactions that take place on surfaces. A significant portion of the mass of fine particles typically resides in this mode.

The third mode is the coarse mode. Coarse particles come from different sources than do the Aitken and accumulation mode particles. Such particles are partly the result of soils and crustal materials being lofted into the atmosphere. Sea salt particles are typically coarse aerosols. Most of the mass of atmospheric particles is located in the coarse mode. Particles larger than these tend to settle out of the atmosphere quickly, having minimal effects on atmospheric chemistry and public health.

Most particles are likely mixtures of different substances, the product of growing by collisions with other particles and by taking on gases. The composition of particles varies with their size. The smallest particles tend to be made up of metals and organics. Larger ones grow by adding water, acids, and organics, so metals are a relatively small fraction of their mass. The largest particles are quite different, owing to their different sources, and are usually made up of soils and other crustal materials. Most individual particles are likely mixtures of different substances, the products of growing by collisions with other particles and by taking on gases.

#### Haze

Fine particles and haze are inextricably linked, since fine particles scatter and absorb light, which is the very nature of haze. Haze is simply the visibility obstruction caused by fine particles. In the United States, under natural conditions, a visual range is roughly 120 miles in the West and 90 miles in the East.

Currently, the EPA estimates that typical visibility in the West is only 1/2 to 2/3 of what it would naturally be, while visibility in the eastern U.S. is roughly 20 percent as good as natural conditions.

Haze should not be confused with fog or mist, which are largely composed of water and are essentially lowlying clouds. In weather reports, conditions are called Haze and fine particles are inextricably linked, since fine particles cause the scattering and absorption that lead to visibility reduction. Some amount of haze is natural, caused by aerosols and gases in the atmosphere.



Class I Areas in MANE-VU



#### **Class I Areas in VISTAS**

#### Figure 4 Class I Federal areas in the East and Southeast

There are 10 Class I Federal Areas in the MARAMA Region. MARAMA member agencies participate in two regional planning efforts to improve visibility. States in the northern MARAMA Region are part of the Mid-Atlantic / Northeast Visibility Union (MANE-VU, www.mane-vu.org). MARAMA members to the south are part of the Visibility Improvement State and Tribal Association of the Southeast (VISTAS, www.vistas-sesarm.org).

hazy when the air is dry, and foggy or misty otherwise. The term fog applies when visibility is 5/8 of a mile or less, and mist applies when visibility is between 5/8 of a mile and 7 miles (about 1 km to 11 km).

There are three components to visibility obstruction: scattering by the atmosphere, scattering by natural particles, and scattering by human generated particles. Through a process known as Rayleigh scattering, atoms and molecules in the air scatter light in all directions, so even if the atmosphere were entirely free of particles, visibility would be somewhat limited. Rayleigh scattering limits visibility to roughly 180 miles (300 km) at sea level. Nitrogen is the most notable molecule in this regard, since it preferentially scatters blue light, giving the Earth's sky its brilliant blue color.

Visibility is measured in three ways: as a visual range in meters, as extinction in inverse megameters, and in deciviews. Visibility disruption is fundamentally the same, regardless of which measure is used. Instead of traveling directly from a target to your eye, light is absorbed or scattered away from your line of sight and light from other objects is also scattered into your line of sight. The combination of increased light from other sources and decreased light from the desired source produces a reduction in visibility.

The term visual range is straightforward, since it just refers to how far away an average observer can still discern an object from its surroundings. Haze scatters and absorbs light. An average human can generally distinguish a two percent contrast between a black object and its surroundings if that object sits in broad daylight. This assumption leads to the 180 mile visibility limit due to Rayleigh scattering mentioned previously.

The visual range can be related to an intrinsic property of the particles in the atmosphere, namely light extinction. Since particles



Clear Day View 43 Miles



View 12 Miles



Hazy Day View 6 Miles

Figure 5 Comparison of hazy vs. clear day at Shenandoah National Park

affect visibility both by scattering and by absorbing light, we have to consider the two processes together to estimate a visual range. If our goal is to see a mountain, and particles are in the way, it does not matter much whether those particles are scattering or absorbing light—less light reaches our eyes, reducing our ability to see the mountain. Extinction represents the combined effects of both scattering and absorption, which reduce our ability to see. As extinction goes up, visibility goes down. The term artification links particle properties and visual range.

term extinction links particle properties and visual range.

Extinction can be calculated from the properties of the particles in the atmosphere, since each particle contributes a little bit to extinction. Extinction is measured in inverse megameters or inverse kilometers, which appear to be clumsy units, but really just show that increased extinction results in decreased visibility. The daytime Visibility is measured in meters, deciviews, and inverse megameters. Each scale has its own purpose. Visibility may be measured directly, but is often reconstructed from mass and composition measurements of fine particles. formula for visual range is a constant (determined by the two percent assumption mentioned above) divided by the extinction. Taking that constant and dividing it by the extinction in inverse kilometers gives the visual range in kilometers. So, the units of extinction are set up so that the visual range comes out as a distance.

Visibility is also measured in deciviews. The deciview scale was designed in hopes of doing for visibility what the decibel scale did for sound. Decibels relate changes in sound energy in a way that makes sense for the human ear. Likewise, deciviews represent changes in extinction and visibility in a way that makes sense for the human eye. The deciview scale was also designed to increase as visibility gets worse in much the same way that air quality gets worse when ozone and fine particle concentrations increase.

Mathematically, deciviews are defined as ten times the natural log of extinction divided by 10, or 10 x ln (extinction/10), where ln is the natural logarithm (to base e) and the extinction is measured in inverse megameters. Logarithms appear in the definitions of both deciviews and decibels because that is how human eyes and ears respond to light and sound. A speaker that produces twice as much sound energy does not sound to us like it is twice as loud. Likewise, a light source that produces twice the energy does not appear to us to be twice as bright. Instead, it takes far more sound energy and far more light to produce a response in our ears and eyes that is twice as large. The result is a far larger range of

A change of one deciview is perceived as the same amount of change whether the visibility goes from 10 to 11 deciviews or from 30 to 31 deciviews. In contrast, a change of visual range from 5 miles to 10 miles is perceived as a much larger change than a change from 100 miles to 105 miles. detectable sights and sounds. An ear that hears the roar of an ocean can also hear the squeak of a mouse, while eyes that let us see in broad daylight can also see by the light of the crescent moon.

Deciviews are convenient in that they correlate well with human perceptions of visibility changes, regardless of what the visibility may be. A change of one deciview is perceived as being the same if visibility goes from 10 to 11 deciviews or from 30 to 31 deciviews.

Visibility differs between night and day. In daytime, one wants to be able to discern an object from its surroundings, all of which are typically well-lit by the sun. At night, one is typically concerned with being able to see bright objects such as runway lights, stars, and car taillights.

These two needs are fundamentally different. Methods for calculating visibility at night and in the daytime are different because picking out bright lights against a dark sky is different from picking out an object from its well-lit surroundings. As a concrete example, lights from distant radio towers may be visible at night, even though those towers are not visible in the day. This change is not due to a change in the particles in the atmosphere, but because distinguishing a light from the black sky is typically much easier than picking out a distant object in the daytime.

Some instruments measure the scattering or absorption of light by particles directly, either in the ambient atmosphere or by drawing outdoor air into an instrument. On the other hand, visibility is often not measured directly, but is instead calculated or "reconstructed" from measurements of the mass and composition of fine particles. This helps us figure out the major sources causing poor visibility, since different kinds of particles come from different sources. (See Appendix E for a discussion on calculating visibility.)



#### Figure 6 Types of particles that impaired visibility on the 20% of days with the poorest visibility

The pie charts above show the relative composition of visibility reducing pollutants at various sites. Note the increasing importance of sulfates  $(SO_4)$ in the southern part of the Region. Organic carbon (OC), nitrates  $(NO_3)$ , and elemental carbon are all important contributors to haze.

#### Interconnections

While it may be useful to break down atmospheric chemistry compound by compound, the atmosphere recognizes no such divisions. Pollutants interact, and the result of those interactions can be to accelerate, slow down, or alter the production Pollutants interact, and the result of those interactions can be to accelerate, slow down, or alter the production of other pollutants.

of other pollutants. Haze and ozone may appear at first to be unrelated, but haze increases the scattering of light, which in turn increases ozone production under certain conditions. So particles may accelerate the production of certain gases. Conversely, gases also form particles. The same VOCs and  $NO_x$ that lead to ozone production also form organic and nitrate particles. Sulfate is commonly formed in cloud droplets when sulfur dioxide reacts with hydrogen peroxide. Hydrogen peroxide is formed as a result of the same cycles that form ozone. These interactions have led to the concept of "oneatmosphere modeling," which recognizes that changes in emissions of one pollutant will necessarily affect others.

#### **Pollutant Fate**

What happens to all these pollutants? Ultimately, most compounds end up on the Earth's surface. Exactly how these pollutants get to the surface affects their concentrations in the atmosphere.

#### Gases

Ozone reacts with surfaces and other compounds directly, forming a chemical product plus oxygen. It will also react with itself, returning breathable molecular oxygen. Nitrogen oxides form nitrates, nitric acid, and nitrogenated hydrocarbons, all of which ultimately deposit to the Earth's surface. Sulfur dioxide is deposited on the surface through various mechanisms involving both wet and dry deposition. Volatile organic species are broken down in the atmosphere into carbon dioxide and water unless they deposit first to the surface. Carbon monoxide has a more interesting fortune, since it eventually turns into carbon dioxide, which is Each pollutant suffers its own particular fate. Most participate in global cycles that take place on time scales much longer than the atmospheric lifetimes of these pollutants. All, at some point, end up back on the ground or in the water. associated with global warming. Carbon dioxide is taken up by plants, which can release that carbon in forest fires or when they decay. The only way to truly sequester carbon is by burial, where the carbon may eventually form coal and oil deposits. Carbon dioxide may also be turned into carbonate shells by microorganisms in the ocean which die and settle to the bottom where they are turned into deposits of lime-stone and chalk.

#### Particles

Fine particles are affected by a variety of loss processes, depending on their solubility and size. If particles grow too large, gravity will ensure

that they settle quickly out of the air. Rain storms, fog, snow, clouds, and all other precipitation phenomena will also remove fine particles from the atmosphere.

#### The Big Picture: Geological Cycles

Atmospheric pollutants all participate in various cycles. Their time as air pollutants is typically very limited, and they spend most of their time in other parts of the cycle. One such example is the carbon cycle, where carbon-containing compounds eventually turn into coal, oil, and limestone. Coal and oil deposits may burn, releasing carbon back into the atmosphere. Limestone rock might seem like a fairly permanent fate, but rocks of all kinds continuously return to the Earth's mantle, where they are melted down to be reborn later in a volcano or a new mountain range. The carbon that was tied up in limestone can then return to the atmosphere as carbon dioxide when a volcano erupts.

Other cycles form important links between different parts of the biosphere. The nitrogen cycle and the sulfur cycle have parts in both the air and the water, as does the carbon cycle. Therefore, an air pollution problem will likely have impacts on a water pollution problem and vice versa.

# How's the Air Out There?

This section presents a brief snapshot of air pollution conditions in the Mid-Atlantic Region. The purpose here is to give a broad overview, not to discuss particular areas at particular times. Since  $PM_{2.5}$  and ozone are the two pollutants that violate health standards in the Mid-Atlantic Region, they are the focus of this section. Maps and charts of pollutant concentrations across the Region are also included. The maps of nonattainment areas highlight the places with the highest concentrations, though emissions from other areas also contribute to air pollution in nonattainment areas.

Trends in pollutant concentrations do indicate a region's progress toward healthful air quality. Ozone trend data available in Appendix D have not been adjusted to account for differences in meteorology, and weather patterns do significantly affect ozone concentrations. The  $PM_{2.5}$  record is not yet long enough for discussion of trends.

### Nonattainment Areas

Areas where air quality does not meet national health standards for several years are designated as nonattainment areas. Figures 7 and 8 show the designated ozone and  $PM_{2.5}$  nonattainment areas in the Mid-Atlantic Region.

High ozone and  $PM_{2.5}$  episodes occur in broad, multi-state regions, though the highest levels occur in smaller areas. Many nonattainment areas include an entire metropolitan area, and nonattainment areas often cross state boundaries. Rural areas can also be designated nonattainment.

Ozone nonattainment areas are classified according to the severity of the air quality problem as marginal, moderate, serious, or severe nonattainment areas. There are also basic nonattainment areas that

generally experience less frequent or less severe air quality problems.  $PM_{2.5}$  nonattainment areas are not classified.

EPA revised ozone nonattainment areas in the Mid-Atlantic Region in 2003 to reflect the shift from the 1-hour ozone standard to the newer and stricter 8-hour ozone standard. Some areas that had complied with the 1-hour ozone standard exceed the 8-hour standard because it is a stricter standard. Larger areas are designated nonattainment than before, but the severity *classification* of the violations is often less. For example, several areas that were classified as severe ozone nonattainment areas under the 1-hour standard are now classified as moderate nonattainment areas under the 8-hour ozone standard.

In the Mid-Atlantic Region, the areas surrounding New York City, Philadelphia, Baltimore, Washington,

#### Early Action Compacts

Communities that are close to exceeding, or exceed the 8-hour ozone standard may choose to enter into an Early Action Compact (EAC) with EPA. The goal of the compact is to take actions to clean the air as soon as possible, rather than waiting for the 2007 deadline.

In 2004, communities participating in the EACs submitted plans for meeting the 8-hour ozone standard by December 31, 2007. EAC requirements include: developing and implementing air pollution control strategies, accounting for emissions growth, and achieving and maintaining the 8-hour standard.

As long as EAC areas meet agreed upon goals, an 8-hour ozone nonattainment designation will be deferred.

Source: http://www.epa.gov/ttn/naaqs/ozone/eac/



Figure 7 Eight-hour ozone attainment/nonattainment areas in the MARAMA Region



Figure 8  $\ensuremath{\mathsf{PM}_{\text{2.5}}}$  nonattainment/attainment areas in the MARAMA Region

D.C., and Charlotte, N.C. usually record the highest number of days with unhealthy air quality for ozone. These areas also usually experience the highest levels of ozone in the Region.

 $PM_{2.5}$  nonattainment areas range from small parts of counties to entire metropolitan areas. High levels of  $PM_{2.5}$  may be experienced in industrial, urban, or rural areas due to the diversity of sources affecting PM concentrations.

### How Many Days of Unhealthful Air Quality?

The number of days on which monitored air quality exceeds the federal health standard for ozone is one measure of how serious the air pollution problem is in an area. (The 24-hour  $PM_{2.5}$  standard is met throughout the Region.) Tables D-4 through D-7 in Appendix D record the number of days exceeding the 1-hour and 8-hour ozone standards for each state in the Region, and for each current or former ozone nonattainment area in the Region.

An ozone exceedance day occurs when air quality surpasses the level of the National Ambient Air Quality Standard (NAAQS) at a particular monitoring site. A day with widespread high ozone levels

An ozone exceedance is a day at a particular monitoring site when air quality surpasses the level of the National Ambient Air Quality Standard (NAAQS). can result in multiple ozone exceedances. As shown in Tables D-4 through D-7 in Appendix D, the Region had fewer ozone exceedances in 2003 than in 2002. During 2002 the weather conditions (drought, clear skies, and high temperatures) were conducive to ozone formation. In contrast, 2003 weather conditions made ozone production more difficult. These conditions were characterized by lower temperatures and increased rainfall. For example, Table D-5 shows that from 2002 to 2003 Pennsylvania dropped from 50 days with exceedances to 19 days, New Jersey fell from

44 days to 19, and Maryland went from 39 days to just nine days with exceedances of the 8-hour standard.

Table D-6 in Appendix D demonstrates that, for the most part, 1-hour ozone exceedances have decreased since the late 1980s. Table D-4 lists the number of days above the 8-hour standard since 1998. Year-to-year variations reflect both efforts to control pollution and the impact of the weather.

## **Design Values**

Another way to judge the severity of an area's air pollution problem is to consider its "design value." The design value is the average concentration that is compared to the air quality standard to determine whether air quality has violated the standard. (See Appendix C for more information about the National Ambient Air Quality Standards.) Design values for both the  $PM_{2.5}$  and the 8-hour ozone standards are calculated for a 3-year period to remove some of the year-to-year variability caused by the weather. If the design value is below the standard, then the area meets the standard. In areas with multiple monitors, the design value for a nonattainment area is determined by the monitoring site in the nonattainment area with the highest design value.

For the 8-hour ozone standard, the design value is a three-year average of each year's fourth-highest daily maximum 8-hour ozone concentration. For  $PM_{2.5}$  the design value is also a three-year average. The daily average  $PM_{2.5}$  levels are first combined into quarterly averages, then the those averages are combined into an annual average. Finally, three consecutive annual averages are combined to determine a 3-year  $PM_{2.5}$  design value.



#### Figure 9 MARAMA Region 2000-2002 8-hour ozone design values by site

Data obtained from MARAMA member agencies. Design values have been grouped according to the classifications used in the Air Quality Index (AQI), although the AQI is meant for use with 8-hour concentrations, not averages such as the design value.

#### **Ozone Design Values**

The 8-hour design value standard is 0.08 ppm averaged over eight hours (0.085 rounds up). Ozone data are usually listed in parts per billion (ppb), so a design value of 85 ppb violates the standard. Many counties in the Region are classified as nonattainment for the 8-hour standard. Tables D-2a and 2b in Appendix D list 8-hour ozone design values for 2001 through 2003 by county. They are grouped into counties in attainment and those designated nonattainment. (Counties without monitors are not listed.) Design values for the previous three-year period are mapped in Figure 9.

In counties with monitors that are classified attainment, 11 design values were 80 ppb or less, and 10 were between 81 and 84 ppb, just below the standard. In counties classified as nonattainment, 43 slightly exceeded the standard, with design values of 85-90 ppb, 50 counties had design values of between 91 and 100 ppb, and three counties exceeded 100 ppb (Ocean and Camden Counties in New Jersey and Harford County in Maryland).



Design Value Less Than 15.1 ug/m3

#### Figure 10 MARAMA Region $PM_{2.5}$ design values 2001-2003

Data obtained from EPA's AIRS website

The county with the highest ozone design value in the Region (109 ppb) was Ocean County, New Jersey. This county borders New Jersey's Atlantic Coast and is characterized by the commercial activities associated with seasonal resorts. Ocean County's air quality is affected by sources in Philadelphia and New York City. The county with the lowest ozone design value (74 ppb) is Swain County, North Carolina. Located in the western part of the state, Swain County is 93 percent forestland and is home to most of the Great Smoky Mountains National Park.

Table D-3 in Appendix D lists 8-hour design values for 2001-2003 by nonattainment area rather than by county. The nonattainment area with the highest design value (106 ppb) is the Philadelphia-Wilmington-Atlantic City area, which includes portions of Pennsylvania, New Jersey, Maryland, and Delaware.

#### Particulate Matter Design Values

For the annual  $PM_{2.5}$  standard, design values greater than or equal to 15.1 micrograms per cubic meter ( $\mu g/m^3$ ) indicate a violation of the annual standard. Most of the  $PM_{2.5}$  design values in the Region show
compliance with the annual standard of  $15 \,\mu g/m^3$ . Table D-1 in Appendix D lists PM<sub>2.5</sub> design values for 2001 through 2003 for each monitoring site in the Mid-Atlantic Region. These values are mapped in Figure 10.

The highest  $PM_{2.5}$  design value in the Region (21.2 µg/m<sup>3</sup> for 2001 to 2003) is located near Pittsburgh (Liberty), and is influenced both by regional transport of fine particle pollution and by local sources, including a large coke plant. The site with the lowest design value in the region for 2001-2003 was at Keeney Knob in Summers County in southwestern West Virginia.

Most of the  $PM_{2.5}$  design values in the Mid-Atlantic Region are relatively close to the annual standard of 15 µg/m<sup>3</sup>. Table D-1 in Appendix D shows that 25 monitors recorded design values between 15 and 16 µg/m<sup>3</sup>, and another 25 were between 14 and 15 µg/m<sup>3</sup>. Monitors with design values of 16 µg/m<sup>3</sup> or greater were limited to one monitor in the Baltimore area, eight sites in Pennsylvania, seven sites in West Virginia, and one in Delaware.

## PM<sub>2.5</sub> Composition

Data from the urban speciation network run by state and local air quality agencies, and data from the National Park Service's more rural Interagency Monitoring of Protected Visual Environments (IMPROVE) network show that, on average, particulate matter across the Mid-Atlantic Region is dominated by sulfates, and that organics are generally higher in cities than in rural areas. (See Figures 11 and 12.) The sizes of the pie charts in Figures 11 and 12 represent the overall PM mass present at each site. Figure 12 shows very similar rural concentrations across much of the Eastern U.S. Concentrations of particulate matter at Mid-Atlantic urban sites are all near the annual standard of  $15 \,\mu g/m^3$ , while rural sites are consistently somewhat lower.

Sulfate is a large fraction of the fine particles and haze in the Mid-Atlantic Region throughout the year, though its role is considerably larger in summer than in winter. In winter, the chemical reactions that turn sulfur dioxide into sulfate are much slower, so most of the atmospheric sulfur is present as sulfur dioxide instead of sulfate. In summer, the opposite is true, and most atmospheric sulfur is present as sulfate. This leaves the significant, but nowhere near as dominant, annual contribution from sulfate shown in Figures 11 and 12. Ammonia is also quite significant, since it is generally found as ammonium sulfate in the summertime.

When  $PM_{2.5}$  is broken down in terms of contributions to haze on the 20% worst days, sulfate is also the dominant component of haze throughout the Mid-Atlantic Region. This is partly because sulfate aerosols take on water readily, growing rapidly, and scattering light efficiently, and partly because of their greater concentration. (See Figure 6 in Part I.)

Comparing nearby urban and rural sites can help determine the fraction of particulate matter due to a particular city's emissions and the fraction that is due to sources affecting the entire region. Rural IMPROVE sites are taken to represent the regional load entering a city, while urban sites are taken to represent the sum of both the regional load and the local contribution. Subtracting the IMPROVE concentrations from their paired urban site counterparts provides an estimate of the mass and speciation of aerosols from the urban area. This analysis reveals that over a year, roughly two thirds of the fine particle mass in Mid-Atlantic cities is the result of a widespread regional load. The other third has been termed the "urban excess" PM <sub>25</sub> concentrations, as shown in Figure 13.



# Figure 11 Annual average composition of fine particles at urban sites throughout the United States

This map was developed using data from the Speciation Trends Network (March 2001- February 2002). Concentrations at these urban sites are higher than at the rural sites shown below, especially in the western U.S.



# Figure 12 Annual average composition of fine particles at rural sites throughout the United States

*This map was developed using annual average data from the IMPROVE network (March 2001- February 2002). In the eastern U.S., sulfate is highly significant both at urban sites shown in figure 11 and at these rural sites.*  EPA's data analysis represented in Figure 13 shows that the excess mass in urban areas is largely organic carbon and soot. Of that excess, organic carbon is by far the largest constituent.

A similar analysis of preliminary results from the Pittsburgh "super site" (see page 26) indicates that the city's haze has a strong regional component for both sulfate and organics. This field project used a network of nearby stations outside the Pittsburgh metro-

politan area to determine the regional load. Monitors closer to the city center measured the urban contribution. Conceptually, the experiment worked the same as the comparisons between urban and IMPROVE data, though the monitors outside Pittsburgh were closer to the city than most of the IMPROVE sites were to their urban counterparts. High aerosol loads were present at both the satellite site and the urban site, with somewhat higher loads of carbon compounds in the city.

The importance of different species shifts from summer to winter in the Mid-Atlantic Region. In summer, sulfate and organic carbon dominate fine particulate matter mass, with sulfate most important in the north and nearly equal contributions from both organic carbon and sulfate in the southern part of

the Region. In winter, sulfate is still significant, but not as dominant as in the summer. Nitrates become far more prominent in winter, since they are more stable in cold weather and break up readily in the heat of summer. Organic carbon remains constant throughout the year.

## Seasonal Variation in Total PM<sub>2.5</sub>

PM concentrations can be high at any time of the year, though the highest values usually occur in the summer. Summertime  $PM_{2.5}$  concentrations often show patterns similar to those shown by ozone, since the meteorology that

generates  $PM_{2.5}$ , haze, and ozone events is often identical. Notable exceptions are found when, for example, a humid, cloudy summer day with no rain may show high levels of  $PM_{2.5}$ , but low levels of ozone. Winter is another matter entirely, since  $PM_{2.5}$  is often high in winter, when ozone is not.

Figures 16-19 demonstrate that  $PM_{2.5}$  levels are at their highest levels in the summertime. Figures 14 and 15 show that peak values tend to occur throughout the eastern part of the Region on the same days. (Note that Figures 14 and 15 do not include sites in West Virginia and western Pennsylvania.) The broad consistency shown on these charts reflects data showing that the highest  $PM_{2.5}$  levels consist primarily of sulfate, which is a secondary pollutant formed downwind of large sources of sulfur dioxide. The MARAMA report, *The Development of PM\_{2.5} Forecasting Tools for Selected Cities in the MARAMA Region* concluded that there are several types of high  $PM_{2.5}$  events, but that many days with high  $PM_{2.5}$  levels are influenced by a slow-moving or stationary high pressure system that results in suppressed vertical mixing of emissions and low wind speed or stagnation.

As explained in Appendix C, the daily  $PM_{2.5}$  standard is 65 µg/m<sup>3</sup>, and the Mid-Atlantic Region complies with this level. However, the Air Quality Index (AQI), described in Appendix A, provides a stricter level for reporting potential adverse health impacts. Concentrations of 40 µg/m<sup>3</sup> or more for 24 hours triggers an AQI of "unhealthy for sensitive groups." At these levels, people with heart or lung disease, older adults and children are advised to reduced prolonged or heavy exertion.

Much of the fine particle and haze problem throughout the Mid-Atlantic is regional in nature, especially in summer. In winter, the problem becomes much more localized.

> Sulfate is a large fraction of the fine particles and haze in the Mid-Atlantic Region throughout the year, though its role is considerably larger in summer than in winter.



#### Figure 13 Ambient urban excess PM concentration for 13 example areas

EPA mapped the difference between urban and rural  $PM_{2.5}$  levels in the 13 areas examined. For this map, the difference was calculated for five categories of particles: sulfates, ammonium, nitrate, total carbon mass (TCM), and crustal matter. For each category, the height of the bar represents the amount by which the urban concentration exceeds the nearby rural concentration. In the Eastern U.S., sulfate, nitrate, and ammonia concentrations are very similar in urban and rural areas, so the differences are small. Most of the "urban excess" that causes higher concentrations in urban areas is total carbon mass. (Total carbon mass is the sum of elemental and organic carbon.) Two assumptions about how to calculate total carbon mass are represented, one by the light gray part of the bar, and the other by the taller, darker gray. The biggest difference in PM concentrations between the eastern rural and urban areas is that urban areas have higher levels of total carbon.

see http://www.epa.gov/airtrends/aqtrnd03/pdfs/2\_chemspecofpm25.pdf page 22

Figures 14 and 15 show that on about 10 days during the summer of 2002,  $PM_{2.5}$  levels were unhealthy for sensitive groups at one monitor, at least once in the Region. These were all summer days, occurring between late June and August and were associated with high pollution episodes.

Figures 14 and 15 show that the first of these four 2002 episodes affected only the northern part of the Region. These charts also show that the more southern parts of the Region tended to have lower concentrations in 2002.

Figures 16-19 show data for the entire year for selected areas. The data for 2002 are not necessarily representative of long-term averages, since weather and emissions can vary from year to year, but

these charts illustrate the regional, episodic nature of many high pollution events.

## An Ozone Episode

Day-to-day 8-hour ozone levels show a substantial influence from short-term changes in the weather. An episode of high ozone days invariably shows a pattern of high ozone that moves The importance of some species shifts throughout the year. Organic carbon is significant throughout the year; sulfate is dominant in summer and important in winter, while nitrate is only significant in winter.

as weather patterns move across the Mid-Atlantic Region. Episodes involving a particularly large weather feature such as the Bermuda High may last weeks, as high ozone moves from Texas and Louisiana, up through the industrialized Midwest, over the Appalachians, and into the Mid-Atlantic Region.

The mid-August 2002 episode is a good example of a lengthy episode. The pattern started as early as August 5, 2002, when a cold front pushed deep into the South, bringing clean air with it. As the cold front pushed on, the Bermuda High pushed westward, first over the southern U.S., and then farther north. High ozone was observed on the 6th in Texas, around Houston. Before long, North Carolina started experiencing high ozone. High ozone then began the push to the north and east, ending up in the Mid-Atlantic Region around the 10<sup>th</sup> of August. Different parts of the region showed the influence of a myriad of transport patterns in this episode, with recirculation, localized stagnation, a low-level jet, and long-range transport driven by the Bermuda High all showing up before the episode finally came to an end with thunderstorms and instability in the Midwest. Ozone along the Eastern Seaboard cleared out from south to north, and the influence of transport along the populated I-95 corridor was seen clearly as pollutants pushed from the southwest to the northeast. Some parts of the region experienced their worst air quality in this end phase.

Since meteorology drives air quality episodes, the pattern of poor air quality in Mid-Atlantic ozone episodes tends to take on the scale and character of the weather that drives them. The next part of this report explains more about the influence of weather patterns on air quality.

# Pittsburgh Air Quality Study (PAQS)

The Pittsburgh Air Quality Study (PAQS) was a comprehensive multi-disciplinary set of projects designed to improve our understanding of airborne PM in the Pittsburgh region. PAQS was led by Carnegie Mellon University (Professors Spyros Pandis (ChE/EPP), Cliff Davidson (CEE/EPP), and Allen Robinson (ME/EPP)) and included investigators from twelve universities, two national laboratories, two private companies, and state and local air pollution agencies. PAQS was supported by the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Energy National Energy Technology Laboratory (NETL).

#### **Objectives**

- Characterize PM (size, surface, and volume distribution; chemical composition as a function of size and on a single particle basis; morphology; and temporal and spatial variability) in the Pittsburgh region.
- Quantify the impact of various sources (transportation, power plants, biogenic, etc.) on the PM concentrations in the area.
- Develop and evaluate the next generation of atmospheric aerosol monitoring techniques (single particle measurements, continuous composition measurements, ultrafine aerosol measurements, improved organic component characterization, etc.).

# USX Tower USX Tower

*Top: July 2,2001, PM*<sub>2,5</sub> =  $4 \mu g/m3$ 

Bottom: July 18, 2001, PM<sub>25</sub> =45 µg/m3

Photo: Carnegie Mellon University

#### Lessons Learned

• Regionality of pollution does not imply the same concentration everywhere. There are gradients, and pollution moves around.

Concentrations of both sulfate and organics in Pittsburgh are influenced by large regional contributions.

- For Pittsburgh, modeling indicates reducing  $SO_2$  emissions will reduce sulfate and  $PM_{2.5}$ , but nitrate will also increase in all seasons. Modeling also indicates ammonia reductions can prevent nitrate increases, and  $NO_x$  emission reductions can help in winter.
- Biogenic (natural) sources, transportation, and biomass burning are important sources of organics. In summer, about 30-40% of organic PM is secondary, and around 10% in winter.
- New monitoring technologies (single particle mass spectrometry, semi-continuous metal measurements) allow fingerprinting of point sources.

#### For more information see

http:homer.cheme.cmu.edu



Figure 14 PM<sub>25</sub> time series for the northeastern MARAMA Region, summer 2002

Based on data from Federal Reference Method (FRM) monitors, five cities in the northeastern part of the Region experienced very similar  $PM_{25}$  levels in the summer of 2002.



Figure 15 PM<sub>25</sub> time series for the southeastern MARAMA Region, summer 2002

Based on data from Federal Reference Method Monitors, four cities in the southeastern part of the Region experienced many similar and some different patterns of  $PM_{2.5}$  concentrations. During most of this season concentrations tended to be lower than in the northern cities shown in Figure 14.





Figure 16 Average FRM values for 2002, Baltimore, MD

Average daily  $PM_{2.5}$  values exceeding 40  $\mu g/m^3$  occurred on only six days in 2002 in Baltimore. Daily values above 40 trigger public health notices that air quality conditions are unhealthy for sensitive groups.





Richmond's average daily  $PM_{2.5}$  values in 2002 were somewhat lower than Baltimore, but high values occurred in both cities on many of the same days.



Figure 18 Average FRM values for 2002, Wilmington, DE

Average  $PM_{2.5}$  daily values for Wilmington for 2002 show a similar pattern to Baltimore and Richmond, with five summer days exceeding 40  $\mu$ g/m<sup>3</sup> and many days exceeding 15  $\mu$ g/m<sup>3</sup> throughout the year.



Figure 19 Average FRM values for 2002, Pittsburgh, PA.

Data for the Liberty monitor were not included in this chart. The pattern of high daily values is similar to the other cities in the Region.

# Mid-Atlantic Regional Air Management Association -30-

#### Part III

# Meteorology and Transport in Air Pollution Episodes

Summertime air pollution episodes in the Mid-Atlantic Region are typically hazy, hot, and humid, with light winds and few clouds. Throughout the Mid-Atlantic Region, polluted air from elsewhere, often the industrialized Midwest, nearly always brings elevated pollution levels into the Region before any pollution from the Mid-Atlantic Region joins the mix. Wintertime air pollution episodes, in contrast, are typically cool, with light winds, and are more dominated by local stagnation and local emissions. Conditions favorable to pollution are produced by a combination of meteorological features of all sizes, though the largest features typically receive the most attention. This section begins with a description of the local meteorological conditions generally present during pollution episodes, and then takes a step back to examine their large-scale causes, before revisiting the small scale to look at the local breezes that also play a role in air quality. At the end of this section, the meteorological phenomena are brought together to see how they influence pollutants in an air pollution episode.

## The Basics: Mixing, Temperatures, and Daily Cycles

What makes a day in an air pollution episode different from any other day? Among other things, pollution is typically confined to a shallow layer near the surface, either in winter or summer. On cleaner days, pollution typically mixes more freely to a greater depth, or it might be blown away by strong winds. The cap that confines pollution near the surface is known as a temperature inversion. A temperature inversion occurs when warmer, more buoyant air sits over colder, denser air.

Anyone who has hiked in the mountains knows that air usually cools with increasing altitude. Where there are no mountains, the temperature decreases even more rapidly. This is the natural result of two facts: air cools as it expands to a lower pressure, and the source of most of the atmosphere's heat is at the surface of the Earth. In general, when the atmosphere is well mixed, the temperature drops uniformly as one rises in altitude. The temperature decrease with distance from the surface sets the stage for considering what happens to a small, polluted parcel of air near the surface.

Let us start with the common saying "hot air rises," which should also be paired with "cold air sinks." This simple phenomenon is very important in air quality. In the atmosphere, this should be extended to "hotter air rises, cooler air sinks." So if a parcel of air is warmer than its surroundings, it will tend to rise.

Now consider stability. If we grab an air parcel near the surface, and give it a nudge upwards, what will happen to it? If the atmosphere is well mixed, then the air parcel will expand and cool at the same rate as the rest of the air around it. This parcel has no reason to keep moving up or down because

it is always cooling at the same rate as the rest of the atmosphere, and is never hotter or cooler than its surroundings. If the atmosphere's temperature does not decrease uniformly with altitude, but increases in a temperature inversion, then, when an air parcel is pushed

Ordinarily, temperature decreases uniformly with altitude, and the atmosphere is free to mix vertically. A temperature inversion occurs when warmer air sits atop cooler air. Temperature inversions prevent mixing, dividing the atmosphere into two parts: that above the inversion and that below it. upwards, it suddenly encounters warmer air above it. Since the air parcel is now cooler than its surroundings, it tends to sink. The temperature inversion acts as a cap, inhibiting mixing. Pollutants emitted from the surface cannot move through the inversion and are trapped near the surface. Likewise, any air above the temperature inversion will be hotter than its surroundings if it tries to move down through the inversion. The temperature inversion therefore caps air near the surface and divides the atmosphere into two parts.

#### Temperature Inversions: Origins

Though they might not know it, most people have direct experience with the effects of a temperature inversion. On a warm summer night, winds at the surface are generally quite weak because a nighttime or nocturnal temperature inversion has formed overhead. This inversion forms as the sun sets, and the Earth's surface cools. Land surfaces are far more efficient at radiating heat than the atmosphere above, so the Earth's surface cools more rapidly than the air. That temperature drop is then conveyed to the lowest few hundred feet of the atmosphere. The air above cools more slowly, and a temperature inversion forms only a few hundred feet (sometimes only a few feet) above the ground. The inversion divides the atmosphere into two sections, above and below the inversion, which do not mix. In the surface section, winds are weak, and any pollutants emitted overnight accumulate beneath the inversion. Above the inversion, winds continue unabated through the night and can even become stronger as the inversion isolates the winds from the friction of the rough surface. The inversion is similar to an air hockey table, letting the winds aloft blow freely by eliminating surface friction.

In the morning, the nocturnal inversion breaks down as the heating of the day gets into full swing. Eventually, the sun warms the Earth's surface, which in turn warms the cool air near the surface,



#### Figure 20 Temperature inversion

This is a simplified picture of a temperature inversion, where warmer air aloft inhibits vertical mixing, concentrating pollution in a smaller volume of air near the ground.

replacing the heat that radiated away the night before. When the air near the surface warms enough, it rises and breaks through the former nocturnal inversion, so the atmosphere may once again mix freely. Air from above then mixes down to the surface, and air that was near the surface is free to mix with the air above. (Depending on whether the air above the inversion is cleaner or more polluted than the air at the surface, this mixing can either lower or increase air pollution levels.)

A second inversion is often present during an air pollution episode, well above the nocturnal inversion, but with a very different cause. This is a subsidence inversion, caused by subsiding (sinking) air (Figure 21). Air cools as it rises and expands, and warms as it sinks or is forced downward and compressed. This warming leads to a subsidence inversion—a phenomenon associated with the sinking motion that occurs in a high pressure system. (High pressure systems are discussed later in this document.) This kind of inversion is particularly strong, since it is associated with a large scale downward motion of the atmosphere. The subsidence inversion typically caps pollution at a higher altitude in the atmosphere, and it is far more difficult to break than the nocturnal inversion's cap. The subsidence inversion limits vertical mixing in the middle of the day during an air pollution episode.

### Daily Cycles

As temperature inversions build and break down with heating from the sun, they produce daily cycles of winds and air pollution. Consider a typical day, starting at sunrise when the air is at its coolest. At this time, the nocturnal inversion is in full force overhead, and winds at the surface are typically quite calm,



#### Figure 21 Daily cycle of inversions and mixing

A temperature inversion effectively traps pollutants near the surface and allows pollutants above the inversion to travel freely over considerable distances. There are two kinds: a low level "nighttime" or "nocturnal" inversion; and an elevated "subsidence" inversion. The low level inversion typically breaks down in the mid- to late-morning, while the elevated inversion is more difficult to breach and limits vertical mixing at mid-day during air pollution episodes. while winds above the nocturnal inversion continue unabated. As the temperature increases through the morning, the nocturnal inversion eventually breaks down, and the atmosphere mixes up to the height of the subsidence inversion. If the day is particularly hot, the subsidence inversion may also be punctured. In the late afternoon, temperatures are at their hottest, and the atmosphere mixes to its greatest height. As afternoon passes into evening, temperatures cool, and mixing subsides. The following night, the nocturnal inversion forms, once again isolating the surface from stronger winds only a few hundred feet overhead. This process continues uninterrupted until the large-scale weather pattern changes.

The daily cycle of mixing is partially responsible for the daily cycle of air pollutants such as ozone. At night, ozone near the surface cannot mix with ozone above. Instead, ozone below the nocturnal

The Sun's daily cycle of heating results in a daily cycle of mixing. Mixing is driven by the warm surface, which heats the air above it. That warm air rises, causing colder air to fall down to replace it. Temperature inversions inhibit mixing, so the air below an inversion may have completely different characteristics from that above the inversion. Air below the nighttime inversion is rather still, while air above that inversion may be moving quite rapidly. inversion is destroyed as it reacts with the Earth's surface and everything on it. In a city, fresh nitrogen oxide  $(NO_x)$ emissions react with ozone, further reducing its concentration, so that by morning, very little ozone is left below the nocturnal inversion.

Above the nocturnal inversion, the story is entirely different. Ozone from the previous day's emissions remains largely intact. There are no surfaces to react with the ozone and destroy it, so a large reservoir of ozone remains above the inversion. In the morning, when the nocturnal inversion breaks down, all the ozone that remained above the inversion comes mixing back down. Likewise, the air near the surface, laden with the emissions of the night before, mixes up away from the

surface. The result of all this mixing is a sudden surge in ozone levels in the middle of the morning. This surge is almost entirely due to mixing. Readings from elevated monitors and measurements with instrumented aircraft have confirmed this large reservoir of ozone aloft. Those measurements also show ozone mixing down to the surface.

This mixing mechanism will also be important in explaining the significance of long-range transport, because the ozone above the nighttime inversion usually comes from far away and is not local.

Pollutants such as particles that do not react with the surface as readily as ozone do not show such a marked diurnal cycle, but the same mixing mechanism also affects their concentrations. Nighttime emissions of particles can build up under the nocturnal inversion, leading to higher levels in the early morning. In the summertime, regional sulfate levels above the inversion can combine with local emissions as the inversion breaks up. In the winter, with less sunshine, it's harder to break the inversion, and local emissions can continue to build unless washed out by rain or dispersed by winds.

## Meteorological Transport Mechanisms

# Large-scale Transport: Global Circulation, High Pressure, Low Pressure, and Fronts

All weather systems on Earth, from the global circulation pattern to the smallest sea breeze, are driven by differences in temperature. Globally, the largest circulations (such as the trade winds in the tropics and mid-latitude storms) are driven by temperature differences between the steamy tropics and the icy poles. Storm systems serve to even out these differences in temperature by mixing cold and warm air. As the position of the Sun in the sky shifts from its northernmost point at the summer solstice to its southernmost point at the winter solstice, storm tracks shift, too. Over the Mid-Atlantic Region, this shift produces winter weather with frequent storms, which periodically clean out the Region's air. In summer, the storm track shifts far to the north, so summer cold fronts typically pass through the northern Mid-Atlantic Region, occasionally reach the central part, and only rarely push into the far southern parts.

Because the storm track shifts, most of the Mid-Atlantic Region's worst pollution events occur in the summer—wintertime weather is not conducive to the large, regional episodes seen in summer. Winter-time episodes can be locally intense, but they generally do not share the regional nature of their summer-time counterparts.

Other seasonal factors also combine to influence pollution events: temperatures, mixing, and strong winds all shift with the seasons. The next sections discuss the large-scale impacts of global circulation, high and low pressure systems, and fronts.

#### Global Circulation

The global circulation of the atmosphere is driven by the enormous heat engine of the tropics. When the Sun's rays are directly overhead, the surface heats rapidly, pushing copious amounts of moisture skyward. This lift eventually results in the downpours for which the tropics are deservedly famous. Just outside the tropics, the air that was lifted aloft by the strong tropical heat now sinks, creating large areas—the subtropics—where the upward motion of air is strongly discouraged. This large belt of sinking air lies between 20 and 30 degrees north, where many of the world's great deserts are found. Land masses and oceans pinch this belt in places, so, for example, the Southeastern United States is relatively moist, while the Southwestern United States is quite dry. These large areas of sinking air form semi-permanent, high pressure systems that strongly influence weather throughout the subtropics.

For the Mid-Atlantic Region, the most relevant feature of this global chain of subtropical high pressure systems typically lies offshore to our east: the Western Atlantic Ridge, also known as the Bermuda

High. In the summer, it occasionally pushes westward, bringing a heat wave to the Eastern United States. In winter, it retreats to the Azores in the eastern Atlantic.

Winds circulating clockwise around the Bermuda High are also responsible for steering hurricanes as they travel across the Atlantic Ocean toward the Leeward Islands and the Eastern United States. Depending on its position, form, and orientation, the Bermuda High can steer clean, moist air to the Mid-Atlantic Region or it can bring a prolonged pollution episode. Air quality becomes particularly foul when the Bermuda High links up with a polluted continental high pressure system. Because the storm track shifts, most of the Mid-Atlantic Region's worst pollution events occur in the summer—wintertime weather is usually not conducive to the large, regional episodes seen in summer. Wintertime episodes can be locally intense, but they generally do not share the broad regional nature of their summertime counterparts.

In contrast to the conditions in the middle of the Bermuda High, where rainfall is suppressed, at its outer fringes, one often finds numerous strong thunderstorms. These thunderstorms occur partly because the far western edges of these systems tend to be unstable, but circulation around the Bermuda High also brings with it considerable moisture from the Gulf of Mexico. In areas where the suppressing influence of the Bermuda High is weak, this moisture leads to numerous thunderstorms. The Bermuda High is

therefore often referred to in weather forecasts as a "ring of fire," where a parched, polluted center is surrounded by a ring of hefty thunderstorms with relatively good air quality.

In winter, the tropics remain hot, but the region of peak heating shifts south of the Equator. This allows cold air from the Arctic to push farther south. The clashes between this cold Arctic air and the warmer air to the south produce the strong winter storms so common to mid-latitudes such as the Mid-Atlantic Region. These clashes bring frequent storms with strong winds, which in turn limit the extent of winter-time pollution episodes. Instead, wintertime air pollution episodes tend to arise from local stagnation and nearby sources.

Just as the tropics force air upwards, cold air sinks over the poles, completing a hemisphere-wide circuit. The interaction of cold air from the poles and warm air from the tropics, when combined with a steering effect resulting from the rotation of the Earth, leads to the west-to-east motion of winds and storm systems in the mid-latitudes. Near the equator and near the poles this is not the case—the prevailing winds at those latitudes blow from the east to the west. Two things drive all of these prevailing winds: the temperature difference between the equator and the poles, and the rotation of the earth.



#### Figure 22 Bermuda High

A semi-permanent area of high pressure, commonly known as the Bermuda High, forms over the Atlantic Ocean during the summer and is the key player in the summer climate for most of the East. The clockwise circulation around the high pressure center brings southerly winds to the East, especially the Southeast.

#### High and Low Pressure Systems

High pressure systems bring calm, cloudless, hot sunny days in summer, and may bring bitter cold in winter. They also bring high humidity (in summer), limited vertical mixing, and stagnation—all the signatures of a heat wave in the Mid-Atlantic summertime. Air in a high pressure system circulates clockwise in the Northern Hemisphere, and sinks. A high pressure system should be thought of as a threedimensional flow which draws air in at high altitude, pushes it downward to the surface, and spreads out. The sinking motion suppresses vertical mixing, clouds, and rainfall. The slow spreading motion also means that winds at the surface will be quite weak. High pressure systems bring clear skies and stable conditions, exactly the situation needed for an air pollution episode. In contrast, low pressure systems bring instability and storms, leading to considerable mixing and high winds. Most Mid-Atlantic air pollution episodes occur when high pressure is in the area and the air stagnates.

In contrast, a low pressure system is a fountain of air, drawing strong

surface winds in toward the center, and forcing them out the top. Low pressure systems circulate in the opposite direction of high pressure systems, or counterclockwise in the Northern Hemisphere. The upward motion in a low pressure system produces increased mixing, showers, stronger winds, and the end of a pollution episode.

High pressure systems can produce particularly strong pollution episodes if their circulation drives air from one polluted area to another. Of particular importance to the Mid-Atlantic Region are episodes where the Bermuda High produces stagnant conditions over the Mid-Atlantic and winds are either from the industrialized Midwest or aligned along the East Coast's urban corridor. Often, this occurs when the Bermuda High combines with a high pressure system over the North American continent that has been collecting pollution for days. Most of the longest-lasting Mid-Atlantic pollution episodes have occurred when the Bermuda High combines with a continental high pressure system. When this happens, the two form a very large high pressure system. Conditions are made worse because the continental part of the new, larger high pressure system is already laden with pollution.

The high temperatures and clear skies that accompany summertime high pressure systems also accelerate smog chemistry, forming ozone, sulfate, and organic carbon aerosols, among others, more quickly. Cloudless skies let through more of the ultraviolet and visible light that drives smog photochemistry. Because they bring higher temperatures and cloudless skies, slow moving high pressure systems usually cause air pollution episodes when they remain over the continent.

In winter, high pressure systems often descend out of Canada, ushering in a severe cold snap with very clean clear air. Wintertime pollution episodes are in some ways different from those in the summer. The

local stagnation and tight cap on mixing that accompany wintertime high pressure systems will produce a localized pollution episode.

Until recently, the focus of most air pollution studies has been on summertime ozone, so wintertime particle pollution has been less well studied. It appears, however, that wintertime episodes are more the result of local stagnation than their summertime cousins. Summertime episodes typically produce a broad region of high pollution (ozone or particle), whereas wintertime particle pollution episodes are localized in cities and near pollution sources. Air in a high pressure system circulates clockwise in the Northern Hemisphere, and sinks. A high pressure system should be thought of as a three-dimensional flow which draws air in at high altitude, pushes it downward to the surface, and spreads out. The sinking motion suppresses vertical mixing, clouds, and rainfall. Most of the longest-lasting Mid-Atlantic pollution episodes have occurred when the Bermuda High combines with a continental high pressure system. When this happens, the two form a very large high pressure system. Conditions are made worse because the continental part of the new, larger high pressure system is already laden with pollution. Under unusual circumstances, high and low pressure systems can team up to produce an air pollution episode. In July 2002, a departing low pressure system and an advancing high pressure system over central Quebec combined to deliver strong northerly winds to the Mid-Atlantic Region. Ordinarily, northerly winds bring very clean air to the Region, since there are very few large sources of emissions in central and northern Quebec. In early July 2002, this was not the case. Between these two systems, several forest fires were burning out of

control in central Quebec. Instead of bringing clean air, the colliding high and low pressure systems funneled smoke from these fires to much of the Eastern United States. The stability of the trailing high may have helped the smoke to make such a long journey. High concentrations of both particulate matter and ozone were reported, and woodsmoke could be smelled as far south as Maryland and Virginia.

#### <u>Fronts</u>

Fronts are the familiar serrated lines shown on weather maps. Warm fronts and cold fronts represent the boundaries between air masses—large bodies of air with similar properties. Fronts are named after the character of the advancing air, so a cold front indicates colder or drier air moving into an area of warmer, moist air, while a warm front indicates warm, moist air moving into colder, drier air.

Cold fronts tend to mark a sharp contrast between air masses, and this contrast often causes the thunderstorms that bring an air pollution episode to an end. Since cold air tends to stay near the surface, a cold front is a wedge of cold air that forces warm, moist air upward. This upward forcing produces the sometimes violent storms associated with the front. Behind the front, the advancing cold air is typically quite clean, so by bringing cleansing storms and cleaner air, a passing cold front usually



# Figure 23 Satellite picture of smoke from 2002 Quebec wildfires

On July 7, 2002 smoke from Quebec, Canada wildfires blew southward over the United States.

ends an air pollution episode. As the front pushes from west to east, winds ahead of the front will blow along it from the southwest to the northeast. In the Mid-Atlantic Region, this typically means that winds will be blowing from the southwest before the front passes through. In the summer, southwest winds ahead of an approaching cold front can alter the transport of pollutants on the final day of a pollution episode.

Unlike the violent weather of a cold front, a much broader area of milder showers generally marks warm fronts. A warm front is a wedge of warm air that rides gradually over cold air that is already in place. Since cold air stays near the surface, a warm front does not immediately replace the surface air with warmer air. The transition occurs more gradually as the cold air retreats. Since they cause broad areas of showers, the atmosphere in the area of the warm front is generally quite clean.

# Maryland Aerosol Research and Characterization (MARCH Atlantic)

photo: Bruce Doddridge

Located between Baltimore and Washington, at Fort Meade, Maryland, and coordinated with other studies in the region,

MARCH Atlantic began ground- and aircraft-based measurements in 1999 and ended in 2002, conducting one month of intensive air quality measurements each season. Active data analysis continues. Peter Mueller [Electric Power Research Institute-EPRI], Bruce Doddridge and Russ Dickerson [University of Maryland], and Judy Chow [Desert Research Institute - DRI] led the study, which also included investigators from the University of Southern California [Ron Henry] and the National Park Service [Bill Malm].

#### **Objectives**

- Characterize the seasonal, daily, and spatial changes in the chemical composition of both gases and particles.
- Identify the most likely sources of airborne particulate matter (PM).
- Contribute to the development of state and federal PM monitoring methods.

#### Lessons Learned

- In summer and winter, PM exhibits the highest seasonal concentrations and different chemical composition. In summer, particulate matter reduces visibility more than in winter at similar concentrations and relative humidity.
- Substantial day-to-day differences in PM occur in several 3- to 5-day weather-driven episodes in both summer and winter.
- Fine PM (PM<sub>2.5</sub>) consists primarily of ammonium sulfate and nitrate plus carbonaceous material (C). Sulfate is higher in summer than winter. Nitrate and C are higher in winter than in summer.
- Carbonaceous material is about 20% soot and 80% other organics in all seasons
- The most serious haze and PM episodes in the Mid-Atlantic Region occur with a combination of westerly transport and regional recirculation or with southerly air flow and localized recirculation of emissions.
- Regional and local emissions influence the composition and concentration of PM differently. In summer, within-region emissions may contribute about 30% of PM<sub>2.5</sub> mass. In winter, within-region emissions my contribute over 60%.
- Routine public agency monitoring of 24-hour particulate matter should be supplemented with continuous measurement technology.

**For more information** and a complete bibliography of related publications, contact Peter Mueller at pklausm@mac.com.

Fronts mark boundaries between air masses, and are labeled by the character of the advancing air, so a cold front denotes colder or drier air pushing into warmer or wetter air. All fronts are weather makers, though the conditions caused by each kind of front are different. Cold fronts generally usher in cleaner air, while warm fronts may usher in a pollution episode. When a front stalls, it is called a stationary front, marking the boundary between two contrasting air masses. This is often the fate of summertime cold fronts, which advance as far south as they can before running out of steam. Stationary fronts sometimes persist for days, serving as a focal point for storm development. Ripples tend to form along the frontal boundary, resulting in a series of small disturbances that roll along the front, usually from west to east. As these disturbances move along, they mix warm, moist air south of the front with cool, dry air to the north of it, producing showers and thunderstorms. A persistent stationary front can generate storm after storm, often producing copious rain over the same region and causing flooding.

To the north of a stationary front, conditions are generally quite clean, since fresh clean air from Canada is transported south to the frontal boundary. In contrast, the stagnant, hot conditions south of the front often lead to poor air quality. In the Mid-Atlantic Region, a cold front will often descend south, become stationary, and then return north as a warm front. In this case, the returning warm air is often quite polluted since it contains several days of emissions that baked under the warm, cloudless conditions south of the front.

# Smaller Scale Motions: Low Level Jet, Appalachian Lee Side Trough, Sea Breezes, and Mountain Breezes

In addition to the large-scale effects just described, smaller scale weather patterns also influence air pollution. This section discusses four such weather phenomena: the low level jet, the Appalachian lee-side trough, sea breezes, and mountain breezes.

#### Low Level Jet

The low level jet, sometimes called the nocturnal jet, is a low-altitude region of rapid winds that forms at night under the same calm conditions typically present in a pollution episode. Forming just above the nighttime temperature inversion mentioned previously, the low level jet depends on the isolation from the surface provided by the inversion. It is typically found where a range of mountains meets a flat plain. In the Mid-Atlantic Region, those features are the Appalachians and the Atlantic Coastal Plain. The Great

The low level jet is a river of air a few hundred feet above the surface. It is driven by differences in heating between a mountain range and the air above a flat plain. Along the East Coast, it runs from the southwest to the northeast, following the contours of the Appalachian Mountains. The low level jet is typically a few hundred feet thick, and may run from South Carolina all the way up to New England. Plains also have a much stronger low level jet resulting from the differences in heating between the Rocky Mountains and the Great Plains. That low level jet fuels some of the enormous thunderstorms that periodically rumble across the Great Plains.

In some sense, the low level jet is a delicate feature. It only forms when fronts and storm systems are far away. It is generated by the temperature difference between the mountainside and the air at a similar altitude above the coastal plain. As mentioned earlier, land cools much faster than air, so the mountainside cools relatively quickly. In contrast, if one traveled a few miles horizontally away from the mountains so the surface was a few hundred meters below, the air would be warmer, since it would be far from a rapidly cooling land surface. This temperature difference drives the low level jet.



#### Figure 24 Time and altitude profile of a low level jet

The low level jet is a river of fast-moving air sometimes present at night about 500 feet above the ground. It can move air about 200 miles in one night.

In the Mid-Atlantic Region, the low level jet was ignored or missed entirely until recently because the twice-daily weather balloon launches always occurred near dawn and sunset. Since the low level jet is at its strongest in the middle of the night, these balloon launches missed its peak winds. The advent of continuous wind profiler systems made this phenomenon considerably easier to study.

The low level jet, as one might expect, blows over the Atlantic Coastal Plain, running parallel to the ridge of the Appalachians. Physically, it is like a river of air about 500 ft. above the ground that moves from the southwest to the northeast. Typically, it is a few hundred meters deep, a hundred kilometers wide, and persists for about six hours. Its peak wind speeds are typically 30 to 40 miles per hour, which implies that a slug of air could move roughly 200 miles overnight. Once the sun rises the next day, the thermal differences that created the low level jet disappear as the Earth's surface warms. Warming also breaks down the nighttime inversion, eliminating the frictionless surface that the low level jet needs, and mixing the contents of the low level jet down to the surface.

#### Appalachian Lee Side Trough

As its name suggests, the Appalachian lee side trough forms on the leeward (downwind) side of the Appalachian Mountains. In a sense, it is the daytime companion to the low level jet, since it forms under similar, stagnant conditions, though the mechanism for its formation is entirely different. The lee side trough forms when winds blow over the mountains and down to the coastal plain. As these winds descend, the air is compressed, warming it, and making it more buoyant. Its additional buoyancy makes the air rise, leading to a broad area of low pressure at the surface—in short, a trough.

Since the air is typically rather dry, and the trough itself is rather weak, it does not usually lead to showers and thunderstorms the way a trough associated with other weather systems would. It does



Figure 25 Appalachian lee side trough

The Appalachian lee-side trough is an area of low pressure east of the mountains that channels winds to the northeast. cause winds to shift their direction, so a wind that comes over the mountains from the west will turn and blow from the southwest along the coastal plain. Therefore, when surface winds on the coastal plain are from the southwest, if the Appalachian lee side trough is in place, it may be that the air actually came from the west, descended, and turned.

The implication for air quality policy is straightforward. Pollution making its way over the mountains from the west will turn once it reaches the coastal plain and come from the southwest. Since surface winds are then from the southwest, when the Appalachian lee side trough is in place, the limits of a city's airshed will be pushed farther south and west than they might otherwise be.

#### Local winds: Land and Sea Breezes, Mountain and Valley Breezes

In the Mid-Atlantic Region, land and sea breezes, and mountain and valley breezes have important influences on local air quality. These local winds are all driven by the same mechanism, namely a difference in temperature that produces a difference in pressure.

A sea breeze forms in the afternoon when the land is considerably hotter than the ocean or bay. The hot air over land rises, leaving something of a vacuum in its absence. Over the ocean, the opposite happens: the air over the ocean cools and sinks, creating a localized area of high pressure. Air then flows from the high pressure over the ocean toward the low pressure over land, creating the refreshing afternoon breeze loved by beachgoers everywhere. At night, the opposite may happen if the land cools to below the ocean's temperature, and a land breeze blows out to sea. Since the nighttime temperature differ-

The Appalachian lee side trough forms when winds blow over the Appalachians and air warms as it flows down the mountain resulting in an area of low pressure on the downwind side of the mountains. This feature turns winds that come over the Appalachians from the west so they come from the southwest. ences are typically much smaller than in the day, the land breeze is likewise weaker than the sea breeze. Both can form over any sizable body of water, making the winds of coastal bays notoriously difficult for sailors and meteorologists alike. Sea breezes typically only penetrate a few miles inland, since they are driven by temperature contrasts which disappear inland.

Air quality is affected by sea and bay breezes in coastal cities because the sea breeze can act as a bulldozer, pushing a city's polluted air back over the city. Picture a city near the water. Emissions have been pouring out of the city all night and into the early morning, generally moving out towards the sea. Before the sea breeze circulation sets up, a wall of pollution has moved out over the water. If this pattern were to continue, the city's pollution might just be blown out to sea. When a sea breeze circulation sets up, however, that polluted air is pushed back toward the city. Furthermore, air that used to leave the city freely is stuck with nowhere to go. The sea breeze has created a wall and sealed off the exit route for pollutants from the city, making the air stagnant and highly polluted. The sea breeze only pushes a few miles inland, which is where the barrier to mixing lies. Later in the day, if one is fortunate enough to be on the ocean side of the city, the air may be quite clean, but the air is usually quite dirty on the inland side. The city suffers from its own recirculated pollution, and by

the wall set up by the sea breeze that does not allow pollution from the city to flow away from it. The sea breeze is therefore both a bulldozer and a dam.

For example, bay breezes from the Chesapeake Bay often make Baltimore's summertime air quality particularly poor. Air from the city cannot escape directly across the Bay. On the other hand, a few miles closer to the Bay, conditions are often considerably cleaner, since no fresh emissions have gotten into the air there since earlier that morning.

This is not to say that the sea breeze, or in this case, the Chesapeake Bay breeze, is an impenetrable wall that prevents all pollution from crossing it! The bay breeze is a shallow circulation, and may only extend a couple hundred meters above the surface. Polluted air from

the west side of the Bay can still mix upward, where it meets the stronger winds aloft, pass over the Bay breeze circulation and come back down on the east side of the Bay. The sea breeze restricts the flow of air at the surface, where wind speeds tend to be weak anyway, but still allows for transport aloft. This mechanism is described in more detail later as the "up, over, down" mechanism.

Mountain and valley breezes are also driven by temperature differences, but in this case, the difference arises because mountain peaks cool more quickly than the valley at night, and heat up more rapidly in the daytime. At night, cool air sinks and flows down the valley, settling in the lowest points, while in the day, warm winds blow up toward the peaks from the valley below. Local topography is very important in generating this phenomenon, making the breeze unique to a particular area.

Mountains and valleys also serve to isolate air in the valleys, while air at the mountaintops may be coming from very far away. Mountain winds, inversions, and mixing are quite complex. On a quiet night, the mountaintop may be in the free troposphere, open to long-range transport, while the valley below is usually capped by a nocturnal inversion, isolating pollution in the valley. Air quality measurements taken during plane flights in the Shenandoah River Valley have shown that the air pollutants in the valley may be rather different from the air at the nearby peaks. Cities on the western

side of the mountains will find that the Appalachians are capable of damming pollution up against them.

### Stagnation and Transport in Air Pollution Episodes

To some extent, air stagnation is common to all air pollution episodes. If pollutants are not diluted by mixing upward or being blown downwind, they become concentrated near the surface. Pollution episodes that only feature stagnation are typically short-lived, since a small change in the weather will usually provide some relief in the form of increased mixing or increased winds. This is not to say that an extended stagnation Sea breezes, land breezes, mountain breezes, and valley breezes are all local winds driven by differences in temperature. These small-scale winds are difficult to predict and may block flow into or out of a city. When they block air flow out of a city, conditions in the city may be particularly dirty, while conditions a few miles away may be relatively clean.

Stagnation is characteristic of most air pollution episodes, though most also have some other transport feature that increases pollutant levels. Weak winds and poor mixing ensure that the pollution emitted by a city does not go far. Recirculation occurs when a city's pollutants are brought back over it by changing winds. Since the city gets a second dose of its own pollution, this weather pattern typically produces highly polluted conditions. episode is impossible—only that such episodes typically have additional causes.

#### Recirculation

Any weather pattern that brings a region's own pollution back over it can produce a pollution episode. This recirculation of polluted air is effectively the same as having a polluted area upwind, since pollution has time to age in the sun, and air entering the area is already some-

what polluted before it arrives. Recirculation typically results when winds have been blowing from one direction for a time and then reverse, bringing the pollution of the previous hours and days back over the region. In the Mid-Atlantic Region this often happens when a weak cold front pushes slowly from north to south, stalls, and then retreats back north. The air south of that front, as mentioned before, is recirculated, polluted air.

#### Along-Corridor Flow

Since most of the East Coast's population is located along the I-95 corridor on the coastal plain east of the Appalachian Mountains, a particularly smoggy episode can result when winds blow along the corridor. Typically, winds blow from the southwest to the northeast, pushing pollution from one city to the next up the coast. Hypothetically, this pattern could also work for winds from the northeast, but those are usually associated with storm systems and strong winds, which do not produce pollution episodes. The low level jet, the Appalachian lee-side trough, a properly oriented high pressure system, and an advancing cold front can all lead to along-corridor flow. This flow pattern is often associated with the end of an episode where flow is from the southwest ahead of a cold front and behind a retreating high pressure system, though that is not the only time it occurs.

#### Up, Over, Down

In a heat wave, surface winds are ordinarily quite weak, to the great frustration of those who must suffer through it, so it might appear at first that long-range transport of air pollution is rather unlikely. Above the surface, however, winds are considerably stronger than at the surface, so if pollution can be lofted above the well-mixed layer, it may be transported rapidly over long distances. The overall mechanism is simply summarized as "up, over, down."

During the day, air pollution mixes upward, carried by the heat of the day. By the middle of the day, the lowest part of the atmosphere is fairly well mixed. Research aircraft routinely measure constant concentrations of carbon monoxide, ozone, and other pollutants throughout this layer.

For the sake of illustration, suppose that this well mixed layer is 6000 ft. deep, a typical depth in the Mid-Atlantic Region. As the day progresses into night, the nighttime inversion forms a few hundred feet above the surface. Again, for sake of illustration, take the nighttime inversion to be at a height of 1000 feet above the surface, though this is perhaps a bit high. Once the inversion forms, it isolates the surface from the air above, so the lower atmosphere is divided into two reservoirs: one below 1000 ft. and one above, between 1000 ft. and 6000 ft. In the lower reservoir, winds are the familiar calm summertime winds, while in the upper reservoir, winds can be quite strong. So while long-range transport along the surface is not likely, transport above the inversion continues unabated.

So far, only the air above one city has been considered. Now a second city, downwind of the first, will be added to the picture. During the first day, pollution mixed up to 6000 ft., and that night the lowest 1000 ft. remains near the ground of both cities. The top 5000 ft. is free to move about, isolated from the ground the way an air hockey table isolates the surface from a puck on a cushion of air. Overnight, winds above the inversion blow from the first city to the second, carrying this pollution along. The following morning, the downwind city is faced with a new problem. On the previous day, the afternoon heat resulted in mixing of that city's air up to 6000 ft., into a pristine atmosphere. On this day, however, between 1000 ft. and 6000 ft. lies the pollution from an upwind city. So when the heat of the downwind city, since the pollution of two cities is involved. In the middle of the afternoon, the pollution over the downwind city is a mixture of its own pollution and that which came in from the upwind city.

The overall picture involves mixing up to a considerable height over one city, producing a column of pollution up to 6000 ft. At night, the bottom of that column is sealed near the ground by a temperature inversion, while the top 5000 ft. slips away uninhibited. The next day, an unfortunate downwind city has a large plume of air pollution overhead, just waiting to mix down in the heat of the day. In the afternoon, the local plume from that city mixes upward into a dirty, transported plume from a distant city. The result is a surge in ozone and other pollutants in the mid- to late- morning as the nighttime inversion breaks down.

This mechanism has implications for air pollution control strategies and the areas over which they should be implemented. At times, power plants have appeared to take the bulk of the blame for long-range transport of air pollution, but power plants are not the only concern in considering long-range transport. Power plants and other tall-stack industrial facilities do have something of a head start, in that their emissions are typically lofted to greater heights than those from automobiles or other surface sources. But surface-based emissions can also be lofted by mixing and then transported over large distances.

The heights here should not be taken to mean that the downwind city is only responsible for  $1/6^{th}$  of its ozone problem. The concentrations of volatile organic compounds (VOCs) and NO<sub>x</sub> in that surface layer have not been mentioned here, and it should be remembered that the downwind city does not cease emissions once the nocturnal inversion is broken! Emissions from both cities are important in producing the problem, and will have to be taken into account if an effective air pollution control strategy is to be designed for the downwind city.

## The Airshed and the Range of Transport

The term airshed is a useful concept, similar to its cousin, the watershed, only the airshed of a city refers to the area from which that city receives a particular pollutant. As such, it has no concrete boundaries, and differs from pollutant to pollutant. For long-lived pollutants such as methane and chlorofluorocarbons (CFCs), the airshed may be the entire globe, while highly unstable compounds may have an airshed of only a few city blocks. The range that is relevant to transport therefore varies by pollutant. The up, over, down mechanism is responsible for carrying pollutants from the surface over great distances. Pollutants mix upward with daytime heating, and then are caught up in the stronger winds aloft. Overnight, those winds may carry pollutants over great distances, particularly when a nighttime inversion is present. The next day, those pollutants mix back down to the surface when daytime heating breaks down the nighttime inversion, polluting a downwind area. The airshed is the entire area whose emissions affect a city or region. It is not as well defined as a watershed, and varies from pollutant to pollutant. The meteorological patterns alluded to earlier when discussing global circulation dictate that transport distances are necessarily longer in the northern Mid-Atlantic Region than in the southern part of the Region. Subtropical high pressure systems spend more time over the south, limiting the range of transport. In the north, the Region is closer to the storm track, meaning that winds are stronger, and the distances over which pollution may be transported are necessarily longer.

While long-range transport and local stagnation are important throughout the Region, the relevant range of transport is shorter in the south than in the north. Individual episodes vary widely, so an individual episode may be almost entirely due to localized stagnation, while another episode may show a strong influence from long-range transport. On the whole, transport is important throughout the Region, and high local emissions add pollution to long-range transport.

## The Whole Picture: Everything at Once

Breaking the meteorology of an air pollution episode into parts makes it easier to understand, but we must recognize that these weather patterns do not exist in isolation. A typical pollution episode reflects influences of several, if not all of these weather patterns by the time it is over. High pressure typically dominates, producing limited mixing and weak surface winds. Winds aloft will often bring pollution from

The relevant distance of transport is longer in the north than in the south. Transport is important throughout the Region, and local emissions add pollution to long-range transport. the industrialized Midwest across the mountains via the up, over, down mechanism. Those winds will then be steered from the west to the southwest by the Appalachian lee side trough in the daytime and by the low level jet at night. Sea breezes and bay breezes typically recirculate air back over coastal cities and prevent polluted air from those cities from flowing away from them. Vertical mix-

ing is inhibited by the nocturnal inversion at night, and by the overall subsidence of a high pressure system. In the mountains, air may also have a difficult time escaping valleys, and cities on the western side of the mountains will find that the Appalachians are capable of damming pollution up against them.

Some or all of these mechanisms will be active during any given air pollution episode. Together, their combined effect is to confine pollution nearer to the surface, to prevent it from escaping horizontally, and to circulate already polluted air from one region to the next or from one region back onto itself. The

Meteorological processes do not exist in isolation. Any given day in an air pollution episode will typically feature many different transport phenomena. combination of so many different mechanisms gives each episode its own unique character. In addition, for a large-scale episode, conditions typically vary across the Region, so long-range transport may be important in one area, while stagnation rules in another.

# Part IV Pollution Sources

The emissions most important to forming ozone and fine particles are nitrogen oxide  $(NO_x)$ , volatile organic compounds (VOC), sulfur dioxide  $(SO_2)$ , ammonia  $(NH_3)$ , and direct emissions of fine particles  $(PM_{2.5})$ . Before discussing emissions, a few terms should be defined. Emissions sources are grouped in broad categories. Natural sources include vegetation, soils, oceans, and volcanos. Anthropogenic sources involve human activities. The following discussion focuses on anthropogenic sources.

# Anthropogenic Sources

On-road mobile sources are automobiles, trucks, and any other road-based sources of pollution. Non-road mobile sources include motorized equipment used away from roads, such as construction equipment, pleasure craft, ships, airplanes, trains, and farm machinery. Other non-road sources include lawn and garden equipment, recreational vehicles, and logging machinery. Point sources are facilities that are sufficiently large to be considered individually. A single very large facility may emit as much pollution as all other sources in a city combined. Examples of point sources are power plants, oil refineries, and steel mills. Finally, area sources represent something of a catchall category. These are small, non-mobile sources that are so numerous that they can be modeled as coming from an area instead of a specific source. Home heating, evaporation from animal waste, paint fumes, and consumer solvent use are all examples of area sources.

The emissions listed in any inventory are necessarily just estimates of emissions. Other than large point sources, it is impossible to place sophisticated emissions monitoring equipment on every source. Large point sources are required to report their emissions, so theirs are better known than those from other sources.



#### pollutant by source category

#### Figure 26 2002 Annual anthropogenic sources (MARAMA+Northeast)

This chart shows the relative importance of various types of emissions sources for each of the major air pollutants. Emissions from natural sources of VOCs are not included in this chart.

Emissions sources are lumped into broad categories: point sources, on-road and non-road mobile sources, and area sources. Point sources are large industrial facilities, while area sources are numerous smaller sources that are spread out over an area. Onroad mobile sources are road-based vehicles, while non-road mobile sources are off-road engines such as construction equipment and airplanes. Emission inventories represent only the starting point of a pollutant's lifetime in the atmosphere. They cannot, for example, show how pollution transport and transformation affects the Region. To fully answer the question of what emissions are affecting an area, one must employ a number of different techniques including measurements, data analysis, and photochemical modeling.

While this section focuses on emissions from the Mid-Atlantic Region, upwind sources are also important throughout the Region. Maps of sulfur dioxide and sulfate concentrations illustrate this point. (See Figures

27 and 28.) One shows sulfur dioxide concentrations, while the other shows sulfate concentrations as measured. These maps are made by smoothing and interpolating measurements from a national network of air quality monitors, so care must be taken when reading them, since there is not a monitor at every point. That said, the industrialized Midwest clearly has high concentrations of sulfur dioxide. Sulfur dioxide is relatively short-lived in the lower atmosphere, generally turning into sulfate or depositing to the ground within a day. Therefore, higher concentrations of sulfur dioxide tend to be located nearer to its sources, as is the case in the Midwest. The effects of those sulfur dioxide emissions are more readily seen once it has turned into sulfate, which spreads out over the entire eastern United States. This is not to say that atmospheric sulfur comes exclusively from the Midwest, but rather to point out that emissions upwind of the Regions also play a significant role in determining

Emissions inventories are usually composed of estimates of emissions rather than direct measurements. Sources outside the Mid-Atlantic Region are important to air pollution Mid-Atlantic and Northeast Regional air quality. Airborne measurements taken in the western part of the Region consistently show high levels of air pollution being transported into the Region, particularly during pollution episodes.

#### Sulfur Dioxide

Sulfur dioxide emissions are dominated by point sources, particularly coal-fired power plants and industrial facilities. (See Figures 26, 29,

and 30.) Many similar but smaller facilities are incorporated into the area source category. All these facilities emit sulfur dioxide because the fuel they burn contains a small amount of sulfur. The sulfur burns along with the rest of the coal or oil and is emitted from the stack. The spotty geographic distribution of this pollutant arises because most of its emissions are from point sources. (See Figures 27 and 31.) Emissions of sulfur dioxide are relatively well quantified in comparison with those of other pollutants because the largest sources are all monitored by continuous emissions monitors (CEMs).

#### Nitrogen Oxide

Nitrogen Oxides (NO<sub>x</sub>) emissions are also dominated by fuel burning sources, mostly by point and on-road sources. (See Figures 26, 32, and 33.) In the Mid-Atlantic Region NO<sub>x</sub> emissions are dominated by vehicle use, though many large point sources of NO<sub>x</sub> are in and just upwind of the Region.

#### Volatile Organic Compounds

Volatile Organic Compounds (VOC) emissions resulting from human activity (anthropogenic VOCs) are dominated by emissions from mobile and area sources. (See Figures 26, 34, and 35.) Mobile sources emit VOCs in two ways: evaporation from the fuel tank and other parts of the equipment, and discharge



Figure 27 Sulfur dioxide concentrations in the eastern United States

EPA maps show improvement over the decade of the 1990s in  $SO_2$  pollution. Higher concentrations are located near major sources.





 $SO_2$  is gradually converted to sulfate. These maps are based on measurements of sulfates in the air. Reductions in  $SO_2$  emissions since 1990 under the acid rain program have reduced sulfate.



Figure 29 Trends in sulfur dioxide emissions from utilities 1980 - 1997

Sulfur dioxide emissions from electricity generating facilities have declined in much of the eastern U.S. since 1990 due to the federal acid rain control program.

of unburned or partially burned hydrocarbons from the exhaust pipe. VOCs from area sources are dominated by combustion of wood and other fuels in residences, solvent use, and other evaporative emissions.

Most VOC emissions in the Region come from natural sources, which are not shown in Figures 26, 34, and 35. Naturally occurring (biogenic) VOC emissions are caused by evaporation of natural organic compounds from plants in warm weather. Many natural VOCs that contribute to ozone formation are highly reactive. Because biogenic VOC emissions are large and reactive, they are the most important part of the VOC inventory for understanding and predicting ozone formation. Biogenic VOCs are not included in Figures 34 or 35, but nationally, they represent roughly two-thirds of all annual VOC emissions. Biogenic emissions are extremely difficult to estimate, since doing so requires modeling the behavior of many plants and animals as well as their responses to the environment. Further complicating the situation, the processes that govern the release of these compounds are complex and poorly understood.

#### Carbon Monoxide

Carbon Monoxide (CO) results from incomplete burning. Since engines never burn their fuel completely, it is no surprise that CO emissions come predominantly from engines. Indeed, engines will run quite poorly if forced to burn their fuel completely. Non-road and on-road mobile sources make up 90 percent of the CO inventory. Geographically, carbon monoxide emissions tend to be located in the urban centers with people and their cars. In contrast, power plants emit very little carbon monoxide

because they burn their fuel almost completely, removing nearly every bit of energy from the fuel. Emissions inventories only describe the primary sources of carbon monoxide. Carbon monoxide also comes from the breakdown of carbon compounds in the atmosphere, and as such, carbon monoxide is both a primary and secondary pollutant. Much of the global background level of carbon monoxide comes from the breakdown of methane and organic compounds, and effectively comes from an incomplete low-temperature burning process.

#### Ammonia

Ammonia  $(NH_3)$  comes predominantly from animal waste and fertilized soils, though some also comes from vehicles. (See Figure 36.) This leads to an interesting geographic distribution. Large emissions coming from urban centers may seem surprising, but water treatment plants and automobiles also emit ammonia. Peak emissions from the Each pollutant comes from characteristic sources. Sulfur dioxide comes predominantly from point sources such as large coal-fired boilers. Carbon monoxide is a product of incomplete combustion, and is emitted largely by on-road and off-road engines as well as some open burning.  $NO_x$  is emitted by fuel burning sources. VOCs come from biogenic sources as well as from human activities, primarily mobile and area sources. Ammonia comes predominantly from animal waste and fertilized soils.

Primary particle emissions come mostly from soils, sea salt, and soot. Most of the fine particles in the atmosphere are secondary pollutants formed in the atmosphere.

hog farms of eastern North Carolina, the dairies of southeastern Pennsylvania, and the chicken farms of the Delmarva Peninsula may be seen in the annual map (Figure 37), but would be much more noticeable in a summertime map. The uncertainty in ammonia emissions is greater than the uncertainties in emissions of other pollutants, because ammonia sources are diverse, and the data on agricultural activities and the relationship of those activities to emissions are scarce.

#### Direct Fine Particle Emissions

Emission inventories of fine particles must be considered carefully, since these inventories only include the primary particles emitted directly from their sources. Secondary particles (those formed in the atmosphere) are not counted in the inventory of particle emissions. Primary fine particle emissions are largely composed of crustal materials, soils, sea salt, and soot. PM emissions from point sources have been reduced tremendously by emission controls, so that most direct PM emissions now come from area sources. (See Figure 38.)

Particulate matter (PM) is the general term for the mix of solid particles and liquid droplets suspended in the air.

- **PM**<sub>2.5</sub> Particles that are less than 2.5 micrometers in diameter; they are also known as fine particles. Because of their size, these fine particles can travel deep into the lungs. The health impacts of exposure to these particles include aggravation of respiratory and cardiovascular disease, decreased lung function, and premature death. Primary fine particle emissions are largely composed of crustal materials, soils, sea salt, and soot.
- **PM**<sub>10</sub> Particulate matter that is less than 10 micrometers in diameter. Major sources of PM<sub>10</sub> include road dust, soil, and wood smoke. Due to increased wood smoke and meteorological conditions, PM<sub>10</sub> concentrations are greatest in the winter and lowest in the summer.

## Analysis of the 2002 Emissions Inventory

Charts and maps summarizing the inventory help us understand the relative importance of various sources of emissions and their locations. We can also evaluate the accuracy of the inventory by judging whether the distribution and location of emissions makes sense. Air quality managers work hard to improve emissions inventories to get a clearer picture of what is causing air pollution and the effectiveness of pollution control strategies.

EPA released a preliminary 2002 National Emissions Inventory early in 2004. State and local agencies have worked with MARAMA to revise and update these preliminary estimates and produced the MANE-VU inventory. Similarly, VISTAS worked with southern states including North Carolina, Virginia, and West Virginia in improving their regional inventory. The data used for the following charts comes from 1) the MANE-VU regional inventory; 2) the VISTAS regional inventory for point, area, and non-road mobile sources; and 3) EPA's 2002 National Mobile Emissions Inventory for mobile sources for North Carolina, Virginia, and West Virginia.

The characteristics presented in the following summary charts and maps provide a general overview of pollution sources in the Region, recognizing that developing emission inventories is a continual process of updates that may result in changes.



#### Figure 30 Annual sulfur dioxide emissions by state -- 2002

*Emissions from coal fired electric generating units and large boilers dominate the inventory for sulfur dioxide emissions. Larger states and states with more coal-fired units have greater emissions.* 



#### Figure 31 Annual point source sulfur dioxide emissions density map -- 2002

Point sources are responsible for most of the sulfur dioxide emissions in the Region. This emissions density map (by county) highlights counties where large sources are located.



#### Figure 32 Annual nitrogen oxide emissions by state -- 2002

All combustion processes discharge nitrogen oxide emissions. Most large point sources are subject to recent emissions control requirements, so mobile sources (on-and off-road) dominate the remaining inventory.



#### **Figure 33 Annual on-road nitrogen oxide emissions density map --2002** *This density map shows higher motor vehicle NO<sub>x</sub> emissions from major highways and urban areas.*





Annual anthropogenic VOC emissions are primarily from area and mobile sources. This graph does not include natural sources of VOCs, which are very large.



#### Figure 35 Annual area source volatile organic compound emissions density map -- 2002

Area source VOC emissions are higher in populated areas and in areas with commercial or industrial use of solvents and other VOCs



## Part IV Pollution Sources

#### Figure 36 Annual ammonia emissions by state -- 2002

Ammonia emissions are dominated by area sources. States with large animal feeding operations have higher total emissions. Motor vehicles with catalytic converters also discharge ammonia.



#### Figure 37 Annual area source ammonia emissions density map -- 2002

This map shows the link between agricultural areas and area-source ammonia emissions.


#### Figure 38 Annual fine particle (PM<sub>2.5</sub>) emissions by state -- 2002

Primary fine particle emissions are dominated by road dust. In some states, major point sources also make significant contributions. Fire emissions can be substantial on an episodic basis but do not have much influence on this annual summary.

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#### Part V

# Measurements, Data Analysis, and Modeling

Scientists have several techniques to determine the nature and causes of the air pollution problems in a given area. Direct measurement, data analysis, and photochemical modeling are three broad categories of these techniques. Each has strengths and weaknesses, and they can effectively complement each other. The details of each technique would consume volumes, so they are not presented in this report. However, knowing the general characteristics of each technique helps ensure that their results are used appropriately.

#### Measurement

Direct measurement of air pollution has the most appeal of the three techniques, since it is difficult to argue with someone who has gone out in the field and measured the concentration of an air pollutant such as ozone in the atmosphere at a particular time and place. MARAMA member agencies operate an extensive network of air quality monitors throughout the Region. Most of these monitors are located in urban areas and downwind of cities or major emissions sources. These monitors are intended to measure the highest levels of pollution in the area. Some monitors are also placed at rural sites and in national parks and wilderness areas. It is important to measure rural background as well as urban levels.

Measurements are reliable but expensive, and pollution cannot be measured everywhere all the time. Furthermore, most measurements are confined to the surface, whereas the atmosphere is a three-dimensional system. Measurements made from balloons and aircraft are more expensive than their ground-based cousins, and unlike surface measurements, they cannot run unattended.

New techniques are emerging that allow more pollutants to be measured throughout a greater part of the atmosphere. Satellites and laser instruments offer the possibility of attaining uninterrupted and largely unattended measurements. These techniques do have their own limitations. Satellites have difficulty measuring pollutants close to the ground and over complex terrain. Most laser techniques have trouble with clouds and suffer from interferences from other pollutants.

Obtaining quality measurements requires great attention and care in both experimental design and instrument maintenance. All instruments suffer from interferences—compounds which either impede the instrument's ability to measure a particular pollutant or give a false response, indicating the presence of a pollutant when none is there. All instruments must be calibrated in some way. For

satellite instruments and other remote sensing measurements such as lidar and radar, this problem is particularly difficult, since the pollutant must be observed over a large area and depth to evaluate the measurement. Finally, some measurements are difficult to obtain, and necessarily subject to interpretation, because the measurement technique defines the measurement itself. An example of this phenomenon is dividing carbon compounds between

Measurements are the most straightforward tool in the atmospheric scientist's toolbox, but they must be interpreted with caution. Users of measurements should be aware of the limitations of the techniques used to gather the data. organic carbon and soot (elemental carbon).

While it might seem simple to distinguish organic carbon, which is oily, from elemental carbon, which is a sooty solid, separating the two requires complex physicalchemical analyses. The carbon sample is collected on a filter for a specified time and then baked in a chamber, first under a heliumonly atmosphere, and then under a helium-oxygen atmosphere. The gases coming off the sample while it bakes are analyzed to determine the amount of carbon released. Depending on the temperature and the time for which the sample is baked, a different organic carbon /elemental carbon split may be obtained. Further complicating things, the total masses of organic carbon and elemental carbon are not measured directly-just the mass of the carbon they contain is measured. To get the total mass of organic carbon compounds, the measured organic carbon mass is multiplied by an assumed factor to



# Figure 39 Monitors used for nonattainment designations in the MARAMA Region

MARAMA's member agencies operate an extensive air quality monitoring network throughout the Region. Monitors may collect data about ozone, carbon monoxide, sulfur dioxide, nitrogen oxide, coarse and fine particles, as well as other contributors to poor air quality.

account for all the non-carbon portion of these oily compounds. This factor actually varies with the mix of hydrocarbons present in the sample. Organic carbon measurements therefore can change with the technique used and the assumptions made in analyzing the data. This is one of the most difficult measurements routinely made in atmospheric chemistry, and it illustrates that measurements are subject to some interpretation by the users of the data.

In addition to the ongoing air quality monitoring networks maintained by MARAMA state and local agencies, there have been several special scientific monitoring projects in the Region over the past few years. Many of these projects are highlighted in this report (Northeast Oxidant and Particle Study, page 6; Pittsburgh Air Quality Study, page 26; MARCH Atlantic, page 39; Southern Appalachian Mountain Initiative, page 65).

Air Quality data collected by MARAMA members is stored in a national database called AQS, which is accessible via the EPA website at http://www.epa.gov/air/data. Daily information about air quality is available on the internet at www.airnow.gov.



# Figure 40 Air quality monitoring sites measuring additional pollutants

In addition to the network of monitoring sites shown in Figure 39, various state, local, and federal agencies operate air quality monitors in the region that measure concentrations of other pollutants. NADP and CASTNet sites help study acid deposition; CASTNet, PAMS, and RAIN sites help study ozone; and IMPROVE, PM speciation, and RAIN sites focus on particulate matter and haze. (See page 62.)

a data set. Many combine measurements of pollutant concentrations with meteorological data to get an impression of the source regions and transport patterns that bring air pollution to a region. These techniques typically group measurements by pollutant concentration or by meteorological conditions.

For example, daily measurements of particle composition may be classified first into similar categories

according to their composition, producing several groups. One group might be dominated by high sulfate while another might contain a fair amount of sea salt. Subsequent analysis can find the weather conditions present when sulfate particles dominate and when sea salt dominates. If more chemical species are measured, more patterns linked to various types of sources may emerge. This technique is called source apportionment analysis or source attribution by receptor-based methods.

### Data Analysis

Data analysis includes assessing current air quality, determining spatial and temporal trends and patterns, and identifying potential air pollution sources.

Most air quality measurements are of limited worth by themselves, and must be combined with other data sets to broaden their value. Sometimes a pollutant may be so ubiquitous that only a few measurements are necessary to determine the uniform concentration of that pollutant. Outside of a few rare cases, however, measurements need to be placed in a broader context and combined with other data to allow broader conclusions to be drawn.

Data analysis is the process of capturing the essence of what is happening through the analysis of large data sets. This process involves many data analysis techniques, both simple and complex. Most analysis techniques are statistical, seeking underlying relationships in

#### Air quality data analysis

• Assesses current air quality Does it meet national standards?

- Determines spatial and temporal trends Is it getting better or worse?
- Identifies potential air pollution sources What's causing high concentrations?

# Air Quality Monitoring Sites Measuring Additional Pollutants (See map page 61.)

#### Rural Aerosol Intensive Network - RAIN

The monitoring site at Piney Run in western Maryland is a research site operated by the State in collaboration with the Appalachian Laboratory and the University of Maryland. It is part of the RAIN network organized by NESCAUM. The site tracks the impact of interstate pollutant transport via measurements of ozone,  $PM_{2,5}$ , and precursor and constituent species.

#### Enhanced Ozone Monitoring – PAMS

New Jersey, Philadelphia, Maryland, the District of Columbia, and Virginia have established Photochemical Assessment Monitoring Stations (PAMS), which collect and report data for ozone and its precursors, including numerous individual volatile organic compounds and  $NO_x$ . Data from these and other PAMS locations in the US help EPA and the states in understanding the causes of ozone pollution. <u>http://www.epa.gov/oar/oaqps/pams</u>

#### National Atmospheric Deposition Program – NADP

The NADP is a cooperative monitoring network used to collect weekly data on the chemistry of precipitation. Precipitation is collected and analyzed for acidity, sulfate, nitrate, ammonium, chloride, calcium, magnesium, potassium, and sodium. The network has also expanded to monitor the amount of mercury found in precipitation. Key Mid-Atlantic NADP monitoring stations are operated by the University of Maryland, Penn State University, the National Oceanic and Atmospheric Administration, Canaan Valley Institute, and others. http://nadp.sws.uiuc.edu/nadpoverview.asp

#### Interagency Monitoring of Protected Visual Environments – IMPROVE

Federal Land Managers at Class I national parks and wilderness areas in the Mid-Atlantic Region operate IMPROVE monitors to measure particles that degrade visibility (as described in Appendix E). Monitors of the IMPROVE design have also been sited in several other rural locations in Pennsylvania and Maryland as well as in the District of Columbia. Measurement of PM species helps identify the sources of fine particles in the air. Monitors that are not at Class I sites are referred to as "IMPROVE Protocol" monitors because they use the monitoring protocols required for the Class I sites. <u>http://vista.cira.colostate.edu/improve/</u>

#### PM Speciation Network

These urban monitors provide data on the concentration of key species of  $PM_{2.5}$ . The monitors are operated by state and local agencies pursuant to EPA guidance. Data on species of  $PM_{2.5}$  helps identify the sources of PM and supports health effects and exposure research.

#### Clean Air Status and Trends Network (CASTNet)

EPA and the National Park Service operate CASTNet monitoring stations to provide data on dry acidic deposition and rural ground-level ozone. CASTNet data is used in conjunction with other monitoring networks to evaluate the effectiveness of national emission control programs. http://www.epa.gov/castnet/ Emissions-based models begin with emissions inventories and act on them in a "forward" direction with atmospheric physical and chemical processes to predict downwind concentrations at multiple "receptor locations." Once validated by comparison to ambient measurement data, these models can be used for apportioning ambient pollution concentrations to specific sources,

"One-atmosphere" modeling recognizes the importance of interactions between different pollutants by modeling all processes simultaneously.

as well as for evaluating potential effects of future changes in emissions or meteorology. Receptor based models begin with ambient measurement data at one or more receptor locations and work "backward" to identify sources contributing to historical ambient pollutant concentrations at the receptor locations. Receptor models cannot be used to predict effects of future emissions changes, but can be applied to long historical records, providing a long-term "climatological" indication of past sourcereceptor relationships and to evaluate the effects of historical emissions changes, thus providing a valuable complement to emissions-based models for determining effective future emissions control technologies.

Data analysis techniques provide general information about the types of sources affecting air quality at one or more monitoring stations. While general assertions about conditions at a site or throughout a region are possible, these techniques typically do not pin down a specific power plant, smelter, or city as the source of a region's problems. Data analysis can help identify gaps in emissions inventories and vice versa. Additionally, the statisticians adage "correlation does not imply causality" is particularly relevant in this type of analysis. Perhaps the simplest example of this kind of limitation is where two unrelated sources sit near each other. If a smelter, the intersection of two enormous freeways, and a feed lot all are within a mile of each other, analysts must be very careful in drawing conclusions about the air coming from such an area. Results must be interpreted in the context of other information about emissions and sources in the area and with an understanding of how pollutants are transported and transformed in the atmosphere.

# Air Quality Modeling

Measurements and data analysis help assess current and past air quality. To predict future air quality and evaluate the air quality benefits of potential controls, scientists use computer-based models. Air quality models are mathematical representations of the relationships between emissions, weather, and air quality.

Photochemical models are one of the most powerful tools in the scientist's toolbox, but the results must be used with great caution. Because they can produce maps showing simulated air quality throughout a region, it is tempting to view photochemical models as providing an all-encompassing view of air quality. However, when interpreting these results, the limitations of the model must always be considered.

Models can only represent the physics and chemistry that are understood by their developers. In fact, models typically only represent a small fraction of the known atmospheric chemistry and physics.

Compromises are always made to get the model to run in a reasonable time. Over 10,000 reactions are important to atmospheric chemistry, while most air quality models contain only a hundred or so. To obtain this simplification, compounds with similar properties are

Photochemical grid models are very powerful tools that allow one to simulate experiments that would be too costly or difficult to perform. The results should always be interpreted with a keen eye for the limitations of the model.

### Part V Measurements, Analysis & Modeling

A "weight of evidence" approach allows scientists to review several studies, seeking similarities and noting differences. If several methods yield similar results, there is greater confidence in the conclusions. grouped to avoid calculating the reactions of, for example, each hydrocarbon in the atmosphere.

Models represent some phenomena in a very simple way because they are not well understood. Interactions between aerosols and gases fall into this category, as do small-scale winds like the low level jet. Sometimes these simplifications can be so severe as to give the wrong answer when attempting

to diagnose a problem. Model results, therefore, should always be interpreted with an eye towards the potential shortcomings of the model.

Models are only as good as the data that goes into them. Emissions inventories often are uncertain. Even weather models that use an enormous weather database from the National Weather Service suffer from incomplete, missing, and sparse data. There is no way, for example, to accurately measure the extent of the sea breeze or the low level jet using National Weather Service data.

A model should not be expected to simulate every nuance of air quality measurements at a given time and place. Instead, regional models can best be used in a general, relative sense, to estimate trends, the relative impacts on different regions, or the relative impacts of different control programs.

Comparing model output with measurements indicates how well the model is simulating reality. Perhaps it is obvious that model results should be compared with observations, but the key is that the model must be tested with relevant data. Many processes could be entirely misrepresented in a model if, for example, its results were only compared with surface measurements. The goal is to examine the processes in the model, not just the final output of the model. This is difficult, since it involves detailed measurements of multiple species, but it is the best way to truly evaluate a model's abilities.

These caveats are not to say that models should not be used—only that they should not be used blindly. Processes do not need to be represented perfectly in the model for the results to be useful. If a model is used for its intended purpose, and evaluated carefully, it may be very helpful.

# **Combining Techniques**

Air quality analysts increasingly combine measurement, data analysis, and modeling into a comprehensive "weight of evidence" approach. Rather than rely on one model, or a few data analysis projects, analysts review numerous studies seeking similarities and noting differences. If several methods yield similar results there is greater confidence in the conclusions. The SAMI Integrated Assessment described on the following pages is an example of an assessment using many analytical techniques.

# Southern Appalachian Mountain Initiative (SAMI)

#### Overview

SAMI was a voluntary partnership of state and federal environmental regulatory agencies, federal land managers, industry, academia, environmental groups, and interested public participants. SAMI provided a forum for stakeholders with diverse interests and viewpoints to work together constructively to conduct the technical and policy assessments necessary to recommend regional solutions to air pollution problems.

SAMI focused on the impacts of ozone, regional haze, and acid deposition on the natural resources of the Southern Appalachian Mountains. The SAMI Integrated Assessment linked the understanding of air emissions, atmospheric transport, environmental effects, and socioeconomic consequences to assess emissions management alternatives.

SAMI evaluated the costs and benefits in the years 2010 and 2040 of current air regulations, and of emissions management strategies that SAMI might recommend. The Assessment results were summarized in a final report issued in August 2002, which is the basis of SAMI's recommendations to policy makers.

Among SAMI's key findings from atmospheric modeling were that each state benefits most from emissions reductions that occur in that state and each state will also benefit from emissions reductions in surrounding states.

#### Conclusions

- To improve visibility, it is most important to reduce sulfur dioxide emissions, and it could become necessary, under certain future sulfur dioxide control strategies, to reduce ammonia emissions.
- To reduce acid deposition affecting streams in the central and northern part of the SAMI region, it is important to reduce sulfur dioxide emissions.
- To reduce acid deposition affecting streams in some geographically limited areas, it is important to reduce nitrogen oxide and ammonia emissions.
- For high elevation spruce-fir forests, it is important to reduce nitrogen oxide and ammonia emissions.
- Ozone exposure does not produce a region-wide effect on forest basal areas, so nitrogen oxide or volatile organic compound reductions are not needed for this purpose. However, site-specific ozone effects to certain forest species are a concern for Federal Land Managers and other stakeholders. Nitrogen oxide emission reductions are important to address that concern.

more...

#### Recommendations

The SAMI Governing body adopted the recommendations listed below on April 18, 2002 by consensus among the state representatives.

• The SAMI states support and will promote strong national multi-pollutant legislation for electric utility plants to assure significant sulfur dioxide and nitrogen oxides reductions both in and outside the SAMI region. This national multi-pollutant legislation should



result in no less than the reductions for sulfur dioxide and for nitrogen oxides represented by the Administration's Clear Skies Initiative. Reductions from other source categories should also be considered in national legislation, and such national legislation should contain sufficient measures to protect Class I areas. Should the national legislation fail to materialize, the states that participated in SAMI will work together to consider regulatory alternatives and to encourage non-SAMI states to participate. Leadership by states ahead of national legislation is encouraged.

- Each SAMI State should seek ways to reduce ammonia emissions from animal feeding operations. Also, support should be given in future work such as VISTAS to improve the understanding of the sources of ammonia, to develop better inventories, and to seek more effective control approaches.
- Where States have control strategy choices in their eight hour ozone and fine particle State Implementation Plans, they should choose options that also have co-benefits for the environmentally sensitive Class I areas. Ambient ozone monitoring should be conducted near all Class I areas in the future.
- Each SAMI state should encourage energy efficiency, conservation, and use of renewable energy to reduce the emissions from stationary and mobile sources.

The states agreed to work towards the implementation of these recommendations. Each SAMI state will determine the most appropriate strategy for its own unique circumstances that will lead to successful implementation of SAMI's final recommendations.

# **Closing Thoughts**

# Understanding A Diverse Region

The MARAMA Region reaches from Pennsylvania and New Jersey through North Carolina, and from the Ohio Valley to the Atlantic shore. In this diverse region, air pollution problems vary greatly, but share many common characteristics.

To continue to frame appropriate air pollution control strategies, it is important to understand how weather patterns affect air quality. A typical air pollution episode will last several days and contain several weather patterns affecting different parts of the Region. One source of variation is the effects of the Region's major topographical features on meteorology and air quality.

High pressure systems typically dominate air pollution episodes, producing stagnant air and weak winds at the surface. Winds aloft often bring pollution from the industrialized Midwest across the mountains. Those same winds are frequently steered northeast by various meteorological phenomena.

For example, the low-level jet that often forms at night east of the Appalachian Mountains transports air northeast along the Piedmont. This natural phenomenon can transport polluted air from one part of the region to another very efficiently.

The location of the Bermuda High pressure system as it moves into the Region, and the tracks of frontal boundaries, also affect the nature and severity of air pollution within the Region. For example, subtropical high pressure systems spend more time over the southern part of the Region, limiting the range of transport there and making local air pollution sources more important. In the northern part of the Region, which is closer to the usual storm track, winds are often stronger, and the distances over which pollution may be transported are generally longer than in the southern part of the Region.

The combination of many different natural phenomena gives each air pollution episode its own unique character. For a large-scale episode, conditions typically vary across the region and change from day to day, so long-range transport may be important in one part of the region while stagnation dominates in another part. Understanding which factors typically generate a pollution episode in a given area is essential to being able to address the sources of pollutants and improve air quality.

# Pollutant Interactions are Important

The nature of air pollutants themselves also affects the choice of appropriate control strategies. Air pollutants exist in complex mixtures, and pollutants react and re-react with each other and with other compounds and surfaces. Some of the most important interactions are summarized here.

# NO<sub>x</sub> Titration

 $NO_x$  titration is one example of an interaction between cycles and families of compounds. When  $NO_x$  is very abundant, as is the case in the plume from a major city or power plant, it reacts with ozone directly, destroying the molecule, and reducing ozone concentrations. Later, as the plume disperses and more VOCs mix into the plume, conditions become more favorable for ozone production, and ozone increases again.

#### NO<sub>x</sub> Limited and VOC Limited Ozone Production

The amount of ozone produced in an area depends in part on the balance of  $NO_x$  and VOC in the area. The amount of ozone produced may be limited when there is not enough VOC or  $NO_x$  for rapid ozone production.  $NO_x$  limited conditions occur when the amount of ozone produced is limited by the amount of  $NO_x$  available. In this situation, the best way to reduce ozone pollution is by further reducing the amount of  $NO_x$  emissions. When VOCs are relatively scarce, conditions are VOC limited, and VOC controls will have a greater effect.

It can be difficult to determine whether an area is  $NO_x$  limited or VOC limited, because conditions vary depending on how much  $NO_x$  is being transported into the area, traffic conditions, temperature variations that affect the production of VOCs, the effects of emissions controls, and many other factors. The plume from a city, for example, is typically VOC limited in the city, and switches over to  $NO_x$  limited some distance downwind. The same area may change back and forth from being  $NO_x$  limited to being VOC limited, meaning that reducing both pollutants will be necessary.

#### Nitrate Replacement

Sulfur dioxide emissions are converted to sulfates, which then form fine particles in a variety of reactions. The presence of ammonia speeds the process of particle formation. Reducing emissions of sulfur dioxide can be expected to reduce airborne particle pollution. However, the effect on fine particle concentrations may not be as dramatic as might be expected. Some of the sulfate may be replaced by increased amounts of particulate nitrate. Nitrate formation increases if ammonia in the atmosphere cannot react with sulfate, but is instead available to help form nitrate particles. This process is called "nitrate replacement." Nitrate replacement is not as big an issue in the eastern U.S. as it is in Southern California, where sulfur dioxide emissions are considerably lower.

Sulfates are the major component of fine particle pollution in the eastern U.S. in the summer, when concentrations are the highest. Significant reductions of sulfur dioxide will be needed in order to reduce fine particle pollution and regional haze. In some areas, particularly in the winter, it will also be important to reduce various nitrogen emissions, such as  $NO_x$  and ammonia ( $NH_3$ ).

### **Emissions Must be Reduced**

Scientists have learned much about the Mid-Atlantic Region's air quality and are continuing to explore outstanding questions. Some of the major studies that have helped us understand air pollution in the region have been highlighted in this report.

We know we need substantial reductions in  $NO_x$  emissions in order to reduce ozone pollution. Exactly how much will be enough is difficult to predict, but we know enough to move ahead. We know we need substantial reductions of  $SO_2$  emissions in order to help address particle pollution and haze. Power plants will have to scrub more of their emissions. Emissions from trucks and automobiles will need to be cleaner.

We are less certain about what measures are needed to reduce organic carbon particles, but it is clear that air quality will improve if more diesels use clean fuels and are fitted with particle traps.

Reducing acid rain and the impacts of air pollution on ecosystems will require cuts in emissions on a year-round basis. Some current ozone control programs are seasonal, whereas controls to address acid rain, particle pollution, and haze will have to be implemented year-round. The best available information indicates emission reductions have and will continue to improve air quality.

# Transport and Local Sources are Both Important

#### The question is not whether there is transport, but how much? And from where?

To improve air quality, we must reduce pollutant emissions from sources affecting polluted areas. This includes local sources as well as distant sources. In particular, emission reductions from the industrialized Midwest will greatly aid Mid-Atlantic Regional air quality. Local emissions are significant as well, and we cannot lay all the blame for our air pollution problems at the doorstep of the Midwest—we must also reduce our own emissions.

While long-range pollution transport and local pollution stagnation are important throughout the Region, the relevant range of transport is generally shorter in the south than in the north. It is also important to note that despite this general tendency, the characteristics of individual episodes vary widely. For example, despite the importance of transport in the northern states, a specific episode in the northern Mid-Atlantic Region may be almost entirely due to localized stagnation, while a particular episode in the southern Mid-Atlantic Region may show a strong influence from long-range transport. Transport is important throughout the Region, and high local emissions add pollution to long-range transport.

# A Commitment to Improving Air Quality

Effective air pollution control requires a partnership of local, state, and federal authorities as well as private citizens, businesses, and industry. Reducing pollution is important to everyone's health and well-being. It requires development of cleaner technology (such as low emission vehicles), the use of pollution control devices (such as scrubbers to remove  $SO_2$  from smokestacks or filters to trap diesel smoke), energy efficiency and pollution prevention measures to improve industrial processes, cleaner fuels (such as low-sulfur gasoline), and decisions that exhibit good stewardship of the environment, such as carpooling, doing more walking or bicycling, and observing burn bans.

Above all, achieving good air quality requires a commitment to continue to seek ways to reduce emissions of VOCs,  $NO_x$ ,  $SO_2$ , and particles. Each state and local government must develop and implement plans to improve air quality, recognizing the need for both local and regional improvements.

The problem will not be solved by local controls alone, nor will it be solved by upwind controls alone. The problem is not just automobiles, nor is it just power plants. A wide variety of sources must reduce emissions for citizens of the Mid-Atlantic Region to breathe clean air.

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# **Appendix List**

Appendix A Health Effects of Air Pollutants
Appendix B Air Pollution Effects on Ecosystems and the Environment
Appendix C Air Quality Standards and Goals
Appendix D MARAMA Region Data Tables
Appendix E Measuring and Calculating Visibility Impairment
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#### Mid-Atlantic Regional Air Management Association

# Appendix A Health Effects of Air Pollutants

# Pollutants

#### Ozone

The reactivity of ozone causes health problems because it damages lung tissue, reduces lung function, and sensitizes the lungs to other irritants. Ozone has long been known to increase the incidence of asthma attacks in asthmatics. The general mechanism is fairly simple, though the exact details of how ozone or any other pollutant causes these problems are considerably more complex.

As air enters the lungs, it passes through the trachea and then into passages called bronchi that divide into smaller and more numerous passageways. Farther down in the lung, the passages only split, and do not become smaller. At the ends of the last bronchi are tiny sacs called alveoli, which increase in volume when a breath is taken. The alveoli exchange incoming oxygen for outgoing carbon dioxide, so they are home to the most crucial part of the breathing process. If the alveoli cannot get fresh air to replace the carbon dioxide, you cannot breathe. The bronchi that lead to those sacs are very narrow. Here, ozone and other lung irritants have their worst effects.

Ozone and fine particles irritate the lining of these small passageways, making them swell and secrete extra mucus. The swelling narrows the tiny passageway, letting very little air through to the alveoli, and dramatically reducing the lung's capacity. The lung's capacity drops further in asthmatics when the

muscles surrounding the bronchi contract and irritated tissues respond by producing more mucus. Muscle spasms and excess mucus further narrow the bronchial passages, making it still more difficult to breathe.

Ozone exposure also makes the lungs more vulnerable to lung diseases such as pneumonia and bronchitis. Ozone not only affects people with impaired respiratory systems, such as asthmatics, but healthy adults and children as well. Exposure to ozone for several hours at relatively low concentrations significantly reduces lung function and induces respiratory inflammation in normal, healthy people during exercise. This decrease in Ozone burns the tissues of the lungs, causing swelling, and making breathing difficult. Ozone exacerbates asthma and reduces lung function. Recent studies suggest that ozone may also cause asthma.

lung function is generally accompanied by symptoms such as chest pain, coughing, sneezing, and pulmonary congestion. Recent research in Southern California strongly suggests that, in addition to exacerbating existing asthma, ozone also causes asthma in children. Longer term exposure to ozone can also lead to scarring of the lung tissue and permanent reductions in lung capacity.

#### Carbon Monoxide

Carbon monoxide is a colorless, odorless, poisonous gas. Carbon monoxide is absorbed more readily than oxygen in the bloodstream and takes up oxygen-carrying sites in the blood. When carbon monoxide enters the bloodstream, it reduces the delivery of oxygen to the body's organs and tissues. Health threats from carbon monoxide are most serious for those who suffer from cardiovascular disease, particularly those with angina or peripheral vascular disease. Exposure to elevated carbon monoxide levels can impair visual perception, manual dexterity, learning ability, and the performance of complex tasks.

#### Sulfur Dioxide

High concentrations of sulfur dioxide affect breathing and may aggravate existing respiratory and cardiovascular disease. Longer-term exposure to high levels of sulfur dioxide causes respiratory illness and aggravates existing heart disease. Sulfur dioxide reacts in the air and turns into sulfate, which is associated with negative health effects as part of particulate matter. Sensitive populations include asthmatics, individuals with bronchitis or emphysema, children, and the elderly.

#### Nitrogen Dioxide

High concentrations of nitrogen dioxide can irritate the lungs, cause bronchitis and pneumonia, and lower resistance to respiratory infections. While concentrations of nitrogen oxides in the Mid-Atlantic Region are low enough to meet health standards, nitrogen oxides are important precursors to both ozone and acid rain, and may affect both terrestrial and aquatic ecosystems. When nitrogen oxides react with volatile organic compounds in the atmosphere, they may form nitrogenated hydrocarbons, most of which are extremely toxic. Some nitrogenated hydrocarbons are known to cause mutations.

#### Particulate Matter

Studies of people exposed to high concentrations of particles (sometimes with gaseous pollutants) and laboratory studies of animals and humans have shown that fine particles can cause serious health effects. These include increased coughing, difficult or painful breathing, chronic bronchitis, decreased lung function, aggravation of existing respiratory and cardiovascular disease, alterations in the body's defense systems against foreign materials, damage to lung tissue, cancer, and premature death. The major subgroups of the population that appear to be most sensitive to the effects of particulate

The exact details of the mechanism by which fine particles cause health effects is not well understood. Size and composition are likely important, since smaller particles are inhaled more deeply into the lungs and particles in different areas of the country appear to generate health effects of differing severity. matter include individuals with chronic obstructive pulmonary or cardiovascular disease or influenza, asthmatics, the elderly, and children.

A number of studies are underway to determine which components of particulate matter cause health problems. The answers are likely to be quite complex, owing to the complex nature of the pollutant. Composition likely plays a role, since some aerosols are thought to be considerably more harmful than others. Aerosols are also efficient carriers of toxic compounds, which are dangerous by themselves. Particle size likely also plays a role, since smaller particles are inhaled more deeply into the lungs.

Furthermore, composition varies widely with size, so these two are

linked. The finest particles tend to contain more metals, while larger particles tend to be mostly soils and other crustal material. Finally, individual variability will probably play a role as well—some individuals may be sensitive to a particular component, while others may be sensitive to the number of particles, and still others may only be sensitive to the total mass of particles they inhale.

#### Lead

Exposure to lead can occur in many ways, including inhalation of air and ingestion of lead in food, water, soil or dust. Excessive lead exposure can cause seizures, mental retardation, and behavioral disorders. A recent National Health and Nutrition Examination Survey reported a 78 percent decrease in blood lead levels from 12.8 to  $2.8 \mu g/dL$  between the periods 1976-1980 and from 1988-1991. This dramatic decline can be attributed to the reduction of leaded gasoline and to the removal of lead from soldered

cans. Although this represents great progress, infants and young children are especially susceptible to low doses of lead, and this age group still shows the highest levels. Low doses of lead can lead to central nervous system damage. Recent studies have also shown that lead may be a factor in high blood pressure and in subsequent heart disease in middle-aged men.

# Air Quality Index (AQI)

The AQI is a tool for reporting daily air quality. It tells you how clean or polluted your air is, and what associated health effects might be of concern. The AQI focuses on health effects an individual may experience within a few hours or days after breathing polluted air. EPA calculates the AQI for five major air pollutants regulated by the Clean Air Act: ground-level ozone, particle pollution (also known as particulate matter), carbon monoxide, sulfur dioxide, and nitrogen dioxide. For each of these pollutants, EPA has established national air quality standards to protect public health.

### How Does the AQI Work?

Think of the AQI as a yardstick that runs from 0 to 500. The higher the AQI value, the greater the level of air pollution and the greater the health concern. For example, an AQI value of 50 represents good air quality with little potential to affect public health, while an AQI value over 300 represents hazardous air quality.

An AQI value of 100 generally corresponds to the national air quality standard for the pollutant, which is the level EPA has set to protect public health. AQI values below 100 are generally thought of as satisfactory. When AQI values are above 100, air quality is considered to be unhealthy-at first for certain sensitive groups of people, then for everyone as AQI values get higher.

### Understanding the AQI

The purpose of the AQI is to help people understand what local air quality means to their health. To make it easier to understand, the AQI is divided into six categories. Each category corresponds to a different level of health concern.

### AQI colors

EPA has assigned a specific color to each AQI category to make it easier for people to understand quickly whether air pollution is reaching unhealthy levels in their communities. For example, the color orange means that conditions are "unhealthy for sensitive groups," while red means that conditions may be "unhealthy for everyone," and so on.

## Reporting & Forecasting

Each MARAMA member reports the daily AQI level via websites or other public announcements. For major cities in the Region a daily forecast of the AQI can be found at http://airnow.gov/.

# Appendix A

Air Quality Index Levels of Health Concern	Numerical Value	Meaning
Good	0-50	Air quality is considered satisfactory, and air pollution poses little or no risk.
Moderate	51-100	Air quality is acceptable; however, for some pollutants there may be a moderate health concern for a very small number of people who are unusually sensitive to air pollution.
Unhealthy for Sensitive Groups	101-150	Members of sensitive groups may experience health effects. The general public is not likely to be affected.
Unhealthy	151-200	Everyone may begin to experience health effects; members of sensitive groups may experience more serious health effects.
Very Unhealthy	201-300	Health alert: everyone may experience more serious health effects.
Hazardous	> 300	Health warnings of emergency conditions. The entire population is more likely to be affected.

AQI Index, Color Ranges and Messages

AQI Range	AQI Color	8-hour Ozone Range (ppb)	24-Hour PM2.5 Range (ugim3)
Good 0-50	Green	0-64	0-15.4
Moderate 51-100	Yellow	65-84	15.5-40.4
Unhealthy for Sensitive Groups 101-150	Orange	85-104	40.5-65.4
Unhealthy 151-200	Red	105-124	65.5-150.4
Very Unhealthy 151-200	Purple	125-374	150.5-250.4

AQI Color Ranges, Index and  $PM_{_{2.5}}$  and 8-Hr Ozone Breakpoints

Air Quality	Air Quality Index	Protect Your Health
Good	0-50	No health impacts are expected when air quality is in this range.
Moderate	51-100	Unusually sensitive people should consider limiting prolonged outdoor exertion.
Unhealthy for Sensitive Groups	101-150	Active children and adults, and people with respiratory disease, such as asthma, should limit prolonged outdoor exertion.
Unhealthy	151-200	Active children and adults, and people with respiratory disease, such as asthma, should avoid prolonged outdoor exertion; everyone else, especially children, should limit prolonged outdoor exertion.
Very Unhealthy (Alert)	201-300	Active children and adults, and people with respiratory disease, such as asthma, should avoid all outdoor exertion; everyone else, especially children, should limit outdoor exertion.

AQI Color Ranges, Index and Health Messages for 8-Hr Ozone

Air Quality	Air Quality Index	Health Advisory
Good	0-50	None.
Moderate	51-100	Unusually sensitive people should consider reducing prolonged or heavy exertion.
Unhealthy for Sensitive Groups	101-150	People with heart or lung disease, older adults, and children should reduce prolonged or heavy exertion.
Unhealthy	151-200	People with heart or lung disease, older adults, and children should avoid prolonged or heavy exertion. Everyone else should reduce prolonged or heavy exertion.
Very Unhealthy (Alert)	201-300	People with heart or lung disease, older adults, and children should avoid all physical activity outdoors. Everyone else should avoid prolonged or heavy exertion.

AQI Color Ranges, Index and PM<sub>2.5</sub>

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# Appendix B Air Pollution Effects on Ecosystems and the Environment

#### Ozone

Ozone interferes with the ability of plants to produce and store their own food. The additional stress makes them more susceptible to disease, insects, other pollutants, and harsh weather. Ozone damages the leaves of trees and other plants. Certain plant species are so susceptible that they may be used as indicators of long-term exposure to ozone. By interfering with the ability of plants to produce and store food, damaging their leaves, and increasing the stress on plants ozone also reduces the yield of certain crops and the growth of certain trees.

#### Sulfur Dioxide

Sulfur dioxide is a primary contributor to acid rain, or acid deposition, which causes acidification of lakes and streams and can damage trees, crops, historic buildings, and statues. In part, this damage occurs when sulfur dioxide deposits directly to surfaces, but sulfur dioxide also reacts in the atmosphere to become sulfate and sulfuric acid. Sulfates dominate visibility impairment throughout the Mid-Atlantic Region. Sulfuric acid is one of the dominant components of acid rain.

#### Nitrogen Dioxide

Nitrogen dioxide forms nitric acid in the atmosphere, contributing to acid rain. Nitrogen oxides also react with volatile organic compounds to form ozone and may contribute to a whole host of nitrogenated hydrocarbons, most of which are extremely toxic. Some nitrogenated hydrocarbons serve as reservoir species which exist for some time in the atmosphere before breaking down to re-release nitrogen oxides.

Nitrogen dioxide also forms nitrate, which is a fertilizer for plant and algae growth. When nitrate (as either nitric acid or nitrate itself) deposits directly to a body of water, it enters via the most active part: the surface. Atmospheric nitrogen is thought to comprise between 10 percent and 45 percent of the nitrogen reaching bodies of water such as the Chesapeake Bay. As such, atmospheric nitrogen leads directly to excessive nutrient loading of those water bodies. Nitrogen loading accelerates eutrophication, which is the aging process of a body of water. Among other effects, excessive nutrient loading causes algae blooms, low oxygen levels, red tides, fish kills, and general ecological degradation. The ecosystem can no longer support certain fish species, which may be replaced by less desirable species, if at all. Oysters are stressed, and greatly reduced in number. Atmospheric nitrogen is not the sole contributor to these effects, but is certainly one of many that must be controlled to improve the health of streams, rivers, and estuaries.

#### Particulate Matter

The impacts of fine particles are largely those of acid rain, increased nutrient loading, and the effects mentioned under sulfur dioxide and nitrogen dioxide. Fine particles are also very efficient carriers of air toxics, which each have their own impacts on ecosystems. Since fine particles are the dominant cause of haze, they also lead to significant visibility reduction, as discussed previously in this document. Fine particles also form grimy deposits on, stain, and damage buildings, cars, and other surfaces.

#### Lead

Wild and domestic animals can ingest lead while grazing, and can experience the same kind of effects as people who are exposed to lead. Low concentrations of lead can slow plant growth near industrial facilities. Lead can enter water systems through runoff and from sewage and industrial waste streams. Elevated levels of lead in the water can cause reproductive damage in some aquatic life and cause blood and neurological changes in fish and other animals.

#### Acid Rain

Acidity is measured on the pH scale, where 7.0 is neutral, 0.0 is strongly acidic, and 14.0 is strongly basic. The scale is logarithmic, so a pH of 5.0 represents ten times more acidity than a pH of 6.0. The scale allows a wide range of acid content to be communicated with a single number.

Nitrogen oxides and sulfur dioxide may both deposit directly to the surface, where they can form acids in the ecosystem. Much of the time, nitrogen oxides form acids before they reach the surface, and are deposited directly to the ecosystem as such. The effects of acid rain range from degradation of buildings and surfaces to acidification of streams and soils. Acids also leach metals and other nutrients from soils. Certain metals, particularly aluminum, are toxic to trees. By increasing the load of certain metals in the soil, many trees and plants are stressed or may be killed outright. Increased stress on plants and trees makes them more susceptible to disease and insect infestations, leading to an overall decline of the ecosystem.

Once acids make it into a stream, pond, or lake, the impact depends on the nature of the body of water. If the area is surrounded by limestone, the lime may be sufficient to neutralize the acid. If not, the body of water will tend to acidify. The nutrients leached from the soil will have additional effects on the ecosystem. Aluminum, for example, is particularly toxic to fish. Streams and lakes can be rendered barren of certain acid sensitive species such as bass, clams, snails, and crayfish. The eggs and young tend to be the most sensitive to acidity. Below a pH of 5, most fish eggs cannot hatch.

The impact of acid rain is felt throughout the ecosystem. For example, frogs can tolerate relatively acidic conditions, but the mayflies they eat cannot, so frogs may disappear from an acidified pond at a pH they are supposedly able to tolerate. The pH of a body of water need not always be low to have

Though many of the air quality standards in the United States are health-based standards, it is important to remember that air pollution harms the environment as well. Many of the same pollutants that lead to elevated ozone and PM also affect the environment directly via acid rain, excess nutrient loading, and visibility impairment, not to mention the direct effects of these pollutants themselves. disastrous effects on the animals living in it. A sudden acidic rainstorm or snowmelt can produce a pulse of acidity that pushes the pH below the limit which a particular fish can tolerate, resulting in a sudden fish kill.

Much of the Mid-Atlantic Region, particularly the Mid-Appalachian highlands, is highly sensitive to acidity. Many of the streams in the Mid-Atlantic Regional coastal plain are acidic, due to acid deposition in their watersheds. In the New Jersey Pine Barrens, for example, over 90 percent of the streams are acidic.

# Appendix C Air Quality Standards and Goals

EPA uses six "criteria pollutants" as indicators of air quality, and has established a maximum concentration for each. Concentrations above these limits may cause adverse health effects. These threshold concentrations are called National Ambient Air Quality Standards (NAAQS). There are two classes of standards, primary and secondary, which are not to be confused with primary and secondary pollutants. Primary standards set limits to protect public health, including the health of sensitive populations such as asthmatics, children, and the elderly. Secondary standards set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings. This section gives a quick overview of the standards.

### Ozone

The first ozone threshold value is 0.12 parts per million (ppm), averaged over one hour. An area meets the ozone standard if the highest hourly value exceeds the threshold on average no more than one day per year at each monitor. Each monitor in an area is treated individually under this standard, so the ozone concentration at a given monitor is allowed to exceed the standard only three times in a three year period. The fourth highest hour-average ozone concentration in a three year period therefore becomes the figure of merit for determining whether or not an area is in compliance with the standard. The fourth highest ozone value is termed the "design value" for that monitor. The highest design value for any monitor is then used as the design value for the entire area.

The threshold value for the 8-hour standard is 0.08 ppm of ozone for an eight-hour average. On a monitor-by-monitor basis, the design value is the annual fourth highest 8-hour value averaged over a three-year period. The 8-hour standard has replaced the 1-hour standard, and is stricter .

## Carbon Monoxide

The standard for carbon monoxide is a 9 ppm 8-hour average not to be exceeded more than once per year. An area meets the carbon monoxide standard if no more than one 8-hour value per year exceeds the threshold, provided the area meets the standard for two consecutive years and carries out air quality monitoring during the entire time. In addition, there is a 1-hour standard for carbon monoxide at 35 ppm, that also may not be violated more than once per year. The areas in violation of the carbon monoxide standard are predominantly in the West. Currently, no areas in the eastern United States are in violation of the carbon monoxide standard. Reformulated gasoline and improved emissions control technologies have greatly reduced carbon monoxide levels.

## Sulfur Dioxide

There are three standards for sulfur dioxide:

- $\cdot$  an annual average of 0.03 ppm (80 micrograms per cubic meter,  $\mu g/m^3)$
- $\cdot$  a 24-hour average level of 0.14 ppm (365  $\mu g/m^3)$
- $\cdot$  a 3-hour average level of 0.50 ppm (1300  $\mu g/m^3)$

### NAAQS Summary Table

The Clean Air Act, which was last amended in 1990, requires EPA to set National Ambient Air Quality Standards (NAAQS) for wide-spread pollutants from numerous and diverse sources considered harmful to public health and the environment. The Clean Air Act established two types of national air quality standards. Primary standards set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. Secondary standards set limits to protect public welfare, including protection against visibility impairment, damage to animals, crops, vegetation, and buildings. The Clean Air Act requires periodic review of the science upon which the standards are based and the standards themselves.

Pollutant	Primary Stds.	Averaging Times	Secondary Stds.
Carbon Monoxide	9 ppm (10 mg/m <sup>3</sup> )	8-hour <sup>1</sup>	None
	35 ppm (40 mg/m <sup>3</sup> )	1-hour <sup>1</sup>	None
Lead	1.5 µg/m <sup>3</sup>	Quarterly Average	Same as Primary
Nitrogen Dioxide	0.053 ppm (100 µg/m <sup>3</sup> )	Annual (Arithmetic Mean)	Same as Primary
Particulate Matter	50 μg/m <sup>3</sup>	Annual <sup>2</sup> (Arith. Mean)	Same as Primary
(PM <sub>10</sub> )	150 µg /m³	24-hour <sup>1</sup>	
Particulate Matter	15.0 µg/m <sup>3</sup>	Annual <sup>3</sup> (Arith. Mean)	Same as Primary
(PM <sub>2.5</sub> )	65 µg m <sup>3</sup>	24-hour <sup>4</sup>	
Ozone	0.08 ppm	8-hour <sup>5</sup>	Same as Primary
Sulfur Oxides	0.03 ppm	Annual (Arith. Mean)	
	0.14 ppm	24-hour <sup>1</sup>	
		3-hour <sup>1</sup>	0.5 ppm (1300 µg /m³)

<sup>1</sup> Not to be exceeded more than once per year.

- <sup>2</sup> To attain this standard, the 3-year average of the weighted annual mean  $PM_{10}$  concentration at each monitor within an area must not exceed 50  $\mu$ g/m<sup>3</sup>.
- <sup>3</sup> To attain this standard, the 3-year average of the weighted annual mean  $PM_{2.5}$  concentrations from single or multiple community-oriented monitors must not exceed 15.0 µg/m<sup>3</sup>.
- <sup>4</sup> To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed  $65 \,\mu g/m^3$ .
- <sup>5</sup> To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.08 ppm.

Source ---- http://www.epa.gov/air/criteria.html

The first two standards are primary (health-related) standards, while the 3-hour standard is a secondary (welfare-related) standard. Annual mean sulfur dioxide concentrations cannot exceed the standard. The short-term standards cannot be exceeded more than once per year. A few areas in the Mid-Atlantic currently violate the sulfur dioxide standard.

# Nitrogen Dioxide

The nitrogen dioxide standard is an annual average concentration of 0.053 ppm ( $100 \mu g/m^3$ ). All areas of the United States are currently in compliance with the nitrogen dioxide standard.

# Particulate Matter

Standards for particulate matter (PM) are set for different sizes of particles. There are standards for PM with a diameter of 10 micrometers  $(PM_{10})$  or less and for smaller particles of 2.5 micrometers  $(PM_{25})$  or less.

The standards in effect for  $PM_{10}$  are an annual mean of 50 µg/m<sup>3</sup> and a daily standard of 150 µg/m<sup>3</sup>. For the daily standard, the annual mean  $PM_{10}$  may not exceed 150 µg/m<sup>3</sup> more than three times in three years. For the annual standard, the average of three sequential annual averages must fall below 50 µg/m<sup>3</sup>. Annual averages are calculated from previously obtained quarterly averages.

Two standards are in effect for  $PM_{2.5}$ : an annual standard of 15 µg/m<sup>3</sup>, and a daily standard of 65 µg/m<sup>3</sup>. All areas in the Mid-Atlantic will comply with the daily standard, but some exceed the annual standard. The annual standard appears to have been placed very near the average annual concentration of  $PM_{2.5}$  in the Region. The rules for calculating design values for these standards are somewhat complex, so they are best broken down into step-by-step procedures.

#### Annual standard

- 1. Average 24-hour measurements to obtain quarterly means at each monitor.
- 2. Average quarterly means to obtain annual means at each monitor.
- 3. Average across designated monitoring sites to obtain an annual spatial mean for an area. (Optional for areas designated for spatial averaging. Such averaging may be used to blend data from more than one monitoring site if approved by the state and EPA.)
- 4. Average three years of annual means to obtain a three-year average of annual means.

#### Daily standard

- 1. Calculate the 98th percentile 24-hour average PM concentration for each year.
- 2. Average the 98<sup>th</sup> percentile concentration over three years.

#### Lead

The lead standard is a quarterly average particulate concentration of 1.5  $\mu$ g/m<sup>3</sup>. Only three areas in Montana and Missouri currently do not comply with the lead standard.

### Haze: A 60-Year Return to Natural Conditions

The haze rule is fundamentally different from those mentioned previously in that it is not a health-based standard, and goals are to be set individually for each area that represent natural conditions at that site. EPA's haze rule requires that Class I areas (large national parks and wilderness areas) return to natural visibility by 2064. The regulation has two parts: one concerns sources that have a readily discernible impact on a Class I area, while the other concerns regional haze where specific sources may not be identifiable.

The haze rule divides days into the 20 percent best and 20 percent worst visibility days. Visibility on the best days can get no worse, while visibility on the worst days must make steady progress as measured in deciviews back toward natural conditions. The logarithmic nature of the deciview scale means that big reductions in particle concentrations are required at first, with smaller ones later. While this may sound like the big burden is up front, it is likely that the most difficult part will come later. By 2064, if visibility is to return to natural conditions, emissions from human activities will have to be quite small.

Most Class I areas are in the West, but there are some in the eastern United States. In the Mid-Atlantic, the Class I areas are: Brigantine Wilderness (NJ), Dolly Sods Wilderness (WV), Otter Creek Wilderness (WV), Shenandoah National Park, (VA), James River Face Wilderness (VA), Linville Gorge Wilderness (NC), Swanquarter Wilderness (NC), Shining Rock Wilderness (NC), Great Smoky Mountains National Park (NC), and Joyce Kilmer-Slickrock Wilderness (NC). All states in the Mid-Atlantic Region will be affected by this regulation, since pollution transport from neighboring states is part of the regional haze problem. Mid-Atlantic Region states will also have to reduce emissions to improve visibility in Class I areas outside the Mid-Atlantic Region.

# Appendix D MARAMA Region Data Tables

- Table D-1 PM <sub>25</sub> Design Values for the Annual Standard (2001-2003)
- Table D-2a 8-hr Ozone Design Values by Nonattainment County (2001-2003)
- Table D-2b 8-hr Ozone Design Values by Attainment County (2001-2003)
- Table D-3 8-hr Ozone Design Values by Nonattainment Area (2001-2003)
- Table D-4 Days Above the 8-Hour Ozone Standard 1998-2003 by EPA Planning/ Nonattainment Area
- Table D-5 Days Above the 8-Hour Ozone Standard 1998-2003 by State

#### Table D-6 Days Above the 1-Hour Ozone Standard 1986-2003 by Nonattainment Area

Table D-7 Days Above the 1-Hour Ozone Standard 1986-2003 by State

State	Monitor Site	County	PM 2.5 Design Value µg/m <sup>3</sup>	EPA Site Code
DE	MLK	New Castle	16.2	100032004
DE	Newark	New Castle	15.1	100031012
DE	Bellefonte	New Castle	15.0	100031003
DE	Seaford	Sussex	13.6	100051002
DE	Dover	Kent	13.1	100010003
DE	Killens Pond State	Kent	13.0	100010002
				100010002
DC	River Terrace	Washington DC	15.9	110010041
	301001	Washington DC	15.0	110010041
DC	McMillan Reservoir	Washington DC	15.2	110010043
	Weivinian Reserven	Washington DO	10.2	110010043
MD	Old Town	Baltimore City	16.6	245100040
		Dalamore eny		210100010
MD	FMCA	Baltimore City	15.9	245100035
MD	Westport	Baltimore City	15.4	245100049
	•			
MD	Glen Burnie	Anne Arundel	15.3	240031003
MD	Essex	Baltimore Co.	15.2	240053001
MD	NWPS	Baltimore City	15.0	245100007
MD	Riviera Beach	Anne Arundel	14.2	240032002
MD	Padonia	Baltimore Co.	14.2	240051007
MD	Hagerstown	Washington	13.9	240430009

Table D-1 PM  $_{\rm 2.5}$  Design Values for the Annual Standard (2001-2003)

State	Monitor Site	County	PM 2.5 Design Value µg/m <sup>3</sup>	EPA Site Code
MD	Fort Meade	Anne Arundel	13.0	240030019
MD	Edgewood	Harford	12.8	240251001
MD	Rockville	Montgomery	12.6	240313001
MD	Davidsonville	Anne Arundel	12.1	240030014
NJ	Elizabeth Lab	Union	15.7	340390004
	Jersey City			
NJ	Firehouse	Hudson	14.8	340171003
NJ	Trenton	Mercer	14.0	340210008
NJ	Phillipsburg	Warren	13.5	340410006
NJ	Rahway	Union	13.1	340392003
NI	Now Brupswick	Middlesex	12.7	340230006
INJ	New Drunswick	Wildulesex	12.1	340230000
NC		Davidson	15.9	270570002
INC.	Lexington	Davidson	15.6	370370002
NC	Hickory 1st Street	Catawha	15.5	270250004
INC.	Theory ist Street	Calawba	15.5	370350004
	Charlotte #10 Fire			
NC	Station	Mecklenberg	14.9	371190010
NC	Winston-Salem	Forsyth	14.6	370670022
			14.0	310010022
NC	Kannanolis	Cabarrus	14.5	370250004
	Каппаронь		14.0	570250004
	Charlotte			
NC	Montclaire	Mecklenberg	14.2	371190042
NC	Marion	McDowell	14.1	371110004

Table D-1, continued PM  $_{\rm 2.5}$  Design Values for the Annual Standard (2001-2003)

State	Monitor Site	County	PM 2.5 Design Value µg/m <sup>3</sup>	EPA Site Code
NC	Charlotte Garinger	Mecklenberg	14.1	371190041
		-		
	Winston-Salem	E a rea dh	44.0	070070004
NC	North	Forsyth	14.0	370670024
NO	Ocatania	Oratan	44.0	070740040
NC	Gastonia	Gaston	14.0	370710016
	Greensboro			
NC	Mendenhall	Guilford	14.0	370810013
NC	Fayetteville	Cumberland	13.9	370510009
NC	Durham	Durham	13.9	370630001
NC	Raleigh Millbrook	Wake	13.8	371830014
NC	Burlington	Alamance	13.7	370010002
NC	Goldsboro	Wayne	13.6	371910005
	Delaist Or			
NC	Raleigh St. Augustine	Wake	13.5	371830015
NC	Waynesville	Haywood	13.4	370870010
	<b>,</b>			
NC	Cherry Grove	Caswell	13.3	370330001
	·			
NC	Spruce Pine	Mitchell	13.3	371210001
NC	Chapel Hill	Orange	13.1	371350007
NC	Asheville	Buncombe	12.9	370210034
NC	Lumberton	Robeson	12.8	371550005
			12.0	371330003
NC	Cherokee	Jackson	12.6	370990006

Table D-1, continued PM <sub>2.5</sub> Design Values for the Annual Standard (2001-2003)

State	Monitor Site	County	PM 2.5 Design Value μg/m <sup>3</sup>	EPA Site Code
NC	Bryson City	Swain	12.6	371730002
NC	Greenville	Pitt	12.3	371470005
NC	Pittsboro	Chatham	12.2	370370004
NC	Candor	Montgomery	12.1	371230001
NC	Kenansville	Duplin	11.9	370610002
NC	Kinston	Lenoir	11.4	371070004
NC	Jacksonville	Onslow	11.1	371330005
PA	Liberty	Allegheny	21.2	420030064
PA	Clairton	Alleghenv	17.2	420033007
PA	Lancaster	Lancaster	17.0	420710007
PA	York	York	17.0	421330008
PA	North Braddock	Alleghenv	16.9	420031301
PA	Reading	Berks	16.4	420110009
	Ŭ			
	500 South Broad			
PA	Street	Philadelphia	16.2	421010047
PA	Beaver Falls	Beaver	16.0	420070014
PA	Harrison	Allegheny	15.9	420031008
PA	Johnstown	Cambria	15.8	420210011
PA	Lawrenceville	Allegheny	15.7	420030008

Table D-1, continued PM  $_{\rm 2.5}$  Design Values for the Annual Standard (2001-2003)

State	Monitor Site	County	PM 2.5 Design Value µg/m <sup>3</sup>	EPA Site Code
PA	Harrisburg	Dauphin	15.7	420430401
PA	Charleroi	Washington	15.5	421250005
		Ŭ		
PA	Greensburg	Westmoreland	15.5	421290008
PA	Chester	Delaware	15.4	420450002
PA	AMS Laboratory	Philadephia	15.2	421010004
PA	Washington	Washington	15.0	421250200
PA	Freemansburg	Northampton	14.6	420950025
	Troomanobarg			120000020
PA	Allentown	l ehiah	14.4	420770004
				120110001
PA	Bristol	Bucks	14.3	420170012
				120110012
PA	Farrell	Mercer	14.3	420850100
	Belmont Water			
PA	Treatment	Philadelphia	14.3	421010020
PA	Norristown	Montgomery	14.1	420910013
PA	Arendtsville	Adams	13.4	420010001
PA	Perry County	Perry	13.0	420990301
PA	WilkesBarre	Luzerne	12.9	420791101
PA	Scranton	Lackawanna	12.5	420692006
VA	Market Street Fire	Salem	14 7	517750010

#### Table D-1, continued PM <sub>2.5</sub> Design Values for the Annual Standard (2001-2003)

State	Monitor Site	County	PM 2.5 Design Value µg/m <sup>3</sup>	EPA Site Code
VA	Aurora Hills Visitors Center	Arlington	14.6	510130020
				010100020
VA	Highlands View Elementary School	Bristol	14.3	515200006
VA	Raleigh Court Library	Roanoke	14.2	517700014
VA	Lewinsville	Fairfax	14.0	510595001
VA	DEQ Air Monitoring Office	Richmond	14.0	517600020
VA	Mathematics &	Henrico	13.7	510870014
			10.1	
VA	Bensley Armory	Chesterfield	13.6	510410003
VA	Lee District Park*	Fairfax	13.6	510590030
VA	Broad Run High School	Loudoun	13.6	511071005
VA	NOAA Facility	Norfolk	13.0	517100024
VA	DEQ Regional Office	Henrico	12.9	510870015
VA	Luray Caverns Airport	Page	12.9	511390004
VA	Off Routh #608	Charles City	12.8	510360002
VA	DEQ Regional Office	Virginia Beach	12.6	518100008
VA	Oscar Smith Stadium	Chesapeake	12.5	515500012

# Table D-1, continued PM $_{\rm 2.5}$ Design Values for the Annual Standard (2001-2003)

\*The completeness criteria were not met for Lee District Park (510590030)

State	Monitor Site	County	PM 2.5 Design Value µg/m <sup>3</sup>	EPA Site Code
VA	Virginia School	Hampton	12.5	516500004
		·		
VA	Pump Station #103	Newport News	11.9	517000013
	•			
WV	Weirton/Oak Street	Hancock	17.4	540291004
WV	South Charleston	Kanawha	17 1	540391005
WV	Follansbee	Brooke	16.8	540090005
		Brooke	10.0	010000000
\M/\/	Huntington	Cabell	16.6	540110006
	Turtington	Gaben	10.0	340110000
10/1/	Martinsburg	Berkeley	16.3	540030003
	Martinsburg	Deriveley	10.0	340030003
	Weirton/Marland			
WV	Heights	Hancock	16.2	540290011
WV	Vienna	Wood	16.0	541071002
WV	Moundsville	Marshall	15.7	540511002
WV	Charleston	Kanawha	15.5	540390010
WV	Fairmont	Marion	15.4	540490006
WV	Wheeling	Ohio	15.2	540690008
WV	Morgantown	Monongalia	14.9	540610003
WV	Clarksburg	Harrison	14.0	540330003
WV	Beckley	Raleigh	13.1	540810002
WV	Bluefield	Mercer	12.5	540550002
WV	Keeney Knob	Summers	10.1	540890001

Table D-1, continued PM<sub>2.5</sub> Design Values for the Annual Standard (2001-2003)
#### Table D-2a 8-hour Ozone Design Values by Nonattainment County (2001-2003)

State	County	Design Value (ppb)					
DE	Kent	89					
DE	New Castle	93					
DE	Sussex	91					
DE	Washington	94					
MD	Anne Arundel	98					
MD	Baltimore	93					
MD	Carroll	89					
MD	Cecil	98					
MD	Charles	94					
MD	Frederick	88					
MD	Harford	103					
MD	Kent	95					
MD	Montgomery	88					
MD	Prince George's	93					
MD	Washington	86					
NC	Alexander	88					
NC	Caswell	88					
NC	Cumberland	87					
NC	Davie	93					
NC	Durham	89					
NC	Edgecombe	89					
NC	Forsyth	93					
NC	Franklin	90					
NC	Granville	94					
NC	Guilford	89					
NC	Haywood	85					
NC	Johnston	85					
NC	Lincoln	92					
NC	Mecklenburg	98					
NC	Person	91					
NC	Randolph	85					
NC	Rockingham	91					
NC	Rowan	100					
NC	Union	88					
NC	Wake	92					
NJ	Atlantic	91					
NJ	Bergen	95					
NJ	Camden	102					
NJ	Cumberland	98					
NJ	Gloucester	100					
NJ	Hudson	87					
NJ	Hunterdon	97					

#### Table D-2a, continued 8-hour Ozone Design Values by Non-attainment County (2001-2003)

State	County	Design Value (ppb)
NJ	Mercer	99
NJ	Middlesex	98
NJ	Monmouth	97
NJ	Morris	98
NJ	Ocean	109
NJ	Passaic	88
PA	Allegheny	93
PA	Armstrong	93
PA	Beaver	94
PA	Berks	91
PA	Blair	85
PA	Bucks	100
PA	Cambria	87
PA	Centre	88
PA	Chester	98
PA	Clearfield	90
PA	Dauphin	88
PA	Delaware	93
PA	Erie	92
PA	Franklin	93
PA	Greene	89
PA	Lackawanna	85
PA	Lancaster	92
PA	Lehigh	92
PA	Luzerne	86
PA	Mercer	94
PA	Montgomery	94
PA	Northampton	91
PA	Perry	87
PA	Philadelphia	97
PA	Tioga	86
PA	Washington	89
PA	Westmoreland	91
PA	York	89
VA	Alexandria	92
VA	Arlington	99
VA	Charles City	91
VA	Chesterfield	86
VA	Fairfax	97
VA	Frederick	85
VA	Hampton	90
VA	Hanover	94

#### Table D-2a, continued 8-hour Ozone Design Values by Non-attainment County (2001-2003)

State	County	Design Value (ppb)
VA	Henrico	90
VA	Loudon	92
VA	Madison	87
VA	Prince William	87
VA	Roanoke	85
VA	Stafford	88
VA	Suffolk	88
WV	Berkeley	86
WV	Cabell	88
WV	Hancock	86
WV	Kanawha	86
WV	Ohio	87
WV	Wood	87

State	County	Design Value (ppb)
NC	Northampton	84
NC	Pitt	82
NC	Swain	74
NC	Yancey	83
NC	Avery	78
NC	Buncombe	78
NC	Caldwell	84
NC	Chatham	82
NC	Duplin	79
NC	Lenoir	81
NC	Martin	81
NC	New Hanover	78
PA	Lawrence	80
PA	Lycoming	83
VA	Caroline	84
VA	Fauquier	80
VA	Page	82
VA	Rockbridge	78
VA	Wythe	80
WV	Greenbrier	80
WV	Monongalia	79

#### Table D-2b 8-hour Ozone Design Values by Attainment County (2001-2003)

#### Table D-3 8-hour Ozone Design Values by Nonattainment Area (2001-2003)

State	Nonattainment Area	8-hr Ozone Design Value (ppb)				
DC	Washington DC, MD, VA	99				
MD	Baltimore	103				
MD	Kent and Queen Anne's Counties	95				
MD	Washington County (Hagerstown)	86				
NC	Charlotte-Gastonia-Rock Hill	100				
NC	Fayetteville	87				
NC	Greensboro-Winston Salem-High Point	93				
NC	Haywood and Swain Counties (Great Smoky NP)	85				
NC	Hickory-Morganton-Lenoir	88				
NC	Raleigh-Durham-Chapel Hill	94				
NC	Rocky Mount	89				
NJ	New York-N. New Jersey-Long Island	102				
PA	Allentown-Bethlehem-Easton	91				
PA	Altoona	85				
PA	Clearfield and Indiana Counties	90				
PA	Erie	92				
PA	Franklin County	93				
PA	Greene County	89				
PA	Harrisburg-Lebanon-Carlisle	88				
PA	Johnstown	87				
PA	Lancaster	92				
PA	Pittsburgh-Beaver Valley	94				
PA	Reading	91				
PA	Scranton-Wilkes Barre	86				
PA	State College	88				
PA	Tioga County	86				
PA	York	89				
PA	Youngstown-Warren-Sharon	95				
PA, NJ, MD, DE	Philadelphia-Wilmington-Atlantic City	106				
VA	Frederick County	85				
VA	Fredericksburg	99				
VA	Madison and Page Counties (Shenandoah NP)	87				
VA	Norfolk-Virginia Beach-Newport News	90				
VA	Richmond-Petersburg	94				

#### Table D-3, continued 8-hour Ozone Design Values by Nonattainment Area (2001-2003)

State	Nonattainment Area	8-hr Ozone Design Value (ppb)
VA	Roanoke	85
WV	Berkeley and Jefferson Counties	86
WV	Charleston	86
WV	Huntington-Ashland	91
WV	Parkersburg-Marietta	87
WV	Steubenville-Weirton	86
WV	Wheeling	87

EPA Planning						
Areas/Nonattainment Areas	1998	1999	2000	2001	2002	2003
Allentown-Bethlehem-Easton PA-			_			
NJ	19	23	6	15	19	4
Altoona PA	17	6	2	3	9	3
Cumberland-Keyser Interstate MD	NA	NA	NA	6	15	3
Atlantic City NJ	23	13	4	9	11	4
Baltimore MD	51	41	17	29	37	9
Charleston WV	12	14	4	1	6	4
Charlotte-Gastonia NC	51	43	27	26	36	9
Erie PA	12	13	2	4	17	4
Greenbrier WV	11	2	1	2	2	0
Greensboro-Winston-Salem-High Point NC	31	30	21	21	29	7
Hampton Roads VA	15	16	5	6	15	4
Harrisburg-Lebabnon-Carlisle PA	22	17	5	16	16	3
Huntington-Ashland WV-KY	16	16	1	5	20	3
Johnstown PA	13	11	5	5	6	2
Kent County and Queen Anne's						
County MD	16	23	6	13	17	4
Lancaster PA	27	18	5	15	18	3
Lawrence Co PA	2	5	0	1	6	2
New York-N. New Jersey-Long Island NY-NJ-CT	41	40	18	34	41	14
Norfolk-Virginia Beach-Newport News-VA	15	16	5	6	15	4
Parkersburg WV	19	13	4	2	19	2
Philadelphia-Wilmington-Trenton PA-NJ-DE-MD	41	36	19	31	41	15
Pittsburgh-Beaver Valley PA	44	29	5	24	33	9
Raleigh-Durham NC	43	35	11	9	29	7
Reading PA	18	17	3	8	14	3
Richmond-Petersburg VA	28	27	6	14	25	5
Roanoke VA	12	5	2	5	5	1
Scranton-Wilkes-Barre PA	15	21	1	10	16	3
Sharon PA	25	8	2	15	20	6
Shenandoah National Park	22	15	1	8	6	6
State College	NA	NA	2	5	13	4
Steubenville WV	6	6	1	3	16	2
Sussex Co DE	22	20	7	10	16	5
Washington DC-MD-VA	47	39	10	24	38	7
Wheeling WV	5	7	2	6	11	0
Williamsport PA	1	NA	1	1	7	0
York PA	19	10	6	8	12	0

Table D-4 Days Above the 8-Hour Ozone Standard (1998-2003) by EPA Planning/Nonattainment Area

Table D-5
Days Above the 8-hour Ozone Standard (1998-2003)
by State

All Mid-Atlantic States	1998	1999	2000	2001	2002	2003
Delaware	36	13	10	21	26	7
District of Columbia	47	39	10	24	38	7
Maryland	55	20	21	30	39	9
New Jersey	47	46	19	35	44	20
North Carolina	71	20	33	33	51	14
Pennsylvania	55	51	22	39	50	19
Virginia	49	18	10	22	45	11
West Virginia	30	28	6	19	31	6

Table D-6Days Above the 1-hour Ozone Standard (1998-2003)by Nonattainment Area

	r –				<u> </u>						-		-		<u> </u>		1		-				<u> </u>
2003	0	-	0	0	2	0	e	0	0	0	0	0	0	~	-	-	ۍ	ţ-	0	7	-	0	-
2002	0	0	0	-	16	0	0	0	0	0	~	0	0	ო	0	0	14	3	-	15	0	0	c
2001	2	0	0	0	6	0	0	0	0	0	0	0	0	0	2	0	8	1	0	12	0	0	ç
2000	-	0	0	0	-	0	ю	0	0	0	0	0	0	ო	0	0	4	0	0	ო	0	1	c
1999	2	0	0	0	11	2	5	0	0	ო	~	-	0	7	2	-	12	4	0	11	4	5	ç
1998	-	0	0	0	9	-	9	0	0	~	-	2	0	~	-	0	4	0	0	9	7	4	c
1997	-	0	0	с	12	0	2	0	0	0	0	-	-	4	e	0	7	0	0	11	3	2	
1996	0	0	0	0	e	0	0	0	0	0	0	0	0	0	0	0	4	0	0	ъ С	0	0	c
1995	0	0	AN	0	13	0	٢	0	0	~	0	2	0	~	-	0	16	0	0	11	6	0	c
1994	0	0	ΝA	0	10	0	0	0	0	0	0	e	0	0	0	0	11	0	-	œ	2	0	-
1993	0	0	ΝA	0	11	0	ю	0	0	-	0	-	0	2	0	2	13	ю	0	21	2	2	c
1992	0	0	AN	-	e	0	0	0	0	0	0	0	0	0	0	0	7	2	0	7	0	0	c
1991	-	0	AN	2	14	-	-	0	1	0	0	e	0	9	0	0	25	-	0	28	2	0	
1990	0	0	AN	5	8	0	٢	0	0	7	-	4	0	~	0	0	22	0	0	15	0	0	c
1989	0	0	AN	-	4	0	2	0	0	0	0	-	0	~	0	0	21	0	-	18	4	3	c
1988	12	4	AN	9	36	7	14	9	4	10	œ	14	7	0	e	e	42	4	11	42	19	12	11
1987	<i>с</i> о	2	NA	5	23	0	7	-	0	~	~	ω	0	0	-	0	31	2	e	31	5	4	ç
1986	0	0	ΝA	0	13	-	7	0	0	2	0	e	0	0	0	0	20	٢	-	16	2	-	- -
EPA Planning/ Nonattainment Areas	Allentown-Bethlehem- Easton PA-NJ	Altoona PA	AQCR 113 Cumberland- Kevser Interstate MD	Atlantic City NJ	Baltimore MD	Charleston WV	Charlotte-Gastonia NC	Erie PA	Greenbrier W V	Greensboro-Winston- Salem-High Point NC	Harrisburg-Lebabnon- Carlisle PA	Huntington-Ashland WV-KY	Johnstown PA	Kent County and Queen Anne's County MD	Lancaster PA	Lawrence Co PA	New York-N. New Jersey- Long Island NY-NJ-CT	Norfolk-Virginia Beach- Newport News-VA	Parkersburg WV	Philadelphia-Wilmington- Trenton PA-NJ-DE-MD	Pittsburgh-Beaver Valley PA	Raleigh-Durham NC	Deading DA

	1000	1001	0001	0001		1001	000		1001	1001	000	1001	000	000		1000		0000
	1900	1901	1 2 0 0	202	1 3 3 0	1221	1 3 3 4	1 3 3 3	1 3 3 4	1880	1 3 3 0	1221	1990	1 3 3 3	2000	2001	2002	2003
Richmond-Petersburg VA	0	5	14	0	1	1	1	5	1	2	0	3	3	8	0	1	5	1
Roanoke VA	0	0	2	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0
Scranton-Wilkes-Barre PA	0	1	10	0	0	2	0	0	0	0	0	0	0	1	0	0	1	0
Sharon PA	ΝA	ΝA	NA	NA	ΝA	ΝA	ΝA	NA	ΝA	NA	0	0	0	0	0	0	0	0
Shenandoah National Park	0	0	2	0	0	0	0	0	0	0	0	0	-	0	0	0	0	0
State College	ΝA	NA	ΝA	NA	ΝA	ΝA	ΝA	NA	ΝA	NA	0	0	0	0	0	0	0	0
Steubenville W V	NA	ΝA	NA	NA	ΝA	ΝA	NA	NA	ΝA	NA	0	0	0	1	0	0	0	0
Sussex Co DE	0	0	8	0	1	3	0	0	0	0	0	3	1	0	0	1	0	2
Washington DC-MD-VA	9	18	31	3	5	6	2	8	4	6	1	6	6	7	2	3	6	3
W heeling W V	ΝA	ΝA	ΝA	NA	ΝA	ΝA	ΝA	ΝA	ΝA	ΝA	0	0	0	0	0	0	0	3
W illiamsport PA	NA	NA	NA	NA	ΝA	ΝA	ΝA	NA	ΝA	NA	0	0	0	0	0	0	0	4
W inchester, VA	ΝA	ΝA	NA	NA	ΝA	NA	0	0	0	0	0	0	0	0	0	0	0	0
York PA	0	0	4	0	0	0	0	0	0	0	0	0	0	-	0	0	-	З

Table D-6, continued Days Above the 1-Hour Ozone Standard (1986-2003) by Nonattainment Area

# Mid-Atlantic Regional Air Management Association Page D-18

Year	Delaware	District of Columbia	Marvland	New Jersev	North Carolina	Pennsvlvania	Virginia	West Virginia
1986	0	0	17	22	8	14	5	4
1987	11	6	23	32	8	23	16	4
1988	28	6	36	45	22	39	29	22
1989	4	1	4	18	5	13	3	2
1990	6	0	10	23	3	7	6	0
1991	9	1	16	26	1	14	11	2
1992	2	0	5	9	1	2	3	0
1993	5	8	16	18	6	10	11	1
1994	2	4	11	7	0	5	3	2
1995	6	4	14	14	3	11	5	2
1996	0	0	4	6	5	3	1	0
1997	7	5	14	10	4	7	4	1
1998	6	0	10	4	9	11	9	5
1999	4	3	11	10	10	11	10	4
2000	3	0	4	4	3	2	1	0
2001	2	4	10	11	2	4	3	0
2002	3	9	16	16	12	11	9	1
2003	2	3	2	4	3	3	3	0

#### Table D-7 Days above the 1-Hour Ozone Standard (1986-2003) by State

### Mid-Atlantic Regional Air Management Association Page D-20

# **Appendix E** Measuring and Calculating Visibility Impairment

Visibility is impaired by light scattering and absorption due to particles and gases in the air.<sup>1</sup> Light extinction is the sum of light scattering plus light absorption. Light extinction may be thought of as a measure of the amount of light that is extinguished as the light moves through the atmosphere. The more light that is lost, the greater the loss of visibility.

Scientists have studied the effect of various air pollutants on light extinction and have developed an equation to estimate light extinction based on measurements of these pollutants in the air. Measuring the concentration of sulfates, nitrates, organic carbon, and other particles allows scientists to "reconstruct" the amount of visibility impairment. Sulfates and nitrates have a stronger effect on visibility impairment than other particles because they combine with water, thereby growing larger and scattering more light. Therefore, relative humidity measurements are also needed in order to calculate visibility impairment.

# Interagency Monitoring of Protected Visual Environments (IMPROVE)

The Interagency Monitoring of Protected Visual Environments (IMPROVE) program is a cooperative measurement effort governed by a steering committee composed of representatives from Federal, regional, and state organizations. The IMPROVE monitoring program was established in 1985 to plan to improve and protect the visibility in Class I areas (156 national parks and wilderness areas) as stipulated in the 1977 amendments to the Clean Air Act.

The objectives of the IMPROVE program are:

- (1) to establish current visibility and aerosol conditions in mandatory Class I areas;
- (2) to identify chemical species and emission sources responsible for existing man-made visibility impairment;
- (3) to document long-term trends for assessing progress towards the national visibility goal; and
- (4) as required by EPA's Regional Haze Rule, to provide regional haze monitoring representing all visibility-protected federal Class I areas, where practical.

IMPROVE has also been a key participant in visibility-related research, including the advancement of monitoring instrumentation, analysis techniques, visibility modeling, policy formulation, and source attribution field studies.

Source: "Improve Monitoring Program Overview", http://Vista.cira.colostate.edu/IMPROVE/

<sup>&</sup>lt;sup>1</sup>Light scattered by gases in the atmosphere is termed Rayleigh or natural scattering, and is taken to be a constant at 12 inverse megameters ( $Mm^{-1}$ ) at sea level. The only significant gas that absorbs light is nitrogen dioxide ( $NO_2$ ), and its absorption is generally small, except in concentrated plumes from emission sources.

# Appendix E

In order to determine compliance with the Clean Air Act and EPA regulations, state, federal, and regional agencies have organized a collaborative effort to monitor visibility in Class I areas where visibility is important. This program is called the Interagency Monitoring of Protected Visible Environments (IMPROVE) program. The IMPROVE program uses various equipment to measure air quality at Class I areas. These measurements are used to calculate visibility (light extinction), as explained below.

Scientists can measure the brightness of light at a distance using a transmissometer. This equipment measures the amount of light seen by looking directly at a light and compares that to the amount of light from the same source reflected from a distant mirror. Transmissometers are difficult to operate in remote locations, and measurements can be affected by unknowns such as fogging of lenses, swarming insects, clouds, and the age of the light source, among other things. The transmissometer measurement is not considered a direct measurement of extinction, and only selected IMPROVE monitoring sites have transmissometers, including one at Shenandoah National Park.

Scientists can also measure light scattering (not including absorbtion) using nephelometers. A nephelometer measures scattering in a measured volume of air. This equipment also has operational limitations, so only some Class I sites have nephelometers. IMPROVE sites at Great Gulf Wilderness, Lye Brook Wilderness, Mammoth Cave, and Shenandoah National Park have nephelometers.

The standard equipment at an IMPROVE site measures  $PM_{2.5}$  on three types of filters (quartz, nylon, and Teflon) as well as  $PM_{10}$  on a Teflon filter. In addition to quantifying  $PM_{2.5}$  and  $PM_{10}$  mass, lab analysis of these filters provides measurements of numerous substances, the most prevalent of which are sulfates, nitrates, and various forms of carbon. (See the following text box for more details.)

To calculate light extinction from these measurements, scientists calculate the mass of ammonium sulfate, ammonium nitrate, organic carbon, soil, coarse particles, and light absorbing carbon. Then they multiply these values by constants that reflect how efficient that type of particle is at scattering or absorbing light and, finally, they sum the results. This process is represented by the following equation:

 $b_{ext} = 3.0 \text{ f(RH)}[\text{AS}] + 3 \text{ f(RH)}[\text{AN}] + 4R_{OC}[\text{OC}] + [\text{Soil}] + 6[\text{CM}] + 10.0[\text{LAC}] + b_{Rav}$ 

where

 $b_{ext} = \text{extinction}$ 

f(RH) = a function of Relative Humidity that accounts for absorption of water

 $AS = Ammonium Sulfate (NH_4)_2 SO_4$ 

 $AN = Ammonium Nitrate (NH_{A})NO_{3}$ 

 $R_{oc}$  = the ratio of the mass of the organic aerosol to the total mass of carbon

OC = organic carbon

Soil = calculated from the measurements of aluminum, silicon, titanium, calcium, and iron

= 2.2Al + 2.49Si + 1.94Ti + 1.63Ca + 2.4Fe

 $CM = coarse mass = PM_{10} - PM_{2.5}$ 

 $b_{Rav}$  = Rayleigh (natural) scattering

There are a number of uncertainties in the equation for calculating light extinction. The uncertainties arise from assumptions that all sulfate and nitrate are present as ammonium sulfate and ammonium nitrate, the functions used to estimate the effect of relative humidity on those particles, the use of average rather than site- and day-specific humidity measurements, assumptions about the noncarbon content of organic compounds and their behavior in varying humidity, and the accuracy and precision of measurements.

The Northeast States for Coordinated Air Use Management's (NESCAUM) February 2002 report on "Updated Visibility Statistics for the Mid-Atlantic Northeast Visibility Union (MANE-VU) Region" concluded that there was reasonable agreement between calculated and measured light scattering (measured by nephelometers) at some locations, and that further study of the effects of uncertainties in the IMPROVE equation was warranted. (See <u>www.nescaum.org/</u> select Air Topics, Regional Haze, and find Technical Report #1 listed under Technical Memoranda.)

A May 2005 report by Jenny L. Hand and William C. Malm, "Review of the IMPROVE

The standard IMPROVE sampler has four sampling modules, listed below.

<u>Module A</u>:  $PM_{2.5}$  particles (0-2.5 µm) on Teflon. These are analyzed by five methods:

- gravimetric mass for PM<sub>25</sub>
- hybrid integrating plate/sphere method for optical absorption
- Proton Elastic Scattering Analysis (PESA) for hydrogen
- Proton Induced X-ray Emission (PIXE) for Na-Mn
- X-Ray Fluorescence (XRF) for Fe-Pb

<u>Module B</u>:  $PM_{2.5}$  particles (0-2.5 µm) on nylon. A denuder before the nylon filter removes nitric acid vapors. These are analyzed by ion chromatography (IC) for nitrate (NO<sub>3</sub><sup>-</sup>), chloride (CL<sup>-</sup>), sulfate (BSO<sub>4</sub>), and nitrite (NO<sub>2</sub><sup>-</sup>).

<u>Module C</u>: PM<sub>2.5</sub> particles (0-2.5  $\mu$ m) on quartz. These are analyzed for carbon using the Thermal Optical Reflectance (TOR) combustion method. A secondary filter at selected sites is used to determine artifact. These samples are baked and oxidized at a series of temperatures; the results are reported at 8 temperature steps.

<u>Module D</u>:  $PM_{10}$  particles (0-10 µm) on Teflon. All are measured for  $PM_{10}$  mass. Approximately 4% are analyzed by the other four methods listed for Module A.

Source: "Improve Particulate Monitoring Network Standard Operating Procedures," Air Quality Group, Crocker Nuclear Laboratory, University of California at Davis, http://vista.cira.colostate.edu/improve/Publications/

Equation for Estimating Ambient Light Extinction Coefficients" recommended consideration of several changes in the IMPROVE equation. Their recommended changes would modify the constants used for sulfates, nitrates, and organic carbon, and would add a term to account for the effect of sea salt. (See <a href="http://vista.cira.colostate.edu/IMPROVE/Publications/">http://vista.cira.colostate.edu/IMPROVE/Publications/</a> and select Gray Literature.) These modifications are currently under review. The Regional Planning Organizations developing plans to improve visibility at Class I areas are seeking to use the best available scientific information, including the most appropriate equation for calculating visibility impairment.

The IMPROVE monitoring network continues to generate important information on visibility and trends in the concentrations of particles that affect visibility. While there are uncertainties in the calculation of visibility impairment, and some changes in the equation may be made, the data provide a reasonable and consistent basis for measuring the results of efforts to achieve air quality improvement.

### Mid-Atlantic Regional Air Management Association Page E-4

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## Web Sites

#### General

EPA's AIRNow Web site: www.airnow.gov

EPA's General Pollution information Web site: www.epa.gov/air/urbanair/6poll.html

EPA's monitoring and emissions Web portal: www.epa.gov/air/data/geosel.html

#### Visibility

National Park Service IMPROVE site: http://vista.cira.colostate.edu/improve/

Introduction to Visibility, by W. C. Malm for the National Park Service:

www2.nature.nps.gov/ard/vis/intro\_to\_visibility.pdf

...and a newer version with animated figures:

vista.cira.colostate.edu/improve/Education/IntroToVisinstr.htm

Colorado State IMPROVE site: vista.cira.colostate.edu/improve/

EPA's visibility site: www.epa.gov/air/visibility

Pictures and summaries for Class I areas: www.epa.gov/air/visibility/monitor.html

#### ΡΜ

NARSTO's 1998 PM assessment: www.cgenv.com/Narsto/Finepart.html

#### Ozone

NARSTO's 2000 Ozone Assessment: www.cgenv.com/Narsto/assess.doc.html EPA's Ozone Web site (general information): www.epa.gov/air/urbanair/ozone/index.html

### Health

The Health Effects Institute: www.healtheffects.org EPA's Health effects site: www.epa.gov/airnow/health

### **Regional Organizations**

Mid-Atlantic Regional Air Management Association (MARAMA): www.marama.org Northeast States for Coordinated Air Use Management (NESCAUM): www.nescaum.org Ozone Transport Commission (OTC): www.otcair.org Mid-Atlantic Northeast Visibility Union (MANE-VU): www.mane-vu.org Visibility Improvement State & Tribal Association of the Southeast (VISTAS):www.vistas-sesarm.org Southeast States Air Resource Managers (SESARM): www.metro4-sesarm.org

## **Regional Experiments in the Mid-Atlantic**

Southern Appalachian Mountains Initiative (SAMI): http://www.epa.gov/ttn/gei/samiinfo.html

Southern Oxidants Study (SOS): www2.ncsu.edu/ncsu/CIL/southern\_oxidants

Pittsburgh Air Quality Study (PAQS): http://homer.cheme.cmu.edu

Baltimore PM supersite: www.chem.umd.edu/supersite

Maryland Aerosol Research and Characterization (MARCH-Atlantic)

www.atmos.umd.edu/~bruce/MARCH-Atl.html

Northeast - Oxidant and Particle Study (NE-OPS): lidar1.ee.psu.edu/narsto-neops



## What is MARAMA?

The Mid-Atlantic Regional Air Management Association is a voluntary, non-profit association of ten state and local air pollution control agencies.

MARAMA provides cost-effective approaches to regional collaboration by pooling resources to develop and analyze data, share ideas, and train staff to implement common requirements.

#### Mission

MARAMA's mission is to strengthen the skills and capabilities of member agencies and help them work together to prevent and reduce air pollution impacts in the Mid-Atlantic Region.

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