CHAPTER 1

INTRODUCTION

This report is the second in a series of periodic reports that describe the data collected by the Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring network. The objectives of this report are threefold:

(1) To describe the spatial and temporal variation of visibility, as measured by the light-extinction coefficient, and the chemical composition of the visibility-degrading aerosol[1] for three years of operation of the network: March 1992 through February 1995.

(2) To provide a first estimate of the apportionment of visibility impairment to the fundamental chemical species, such as sulfates, nitrates, organics and elemental carbon, and soil dust.

(3) To document the long-term trends (or lack of trends) of aerosol mass and its principal aerosol species.

1.1 Objectives of Visibility Monitoring

The primary objectives of IMPROVE are the following:

(1) To establish current background visibility levels in 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 toward the national visibility goal.

By measuring visibility routinely over a network and over a sufficiently long period of time, the first and third objectives of IMPROVE can be met. The monitoring also meets a portion of the second objective: the identification of the chemical composition of the visibility-degrading aerosol.

---

[1] An aerosol is a suspension of fine and coarse solid and liquid particles in air. Particles, especially fine particles less than 2.5 ìm, scatter light and degrade the visual information content of a scene (e.g., contrast, color, line, and texture). Fine particles consist of different chemical species either within the same particle (internally mixed) or in different particles (externally mixed). Significant chemical species found in particles include sulfates, nitrates, organics and elemental carbon, and soil dust. The sulfates, nitrates, and some hygroscopic organics absorb water from the atmosphere, thereby increasing significantly the light-scattering particle size and mass.

Each of these IMPROVE objectives are discussed in greater detail below.

Establish Current Visibility. This is necessary for two reasons. First, visibility levels monitored at a Class I area, when compared to surrounding area visibility or area estimates for natural levels, may be sufficient to indicate man-made impairment. Second, knowledge of existing visibility levels is required to model the anticipated visibility effects of proposed emission sources, because increments of pollution are more noticeable in clear conditions.

Establishment of present visibility levels requires monitoring that is appropriate for both surface and elevated layer impairment distributions. Optical monitoring systems, such as the transmissometer, are appropriate for surface haze monitoring, while scene monitoring with photography is the only practical way to routinely monitor elevated layers.

Visibility changes with time: diurnal, seasonal, and yearly variations all exist. Though five to eight years of data would be considered ideal for establishing present seasonal and annual averaged conditions, a minimum of one year is a reasonable compromise if that year is typical from a meteorological and source activity point of view.

Source Identification. Identification of chemical species and emission sources responsible for man-made visibility impairment is necessary to protect Class I areas, as called for by Congress. Monitoring is the principal means of gathering information needed to identify the contribution to impairment by emission sources. Even to distinguish man-made from natural impairment, which is fundamental to the national visibility goals, requires information derived from monitoring data.

Aerosol and scene monitoring are the primary sources of emission source identification information. Photography of a plume emanating from its source and impacting a Class I area is sufficient to indicate impairment. Furthermore, photographs can be evaluated to indicate the density or intensity of the visible plume. Unfortunately, most visibility impairment does not lend itself to this simple type of source attribution. Often sources are not visible from any line of sight that includes the Class I area, or their plumes disperse to a haze layer before reaching it.

Visibility impacts are often caused by aerosols formed over time from gaseous pollutants that are emitted without visibly noticeable plumes. Characteristics of the aerosol that are responsible for the haze provide valuable information that can be used in conjunction with other information to help identify the responsible emission sources. It is possible to statistically relate measured optical data to corresponding aerosol composition data to estimate the relative importance of the various major components of the aerosol. The result, known as an extinction budget, should narrow the list of possible sources responsible for large impacts. For example, if organic carbon is shown to be responsible for 75% of the extinction coefficient, the major sources responsible must emit organic carbon or precursor gases that form organic aerosols.

Another related approach for source identification using aerosol data is known as receptor modeling. Instead of using only the major aerosol components that are directly responsible for the impairment, receptor models use relative concentrations of trace components that can more specifically identify the influence of individual sources (or source types).

Long-Term Trends. With the establishment of a long-term goal of no man-made visibility impairment in protected areas, Congress imposed the responsibility to show progress towards meeting that goal. Trends monitoring is an ideal approach for tracking the visibility conditions of Class I areas.

Optical and scene monitoring conducted to establish present visibility levels (described above), if conducted in perpetuity, can provide the data required to determine long-term visibility trends. Alternatively, tracking levels of ambient aerosols and the key aerosol species will reveal the effectiveness of emission control programs. In either case, in order to determine the effectiveness of individual concurrent emission reduction programs, it is necessary to conduct aerosol monitoring to support extinction budget analysis as described above.

1.2 Overview of the IMPROVE Monitoring Network

The design of the IMPROVE monitoring network was resource and funding limited so that it was not practical to place monitoring stations at all 156 mandatory Class I areas where visibility is an important attribute. Instead, the IMPROVE Steering Committee selected a set of sites that were representative of the Class I areas. For the first IMPROVE report, published in the spring of 1993, data for 36 sites was summarized. In the intervening time the IMPROVE network has evolved; two sites were dropped, some sites were downgraded to the measurement of a subset of the variables measured at a fully complemented site, and other sites have been added. There are currently a total of 58 IMPROVE sites with various configurations of optical and aerosol monitoring equipment. For this report, only the 43 IMPROVE sites that are fully configured as aerosol monitoring sites with data for the three-year period, March 1992 through February 1995, are utilized. However, only 26 of the sites have optical monitoring equipment (e.g., transmissometers or nephelometers to measure visibility-related parameters).

View monitoring at all aerosol monitoring sites was routinely done for the first five years of the IMPROVE program. View monitoring is used to document the range of visibility conditions for a particular scene. Due to resource considerations, five years of scene monitoring was judged to adequately document the range of visibility. Now, view monitoring is only carried out at selected sites with less than five years of data. View monitoring is accomplished by automated 35-mm camera systems. These systems provide three color slides per day to document the appearance of a selected scene at each of the IMPROVE sites. The slides are used to interpret measurements, to communicate perceived visual conditions, and, if needed, to derive quantitative estimates of light extinction by microdensitometry.

Figure 1.1 shows a map of the United States indicating the locations of the 43 monitoring sites analyzed in this report. On the basis of regional similarities, the sites were grouped into 21 regions, listed in Table 1.1.

Figure 1.1 The 42 IMPROVE sites out of 43 included in the report. Denali National Park in Alaska is not shown.

Table 1.1 IMPROVE and NPS/IMPROVE protocol sites according to region.

Alaska (AKA) •Denali NP (DENA) **Appalachian Mountains (APP)** •Great Smoky Mountains NP (GRSM) •Shenandoah NP (SHEN) •Dolly Sods WA (DOSO) **Boundary Waters (BWA)** •Boundary Waters Canoe Area (BOWA) **Cascade Mountains (CAS)** •Mount Rainier NP (MORA) **Central Rocky Mountains (CRK)** •Bridger WA (BRID) •Great Sand Dunes NM (GRSA) •Rocky Mountain NP (ROMO) •Weminuche WA (WEMI) •Yellowstone NP (YELL) **Coastal Mountains (CST)** •Pinnacles NM (PINN) •Point Reyes NS (PORE) •Redwood NP (REDW) **Colorado Plateau (CPL)** •Bandelier NM (BAND) •Bryce Canyon NP (BRCA) •Canyonlands NP (CANY) •Grand Canyon NP (GRCA) •Mesa Verde NP (MEVE) •Petrified Forest NP (PEFO) **Florida (FLA)** •Chassahowitzka NWR (CHAS) •Okefenokee NWR (OKEF) **Great Basin (GBA)** •Jarbidge WA (JARB) •Great Basin NP (GRBA)	**Lake Tahoe (LTA)** •D.L. Bliss State Park (BLISS) •South Lake Tahoe (SOLA) **Mid Atlantic (MAT)** •Edmond B. Forsythe NWR (EBFO) **Mid South (MDS)** •Upper Buffalo WA (UPBU) •Sipsey WA (SIPS) •Mammoth Cave NP (MACA) **Northeast (NEA)** •Acadia NP (ACAD) •Lye Brook WA (LYBR) **Northern Great Plains (NGP)** •Badlands NM (BADL) **Northern Rocky Mountains (NRK)** •Glacier NP (GLAC) **Sierra Nevada (SRA)** •Yosemite NP (YOSE) **Sierra-Humboldt (SRH)** •Crater Lake NP (CRLA) •Lassen Volcanoes NP (LAVO) **Sonoran Desert (SON)** •Chiricahua NM (CHIR) •Tonto NM (TONT) **Southern California (SCA)** •San Gorgonio WA (SAGO) **Washington, D.C. (WDC)** •Washington, D.C. (WASH) **West Texas (WTX)** •Big Bend NP (BIBE) •Guadalupe Mountains NM (GUMO)

NP = National Park

NM = National Monument

WA = Wilderness Area

NWR = National Wildlife Refuge

NS = National Seashore

The routine IMPROVE monitoring approach now involves aerosol, and optical monitoring. Aerosol monitoring measures the mass concentration (in micrograms per cubic meter, $\mu g/m^3$) and the chemical composition of the particles. Optical monitoring measures the light-extinction coefficient (b_{ext}) using a transmissometer or the light-scattering coefficient (b_{scat}) using a nephelometer.

Aerosol monitoring in the IMPROVE network is accomplished by a combination of particle sampling and sample analysis. The sampler employed was designed specifically for the program. It collects four simultaneous samples: one PM_{10} sample (particles less than 10 micrometers, μm, in diameter) on a Teflon filter and three $PM_{2.5}$ samples (particles less than 2.5 μm in diameter) on Teflon, nylon, and quartz filters. Each of the four samples is collected by a separate subsystem (or module) including everything from the inlet to the pump with only the support structure and controller/timer in common. The particle size segregation for the PM_{10} module is accomplished by a wind insensitive inlet with a 10 μm cutoff, while the $PM_{2.5}$ segregation is produced by passing the sampled air through a cyclone separator. Constant sample flow is maintained by a critical orifice in each module. The IMPROVE sampler is programmed to automatically collect two 24-hour duration samples per week.

Only mass analyses are conducted on the PM_{10} samples. The $PM_{2.5}$ samples are analyzed for mass, elements, ions (including particulate nitrate sampled through a denuder), organics and elemental carbon, and optical absorption.

At many sites in the IMPROVE network, long-path transmissometers are employed for optical measurements. These instruments measure the amount of light transmitted through the atmosphere over a known distance, usually 0.5 to 10 kilometers, between the light source (transmitter) and the light-monitoring component (receiver). Transmission measurements are converted electronically to the path-averaged, light-extinction coefficient (b_{ext}). At other sites nephelometers are used that measure the light-scattering coefficient (b_{scat}) from an enclosed volume of air.

In addition to the aerosol and optical monitoring, those sites that have optical monitoring have temperature and relative humidity instruments. Liquid water is a component of the hygroscopic sulfate, nitrate, and possibly organic carbon fractions, but it is not quantified by any of the filter sampling techniques. Relative humidity measurements are used to estimate the amount of liquid water associated with these particles.

1.3 Background Regarding Visibility Impairment and Aerosols

Visibility is usually characterized either by visual range (the greatest distance that a large dark object can be seen) or by the light-extinction coefficient (the attenuation of light per unit distance due to scattering and absorption by gases and particles in the atmosphere). Under certain assumed conditions these two measures of visibility can be shown to be inversely related to each other. Visual range functions well as an aid in military operations and transportation safety. Issues of concern for such use include: the minimum distance required to land an aircraft, the distance to the first appearance of a military target or an enemy aircraft or ship, and safe maneuvering distances under impaired visibility conditions. Because of the use of familiar distance units, the simple definition, and the ability of any sighted person to characterize visual conditions with this parameter without instruments, visual range is likely to remain the most popular measure of atmospheric visibility.

Extinction coefficient is used most by scientists concerned with the causes of reduced visibility. There are direct relationships between the concentrations of the atmospheric constituents and their contribution to the extinction coefficient. Apportioning the extinction coefficient to atmospheric constituents provides a method to estimate the change in visibility caused by a change in constituent concentrations. This methodology, known as extinction budget analysis, is important for assessing the visibility consequences of proposed pollutant emission sources, or for determining the extent of pollution control required to meet a desired visibility condition. Interest in the causes of visibility impairment is expected to continue and the extinction coefficient will remain important in visibility research and assessment.

Neither visual range nor extinction coefficient is linear with humanly perceived changes caused by uniform haze (i.e., as opposed to elevated haze layers and plumes). For example, a given change in visual range or extinction coefficient can result in a scene change that is either unnoticeably small or very apparent depending on the baseline visibility conditions. Presentation of visibility measurement data or model results in terms of visual range or extinction coefficient can lead to misinterpretation by those who are not aware of the nonlinear relationship.

To rigorously determine the perceived visual effect of a change in extinction coefficient requires the use of radiative transfer modeling to determine the changes in light from the field of view arriving at the observer location, followed by the use of psychophysical modeling to determine the response to the light by the eye-brain system. Results are dependent not only on the baseline and changes to atmospheric optical conditions, but also on the characteristics of the scene and its lighting. The complexity of employing such a procedure and the dependence of the results on non-atmospheric factors prevent its widespread use to characterize perceived visibility changes resulting from changes in air quality.

Parametric analysis methods have been used to suggest that a constant fractional change in extinction coefficient or visual range produces a similar perceptual change for a scene regardless of baseline conditions. Simplifying assumptions eliminate the need to consider the visibility effects of scene and lighting conditions. Using the relationship of a constant fractional change in extinction coefficient to perceived visual change, a new visibility index called deciview (*dv*) is defined as:

$$dv = 10 \ln(b_{ext}/0.01 \text{ km}^{-1}) \tag{1.1}$$

where extinction coefficient is expressed in km^{-1} [Pitchford and Malm, 1994]. A one *dv* change is about a 10% change in extinction coefficient, which is a small but perceptible scenic change under many circumstances. The deciview scale is near zero for pristine atmosphere ($dv = 0$ for Rayleigh condition at about 1.8 km elevation) and increases as visibility is degraded. Like the decibel scale for sound, equal changes in deciview are equally perceptible.

1.3.1 Relationship Between Visibility and Aerosol Concentrations

Visibility is degraded by light scattered into and out of the line of sight and by light absorbed along the line of sight. Light extinction (the sum of light scattering and absorption) is usually quantified using the light-extinction coefficient (b_{ext}), which may be thought of as the atmospheric concentration of light-extinction, cross-sectional area. Light extinction has units of 1/length.

The light-extinction coefficient (b_{ext}) is the sum of the light-scattering coefficient (b_{scat}) and the light-absorption coefficient (b_{abs}). Light scattering results from the natural Rayleigh scatter (b_{Ray}) from air molecules (which causes the blue sky) and the scattering caused by suspended particles in the atmosphere (aerosols). Particle scatter (b_{sp}) can be caused by natural aerosol (e.g., wind-blown dust and fog) or by man-made aerosols (e.g., sulfates, nitrates, carbonaceous aerosols, and other fine and coarse particles). Light absorption results from gases (b_{ag}) and particles (b_{ap}). Nitrogen dioxide (NO_2) is the only major light-absorbing gas in the lower atmosphere. Its strong wavelength-dependent scatter causes yellow-brown discoloration if present in sufficient quantities. Soot (elemental carbon) is thought to be the dominant light-absorbing particle in the atmosphere. Thus, the total light extinction is the sum of its components:

$$b_{ext} = b_{scat} + b_{abs} = b_{Ray} + b_{sp} + b_{ag} + b_{ap} \quad (1.2)$$

The particle light-scattering coefficient (b_{sp}), in turn, is composed of the contributions from individual species. Fine particles are much more efficient at light scattering (per unit mass) than larger particles. Thus, it makes sense to divide the contributions to b_{sp} into the contributions from various species of fine and coarse particles. In this study, we specifically evaluated the following components of fine particles (those with diameters less than 2.5 ìm): sulfate (SO), nitrate (NO), organic carbon, elemental carbon (soot), and soil. In addition to these chemical species, the effect of water associated with sulfates, nitrates, and some organics need to be considered in the overall assessment of light extinction. Finally, the coarse fraction of PM_{10} (those with diameters between 2.5 and 10 ìm) are separately considered.

The light-extinction coefficient can be written with a number of assumptions, as the sum of the products of the concentrations of individual species and their respective light-extinction efficiencies:

$$b_{ext} = b_{Ray} + \sum \beta_i C_i \quad (1.3)$$

where $\hat{a}_i$ is the light-extinction efficiency (m^2/g) of species *i*, C_i is the atmospheric concentration of species *i* (ìg/m^3), and the summation is over all light-interacting species (i.e., sulfates, nitrates, organic carbon, elemental carbon, other fine particles, coarse particles, and NO_2). The above units, when multiplied, yield units for b_{ext} of 10^{-6} m^{-1} or $(10^6\ m)^{-1}$, or as we prefer to label it here, inverse megameters (Mm^{-1}).

1.3.2 Effect of Relative Humidity on Light Scattering

Sulfates, nitrates, and some organics can combine with water in the vapor phase to form solutions. Thus, at some humidity conditions, considerable water may be associated with these species. Although the overall light-scattering efficiency is on the order of 3 m^2/g for these solutions, if the light-scattering efficiency is stated in terms of the mass of dry sulfate ($SO_4^{=}$), the efficiency must be larger than 3 m^2/g to account for the additional mass (and volume) of the associated water. In addition, the associated cations (H^+ and NH_4^+) must also be included. As a result, light-scattering efficiency per unit of dry sulfate can be much larger than 3 m^2/g. This hygroscopic effect can be described by the following equation:

$$\beta_{wet} = k f_{RH} \beta_{dry} \tag{1.4}$$

where $\hat{a}_{wet}$ is the light extinction efficiency of the wet sulfate, nitrate, and/or organic solution, *k* is the ratio in molecular weight of the neutralized species (e.g., ammonium sulfate or ammonium nitrate) to the anion (sulfate, nitrate), f_{RH} is a factor that accounts for the liquid water associated with the aerosol at the given relative humidity (*RH*), and $\hat{a}_{dry}$ is the light-extinction efficiency of the dry particle.

1.4 Organization of the Report

This report is divided into six chapters. Chapter 2 summarizes the optical and aerosol measurement techniques and details the assumptions for determining the chemical composition of the aerosol species. The spatial and seasonal patterns of aerosol mass and chemical composition are summarized in Chapter 3. Chapter 4 discusses the theory of light extinction in detail and specifies the assumptions used to reconstruct light extinction from aerosol measurements. Using reconstructed light extinction, Chapter 5 discusses the spatial and seasonal patterns of reconstructed light extinction. Chapter 6 discusses the long-term temporal trends of two key aerosol species, sulfur and light-absorbing carbon.

1.5 References

Pitchford, M.L., and Malm, W.C. Development and applications of a standard visual index, *Atmospheric Environment*, **28**(5):1049-1054, 1994.