OVERVIEW AND SUMMARY

This report describes data for the three year period, March 1992 through February 1995, of the Interagency Monitoring of Protected Visual Environments (IMPROVE) measurement program. IMPROVE is a cooperative visibility monitoring effort between the United States Environmental Protection Agency, (EPA) federal land management agencies, and state air agencies.

The objectives of IMPROVE are:

(1) To establish current background visibility in Class I areas;

(2) To identify chemical species and emission sources responsible for existing man-made visibility impairment; and

(3) To document long-term trends.

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, 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). Figure S.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 S.1.

S.1 Optical and Aerosol Data

Aerosol monitoring in the IMPROVE network is accomplished by a combination of particle sampling and sample analysis. The sampler was designed specifically for IMPROVE. It collects four simultaneous samples: one PM$_{10}$ sample (particles less than 10 μm in diameter) on a Teflon filter and three PM$_{2.5}$ samples on Teflon, nylon, and quartz filters. The IMPROVE sampler is programmed to collect two 24-hour duration samples per week (i.e., 26 per season, 104 per year). The PM$_{10}$ filter is used to determine total PM$_{10}$ mass. The PM$_{2.5}$ Teflon filter is used to measure

Figure S.1 The 42 IMPROVE sites out of 43 included in the report. Denali National Park in Alaska is not shown.

Table S.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

total fine aerosol mass, individual chemical species using Proton Induced X-ray Emission (PIXE) and Proton Elastic Scattering Analysis (PESA), and light-absorption coefficient using the Laser Integrating Plate Method (LIPM). The nylon filter is used to measure nitrate and sulfate aerosol concentrations with Ion Chromatography (IC). Finally, the quartz filters are analyzed for organic and elemental carbon using the Thermal Optical Reflectance (TOR) method.

Transmissometers are employed to measure the light-extinction coefficient at 15 of the IMPROVE sites, and 11 sites have integrating nephelometers, which measure the scattering coefficient. Transmissometers measure the light transmitted through the atmosphere over a distance of one to fifteen kilometers. The light transmitted between the light source (transmitter) and the light monitoring component (receiver) is converted to the path-averaged light extinction coefficient (b_{ext}), which is the sum of scattering (b_{scat}) and absorption (b_{abs}). Integrating nephelometers measure the scattering of light over a defined band of visible wavelengths from an enclosed volume of air and represents a point measurement of scattering. By combining the absorption coefficient from the particle sampler with the scattering coefficient from the nephelometer the extinction coefficient can be reconstructed at the 11 nephelometer sites. Relative humidity was measured continuously at the transmissometer and nephelometer sites.

S.2 Spatial and Seasonal Distribution of Aerosol Concentration and Chemical Composition

Fine aerosol concentrations are highest in the eastern United States (in the Appalachian Mountains, Mid South, Mid Atlantic and in Washington, D.C.). Concentrations are also relatively high in southern California. The lowest concentrations occur in the Great Basin in Nevada, the Colorado Plateau in the four corners states, Wyoming, and in Alaska.

The largest single component of the fine aerosol in the East is sulfate, while in the Pacific Northwest it is organics, and in southern California it is nitrate. In general, the largest mass fractions of the fine aerosol are sulfate and organics. Of the 21 regions in the IMPROVE network, organic carbon is the largest single component in 10 regions (Alaska, Cascades, Colorado Plateau, Central Rockies, Pacific Coastal Mountains, Great Basin, Northern Rockies, Sierra Nevada, Sierra-Humboldt, and Lake Tahoe). Sulfate is the largest single component of fine aerosol in seven regions, primarily in the East (Appalachian Mountains, Florida, Northeast, Mid South, Mid Atlantic, Washington D.C., and West Texas). The contributions of organic carbon and sulfate are approximately equal in three regions (Boundary Waters, Sonoran Desert, and Northern Great Plains). Soil is the next largest contributor, followed by nitrate and light-absorbing carbon. Nitrate is the largest component of fine aerosol in southern California only.

With few exceptions, average fine mass concentrations, as well as the sulfate, organic carbon, and light-absorbing carbon components of fine mass, are highest in summer. Soil concentrations are highest in spring or summer. Nitrate concentrations are generally highest in winter or spring.

S.3 Light Extinction and its Relationship to Aerosols

Two unique data sets were used to explore the relationship between optical extinction, absorption, scattering, and various aerosol species. The Measurement of Haze and Visual Effects (MOHAVE) special study provided, at one monitoring site, independent optical measurements of b_{ext}, b_{scat}, and b_{abs}, and the various aerosol species. This data set provided for a variety of ways for exploring absorption and scattering efficiencies. The second data set, IMPROVE, provides for the first time, an opportunity to explore the relationship between measured extinction (as opposed to scattering) and aerosol species over the whole western United States. These are the first data sets where extinction was directly measured as opposed to estimated by summing b_{scat} and absorption as derived from "elemental" carbon measurements.

The most surprising outcome of the analysis relates to estimates of absorption. It has been known for some time that, at remote nonurban locations, b_{abs} as derived from the LIPM, was about twice the absorption as estimated from elemental carbon derived from thermal optical reflectance techniques (b_{lac}). Although there may be alternative interpretations, the most straightforward explanation of the relationships between b_{ext}, b_{scat}, b_{abs}, and b_{lac} is that b_{abs} is a more accurate predictor of absorption than b_{lac}. If this is the case, then absorption is on average at about 30% of the non-Rayleigh extinction budget, as opposed to about 10% as conventional wisdom would have dictated.

An examination of the hygroscopic nature of organics lead to the conclusion that organics are not hygroscopic to weakly hygroscopic. However, it is estimated that they have about a 4.0 m^2/g rather than a 3.0 m^2/g mass scattering efficiency.

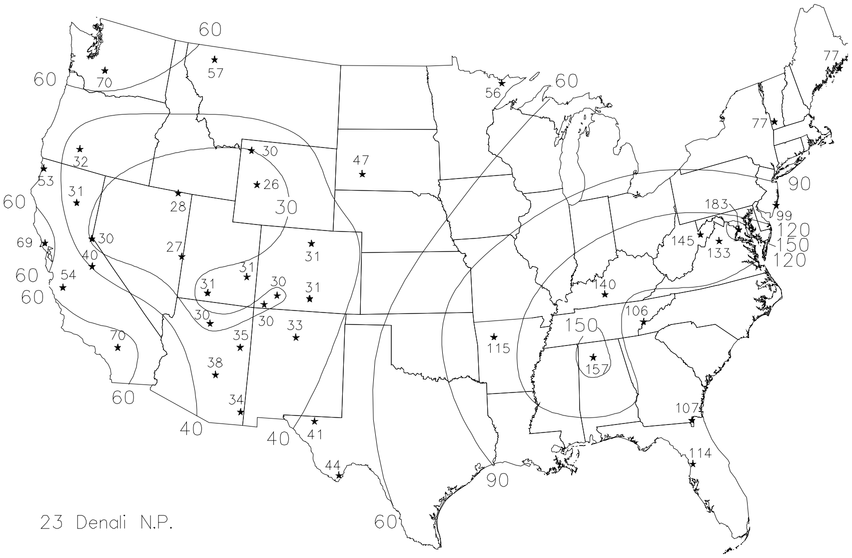
Another result of the b_{abs} analysis is that a significant amount of b_{abs} is linked to light absorption by soil. Of fine mass absorption, 15-20% is soil related, while elemental and organic carbon contribute about equal amounts of absorption.

S.4 Spatial and Seasonal Distribution of Reconstructed Light Extinction and Species Contributions

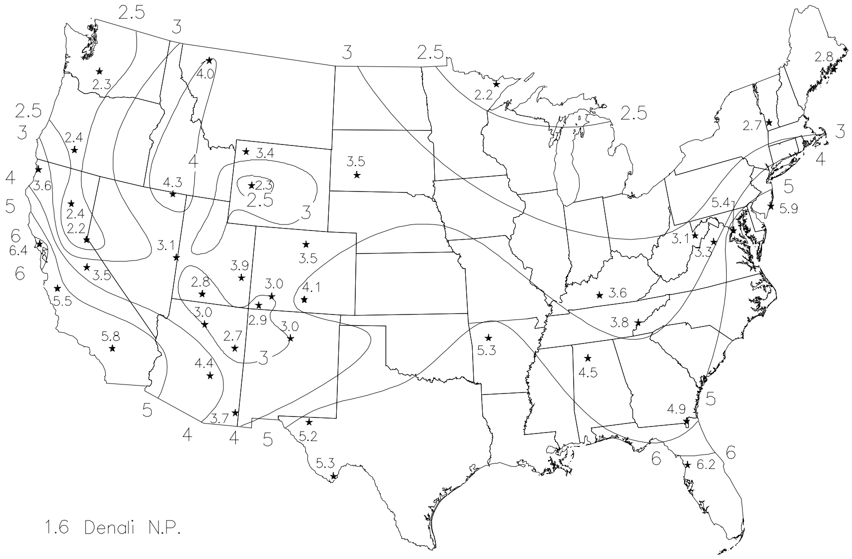
The light-extinction coefficient (b_{ext}) is calculated from the measured aerosol species' concentrations by multiplying the concentration of a given species by its light-extinction efficiency, and summing over all species. Since sulfates and nitrates were assumed to be hygroscopic, their light-extinction efficiencies increase with relative humidity; therefore, extinction efficiencies for soluble species must be adjusted according to the seasonal and annual average relative humidity at each site.

Figures S.2a through S.2f summarize the spatial distribution of reconstructed light extinction (in Mm^{-1}), as well as the contributions to the total extinction from coarse particles and fine soil, sulfate, organics, nitrate, and light-absorbing carbon, averaged over three years of IMPROVE (March 1992 through February 1995).

Reconstructed light extinction varies throughout the United States in a way analogous to fine aerosol concentrations. The greatest light extinction occurs in the eastern United States and in

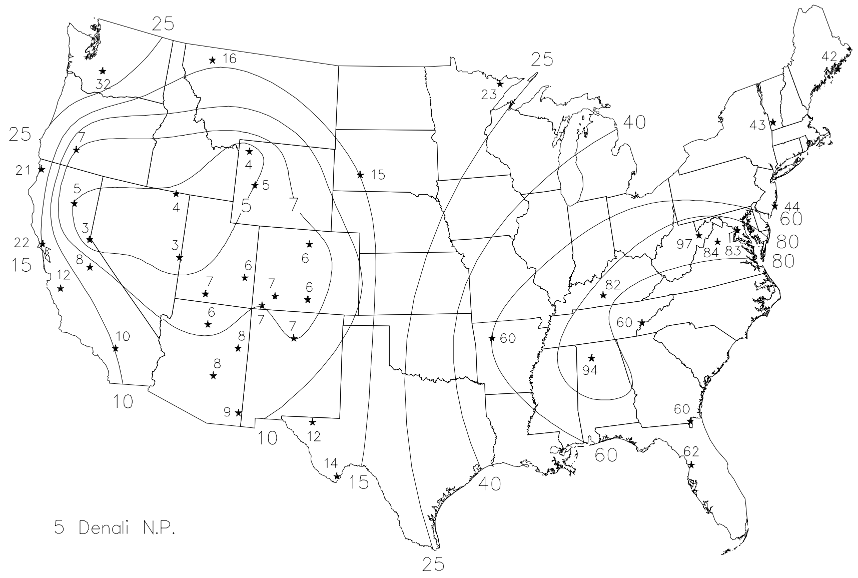


S.2(a) Total light extinction b_{ext} (Mm^{-1})



S.2(b) Extinction due to coarse particles and fine soil (Mm^{-1})

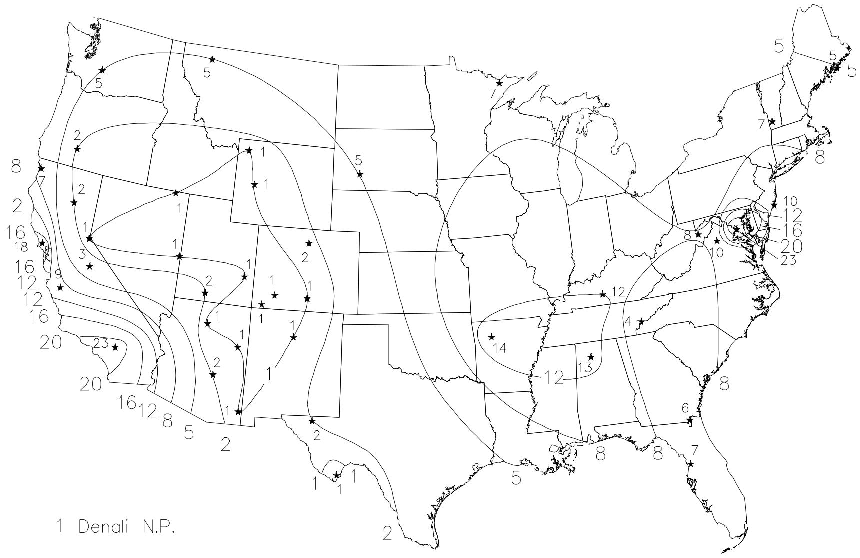
Figure S.2 Average reconstructed light extinction coefficient (Mm^{-1}) calculated from the aerosol concentrations measured during three years of IMPROVE, March 1992 through February 1995. The various panels of this figure show total extinction (including Rayleigh scattering due to air) and the contributions due to the various aerosol components: coarse particles and fine soil, sulfate, organic carbon, nitrate, and absorption.



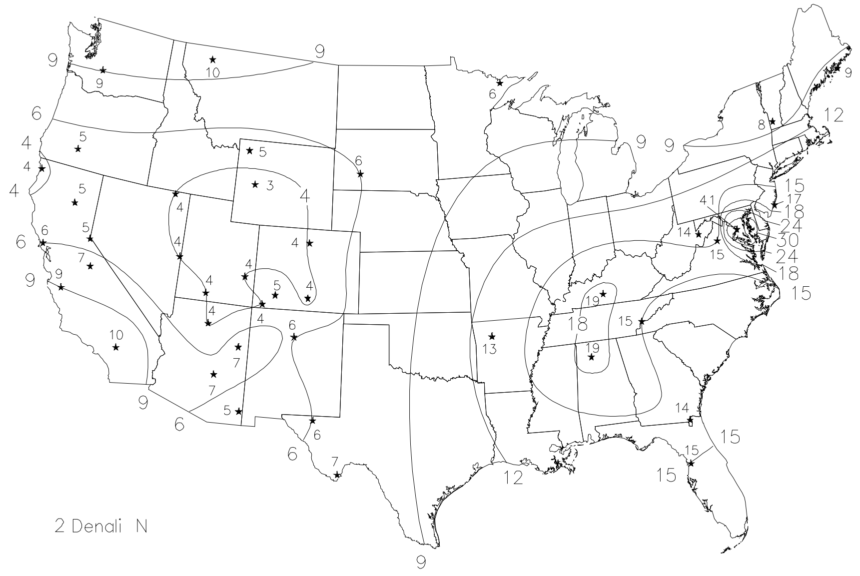
S.2(c) Extinction due to sulfate (Mm^{-1})

S.2(d) Extinction due to organic carbon (Mm^{-1})

Figure S.2 Continued.



S.2(e) Extinction due to nitrate (Mm^{-1})



S.2(f) Extinction due to light absorption (Mm^{-1})

Figure S.2 Continued.

southern California, while the least light extinction occurs in the nonurban west (e.g., the Great Basin of Nevada and the Colorado Plateau) and in Alaska. However, since relative humidity (and hence the light-scattering efficiency of sulfate and nitrate) is higher in the East than in the West, the difference between eastern and western light extinction is even more pronounced than the difference in aerosol concentrations.

Fine aerosols are the most effective in scattered light and are the major contributors to light extinction. In most cases, the sulfate component of fine aerosol is the largest single contributor to light extinction. This is because sulfate, being hygroscopic, generally has a higher light extinction efficiency than other species due to associated liquid water. This is especially true in the eastern United States, where relative humidity is high. In the Appalachian Mountains (Shenandoah and Great Smoky Mountains), sulfate accounts for 2/3 of the total aerosol light extinction throughout the year, and 3/4 of the total in summer. Sulfate is the largest single contributor to light extinction in 14 of the 21 regions, and is comparable with organics as the most significant contributor in three additional regions (Northern Rockies, Central Rockies, and Sierra-Humboldt). Organic carbon is the largest single contributor to light extinction in three of the 21 regions (Great Basin, Sierra Nevada, and Lake Tahoe) and is a major contributor in the two previously mentioned regions. Smaller contributions come from wind-blown dust (coarse particles and fine soil) and nitrate. Nitrate is the single largest contributor to light extinction only in southern California.

Generally, reconstructed light extinction is highest in summer and lowest in winter; however, there are many exceptions to this general rule. Higher extinction occurs in summer generally because of elevated sulfate and carbonaceous aerosol concentrations. Also, higher average RH's occur in the East during the summer, which increases extinction.

S.5 Spatial and Seasonal Trends in Visibility in the United States

To show the effect on visibility of aerosol extinction, the deciview (*dv*) scale is applied to the total (Rayleigh included) reconstructed aerosol extinction (see Chapter 1). By utilizing the *dv* scale, the effect of light extinction on visibility is portrayed in a way that is approximately linear with respect to perceived visual air quality.

Because higher extinction coefficients lead to higher *dv* numbers, the geographic trends in visibility follow the trends in reconstructed extinction. Pristine or Rayleigh conditions correspond to a *dv* of zero.

Figure S.3 shows isopleths of deciviews averaged over three years of IMPROVE, March 1992 through February 1995. The smallest *dv* or best visibility is reported at Denali NP with 8 *dv*. A broad region, which includes the Great Basin, most of the Colorado Plateau, and portions of the Central Rockies, has visibility impairment of less than 11 *dv*. Moving in any direction from this region generally results in increasing *dv*. West of the Sierra Range and including southern California one finds *dv* values in excess of 15, with a maximum value of 19 *dv* at Point Reyes and San Gorgonio. The northwest United States and all of the eastern half of the United States have an excess of 15 *dv* of impaired visibility. The region east of the Mississippi and south of the Great Lakes has impairment in excess of 20 *dv*, with the Appalachian, Mid South and Florida regions exceeding 24 *dv*. The highest annual *dv* is reported in Washington D.C. at 29 *dv*, followed by Sipsey Wilderness at 28 *dv*.

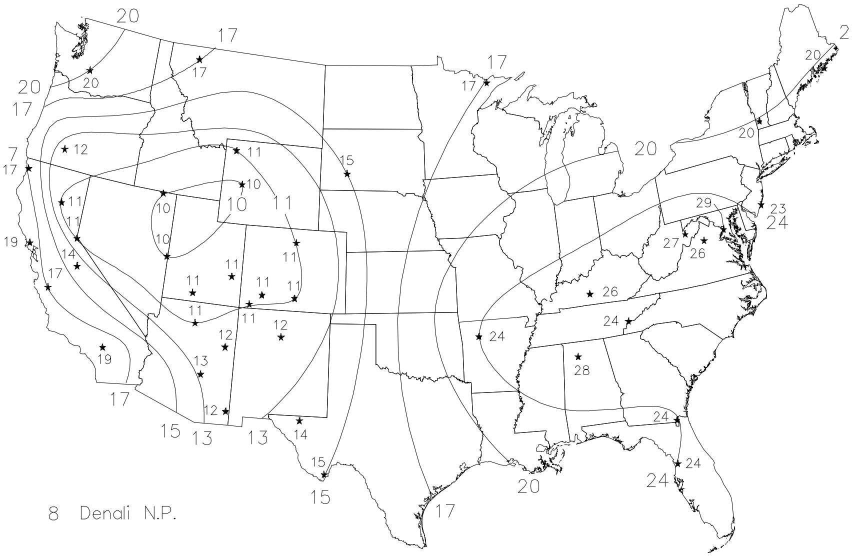


Figure S.3 Average visibility impairment in deciviews calculated from total (Rayleigh included) reconstructed light extinction for three years of IMPROVE, March 1992 through February 1995.

The general spatial trend noted above for the annual average *dv* generally holds true for each season's average *dv* as well. Specifically, the least impairment occurs in all or part of the Great Basin, Colorado Plateau, and Central Rockies, with gradients of increasing *dv* in any direction. The best visibility occurs during the winter and the worst in the summer. Visibility impairment in the spring and autumn are comparable.

S.6 Temporal Trends and Interrelationships of Aerosol Concentrations

The IMPROVE aerosol monitoring network, established in March 1988, initially consisted of 36 sites instrumented with aerosol sampling modules A through D. Many of the IMPROVE sites are successors to sites where aerosol monitoring with stacked filter units (SFU) was carried out as early as 1979. The IMPROVE sites that can be paired with antecedent SFU sites have an almost unbroken record of fine mass and sulfur from as early as 1979, and b_{abs} from 1983. Table S.2 lists the sites and time periods that IMPROVE or SFU samplers were operated. These data provide an excellent opportunity to look for evidence of temporal trends in aerosol concentrations. Two distinct temporal trends are considered here: seasonal, and long-term trends of statistical measures such as maxima, minima, percentiles, and standard deviations.

Table S.2 Sites and time periods for IMPROVE and SFU.

Acronym	Full Name	SFU Start	SFU End	IMPROVE Start	IMPROVE End
ACAD	Acadia NP	9/21/85	11/28/87	3/01/88	Present
ARCH	Arches NP	9/28/79	11/28/87	3/01/88	5/92
BAND	Bandelier NM	10/02/82	2/09/85	3/01/88	Present
BIBE	Big Bend NP	7/27/82	11/28/87	3/01/88	Present
BRCA	Bryce Canyon NP	9/21/79	12/02/87	3/01/88	Present
BRLA	Brooklyn Lake	3/01/91	7/31/93	7/31/93	Present
CANY	Canyonlands NP	9/21/79	11/28/87	3/01/88	Present
CHIR	Chiricahua NM	6/8/82	5/31/86	3/01/88	Present
CRLA	Crater Lake NP	10/12/82	11/28/87	3/01/88	Present
CRMO	Craters of the Moon	7/17/82	3/29/86	5/12/92	Present
DENA	Denali NP &	9/10/86	11/25/87	3/01/88	Present
DEVA	Death Valley NP	6/01/82	3/29/86	10/18/93	Present
GLAC	Glacier NP	9/28/82	12/5/87	3/01/88	Present
GICL	Gila NF	10/1/79	8/31/81	3/28/94	Present
GRBA	Great Basin NP	10/12/82	3/29/86	5/00/88	Present
GRCA	Grand Canyon NP	8/03/79	11/28/87	3/01/88	Present
GRSA	Great Sand Dunes	9/15/80	8/31/81	5/04/88	Present
GRSM	Great Smoky Mtns	1/31/84	11/28/87	3/01/88	Present
GUMO	Guadalupe Mtns NP	2/19/83	12/02/87	3/01/88	Present
LAVO	Lassen Volcanic NP	6/29/82	5/29/84	3/01/88	Present
MEVE	Mesa Verde NP	10/30/82	12/05/87	3/01/88	Present
MORA	Mount Rainier NP	7/23/83	12/16/87	3/01/88	Present
PEFO	Petrified Forest NP	7/30/79	11/25/87	3/01/88	Present
ROMO	Rocky Mountain NP	9/21/79	12/02/87	9/15/90	Present
SAGU	Saguaro NM	7/2/85	8/31/88	3/1/88	Present
SALM	Salmon NF	9/01/90	11/13/93	11/09/93	Present
SHEN	Shenandoah NP	7/13/82	11/28/87	3/01/88	Present
TONT	Tonto NM	8/3/79	11/29/83	3/01/88	Present
VOYA	Voyageurs NP	7/13/85	Present	3/01/88	Present
YELL	Yellowstone NP	9/29/79	12/05/87	3/01/88	Present
YOSE	Yosemite NP	9/25/82	10/28/87	3/01/88	Present

NP = National Park NM = National Monument NF = National Forest

A hallmark of sites impacted by sulfate pollution is a distinct seasonal trend of sulfate concentrations manifested by high concentrations during the summer and lowest during the winter. Sulfate seasonality is attributed to many factors with seasonal changes in meteorology and photochemistry being the most influential. Sites that demonstrate the most sulfate seasonality are in the East and southern California, while sites in the intermountain west have little or no seasonality. Absorption also demonstrates a clear seasonal trend at many sites and tends to be highest during the summer and early autumn. The seasonality of absorption, unlike sulfate seasonality, is driven by seasonal changes of emissions. In the West, where the absorption seasonality is strongest, controlled burning and wildfires have a strong influence, while in the East the seasonality is less pronounced.

Demonstrated long-term trends fall into three categories: increases, decreases, and variable. Sites that demonstrate decreases are at Crater Lake and Rocky Mountain National Parks, where absorption dropped dramatically, and at Guadalupe Mountains National Park where sulfur is decreasing in the autumn. A clear demonstration of decreased sulfur concentrations as a result of emission reductions is in the desert southwest at Chiricahua National Monument. Two sites where increases have been observed are at Grand Canyon National Park in the autumn, where the 25th percentile of sulfur concentrations have increased steadily since 1980, and at Great Smoky Mountains National Park, where autumn concentrations of sulfur and absorption have increased. Other sites that demonstrate little or variable changes in sulfur concentrations are at Bryce Canyon, Rocky Mountain, and Crater Lake National Parks. Variable or little change in absorption was noted at Grand Canyon in the winter and Chiricahua in the summer.

The most notable observation from a national perspective is the lack of a clear uniform trend of sulfur concentration or absorption. There are local success stories related to emission controls, and there are failures most likely associated with increased local emissions or long-range transport. The bulk of the sites show little or variable trends in the long run.

The matrix scatter plots demonstrate correlations ranging between slight to strong between gravimetric fine mass, b_{abs}, and sulfur. Some of the strongest correlations are between fine mass and b_{abs}, even though light-absorbing material is a small fraction of fine mass suggesting an internal mixture of carbon with the primary constituents of the fine mass. The exceptions to this are sites in the eastern United States where sulfur is a large fraction of the fine mass; here sulfur shows strong correlations with fine mass indicative of strong sources. Weak correlations are usually manifested by 'fan shaped' scatters, some with hard edges, which suggest multiple sources with variable ratios of b_{abs} or sulfur.

S.7 Recommended Future Research

There are a number of uncertainties raised by the work described in this report that deserve additional study.

Organic Aerosol Measurement. The measurement of organic mass is still responsible for the most uncertainty in estimates of how various aerosol species affect visibility. Adjustments are made to the organic carbon mass to correct for the adsorption of organic aerosols on the filter. However, this adjustment often results in negative concentrations. This area needs to be considered in future studies. Also, the mass fractions of hydrogen and carbon in organics are based on an assumption of the hydrocarbon type. Future research should evaluate these fractions on the basis of the most common organic molecules in the samples.

Light-Absorbing Carbon Measurement. The work reported here suggests that b_{abs} estimated from LIPM is a more accurate measure of absorption than that derived from elemental carbon measurements. The difference between the estimates is significant at about a factor of two.

Hygroscopicity of Aerosols. The relative humidity correction terms applied to sulfate and nitrate need to be reevaluated. The sulfate and nitrate RH factors are based on ammonium sulfate. Specific curves should be developed for ammonium nitrate, which has a different deliquescence point than sulfate. Also, acidic sulfates (e.g., sulfuric acid and ammonium bisulfate) have higher water contents and higher light scattering efficiencies than ammonium sulfate. Furthermore, the hygroscopicity of organics is not currently well understood. Basic research is required in this area. Until such research is available, alternative assumptions regarding organic hygroscopicity should be tested.

Long-Term Trends. The analysis of long-term trends of fine mass concentrations, sulfur concentrations, and absorption as presented here is based on descriptive statistics and inspection. A major point of contention is the fact that two protocol changes occurred in the middle of the data record (SFU vs IMPROVE samplers; and, 72 hour vs 24 hour duration samples). No IMPROVE and SFU samplers were operated concurrently side by side, nor were any 72-hour duration samples collected concurrently with 24-hour duration samples. Therefore, any bias in the data due to protocol changes should be revealed in the data; moreover, since the protocol changes were system wide any bias should be systematic. If there is a bias in the data then long- term trends, if any, could be masked or exaggerated. A detailed statistical analysis across all sites needs to be carried out to look for and quantify systematic changes in the data behavior that can be attributed to protocol changes. This understanding is required for correct interpretation of long-term trends.

In addition to the above refinements in the analyses conducted in this report, additional data analysis is recommended. For example, back trajectory analysis and spatial/temporal pattern analysis of episodes is recommended to determine the source region contributions to elevated concentrations. Also, the cleanest days should be studied to determine the source areas and meteorological causes of clean air.