OVERVIEW AND SUMMARY

This report describes data obtained from the first three years, March 1988 through February 1991, of the IMPROVE measurement program (Interagency Monitoring of Protected Visual Environments). IMPROVE is a cooperative visibility monitoring effort between the U.S. Environmental Protection Agency, 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.

Due to resource and funding limits, IMPROVE was not able to measure visual air quality in all 156 mandatory Class I areas that are afforded visibility protection by the Clean Air Act. Instead, 36 IMPROVE and NPS/IMPROVE protocol sites were selected to represent the distribution of visibility and aerosol concentrations over the United States. Each site has aerosol monitoring and scene monitoring (automated cameras) equipment. However, only 20 sites have optical monitoring equipment (transmissometers) to measure light extinction. Figure S.1 shows the locations of these sites. On the basis of regional similarities, the sites were grouped into 19 regions as shown in Table S.1.

S.1 Monitoring Methodologies

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 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.

Figure S.1. The 36 IMPROVE sites included in the report. Sites designated by an asterisk have both aerosol and visibility monitoring.

Table S.1 IMPROVE and NPS/IMPROVE protocol sites according to region.

Alaska (AKA)
- Denali National Park (DENA)

Appalachian Mountains (APP)
- Great Smoky Mountains National Park (GRSM)
- Shenandoah National Park (SHEN)

Boundary-Waters (BWA)
- Isle Royale National Park (ISRO)
- Voyageurs National Park (VOYA)

Cascade Mountains (CAS)
- Mount Rainier National Park (MORA)

Central Rocky Mountains (CRK)
- Bridger Wilderness Area (BRID)
- Great Sand Dunes National Monument (GRSA)
- Rocky Mountain National Park (ROMO)
- Weminuche Wilderness Area (WEMI)
- Yellowstone National Park (YELL)

Coastal Mountains (CST)
- Pinnacles National Monument (PINN)
- Point Reyes National Seashore (PORE)
- Redwood National Park (REDW)

Colorado Plateau (CPL)
- Arches National Park (ARCH)
- Bandelier National Monument (BAND)
- Bryce Canyon National Park (BRCA)
- Canyonlands National Park (CANY)
- Grand Canyon National Park (GRCA)
- Mesa Verde National Park (MEVE)
- Petrified Forest National Park (PEFO)

Florida (FLA)
- Everglades (EVER)

Great Basin (GBA)
- Jarbidge Wilderness Area (JARB)

Hawaii (HAW)
- Hawaii Volcanoes National Park (HAVO)

Northeast (NEA)
- Acadia National Park (ACAD)

Northern Great Plains (NGP)
- Badlands National Monument (BADL)

Northern Rocky Mountains (NRK)
- Glacier National Park (GLAC)

Sierra Nevada (SRA)
- Yosemite National Park (YOSE)

Sierra-Humboldt (SRH)
- Crater Lake National Park (CRLA)
- Lassen Volcanoes National Park (LAVO)

Sonoran Desert (SON)
- Chiricahua National Monument (CHIR)
- Tonto National Monument (TONT)

Southern California (SCA)
- San Gorgonio Wilderness Area (SAGO)

Washington, D.C. (WDC)
- Washington, D.C. (WASH)

West Texas (WTX)
- Big Bend National Park (BIBE)
- Guadalupe Mountains National Monument (GUMO)

Transmissometers were employed to measure the light extinction coefficient at 20 of the IMPROVE sites. These instruments 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}). Relative humidity was measured continuously at the transmissometer sites.

S.2 Assessing Aerosol Measurement Quality

The self-consistency and overall quality of the aerosol mass and chemical composition measurements were evaluated by intercomparing independent measurements.

Simultaneous measurements of elemental sulfur and of sulfate ions, on the Teflon and nylon filters respectively, were compared to assess their quality. The two sets of measurements agreed very well, indicating that almost all sulfur was due to sulfate species. The more precise elemental sulfur measurements on the Teflon filters were used to estimate sulfate concentrations in all of the studies, including reconstructions of fine mass and light extinction, acidity, and organic mass calculations.

Organic mass (OM) was estimated two different ways: From hydrogen mass measured on the Teflon filter (OMH); and from organic carbon mass measured on the quartz filter (OMC). Estimation of the organic mass by hydrogen also involved knowing or assuming the aerosol sulfate acidity. The two estimates of organic mass agreed well except for the third year of data, when a positive artifact affected the OMH estimate. This artifact was identified as resulting from problems associated with a batch of Teflon filters. This problem did not affect reconstructed extinction estimates; therefore, extinction calculations were reported for all three years. However, because hydrogen was used in estimates of acidity, only the first two years of data were used to estimate aerosol acidity. The quartz-filter based organic carbon measurements were used to estimate organics in reconstructions of fine mass and light extinction.

Elemental (light-absorbing) carbon, measured on the quartz filters using the Thermal Optical Reflectance method (TOR), was compared to the light absorption coefficient (b_{abs}), measured on the Teflon filters using the Laser Integrating Plate Method (LIPM). b_{abs} should agree very well with the elemental carbon TOR measurements and less well with the organic carbon TOR measurements. However, the portion of elemental carbon extracted at high temperature (ECHT) showed little or no correlation with b_{abs}. Also, b_{abs} correlated well with both low-temperature-extracted elemental carbon (ECLT) and high-temperature-extracted organic carbon (OCHT). Further, the form of the correlation between b_{abs} and ECLT (as shown in scatter plots) follows the form of the correlation between OCHT and ECLT. Finally, the ratio of b_{abs} to elemental carbon mass was approximately twice as large as literature values. These comparisons were all unexpected, and indicated possible errors in the estimation of elemental and organic carbon. A systematic error in the measurement of b_{abs} is possible but less likely, since the correlations noted above would still require explanation. Nevertheless, to be consistent with other studies, light-absorbing carbon was assumed to be the sum of ECLT and ECHT as measured from the quartz filters by the TOR method.

S.3 Aerosol Acidity

Aerosol sulfate can be fully neutralized as ammonium sulfate [$(NH_4)_2SO_4$], partially neutralized as in ammonium bisulfate [NH_4HSO_4], or fully acidic as sulfuric acid [H_2SO_4]. Hydrogen is associated with sulfate, nitrate, and organic carbon. However, the Teflon filters are analyzed in a vacuum during which nitrate aerosol is assumed to volatilize. Therefore, one should be able to estimate the acidity of the sulfate aerosol by using the measured aerosol concentrations of hydrogen, sulfate, and organic carbon in a statistical analysis to determine the hydrogen-sulfate ratio which is indicative of acidity. Sites identified as acidic by this procedure include Hawaii Volcanoes in Hawaii; Mount Rainier in the Pacific Northwest; Point Reyes, Redwoods, and Pinnacles in Northern California; Shenandoah in the East; and Tonto in southeastern Arizona. The uncertainties in the statistical approach used to derive aerosol acidity are significant. However, these results appear to be consistent with the fact that ammonia may not be present in sufficient quantities at coastal sites and in the Appalachian Mountains to neutralize sulfuric acid, and that sites with relatively fresh sulfate (such as Shenandoah, which is near power plants, and Tonto, which is near copper smelters) may not have had time for neutralization.

S.4 Spatial and Seasonal Distribution of Aerosol Concentration and Chemical Composition

Fine aerosol concentrations are highest in the eastern United States (in the Appalachian Mountains 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, 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 19 regions in the IMPROVE network, organic carbon is the largest single component in nine regions (Alaska, Cascades, Colorado Plateau, Central Rockies, Coast Mountains, Great Basin, Northern Rockies, Sierra Nevada, and Sierra-Humboldt). Sulfate is the largest single component of fine aerosol in six regions, primarily in the East (Appalachian Mountains, Florida, Hawaii, Northeast, Northern Great Plains, and Washington, D.C.). The contributions of organic carbon and sulfate are approximately equal in three regions (Boundary Waters, Sonoran Desert, and West Texas). 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.5 Spatial and Seasonal Distribution of Reconstructed Light Extinction and Species Contributions

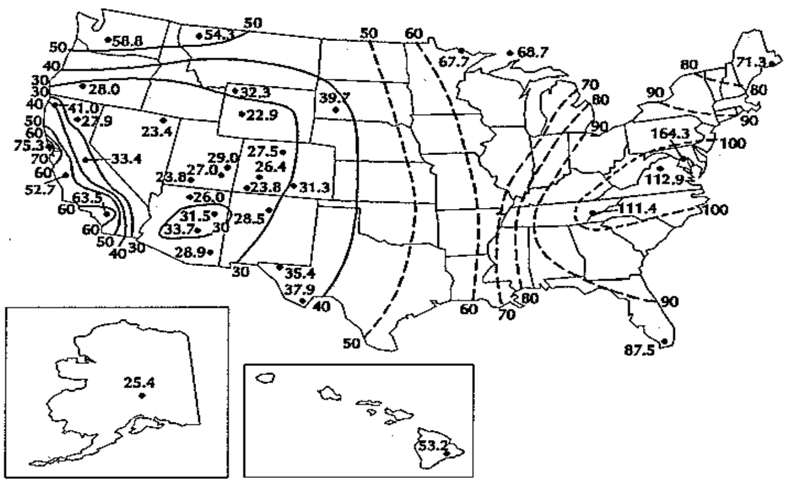
The light extinction coefficient (b_{ext}) is calculated from the measured aerosol species concentrations by multiplying the concentration of a given species by its light extinction efficiency, and summing over all species. Since sulfates and nitrates, as well as some organics, are hygroscopic, their 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 the first three years of IMPROVE (March 1988 through February 1991).

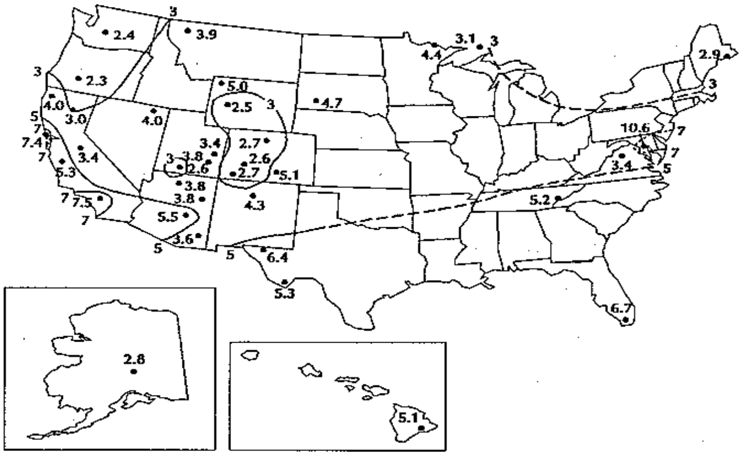
Reconstructed light extinction varies throughout the United States in a way analogous to fine aerosol concentrations. The greatest light extinction occurs in the eastern United States and in Southern California, while the least light extinction occurs in the nonurban West (e.g., the Great Basin of Nevada and the Colorado Plateau) and in Alaska. However, since relative humidity (and hence the light scattering efficiency of sulfate, nitrate, and some organics) 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 scattering 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 12 of the 19 regions, and is comparable with organics as the most significant contributor in two additional regions (Cascades and Central Rockies). Organic carbon is the largest single contributor to light extinction in four of the 19 regions (Great Basin, Northern Rockies, Sierra Nevada, and Sierra-Humboldt) and is a major contributor in the two previously mentioned regions. Smaller contributions come from windblown dust (coarse particles and fine soil) and nitrate. Nitrate is the single largest contributor to light extinction only in Southern California. Light-absorbing carbon is generally the smallest contributor.

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.

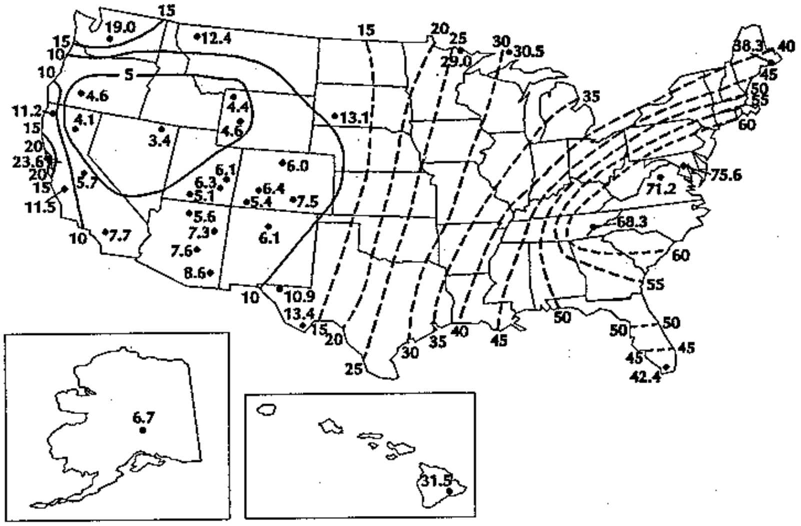


S.2 (a). Total light extinction b_{ext} (Mm^{-1})

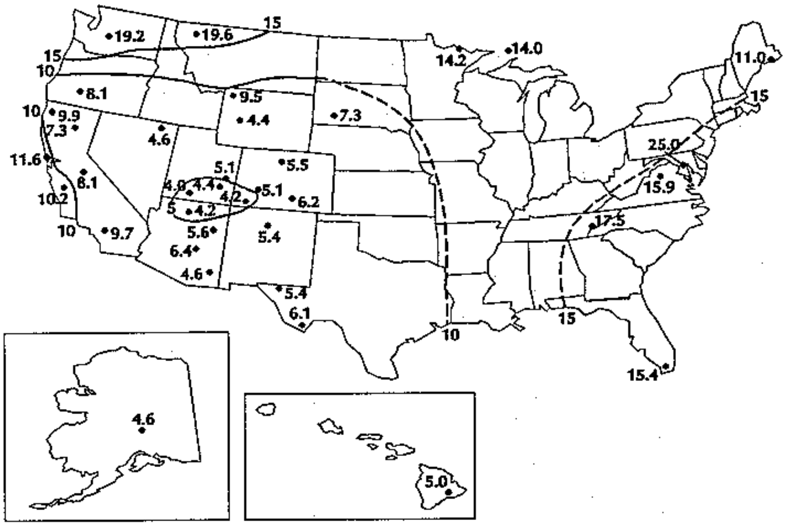


S.2 (b). Extinction due to coarse particles and fine soil (Mm^{-1})

Figure S.2 Average reconstructed light extinction coefficient (Mm^{-1}) calculated from the aerosol concentrations measured during the first three years of IMPROVE, March 1988 through February 1991. 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 light-absorbing carbon.

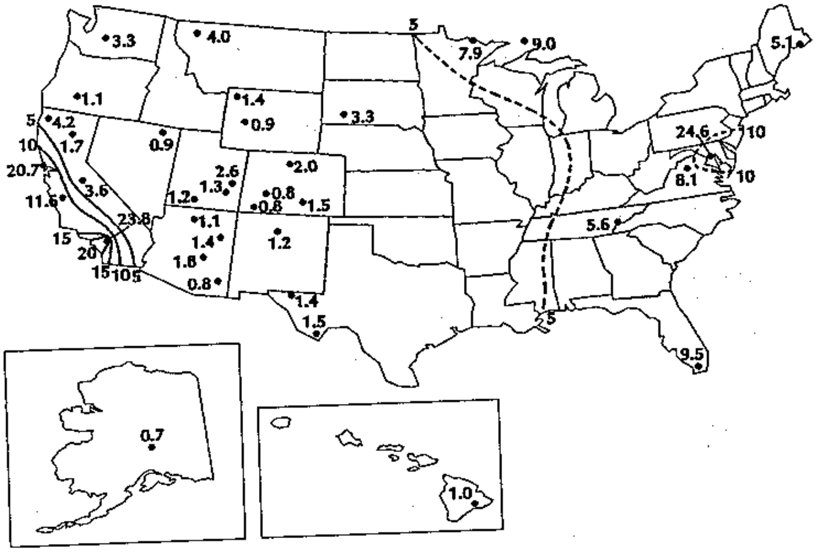


S.2 (c). Extinction due to sulfate (Mm^{-1})

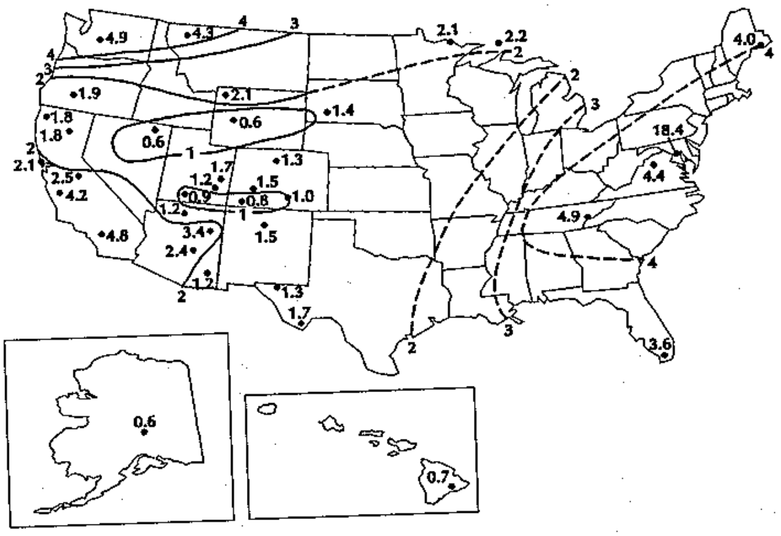


S.2 (d). Extinction due to organic carbon (Mm^{-1})

Figure S.2 Continued.



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



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

Figure S.2. Continued.

S.6 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. A one or two dv change is usually associated with the minimal or just noticeable change (JNC) in visibility that is perceivable by an average individual.

Figure S.3 shows isopleths of deciviews averaged over the first three years of IMPROVE. The smallest dv or best visibility is reported at Bridger Wilderness with 8.3 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 10 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 20.2 dv at Point Reyes. The northwest United States and all of the eastern half of the United States have in 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 region exceeding 24 dv. The highest annual dv, 28 dv, is reported at Washington D.C.

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.7 Measured Light Extinction

Figure S.4 summarizes the light extinction measurements made with transmissometers during the first three years of IMPROVE. This figure shows both the seasonal and annual averages of measured light extinction for all periods, and for periods excluding fog, precipitation, and low clouds. As was the case for reconstructed light extinction, highest measured light extinction occurs in the eastern United States and, to a lesser extent, in Southern California.

Light extinction is significantly higher in the eastern United States when weather-related events are included. Such events affect light extinction approximately two-thirds of the time at Shenandoah and Acadia National Parks.

When measured light extinction is compared to the reconstructed value calculated from the measured concentrations of the major aerosol species, good comparisons are formed (within 10%) for the Appalachian Mountains, Central Rockies, Colorado Plateau, Northeast, Northern

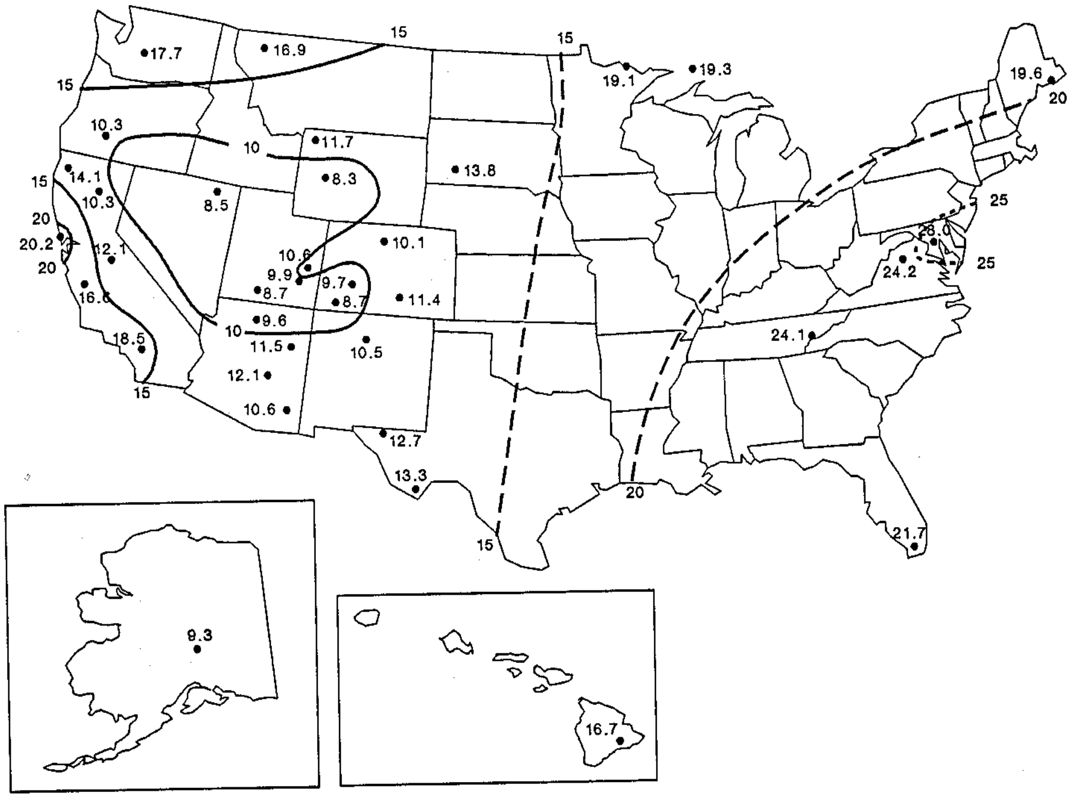


Figure S.3. Average visibility impairment in deciviews calculated from total (Rayleigh included) reconstructed light extinction for the first three years of IMPROVE, March 1988 through February 1991.

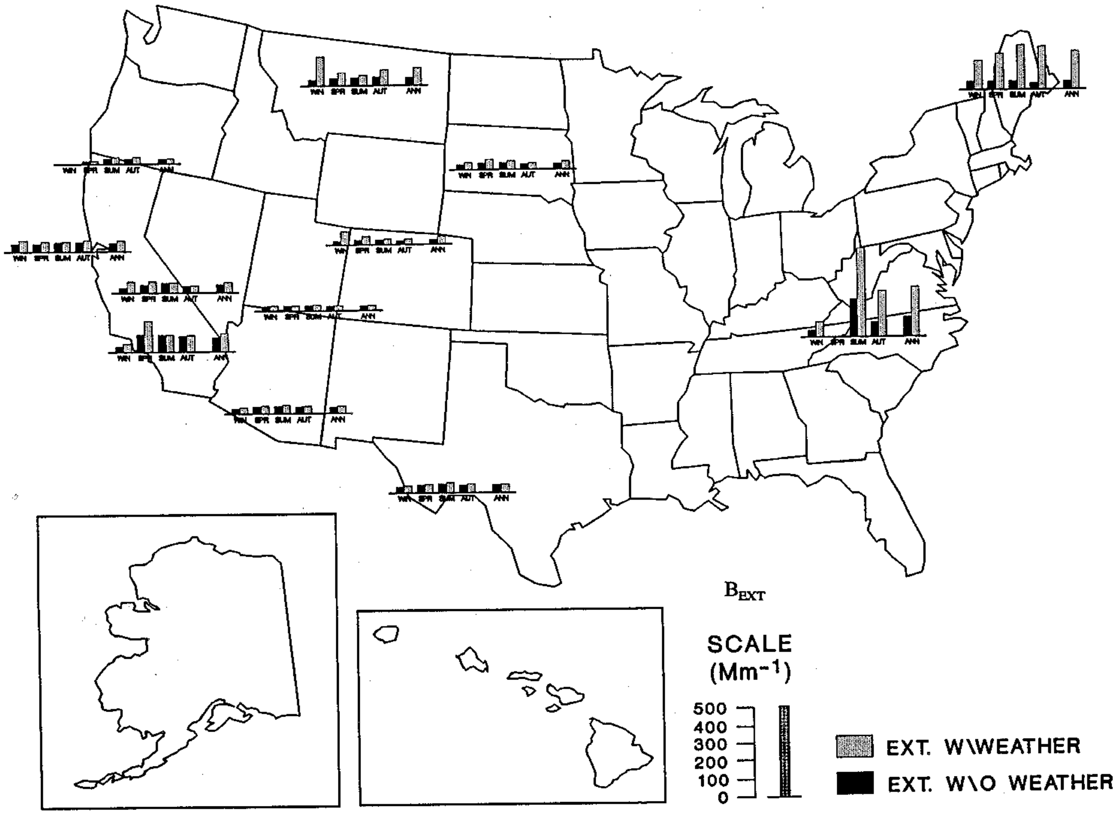


Figure S.4. Spatial and seasonal variation of measured light extinction coefficient (Mm^{-1}) in the U.S. for the three-year period, March 1988 through February 1991. From left to right, the bars show winter, spring, summer, autumn, and annual averages. Open bars include all time periods; dark bars exclude periods with fog, precipitation, and low clouds.

Great Plains, and Northern Rockies. However, reconstructed extinction is about 80% of measured light extinction in the Appalachian Mountains during summer and in the Pacific Coast, Southern California, Sonoran Desert, and West Texas regions. The worst comparison is at Yosemite in Sierra Nevada, where reconstructed light extinction is only 50% of the measured extinction. This may be because the aerosol monitor is above the mixed layer much of the time. The summertime Appalachian Mountains reconstructed extinction may be too low because of the assumption of fully-neutralized sulfate (ammonium sulfate). It is likely that the elevated sulfate concentrations in the Appalachian Mountains are acidic, and therefore have a higher light scattering efficiency than ammonium sulfate. Currently it is not clear why the reconstructed light extinction is less than measured light extinction in the other regions. One reason may be that the reconstructed light extinction is based on a 24-hour average, while measured extinction is hourly and often quite intermittent due to weather influences. Another possible explanation is that measured extinction is an average over the entire length of the transmissometer sight path, while aerosol measurements are at a point.

S.8 Recommended Future Research

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

Organic Aerosol Measurement. Organic aerosol mass is calculated from the organic carbon mass collected on the quartz filters and measured by the TOR process. 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. The organic artifact seen on the Teflon filter in the third year should be carefully evaluated in future studies, when additional years of data are analyzed. Finally, the correlation between light absorption and organic carbon measured on the quartz filter with TOR was unexpected. Additional research should be directed toward determining whether all light-absorbing carbon is in fact elemental as determined by TOR, and in particular whether the TOR pyrolyzed carbon may be light-absorbing in the ambient aerosol.

Light-Absorbing Carbon Measurement. The work reported here shows that light absorption correlates equally well with organic carbon and elemental carbon. It may be instructive to study the sensitivity of the results presented in this report to the elemental carbon measurements. For example, the measurement of the light absorption coefficient b_{abs} can be used directly to assess the light absorption contribution to the light extinction, and to calculate light-absorbing carbon aerosol concentrations (by dividing b_{abs} by the light absorption efficiency).

Hygroscopicity of Aerosols. The relative humidity correction terms applied to the sulfate, nitrate, and organic aerosols need to be re-evaluated. 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. Finally, the humidity correction curve for organics is a very rough approximation based on aerosol measurements in Europe (Hanel, 1981). 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.

Comparisons of Measured and Reconstructed Light Extinction. At many sites the light extinction estimated from concentrations of the major aerosol species underestimates measured light extinction. At some sites improved RH correction factors may provide better agreement. At other sites, it is currently not clear why reconstructed extinction underestimates measured light extinction. More work is required to resolve these differences and to improve the process of reconstructing light extinction.

Aerosol Acidity. The statistical analysis of aerosol acidity was based on a set of assumptions and on linear regression. More advanced variance-weighted regression techniques need to be applied. Physically incorrect results (e.g., overneutralization) are obtained at some sites. Sites with acidic aerosols should be flagged so that RH correction curves for acidic aerosols can be used.

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.