

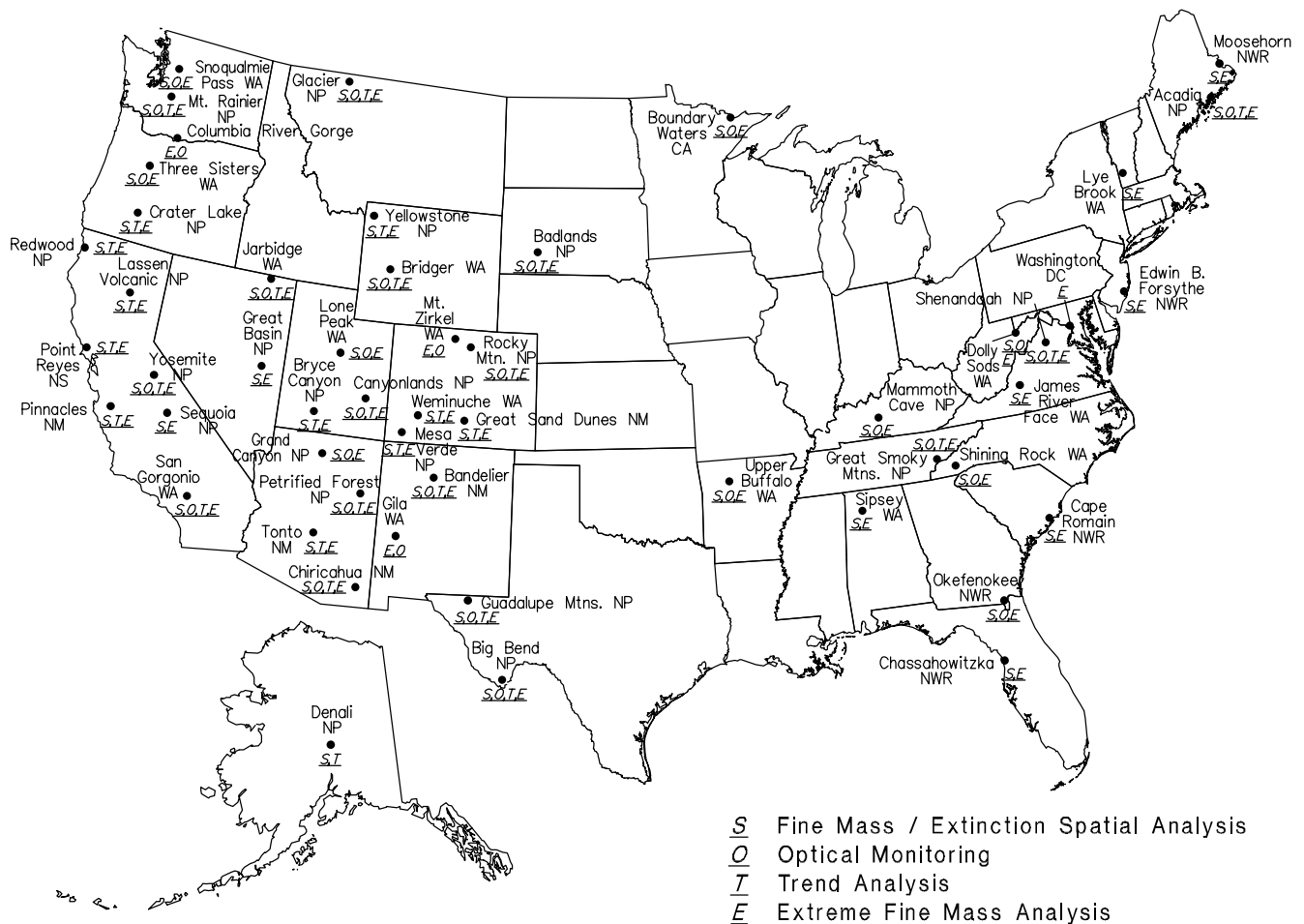
## OVERVIEW AND SUMMARY

This report describes data collected by the Interagency Monitoring of Protected Visual Environments (IMPROVE) measurement program. IMPROVE is a cooperative visibility monitoring effort between the U.S. Environmental Protection Agency (EPA), federal land management agencies, and state air agencies.

The objectives of IMPROVE are:

- (1) to establish current visibility and aerosol conditions in mandatory Class I areas (CIAs);
- (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) with the enactment of the Regional Haze Rule, to provide regional haze monitoring representing all visibility-protected federal CIAs where practical.

When the IMPROVE monitoring program was initiated it 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. Therefore, the first IMPROVE report [Sisler et al., 1993] reflected data that was collected at only 36 sites for the time period March 1988 through February 1991. Over subsequent years the IMPROVE Network evolved and a second IMPROVE report [Sisler, 1996] was published that covered data gathered between March 1992 and February 1995 at 43 sites. Currently, there are a number of sites that use IMPROVE monitoring equipment and operate under IMPROVE protocol, however, for this report, the spatial trend analysis, which covers the time period from March 1996 to February 1999, will use 49 sites. An analysis of species contributions to the extreme (high and low) fine mass concentrations will utilize 51 sites, while an 11-year trend analysis will use 29 sites. Thirty-one of the 49 sites have optical monitoring and these data will be used to explore diurnal variability in the extinction or scattering coefficient. Figure S.1 shows a map of the United States indicating the locations of the monitoring sites along with those sites that have optical monitoring, those sites used in the spatial and temporal trend analyses, and those sites used in the extreme fine mass analysis. Finally, on the basis of regional similarities, the sites are grouped into 21 regions, listed in Table S.1.



**Figure S.1** Map of the IMPROVE sites included in this report.

## 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<sub>10</sub> sample (particles less than 10 μm in diameter) on a Teflon filter and three PM<sub>2.5</sub> 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<sub>10</sub> filter is used to determine total gravimetric PM<sub>10</sub> mass concentration, while the PM<sub>2.5</sub> Teflon filter is analyzed to determine gravimetric mass concentrations and concentrations of selected elements using particle-induced x-ray emission (PIXE), x-ray fluorescence (XRF), and Proton Elastic Scattering Analysis (PESA). The nylon filter is analyzed to determine nitrate and sulfate aerosol concentrations using Ion Chromatography (IC). Finally, the quartz filters are analyzed for organic and elemental carbon using the Thermal Optical Reflectance (TOR) method.

*Table S.1 IMPROVE monitoring sites listed according to region.*

<p><b>Alaska (AKA)</b></p> <ul style="list-style-type: none"> <li>•Denali NP&amp;P (DENA)</li> </ul> <p><b>Appalachian Mountains (APP)</b></p> <ul style="list-style-type: none"> <li>•Great Smoky Mountains NP (GRSM)</li> <li>•Shenandoah NP (SHEN)</li> <li>•Dolly Sods WA (DOSO)</li> <li>•James River Face WA (JARI)</li> <li>•Shining Rock WA (SHRO)</li> </ul> <p><b>Boundary Waters (BWA)</b></p> <ul style="list-style-type: none"> <li>•Boundary Waters Canoe Area (BOWA)</li> </ul> <p><b>Cascade Mountains (CAS)</b></p> <ul style="list-style-type: none"> <li>•Columbia River NSA (CORI)</li> <li>•Mount Rainier NP (MORA)</li> <li>•Snoqualmie Pass WA (SNPA)</li> <li>•Three Sisters WA (THIS)</li> </ul> <p><b>Central Rocky Mountains (CRK)</b></p> <ul style="list-style-type: none"> <li>•Bridger WA (BRID)</li> <li>•Great Sand Dunes NM (GRSA)</li> <li>•Mount Zirkel WA (MOZI)</li> <li>•Rocky Mountain NP (ROMO)</li> <li>•Weminuche WA (WEMI)</li> <li>•Yellowstone NP (YELL)</li> </ul> <p><b>Colorado Plateau (CPL)</b></p> <ul style="list-style-type: none"> <li>•Bandelier NM (BAND)</li> <li>•Bryce Canyon NP (BRCA)</li> <li>•Canyonlands NP (CANY)</li> <li>•Grand Canyon NP (GRCA)</li> <li>•Mesa Verde NP (MEVE)</li> <li>•Petrified Forest NP (PEFO)</li> </ul> <p><b>Great Basin (GBA)</b></p> <ul style="list-style-type: none"> <li>•Jarbidge WA (JARB)</li> <li>•Great Basin NP (GRBA)</li> </ul> <p><b>Mid Atlantic (MAT)</b></p> <ul style="list-style-type: none"> <li>•Edwin B. Forsythe NWR (EBFO)</li> </ul> <p><b>Mid South (MDS)</b></p> <ul style="list-style-type: none"> <li>•Upper Buffalo WA (UPBU)</li> <li>•Sipsey WA (SIPS)</li> <li>•Mammoth Cave NP (MACA)</li> </ul>	<p><b>Northeast (NEA)</b></p> <ul style="list-style-type: none"> <li>•Acadia NP (ACAD)</li> <li>•Lye Brook WA (LYBR)</li> <li>•Moosehorn NWR (MOOS)</li> </ul> <p><b>Northern Great Plains (NGP)</b></p> <ul style="list-style-type: none"> <li>•Badlands NP (BADL)</li> </ul> <p><b>Northern Rocky Mountains (NRK)</b></p> <ul style="list-style-type: none"> <li>•Glacier NP (GLAC)</li> </ul> <p><b>Pacific Coastal Mountains (PCM)</b></p> <ul style="list-style-type: none"> <li>•Pinnacles NM (PINN)</li> <li>•Point Reyes NS (PORE)</li> <li>•Redwood NP (REDW)</li> </ul> <p><b>Sierra Nevada (SRA)</b></p> <ul style="list-style-type: none"> <li>•Yosemite NP (YOSE)</li> <li>•Sequoia NP (SEQU)</li> </ul> <p><b>Sierra-Humboldt (SRH)</b></p> <ul style="list-style-type: none"> <li>•Crater Lake NP (CRLA)</li> <li>•Lassen Volcanic NP (LAVO)</li> </ul> <p><b>Sonoran Desert (SON)</b></p> <ul style="list-style-type: none"> <li>•Chiricahua NM (CHIR)</li> <li>•Gila WA (GILA)</li> <li>•Tonto NM (TONT)</li> </ul> <p><b>Southeast (SOE)</b></p> <ul style="list-style-type: none"> <li>•Chassahowitzka NWR (CHAS)</li> <li>•Okefenokee NWR (OKEF)</li> <li>•Cape Romain NWR (CARO)</li> </ul> <p><b>Southern California (SCA)</b></p> <ul style="list-style-type: none"> <li>•San Geronio WA (SAGO)</li> </ul> <p><b>Wasatch (WAS)</b></p> <ul style="list-style-type: none"> <li>•Lone Peak WA (LOPE)</li> </ul> <p><b>Washington, D.C. (WDC)</b></p> <ul style="list-style-type: none"> <li>•Washington, D.C. (WASH)</li> </ul> <p><b>West Texas (WTX)</b></p> <ul style="list-style-type: none"> <li>•Big Bend NP (BIBE)</li> <li>•Guadalupe Mountains NM (GUMO)</li> </ul>
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NP&P = National Park and Preserve  
 NP = National Park  
 NS = National Seashore

NM =National Monument  
 NWR =National Wildlife Refuge

NSA = National Scenic Area  
 WA = Wilderness Area

Transmissometers are employed to measure the light-extinction coefficient at 15 of the IMPROVE sites, and 16 sites have integrating nephelometers, which measure the scattering coefficient. Transmissometers measure the light transmitted through the atmosphere over a distance of 1 to 15 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 ( $b_{abs}$ ). An integrating nephelometer measures the scattering of light from a small volume of air and thus it is a point measurement of scattering. By combining an estimate of the absorption coefficient from the particle data with the scattering coefficient from the nephelometer the extinction coefficient can be estimated at the 16 nephelometer sites. Relative humidity is measured continuously at the transmissometer and nephelometer sites.

In the next sections the spatial and temporal trends of fine and coarse mass concentrations along with their associated optical extinction and/or scattering characteristics will be summarized.

## **S.2 SPATIAL DISTRIBUTION OF AEROSOL CONCENTRATION AND CHEMICAL COMPOSITION**

Coarse mass, the difference between  $PM_{10}$  and  $PM_{2.5}$ , concentrations are highest along the Southeast, Pacific Coastal Mountains, West Texas, and Sonoran Desert regions, while it is lowest in the Sierra-Humboldt and Cascade Mountains regions.

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

The largest single component of the fine aerosol in the East is sulfate at 60-65% of the mass, while in the Pacific Northwest it is organics, and in southern California it is nitrates. In general, the largest mass fractions of the fine aerosol are sulfates, organics and soil/dust. Of the 21 regions in the IMPROVE Network, carbon (organic plus light-absorbing carbon) is the largest single component in ten regions (Alaska, Cascade Mountains, Central Rocky Mountains, Colorado Plateau, Great Basin, Northern Rocky Mountains, Pacific Coastal Mountains, Sierra-Nevada, Sierra-Humboldt, and Wasatch regions). Sulfate is the largest single component of fine aerosol in ten regions, primarily in the East (Appalachian Mountains, Boundary Waters, Mid-Atlantic, Mid-South, Northeast, Northern Great Plains, Sonoran Desert, Southeast, Washington, D.C., and West Texas regions), while nitrates are slightly greater than carbon in the Southern California region. Sulfates and carbon are approximately the same on the Colorado Plateau and Sonoran Desert.

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 SPATIAL 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 are assumed to be hygroscopic, their light-extinction efficiencies increase with relative humidity; therefore, extinction efficiencies for soluble species must be adjusted according to average relative humidity at each site.

There are two ways reconstructed extinction is calculated in this report that are different from the 1996 IMPROVE report. First, the factor  $f(RH)$  that accounts for the relative humidity effects on hygroscopic aerosols has been upgraded with new relative humidity data from additional relative humidity monitoring sites and second, absorption is estimated from measurements of light-absorbing carbon rather than from transmission measurements of filter media. Therefore, some differences in aerosol extinction between this and the 1996 report are due to changes other than levels of aerosol mass concentration.

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 2). 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.

Figures S.2 and S.3 are the spatial deciview maps using just the IMPROVE data and IMPROVE plus the EPA's Clean Air Status and Trends Network (CASTNet) data, respectively. Figure S.2 incorporates data for the time period March 1996 through February 1999, and Figure S.3 uses data for the time period December 1995 through November 1998. Therefore, the estimates of deciview and extinction are slightly different for the two time periods. These different time periods are used for the respective maps because at the time of this writing the CASTNet data were available only through the end of 1998. The discussion of how the two data sets are combined is presented in Appendix A. The maps of the combined data sets are presented here because of the higher density of deposition sites in the eastern United States. Figures S.4 and S.5 are the corresponding extinction maps for the time periods analogous to Figures S.2 and S.3. Figures S.6a through S.6e show the fractional contribution of sulfates, nitrates, organics, light-absorbing carbon, and dust to total aerosol extinction.

Deciview and 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 and the Colorado Plateau) and in Alaska. However, because relative humidity (and therefore 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.

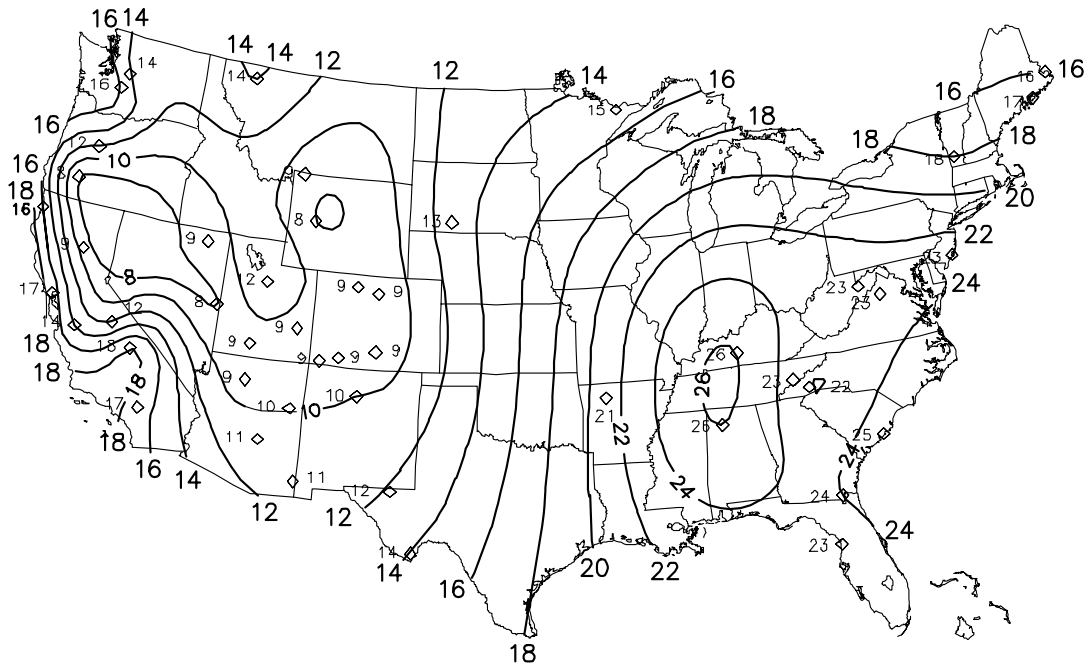
Figures S.2 and S.3 show isopleths of deciviews averaged over the respective time periods previously described. The smallest dv value or best visibility is reported at Denali National Park with 7 dv. A broad region, which includes the Great Basin, most of the Colorado Plateau, and portions of the Central Rockies, has visibility impairment of less than 10 dv. Moving in any direction from this region generally results in increasing dv values. West of the Sierra Mountain Range and including southern California one finds dv values in excess of 15, with a maximum value of 18 dv at Sequoia National Park. The northwest United States and the entire eastern half of the United States have an excess of 14 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 Southeast regions exceeding 24 dv. Figure S.3 shows the highest annual dv values, greater than or equal to 26 dv, occurring in the eastern United States in the general region of the Ohio River and Tennessee Valleys. Total aerosol extinction, shown in Figures S.4 and S.5, show the same general spatial trend as deciviews.

Fine aerosols are the most effective in scattered light and are the major contributors to light extinction. Referring to Figure S.6a, in most cases the sulfate component of fine aerosol is the largest single contributor to total aerosol 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 National Parks), sulfate accounts for nearly 80% of the total aerosol light extinction on an annual basis, and more during the summer months. Sulfates contribute the least in the Great Basin region at about 25%, while along the Rocky Mountains the contribution is about 30-40%. In the Cascade Mountains region, sulfates contribute significantly at 50-60%. Sulfates are the largest single contributor to light extinction in 17 of the 21 regions and are about comparable to organics in two of these regions, Northern Rocky Mountains and Wasatch.

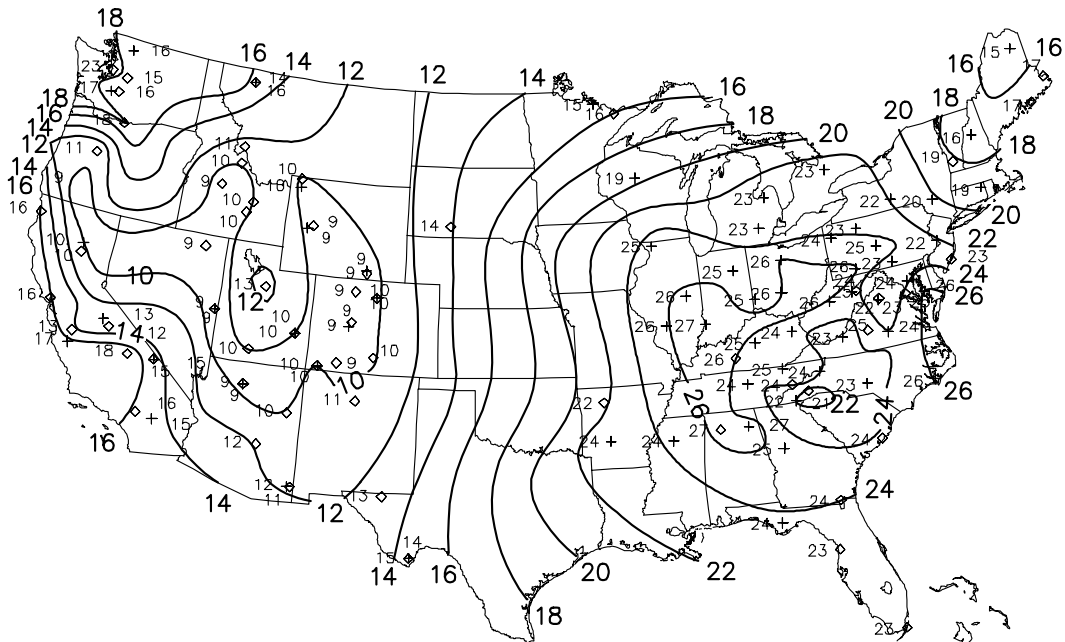
Figure S.6b shows the fractional contribution of nitrates to total aerosol extinction. Nitrates are not only the single largest contributor to extinction in the Southern California region at 39% but also contribute significantly along the coastal areas of California at about 20-25%. Nitrates are 16% of extinction at Lone Peak Wilderness Area, which is near Salt Lake City, while in the rest of the United States it is less than 10%.

Figure S.6c shows the fractional contribution of organics to extinction. Organics are, in general, the second largest contributor to total aerosol extinction. It is the largest contributor in the Great Basin, Sierra-Humboldt, and Sierra-Nevada regions at 33%, 36%, and 32% respectively. It is the largest contributor at Yosemite National Park at 40% and on the order of about 10% in most of the eastern United States. In the Central Rockies and on the Colorado Plateau, its contribution to extinction is about 20-25%.

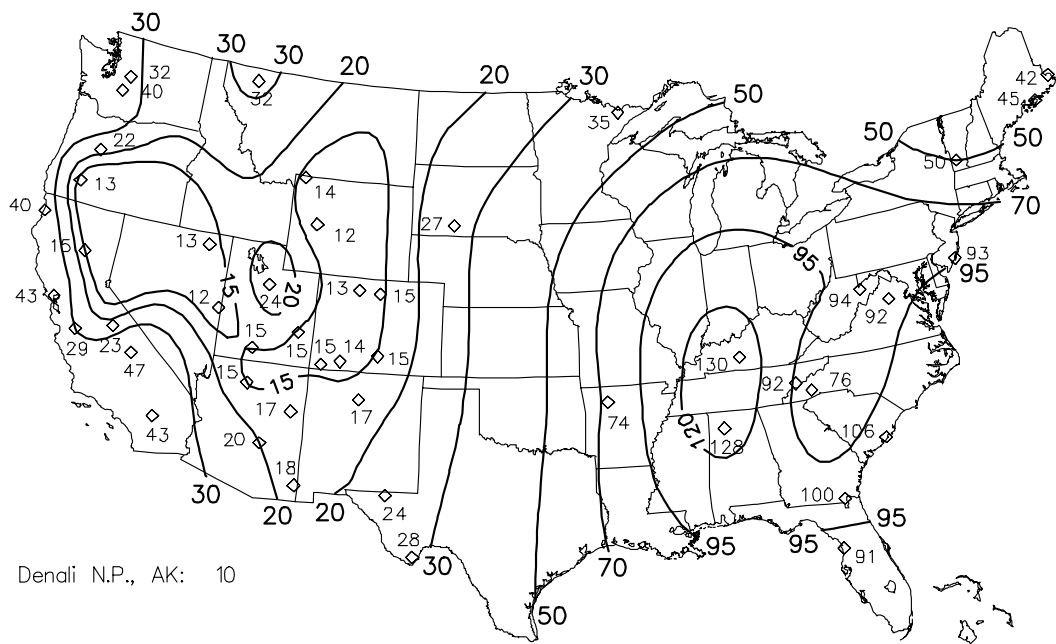
Figure S.6d shows the fractional contribution of light-absorbing carbon to total aerosol extinction. It is on the order of about 10% in much of the western United States and on the order of 5% east of the Mississippi. In the three regions where organics are the largest contributors to extinction, the sum of organic and light-absorbing carbon, or the contribution of carbon in general, to extinction is 40-50%.



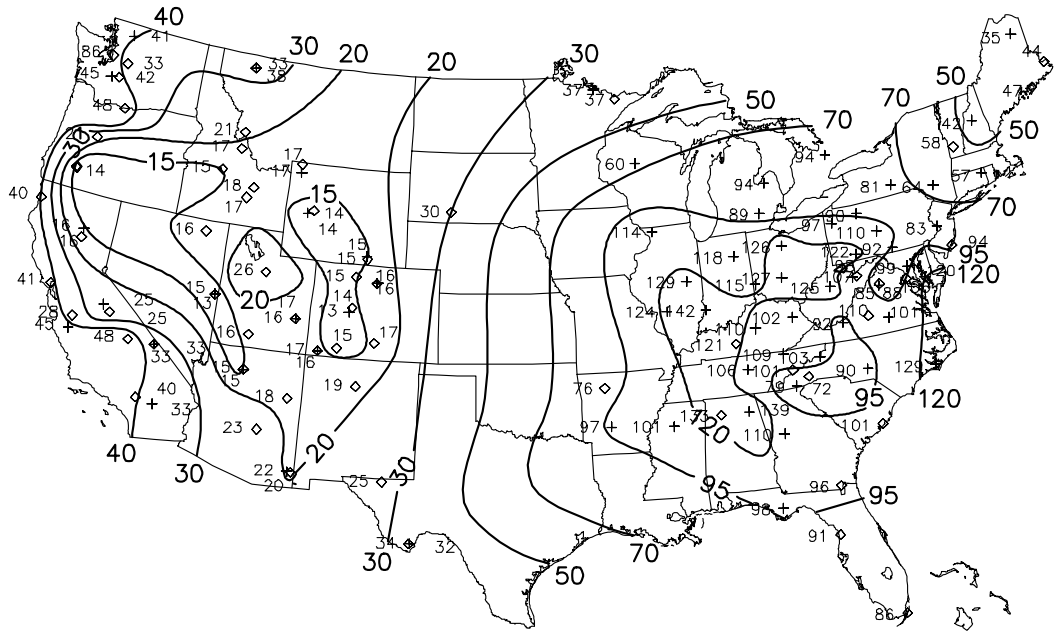
**Figure S.2** Three-year averages of deciview values using only data collected in the IMPROVE Network.



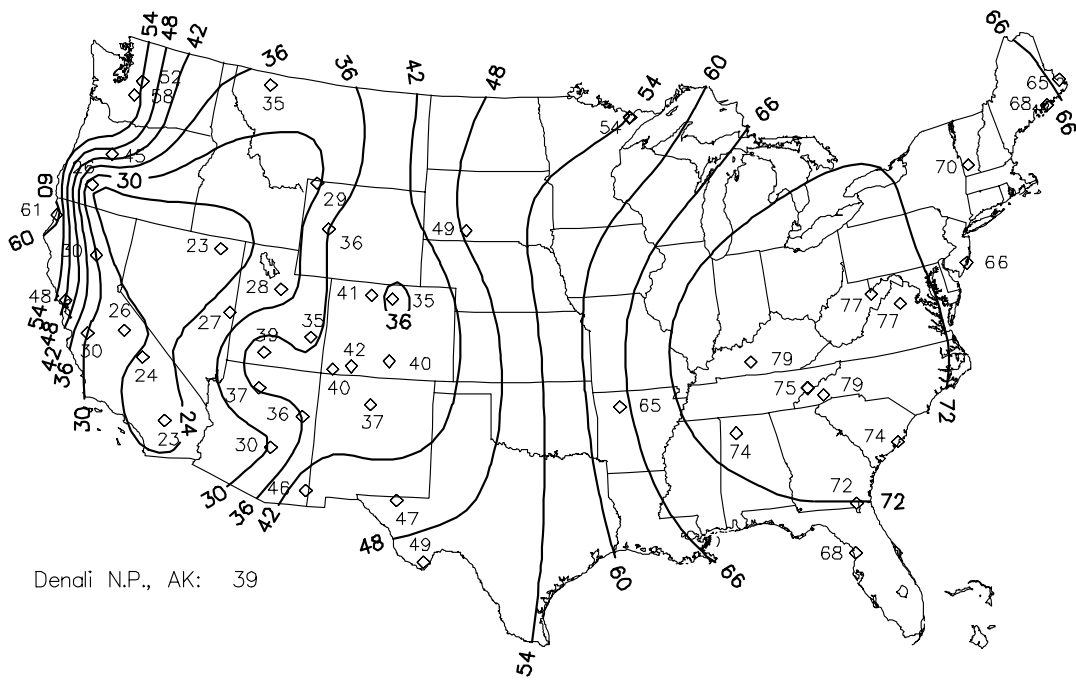
**Figure S.3** Three-year averages of deciview values using data collected in the IMPROVE Network and CASTNet.



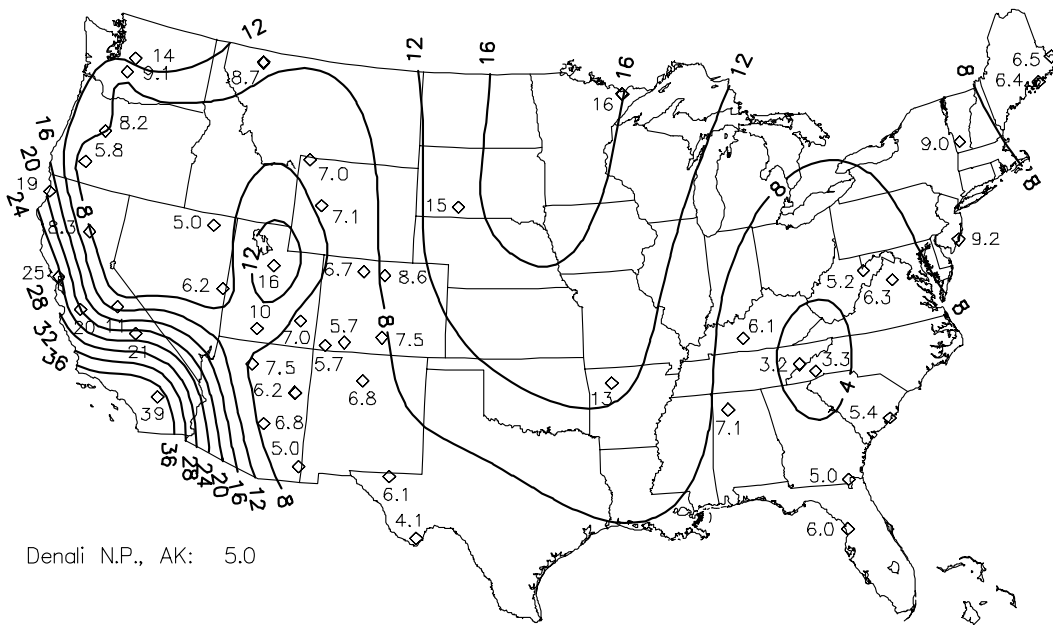
**Figure S.4** Three-year averages of total reconstructed aerosol light-extinction coefficient (1/Mm) using only data collected in the IMPROVE Network.



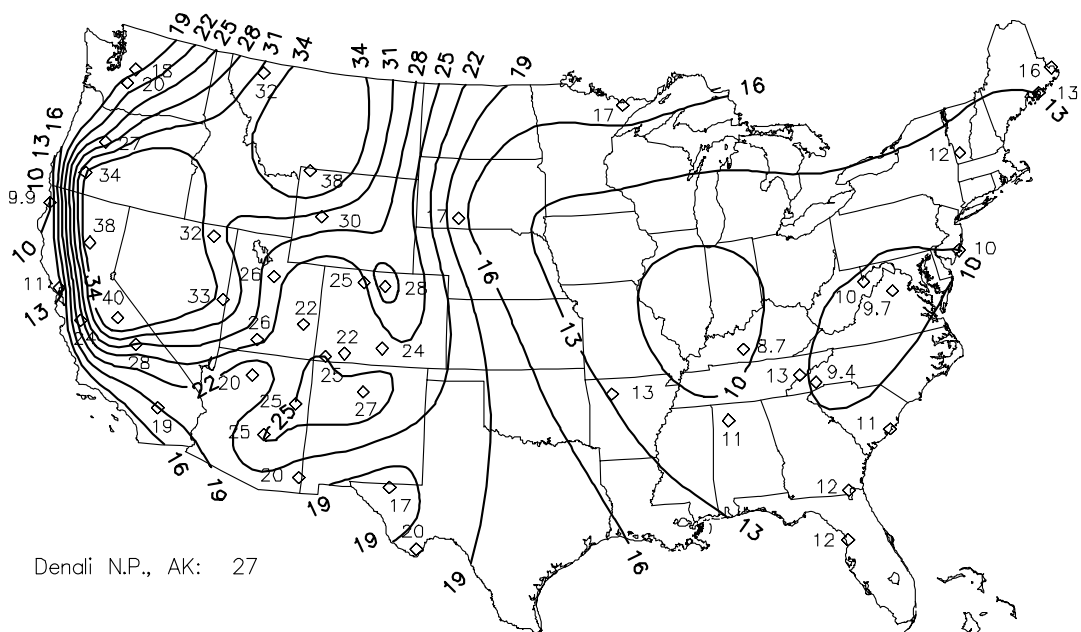
**Figure S.5** Three-year averages of total reconstructed aerosol light-extinction coefficient (1/Mm) using data collected in the IMPROVE and CASTNet.



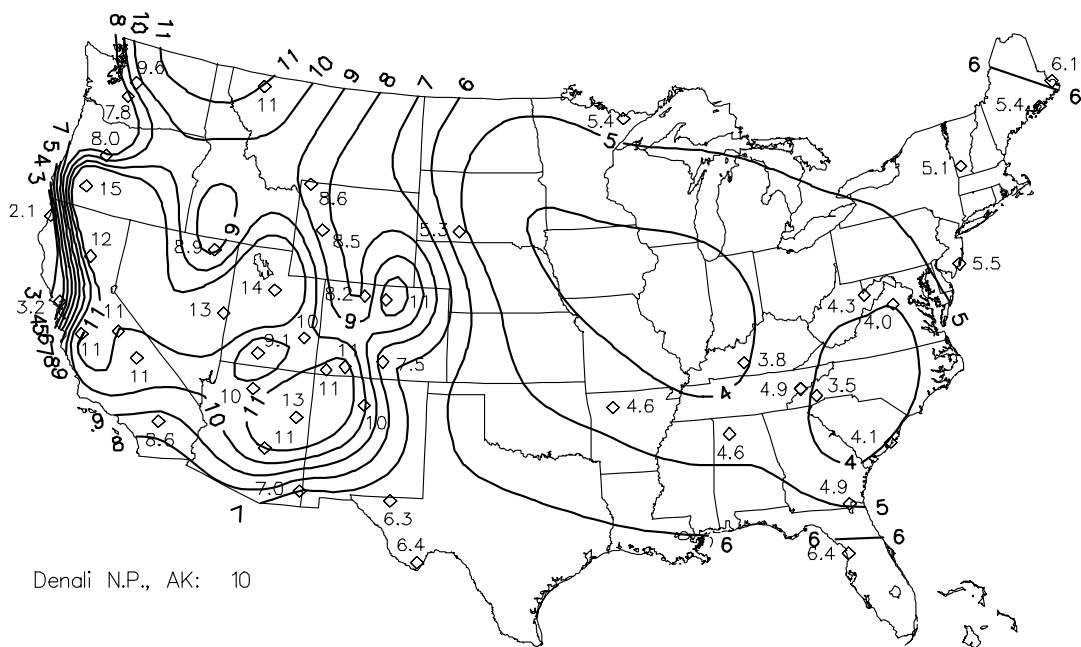
**Figure S.6a** Fractional contribution of sulfates to total aerosol reconstructed light extinction (%).



**Figure S.6b** Fractional contribution of nitrates to total aerosol reconstructed light extinction (%).

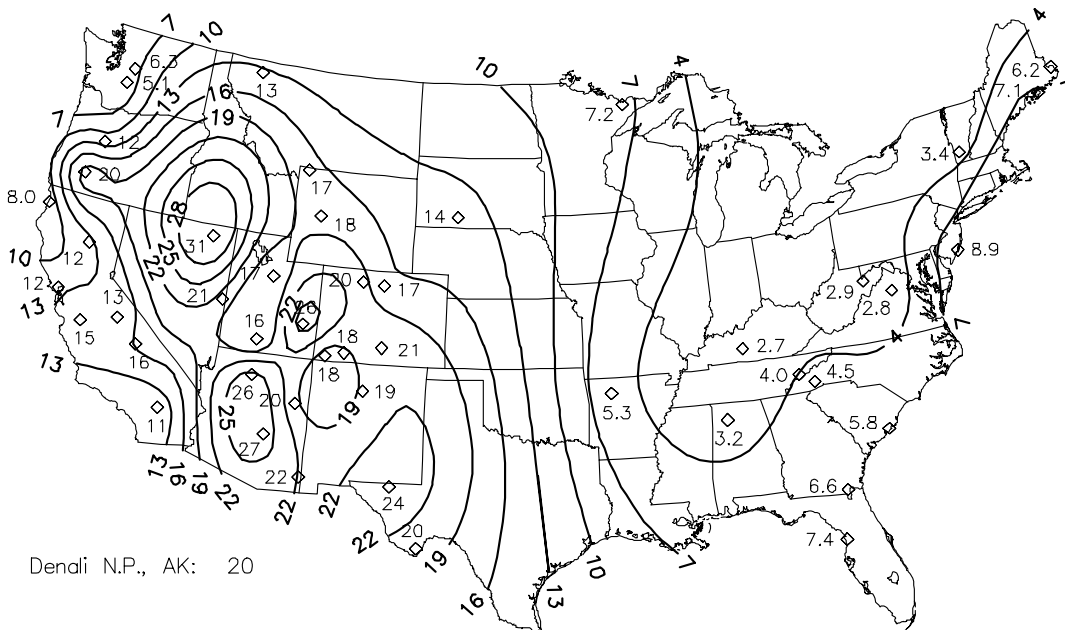


**Figure S.6c** Fractional contribution of organics to total aerosol reconstructed light extinction (%).



**Figure S.6d** Fractional contribution of light-absorbing carbon to total aerosol reconstructed light extinction (%).

Finally, the fractional contribution of fine and coarse soil/dust is shown in Figure S.6e. In the eastern United States, it is generally less than 5%, while in the Sonoran Desert, West Texas, and Great Basin regions its contribution to extinction is on the order of 20-30%. In the Cascade Mountains region, it is about 5%. In the rest of the United States, soil/dust contributes between about 10 and 20% of extinction.

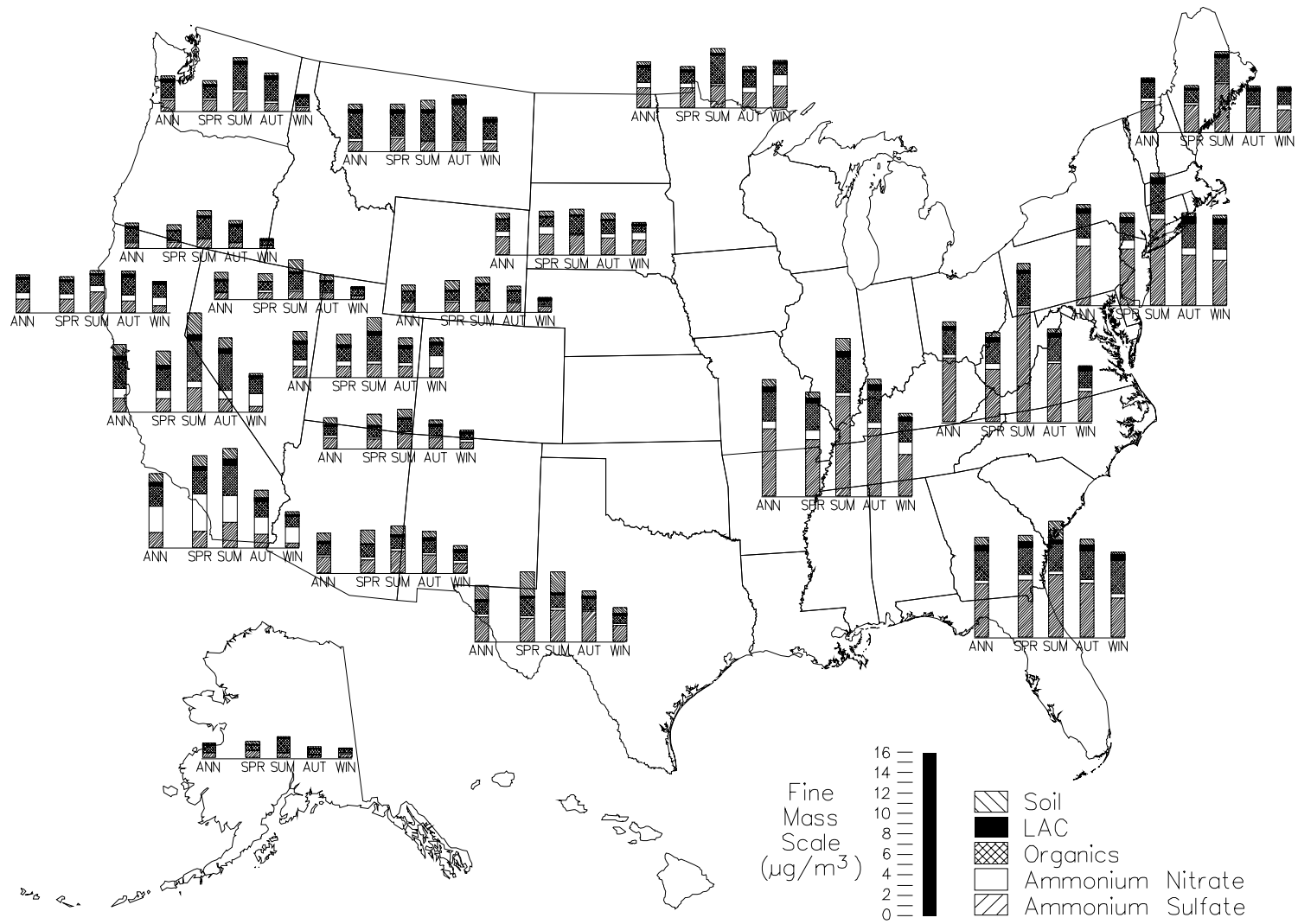


**Figure S.6e** Fractional contribution of soil/dust to total aerosol reconstructed light extinction (%).

#### **S.4 SEASONAL DISTRIBUTION OF FINE MASS AND RECONSTRUCTED LIGHT EXTINCTION**

Figure S.7 is a summary plot of reconstructed fine mass and the contribution of each species for the 20 monitoring regions, excluding Washington, D.C., in the IMPROVE Network. The summer months have the highest fine mass loadings at 19 of the 20 monitoring regions with two regions having nearly identical mass loadings in two seasons. In the Pacific Coastal Mountains region, fine mass concentrations are nearly the same in the summer and autumn seasons, while the West Texas fine mass loadings are nearly the same in spring and summer. In the Northern Rocky Mountains region, fine mass loadings are greatest during the autumn season primarily because of increased organic mass concentration. East of the Mississippi sulfates make up about 60-70% of the fine mass in all seasons, while in much of the inner-mountain west fine mass concentrations are somewhat evenly split between sulfates, carbon, and soil/dust mass concentrations.

Figure S.8 is a summary plot of reconstructed light extinction and the contribution of each species for the 20 monitoring regions, excluding Washington, D.C., in the IMPROVE Network. The addition of the effect of water on hygroscopic aerosols and the addition of coarse mass changes the seasonal trends somewhat. At 13 of the 20 monitoring regions, summer extinction is



**Figure S.7** Summary plot of reconstructed fine mass and the fractional contribution of each species for the 20 monitoring regions in the IMPROVE Network, excluding Washington, D.C.



**Figure S.8** Summary plot of reconstructed light extinction and the fractional contribution of each species for the 20 monitoring regions in the IMPROVE Network, excluding Washington, D.C.

the highest, with the largest difference between seasons being in the eastern United States, where sulfates in combination with high relative humidity make summer substantially hazier than any other season. Notice that sulfates, on a relative basis, contribute significantly more, because of high relative humidity, to extinction than to fine mass. West Texas, Sonoran Desert, Colorado Plateau, Great Basin, Sierra-Humboldt, Sierra-Nevada, Pacific Coastal Mountains, and Cascade Mountains regions also have, on the average, the highest extinction during the summer months, however, the differences between seasons tend to be not as pronounced. Three of the regions, Southern California, Central Rocky Mountains, and Northern Great Plains, have the highest extinction during the spring season. In the Southern California region, the springtime high is driven by increased nitrate extinction. In two regions, Cascade Mountains and Boundary Waters, winter has the highest extinction and again it is driven by nitrates, while in one region, Northern Rocky Mountains, spring is the season with greatest extinction.

## **S.5 CONTRIBUTION OF AEROSOL SPECIES TO PERIODS OF HIGH AND LOW (EXTREMES) FINE MASS CONCENTRATIONS**

The chemical species contribution to extremes in fine mass is relevant to emissions control scenarios for the Class I areas represented by the IMPROVE monitoring sites where it is the goal to improve the haziest days, while maintaining visibility levels on the clearest days. Identification of the chemical species that impact the clearest and/or haziest days will provide a better understanding of potential sources of atmospheric particles responsible for visibility reduction during extreme fine mass events. For example, forest fires, whether they are prescribed burns or natural fires, occur sporadically and can cause particle carbon to have a large contribution to upper extremes of observed particle fine mass concentration at impacted sites. Also, secondary nitrate particles can have large contributions to upper extremes of fine particle mass during cold seasons, particularly in areas impacted by urban sources.

Spatial trends of fine particle data based on measurements from the IMPROVE Network indicate that, on average, sulfates constitute a major portion of particle fine mass in the eastern United States, particle carbon and soil/dust can have large contributions in the United States interior, desert mountain, and northwest regions, while nitrates are often major contributors to fine particle mass near many urban areas. This analysis contrasts the mean contribution of individual chemical species to the contribution of the same species to extremes in observed fine particle mass. It is illustrated that a chemical species contribution to the highest and lowest fine mass concentrations can be quite different from that species mean contribution. The analysis examined the contribution of sulfates, carbon, soil, and nitrate particles to extremes of observed fine particle mass.

On clean days, when fine mass concentrations are lowest, sulfate or carbon is the largest contributor to fine mass. However, on the highest fine mass days, or upper percentiles of observed fine mass, all species, including particle nitrates, can have large contributions, depending on the monitoring site and time of year.

For instance, sulfate is a major contributor to both the mean and upper extremes of fine mass in the eastern United States, with largest contributions to the upper extremes clustered in regions of high sulfur emissions. In the upper 2% of fine mass concentration, the sulfate contribution increases

between 20-30% over the mean sulfate contribution. For example, if the sulfates contribute 50% of the fine mass then, on the average, they contribute between 70-80% of the fine mass on the upper 2% time periods.

Carbon mass concentration exhibits a pattern generally increasing the mean contribution of fine mass concentrations from south-to-north. The carbon concentration increases during extreme high fine mass in the western United States that are likely related to forest fires. In the Central and Northern Rocky Mountains regions, the relative contribution of organics to fine mass increases from about 40-50% on the average to 50-70% on the extreme periods and at Yellowstone from 52% on the average to 75% on the highest fine mass time periods.

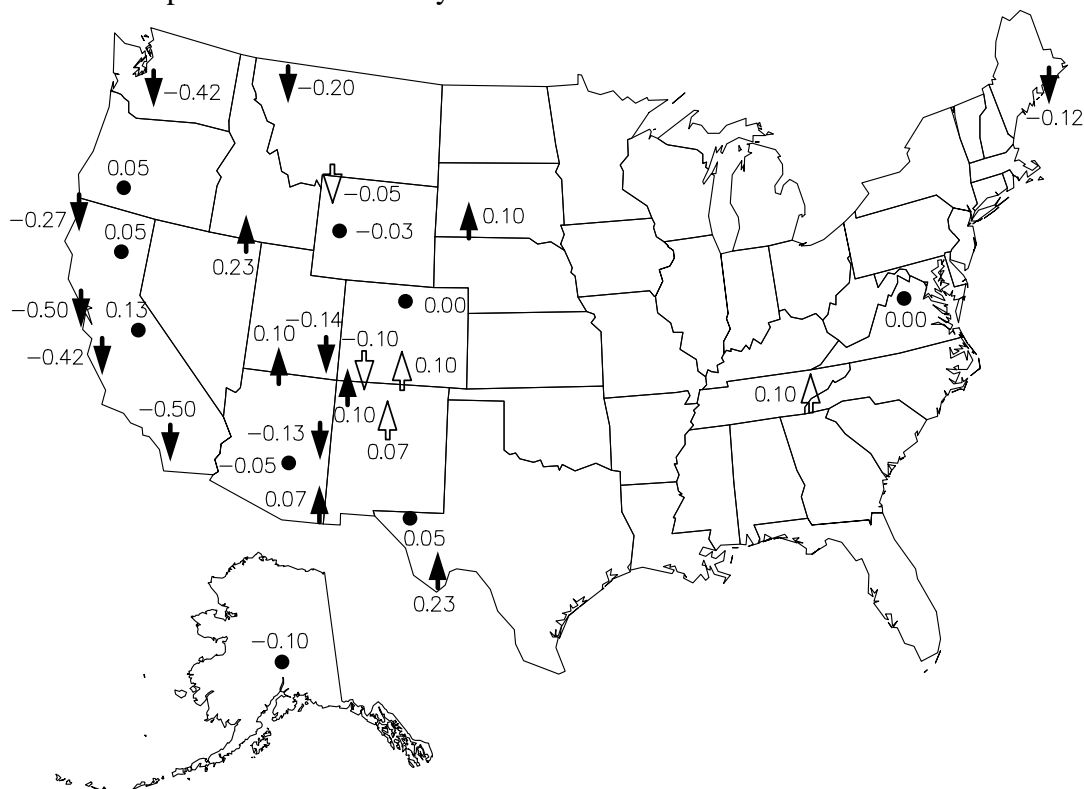
Particle nitrate contributions to fine mass are largest during the winter, and have substantially increased contributions to upper extremes of fine mass near urban areas and in the Midwest. For instance, along the California coast the average nitrate contribution to fine mass is 25-30%, while on the high fine mass days it is 60-65% and in the Midwest it is about 20-30% on the average and 40-45% on the highest fine mass periods. Interestingly, at Rocky Mountain National Park nitrates are only 7.3% of the fine mass on the average but 28.3% on the extreme days. The mean soil contribution to fine mass is largest in the western United States, with high soil contributions to upper extremes in the southwest and southeast coastal regions, where regional and long-range transport of wind-blown dust are responsible for extremes.

## **S.6 TEMPORAL TRENDS IN VISIBILITY AND AEROSOL CONCENTRATIONS**

Referring to Figure S.9, the haziest days as represented by those days with the highest 20% fine mass concentrations, have nine sites with positive and significant  $dv$  slopes indicating that visibility is decreasing on the haziest days, eleven sites where visibility is improving at a statistically significant rate, and nine sites where visibility remains the same. At five of the nine sites that have decreasing visibility, sulfates are increasing at a significant rate (Great Smoky Mountains and Big Bend National Parks, and Chiricahua, Bandelier, and Great Sand Dunes National Monuments), four sites show increasing nitrates (Badlands, Mesa Verde, and Big Bend National Parks, and Chiricahua National Monument), and two sites (Jarbidge Wilderness Area and Bryce Canyon National Park) with increasing organics. The Great Smoky Mountains National Park's increase in haziness is primarily associated with a  $259 \text{ ng/m}^3/\text{yr}$  increase in sulfates. This rate of increase in sulfates is  $2\frac{1}{2}$  times greater than at Big Bend National Park and a factor of 10 greater than at Bandelier and Great Sand Dunes National Monuments. Also, even though there are only two sites where increases in organics correspond to increases in haziness, there are seven sites, all in the inner-mountain west where organics are increasing in a statistically significant way. These are the same sites where the extreme fine mass concentrations are dominated by organics.

Of the eleven sites that show statistically significant trends toward improved visibility, six of these sites (Glacier, Mount Rainier, Redwood, and Canyonlands National Parks, Pinnacles National Monument, and San Geronio Wilderness Area) show decreases in sulfate mass concentration, eight sites (Mount Rainier, Redwood, Canyonlands, Petrified Forest and Acadia National Parks, Point Reyes National Seashore, Pinnacles National Monument, and San Geronio Wilderness Area) in nitrate concentrations, and seven sites (Mount Rainier, Redwood, Petrified Forest and

Acadia National Parks, Point Reyes National Seashore, Pinnacles National Monument, and San Geronio Wilderness Area) in organic mass concentration. At sites along the California coast and at San Geronio Wilderness Area, reductions in nitrate concentrations are the most significant contributors to improvement in visibility.



**Figure S.9** This map summarizes the trends in deciview (dv/yr) for group 90 (top 20% of fine mass) days. The icons mark the site locations, a solid dot indicates an insignificant slope, an empty arrow indicates a positive or negative slope that is significant in the range of  $0.05 < p \leq 0.1$  level of probability, and a solid arrow indicates a positive or negative slope that is significant at better than 0.05 ( $p \leq 0.05$ ) level of probability.

## S.7 DIURNAL TRENDS IN SCATTERING AND EXTINCTION

The previous analysis, which focused on spatial and long-term trends, relied entirely on particle data that was collected twice weekly and each sample was 24 hrs in duration. On the other hand, at a few select sites transmissometers and nephelometers are operated along with the aerosol samplers. The optical instruments serve as a quality assurance check in that measured and reconstructed scattering/extinction should be equivalent and because these instruments run continuously, essentially collecting instantaneous data (10-min or 2-min time intervals), an examination of diurnal variations in visibility, as represented by the extinction and/or scattering coefficient, are possible.

Diurnal and seasonal patterns in measured  $b_{scat}$  and  $b_{ext}$  are similar for many sites. A common pattern is highest scattering or extinction during the summer, lowest during the winter with

scattering or extinction being somewhat higher at night. Usually, the differences between different hours of the day are not as large as the differences between seasons. In some cases, however, the average extinction varies by up to a factor of 5 from one time of day to another largely because of changes in relative humidity and the associated growth of hygroscopic aerosols. RH is typically driven mostly by an inverse relationship to average temperature. There are some sites that have unique diurnal or seasonal patterns in average  $b_{scat}$  or  $b_{ext}$ . In many cases, especially when the site is near a large urban area, there is evidence that these average values are dependent on mixing height. Higher mixing heights allow aerosols associated with local sources to reach the monitoring site.

## **S.8 RECOMMENDED FUTURE RESEARCH**

Developing strategies to improve visibility requires an understanding of the relationship between the various aerosol species and atmospheric extinction. In this report and for applications where detailed physio-chemical aerosol characteristics are not known, a number of simplifying assumptions were made to make estimates of extinction from aerosol concentration measurements. Understanding the inherent uncertainties in linking aerosol species concentrations to extinction is essential if one is going to track progress in extinction change (change in visibility) as a function of changing emissions and resulting aerosol concentrations. Some key concerns are:

Organic Aerosol Measurement. The measurement of carbon mass remains responsible for much of the uncertainty in estimates of how various aerosol species affect visibility. Adjustments are made to carbon mass to correct for the adsorption of organic gases on the filter substrate as well as loss of volatile material from the substrate. 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.

Absorption Estimates and Measurement. The accurate estimation of absorption remains problematic. Absorption can be estimated by assigning a mass absorption efficiency to elemental carbon or it can be estimated from direct measurements of light attenuation as it passes through a filter medium on which the absorbing material has been collected. Some research has suggested that the various filter absorption measurement techniques yield values that are too high by factors on the order of 20-80%, while other techniques may underestimate absorption by the same amount. Even though all techniques are highly correlated, the absorption estimates can vary by more than factors of two. Furthermore, mass absorption efficiencies, which are required to estimate absorption from measurements of elemental carbon, have been reported in the literature that range from about 5–20  $m^2/g$  with a value of 10  $m^2/g$  being used by most researchers in the field. On a theoretical basis, it is hard to justify absorption efficiencies greater than about 5-8  $m^2/g$ .

Apportionment of Carbon to General Source Categories. The attribution of smoke to fine particle mass and visibility impairment at points that are hundreds of kilometers distant are essential for meeting the requirements of the proposed PM<sub>2.5</sub> standard and proposed Regional Haze Rule.

Attribution of smoke to fine mass and/or extinction can only be achieved using yet to be developed monitoring methodologies.

Hygroscopicity of Aerosols. The relative humidity correction terms applied to sulfate and nitrate vary as a function of physio-chemical characteristics such as ammoniation and particle size, which to a large degree are dependent on the region of the country. For instance, sulfates tend to be more acidic in the eastern United States and tend toward larger particles than the western United States.

Coarse Particle Chemical and Optical Characteristics There has been very little work investigating coarse particle chemical and optical characteristics. It is usually assumed that coarse particles are primarily soil/dust, with scattering efficiencies of 0.4-0.6 m<sup>2</sup>/g, and values that were derived from two studies that occurred in desert areas where dust can contribute as much as 50% of the particle extinction budget. Some recent studies suggest that significant fractions of coarse particles are organics and/or nitrates depending on the region of the country.

Other areas of concern that are secondary to these described issues are:

- (1) How important are the mixing characteristics of aerosol species? Externally mixed particles are assumed, while it has been well documented that some species are internally mixed.
- (2) What is the significance of scattering properties of sulfates as a function of ammoniation? This includes the water absorption properties of sulfates as a function of ammoniation.
- (3) How important is the variability of ambient particle size to estimates of dry mass scattering efficiencies?
- (4) Do carbon aerosols, other than elemental carbon, absorb light and if so what are the associated absorption efficiencies?

The answer to these questions may be regionally dependent. For instance, is the east different from the inner-mountain west or the northwest or the southwest?

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.

## **S.9 REFERENCES**

Sisler, J. F., *Spatial and Seasonal Patterns and Long Term Variability of the Composition of the Haze in the United States: An Analysis of Data from the IMPROVE Network*, Cooperative Institute for Research in the Atmosphere, Colorado State University, ISSN 0737-5352-32, 1996.

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