Chapter 8

SUMMARY

8.1 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, can be compared to assess their quality. The two sets of measurements agree very well, indicating that almost all sulfur is due to sulfate species. The more precise elemental sulfur measurements on the Teflon filters are 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) can also be 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 involves knowing or assuming the aerosol sulfate acidity. The two estimates of organic mass agree well except for the third year of data, when a positive artifact affected the OMH estimate of organic mass. This artifact was identified as resulting from problems associated with a batch of Teflon filters. This problem does not affect reconstructed extinction estimates; therefore, extinction calculations are reported for all three years. However, because hydrogen is used in estimates of acidity, only the first two years of data are used to estimate aerosol acidity. The quartz-filter based organic carbon measurements are 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), may be compared to the light absorption coefficient (b_{abs}), measured on the Teflon filters using the Laser Integrating Plate Method (LIPM). One would expect that b_{abs} would 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) shows little or no correlation with b_{abs}. Also, b_{abs} correlates 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 is approximately twice as large as literature values. These comparisons are all unexpected, and indicate 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.

8.2 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.

8.3 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). Nitrate is the largest component of fine aerosol in Southern California only.

After the significant contributions of sulfate and organic carbon, soil is the next largest contributor, followed by nitrate and light-absorbing carbon.

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.

8.4 Spatial and Seasonal Distribution of Reconstructed Light Extinction and Species Contributions

The light extinction coefficient (b_{ext}) may be 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 increasing relative humidity; therefore, extinction efficiencies for soluble species must be adjusted according to the seasonal and annual average relative humidity at each site.

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 the liquid water associated with it. 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 tied for first place (with organics) 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 tied for first place in the two previously mentioned regions. Nitrate is the single largest contributor to light extinction only in Southern California.

After the significant contributions of sulfate and organic carbon to light extinction, smaller contributions come from windblown dust (coarse particles and fine soil) and nitrate. 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, in the East, higher average RH's occur during the summer, which increases extinction.

8.5 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 to perceived visual air quality.

The trends in visibility follow the trends in reconstructed extinction, in the sense that higher extinction coefficients lead to higher dv numbers. 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.

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 is reported at our nations capital, Washington D.C., with 28 dv's.

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 (or lowest dv numbers) generally occur 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.

8.6 Measured Light Extinction

Weather has a significant effect on light extinction in the eastern United States; light extinction is significantly higher when weather-related events are included. Weather-related events affect light extinction approximately two-thirds of the time at Shenandoah and Acadia National Parks.

The measured light extinction is compared to the reconstructed light extinction calculated from the measured concentrations of the major aerosol species. The comparison is quite good (within 10%) for the Appalachian Mountains, Central Rockies, Colorado Plateau, Northeast, Northern 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 last result 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; acidic sulfates have higher light scattering efficiencies 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. A further possible explanation is that extinction is an average over the entire length of the transmissometer sight path, while aerosol measurements are at a point.

8.7 Recommended Future Research

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

Organic Aerosol Measurement. Organic aerosol mass is calculated from the organic carbon mass collected on the quartz filters and with the TOR process. Adjustments were made to the organic carbon mass to correct for the adsorption of organic aerosols on the filter. However, this adjustment often resulted 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. As noted above, the work reported here showed that light absorption correlated 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, as well as 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 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. Finally, the humidity correction curve for organics is a very rough assumption 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 (i.e., "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 reasons for clean air: whether it is due to source area or meteorological causes.