**DRAFT For Comments (**April 19, 2002)

**Visibility monitoring issues: A report to MANE-VU**

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*Introduction*

It has been recognized for more than three decades that photochemical smog and fine particulate matter ($PM_{2.5}$) have reduced visibility in the US on a regional scale ("regional haze"). While these pollutants are generally anthropogenic in nature, they have also contributed to visibility degradation in rural areas. To prevent further visibility impairment in the 156 Federal Class 1 National Parks and Wilderness Areas, the EPA recently promulgated the Regional Haze Rule (64 Federal Register 35714, 1999), as a means to monitor progress toward a national visibility goal (IMPROVE, 2000). The two extended networks that have reported speciated $PM_{2.5}$ have been the Interagency Monitoring of PROtected Visual Environments (IMPROVE) program and the Clean Air Status and Trends Network (CASTNet) Visibility program.

Historically, the CASTNet 24-hour average data were reported every sixth day, while the IMPROVE data were reported every Wednesday and Saturday. In 2001, operation of the CASTNet-Visibility network was taken over by the IMPROVE program, unifying the sampling and analysis protocols under a single network. Currently, these regional haze data are reported as 24-hour averages every third day. Since the two networks differ in their protocols, we investigated the compatibility between them based upon concurrent measurements at one location, Shenandoah National Park, VA. This study differs from the analysis of Ames and Malm (2001), whose comparison was based upon weekly-integrated CASTNet samples and daily average IMPROVE samples for monitor pairs located within about 60 km of each other.

One of the tasks under the regional haze SIP process is to establish the expected improvement in visibility, and as such it is important to have an extended database of all valid measurements. Regional haze is caused by numerous sources over a much larger region than just the Class I areas. Hence, the monitoring data from additional sites may be useful to policy makers in analyzing the sources, transport, and fates of regional haze and precursors, as well as developing and evaluating potential mitigation strategies.

The haze rule calls for the monitoring of particulate matter by mass and by major species, and provides for estimating extinction using aerosol light scattering and extinction theory (IMPROVE, 2000). Some of the monitoring sites are equipped with nephelometers and/or transmissometers to provide a direct measure of scattering and extinction information. It is therefore important to assess whether or not these direct measures of

scattering and extinction are comparable to the indirect means of estimating extinction. This issue is investigated here using data from Acadia National Park, ME.

The total aerosol extinction is assumed to consist of extinction by fine particulate species (ammonium sulfate, ammonium nitrate, organic and light-absorbing carbon compounds, and soil components), as well as coarse particulate matter. At most of these sites, the ammonium ion concentration is not measured. Sulfate and nitrate ion concentrations are reported, although it is recommended to estimate sulfate extinction from elemental sulfur, while for nitrate extinction the recommendation has been to use a site-specific average value, due to network protocol changes. Since the measurements of sulfate, nitrate, and ammonium (where available) ions are generally not used to estimate aerosol extinction using the IMPROVE methodology, there is a potential need for a reassessment of the measurements undertaken as part of the regional haze monitoring program.

These are just a few of the issues pertaining to the analysis of regional haze and visibility data. We feel that these and other concerns need to be addressed at the regional planning level as the measurement programs and modeling efforts are undertaken in the upcoming years.

*Compatibility between the historical CASTNet and IMPROVE data*

Figure 1 displays the locations of the CASTNet-Visibility and IMPROVE monitors in the northeastern US. Although the two networks had different monitoring schedules, site location criteria, and analysis protocols before 2001, the networks complement each other in space; the IMPROVE monitors are generally along the Atlantic coast and the Appalachian Mountains, with one located in the urban area (Washington, D.C.), while the CASTNet monitors tend to fall along the Ohio River Valley region and into upstate New York. Unlike the IMPROVE program which required the placement of monitors in mandated Class I areas, the design of the CASTNet program was oriented towards assessment of regional ozone, sulfur dioxide levels and deposition. However, at the Big Meadows area of Shenandoah National Park (SNP), VA, both networks had monitors. The IMPROVE site is located at an elevation of 1098 m MSL and about 10 km southwest of the CASTNet location, which was at a slightly lower elevation of about 1073 m MSL.

The concurrent data from these two sites are available from November 1993 through November 1995 and should provide an opportunity to compare the historical inter-network differences in sampling and protocols. It should be noted that the CASTNet-Visibility monitor at SNP is no longer operational, even though CASTNet was back in operation in 1996 following the shutdown of the entire network in late 1995. Prior to the shutdown, the CASTNet network operated on a 1-in-6 day sampling schedule, while the IMPROVE network reported data on a twice-per-week basis.
Both networks reported elemental and major ion species, as well as elemental and organic carbon (EC and OC) and $PM_{2.5}$ mass. However, unlike IMPROVE there are no coarse (>2.5 μm) particulate mass measurements reported by CASTNet. Since the intent of this study is to examine the measurements at SNP from these two networks, we considered elemental sulfur (S), sulfate ($SO_4^{2-}$) and nitrate ($NO_3^-$) ions, and $PM_{2.5}$ mass, as these constitute the major components that contribute to visibility degradation. While the IMPROVE data are reported at ambient conditions, the CASTNet data historically had

been reported at STP. We obtained the CASTNet data, corrected to ambient conditions, from Harding ESE (E. Hebert, personal communication, 2001).

Figures 2(a)-(d) display a comparison of elemental S, $SO_4^{2-}$, $NO_3^-$, and $PM_{2.5}$, respectively, using data from common sampling days only. The 1-to-1 line is displayed as a dashed line, while the best-fit line is shown as a solid line. In general, there is a high degree of correlation between the two datasets. In the case of elemental S (see Figure 2(a)) the correlation between the two networks is quite high, and the best-fit line yields a slope of 1.29 and a correlation coefficient ($r^2$) of 0.915. The IMPROVE concentrations are, on average, about 29% higher than the corresponding CASTNet concentrations suggesting possible sampling or analytical differences between the two networks.

Figure 2(b) displays the $SO_4^{2-}$ concentrations from the two networks, and indicates a high correlation with the best-fit line not much different from the 1-to-1 line. This suggests that $SO_4^{2-}$ may be more reliable in estimating visibility than elemental S. However, as noted before, the lack of continuity in measurements beyond 1995, the limited data of about 30 samples, only one location where the two networks had monitored, and the high degree of correlation raise the possibility that the agreement may be fortuitous. This is one issue that needs careful resolution before the data from both networks can be used in further assessment of regional haze.

Figure 2(c) displays the $NO_3^-$ concentrations for the two networks along with the best-fit line and the 1-to-1 line. Again the sample size is 33, and the correlation is slightly lower than that estimated for S and $SO_4^{2-}$. There have been some concerns on the reported measurements of $NO_3^-$ in the case of the IMPROVE network, (see the IMPROVE web site http://vista.cira.colostate.edu/IMPROVE/Default.htm), although by removing one possible outlier the correlation improves to 0.954, a value similar to those estimated for S and $SO_4^{2-}$. Also, the slope of the best-fit line without the outlier is 0.86, which suggests that the estimates of $NO_3^-$ from IMPROVE are, on average, about 14% lower than those from CASTNet. Although not shown here, the annual average $NO_3^-$ concentrations at Arendtsville, PA (CASTNet) were consistently higher than those from Washington, DC (IMPROVE) by >0.5 $\mu g\ m^{-3}$ from 1994-1999, even though Washington is more urbanized. This results differs from the findings of Ames and Malm (2001), who showed than the IMPROVE network generally reported higher $NO_3^-$ concentrations than CASTNet in the eastern US. However, the study by Ames and Malm considered a longer time record (January 1989 to December 1998) and was based upon four-week averages, and all data were corrected to STP. Also, the authors reported that in the western US, CASTNet $NO_3^-$ concentrations were substantially higher than the corresponding IMPROVE values. Regardless of any potential bias between the two networks, it should be noted that, according to the IMPROVE web site, site-specific average ammonium nitrate concentrations rather than the measured $NO_3^-$ concentrations should be used to estimate extinction.

Figure 2(d) displays the scatter plots of fine mass from the two networks, with a correlation of 0.956, similar to the other variables examined in this study. Again the estimated slope is 1.03 indicates that the IMPROVE estimates of fine mass are only slightly (about 3%) higher than those from CASTNet.

Although $SO_4^{2-}$ is measured and contributes to visibility degradation in the eastern US, the recommended procedure has been the use of elemental S to compute the extinction assumed as ammonium sulfate (IMPROVE, 2000). The rationale for this appears to be that the elemental measurements are more reliable than the ionic measurements. However, from Figure 2(a) it is evident that the estimates of S based on IMPROVE are higher than those from CASTNet, while Figure 2(b) suggests that the $SO_4^{2-}$ estimates between the two networks are in very good agreement. For the limited dataset considered here, the average $S/SO_4^{2-}$ mass ratio at the IMPROVE monitor was 0.33, while the average $S/SO_4^{2-}$ ratio at the CASTNet monitor was 0.25. This is in agreement with a recent assessment study involving data from these two networks it was found that the $S/SO_4^{2-}$ ratios are lower (about 0.21 to 0.26) at the CASTNet monitors compared to about 0.31 to 0.36 for the IMPROVE monitors (Coutant et al., 2002)

If all of the ambient S is attributed to $SO_4^{2-}$, then the expected ratio is about 0.33. Since the coincident $SO_4^{2-}$ measurements between the two networks are very similar (see Figure 2(b)), it is possible that CASTNet may have been underpredicting S levels. The use of S in calculating visibility using historical data could lead to a discontinuity and erroneous trend estimates if the two networks are merged. Based upon this limited data, these results suggest that the two networks agree fairly well with each other at this monitoring site, although care must be exercised when translating the S data to aerosol extinction.

*Comparing direct and estimated measures of extinction and scattering*

The regional haze guidance calls for visibility to be computed using measurements of speciated particulate matter even though direct measurements of scattering using nephelometers and or transmissometers are made at a few sites. In this study, we considered the IMPROVE site at Acadia National Park, ME which has had both instruments operating at different time periods. The site is also equipped with a particulate sampler to provide the aerosol concentrations. For this analysis, daily average scattering and extinction were computed from the hourly nephelometer and transmissometer data, respectively, with the requirement that there are at least 12 hours of valid data to obtain the daily average. No relative humidity or STP corrections were applied to either the nephelometer or transmissometer data. These data are available from the IMPROVE web site (see http://vista.cira.colostate.edu/IMPROVE/Default.htm) for the periods of March 1988 to June 1993, and December 1995 to December 1997, respectively.

Figures 3(a)-(d) display the comparison of measured scattering from the nephelometer to the measured $PM_{2.5}$, $SO_4^{2-}$, reconstructed ammonium sulfate ($4.125 \times S$), and the aerosol extinction computed from the reconstructed fine particulate mass, respectively. Note that the reconstructed aerosol extinction was computed with monthly average relative humidity factors, and that these data were obtained directly from the IMPROVE web site. In general, the level of correlation is higher between the nephelometer measurements and the $PM_{2.5}$ mass compared to $SO_4^{2-}$ or reconstructed ammonium sulfate. It is interesting to note that Figures 3(b) through 3(d) indicates that one of the datum (June 11, 1997) may be identified as an outlier, which is not as obvious in Figure 3(a). The identified outlier has the highest measured scattering coefficient of about 118 $Mm^{-1}$ while a majority of the values are generally less than 80 $Mm^{-1}$. On this day, both the EC and OC concentrations

were relatively high compared to other days during June 1997. Similarly, this day also had a relatively high mass (>25 μg $m^{-3}$), while the majority of the data are generally < 20 μg $m^{-3}$. Further, not considering this outlier yields generally slightly higher correlations.

Figures 4(a)-(d) display a similar comparison as shown in Figures 3(a)-(d) but with measured aerosol extinction from the transmissometer data. Note that these data are from a different monitoring period than the nephelometer data. The degree of correlation is much lower compared to the nephelometer data. Most surprising is the fact that the aerosol extinction computed with reconstructed fine mass data is only weakly correlated with the direct transmissometer measurements (see Figure 4(d)).

The NESCAUM (2002) report examined similar comparisons between reconstructed extinction and scattering data and the corresponding transmissometer and nephelometer data at Acadia National Park and Shenandoah National Park. Their results were qualitatively similar, in that the agreement was better for scattering measurements. However, the authors stated that the use of monthly versus day-specific relative humidity factors would affect such comparisons.

Since the total aerosol extinction is a combination of scattering and absorption processes, we also considered the extinction (absorption) due to light absorbing carbon (LAC), as well as the reconstructed aerosol scattering, defined as the difference between constructed extinction and LAC absorption. The LAC is equal to the sum of the EC components minus the pyrolized organic components. The scatter plots are shown in Figures 5(a)-(d). Scattering is generally a small component of the total extinction. While there is a reasonable degree of correlation with the measured scattering data (nephelometer) data (see Figures 5(a) and (b)), there is a poorer degree of correlation with the measured extinction (transmissometer) data (see Figures 5(c) and (d)). Note that the high LAC absorption value (11 $Mm^{-1}$) corresponds to the potential outlier from Figures 3(a)-(d).

*Discussion*

This work builds upon a number of studies involving visibility and fine particulate data in the eastern US (e.g. Coutant et al., 2002; NESCAUM, 2001, 2002). In this study, we examined the compatibility between two national networks collecting particulate mass and speciated data over the northeast U.S. as well as a comparison between direct measurements of scattering and extinction to those estimated using particulate measurements. This work is preliminary, and demonstrates some of the simple analyses that can be made with these data. These comparisons are limited by the availability of cross-network filter-based data, and simultaneous filter, nephelometer, and transmissometer data.

In particular, it is found from these limited data that the two networks are in better agreement with each other in terms of the measured $SO_4^{2-}$ and $PM_{2.5}$ than with elemental S and $NO_3^-$. The analysis demonstrated that reliance on elemental S as a surrogate for reconstructed ammonium sulfate needs to be evaluated, given the differences between the two networks in the determination of S. Even though there are concurrent measurements of $NH_4^+$, $NO_3^-$ and $SO_4^{2-}$ ions at three sites in the eastern US -- Shenandoah National Park, VA; Great Smoky Mountains, TN; and Dolly Sods Wilderness, WV -- none of the

$NH_4^+$ data are recommended for use in reconstructing aerosol mass or extinction according to the IMPROVE methodology. If, at a majority of the monitoring locations, the $NH_4^+$ (where available), $NO_3^-$ and $SO_4^{2-}$ ion data are not being used to estimate aerosol extinction, there may be a need to evaluate why resources are being expended. It should be noted that there are many other comparisons that can be performed between the two networks that report the large number of elemental concentrations, including an examination of minor (e.g. soil) species and chemical tracer species (e.g. V, Se, etc.). Such an assessment could provide a better understanding of the differences between these two sets of historical data.

Another area that was examined in this study is the direct measurement of aerosol extinction and scattering from the transmissometer and nephelometer measurements, respectively. If these measurements are considered as direct measures of the scattering and extinction in the atmosphere then they should have a close linkage to the estimated visibility. However, since there were no readily available cotemporaneous measurements with the two instruments, we examined them individually in this study. The data were obtained from Acadia, ME, and it appears that the nephelometer measurements show a higher degree of correlation with $PM_{2.5}$ mass and reconstructed extinction than with $SO_4^{2-}$ or reconstructed ammonium sulfate. In contrast the transmissometer data was generally poorly correlated even with $PM_{2.5}$ and LAC. Some of this poor correlation may be due to not applying relative humidity factors to the nephelometer and transmissometer data. Currently only a nephelometer is operational at Acadia. However, it is unclear as to how these data from the nephelometer would be factored in the determination of the visibility impairment and improvement

The analysis presented here is far from complete, but illustrates some of the issues that pertain to regional haze and visibility in the eastern US. It is therefore recommended that the regional planning organizations (RPOs) should undertake additional assessments of the type and variety of data that are being collected towards the assessment of visibility in the Class I areas.

*Disclaimer/Acknowledgements*

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*References*

64 Federal Register 35714, July 1, 1999.

Ames, R. B., Malm, W. C., 2001. Comparison of sulfate and nitrate particle mass concentrations measured by IMPROVE and the CDN. Atmospheric Environment 35, 905-916.

Coutant, B., et al., 2002. Source apportionment analysis of air quality monitoring data: Phases 1A and 1B. Draft Final Report prepared for the Mid-Atlantic/Northeast Visibility Union (MANE-VU) and the Midwest Regional Planning Organization under contract from the Mid-Atlantic Regional Management Association (MARAMA), Baltimore, MD.

Interagency Monitoring of PROtected Visual Environments (IMPROVE), 2000. Spatial and seasonal patterns and temporal variability of haze and its constituents in the United States: Report III. ISSN 0737-5352-47, Cooperative Institute for Research in the Atmosphere (CIRA), Colorado State University, Fort Collins, CO.

Northeast States for Coordinated Air Use Management (NESCAUM), 2001. Regional haze and visibility in the Northeast and Mid-Atlantic States. Available at web site http://www.nescaum.org.

NESCAUM, 2002. Technical memorandum #1: updated visibility statistics for the MANE-VU region. Available at web site http://www.nescaum.org.

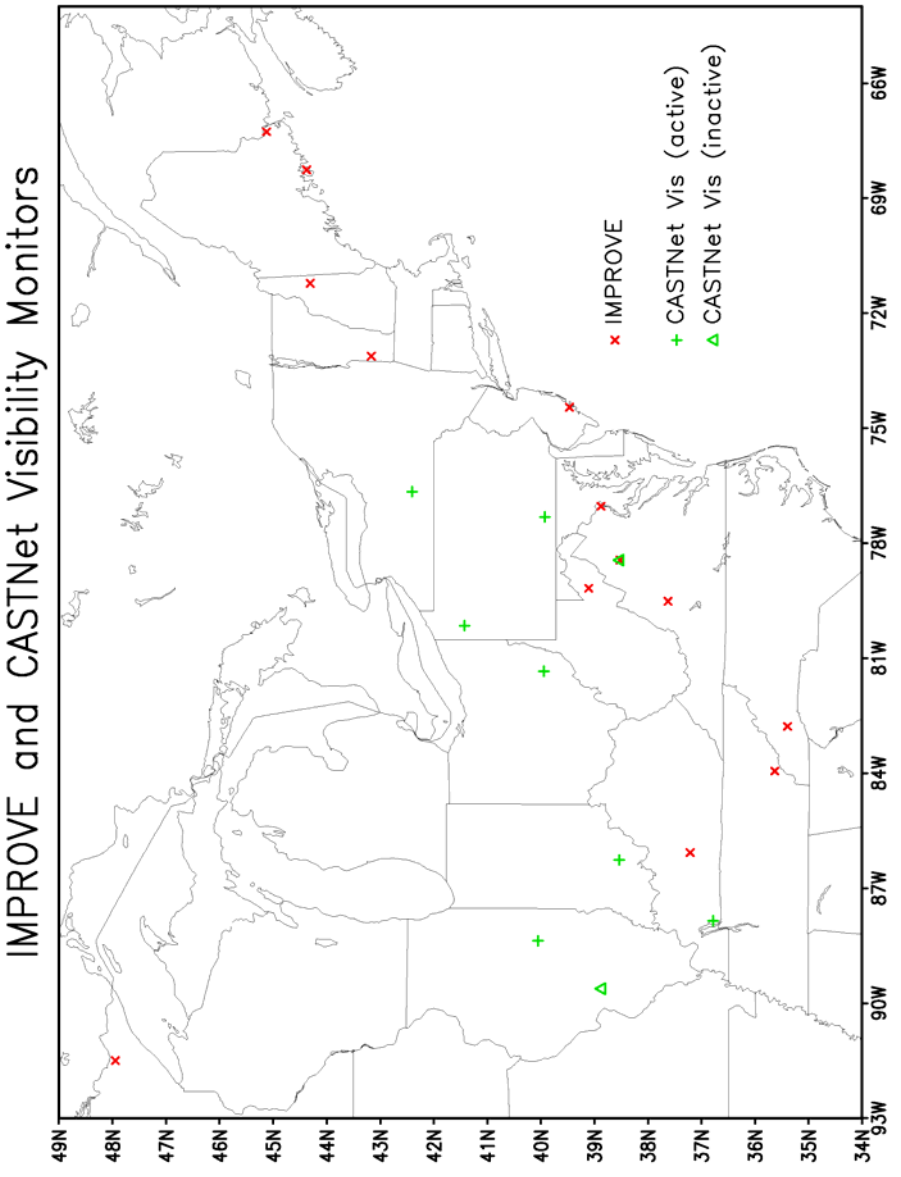


**Figure 1.** Map showing the locations of the IMPROVE and CASTNet Visibility monitors.

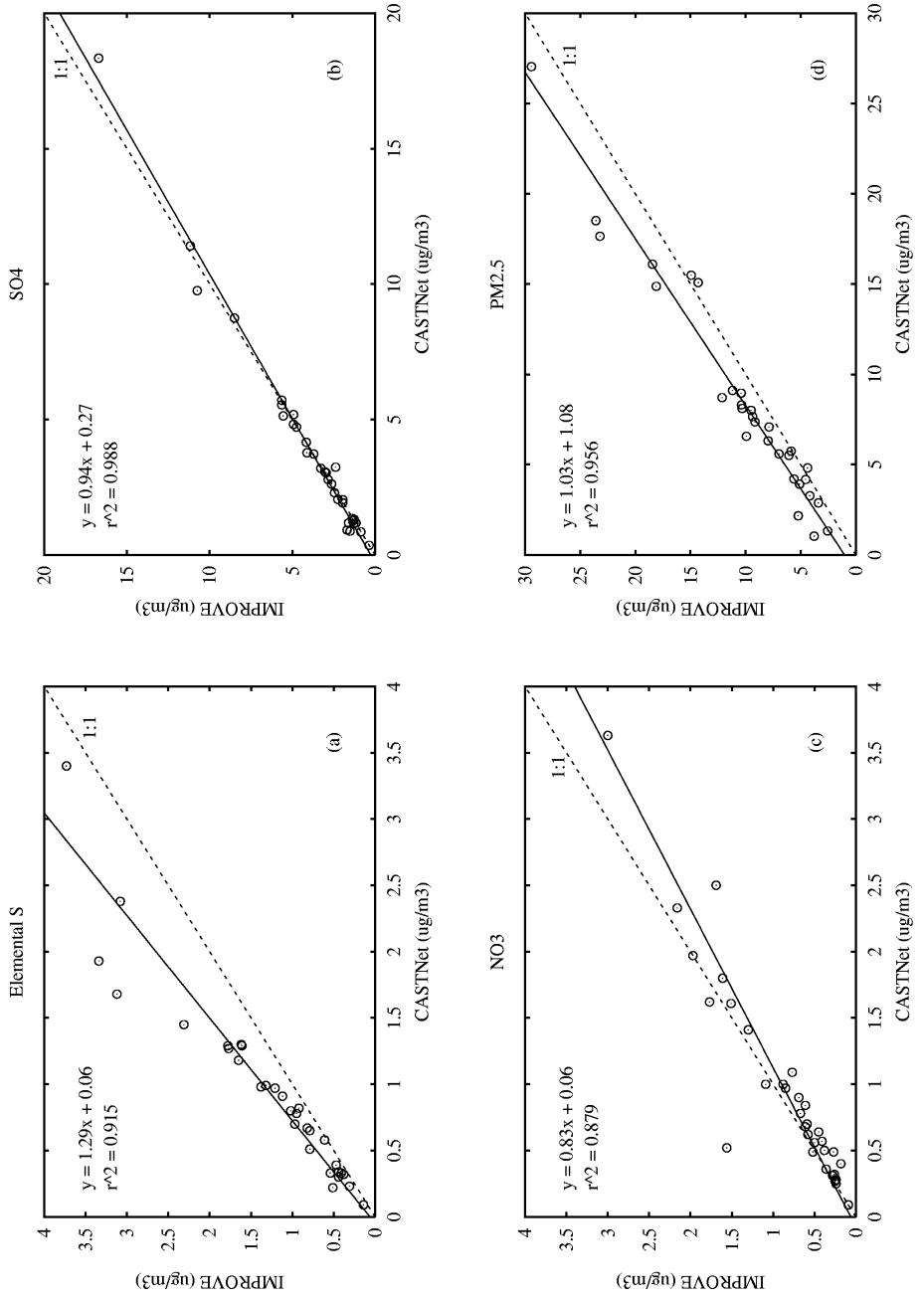


**Figure 2.** Comparison of IMPROVE and CASTNet concentrations at Shenandoah National Park, VA: (a) elemental S, (b) $SO_4^{2-}$, (c) $NO_3^-$, and (d) $PM_{2.5}$.

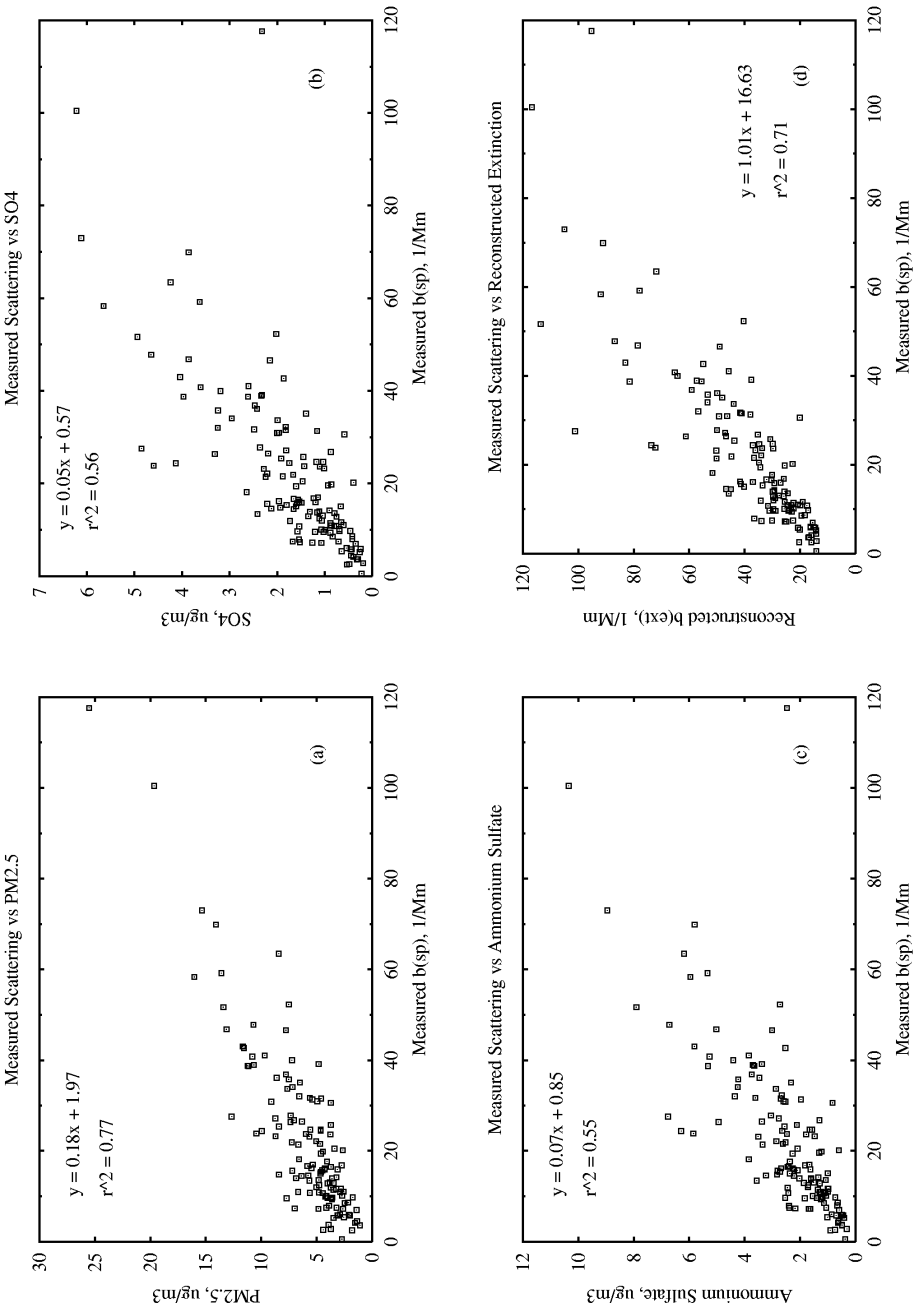


**Figure 3.** Measured aerosol scattering (nephelometer) at Acadia National Park, ME compared to various aerosol species: (a) $PM_{2.5}$ mass, (b) $SO_4^{2-}$ mass, (c) reconstructed ammonium sulfate mass, and (d) extinction due to reconstructed ammonium sulfate.

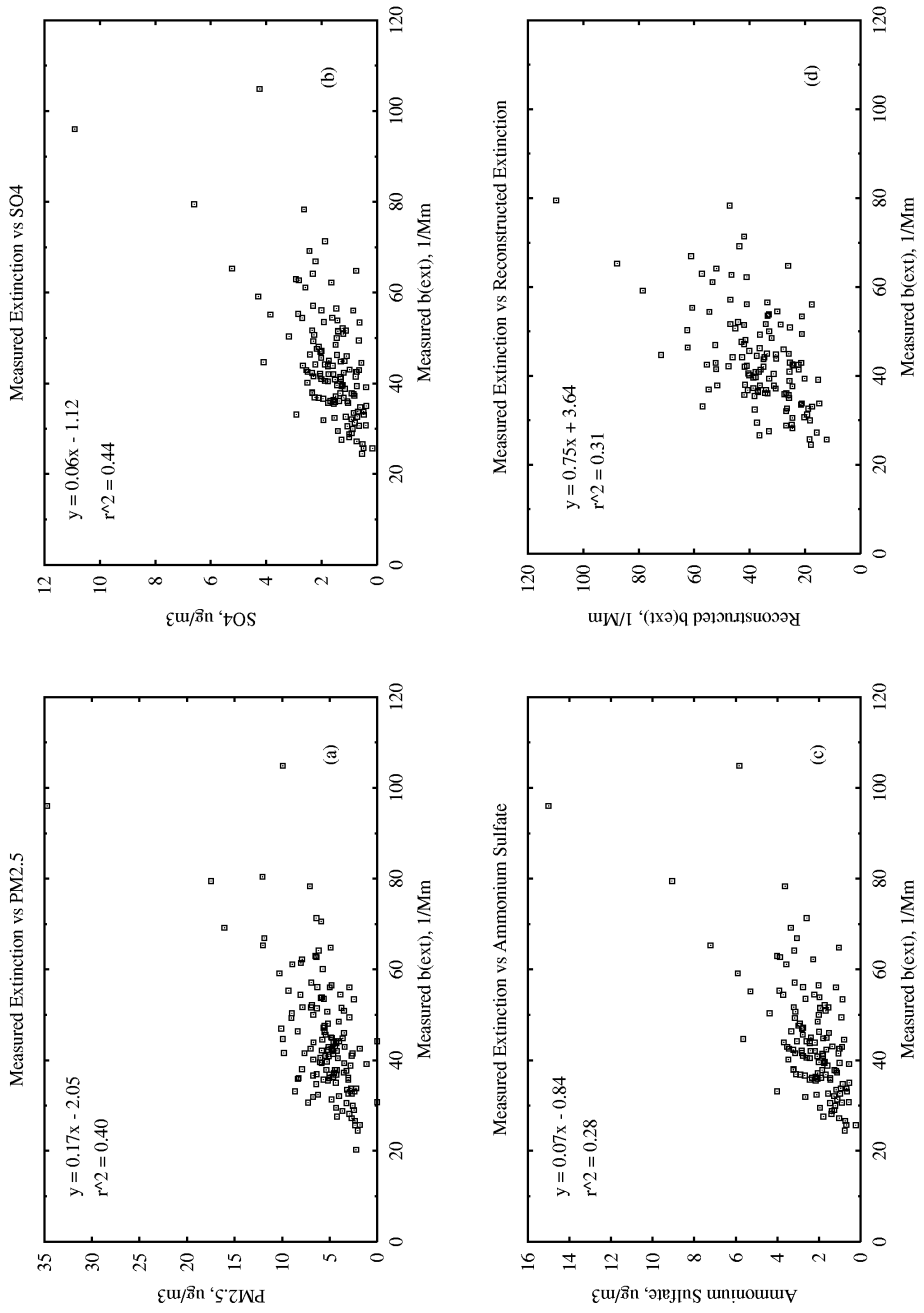


**Figure 4.** Same as Figure 3, except for measured aerosol extinction (transmissometer).

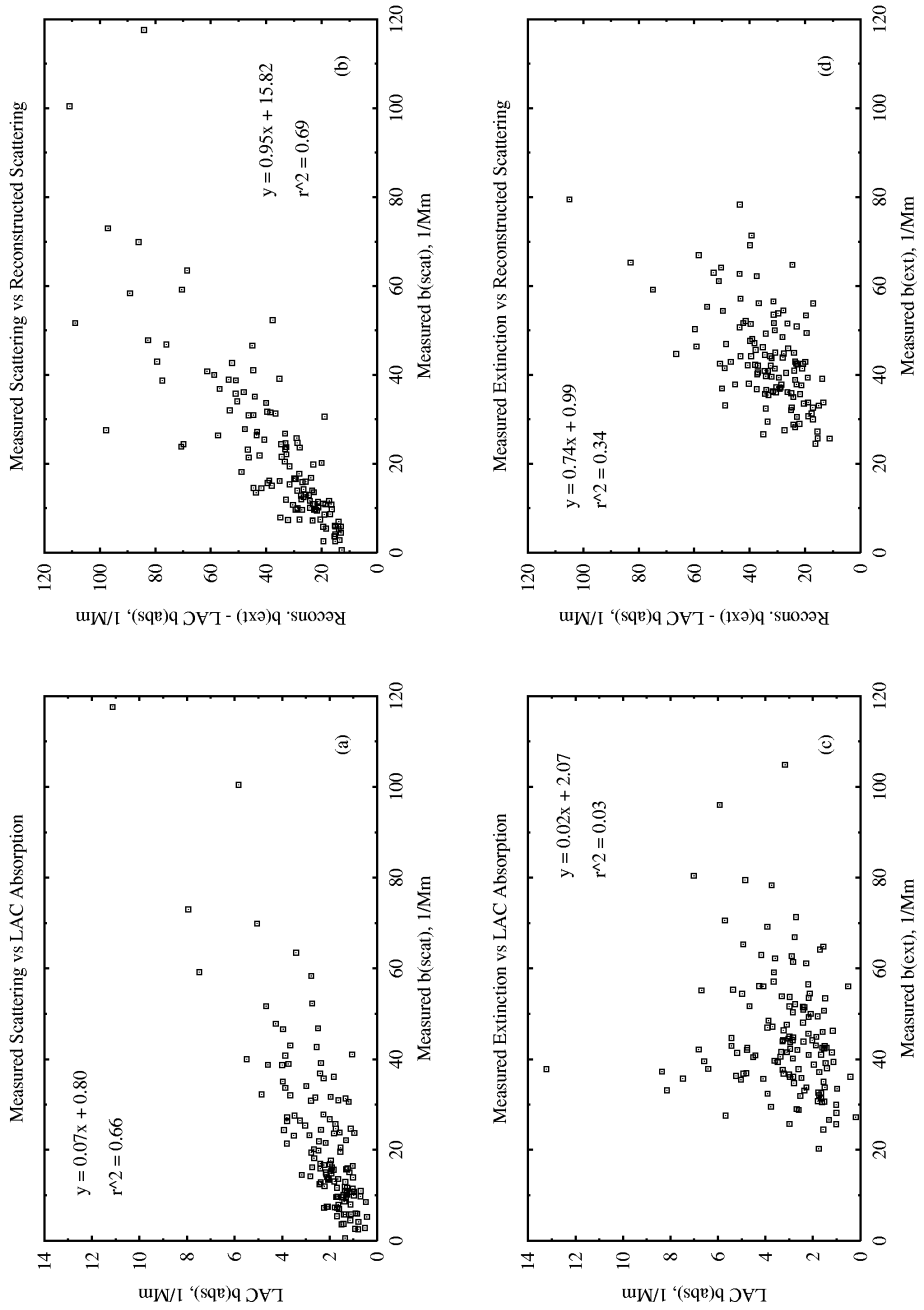


**Figure 5.** Comparisons of aerosol extinction, scattering, and absorption data from Acadia National Park, ME: (a) measured scattering vs. LAC absorption; (b) measured scattering vs. reconstructed scattering; (c) measured extinction vs. LAC absorption; and (d) measured extinction vs. reconstructed scattering.