

Real-time Carbon and Sulfate Measurements from the MANE-VU Rural Aerosol Intensive Network (RAIN): Design, Methods and Early Data

George A. Allen

NESCAUM, 101 Merrimac St., Boston MA 02114

Bradley P. Goodwin, Jay R. Turner

Environmental Engineering Program, Washington University in St. Louis, One Brookings Drive,
St. Louis, MO 63130

ABSTRACT

A rural, high elevation monitoring network of aerosol and visibility related parameters has been recently deployed in the Northeast U.S. under the Mid-Atlantic and Northeast Visibility Union (MANE-VU) regional haze planning organization (RPO). This network is designed to provide detailed characterization of transported pollution with both a visibility and fine particle focus. The initial network has three high-elevation (700-2500') sites with detailed PM and visibility-related measurements. The sites cover a wide geographic area from near the Ohio River valley to Acadia National Park, allowing an assessment of a range of aerosol types ("fresh" vs. aged secondary aerosols) and their precursor gases. Aerosol measurements are made year-round with highly time-resolved (1-2 h) methods, providing enhanced insight into regional aerosol generation and source characterization, and factors that drive short-term visibility. These data will also be used for aerosol model performance evaluation and development. Hourly parameters measured in this network include: PM2.5, sulfate, EC/OC, light scattering, trace SO₂ and CO, ozone, surface meteorology, and visual scene images. IMPROVE third-day 24-hour integrated measurements for carbon, ions and PM2.5 are made at all sites. The network is a multi-year project, with routine operations being integrated into participating state agency's networks. The sites are located in a SW-NE line: Frostburg - western MD (near-source), Mohawk Mt. - northwest CT (mixed-source), and Acadia NP (far-source). This network is the first long-term deployment of the Thermo Electron continuous sulfate and Sunset Laboratories carbon analyzers at routine state agency monitoring sites; these methods are representative of the new breed of mature continuous speciation methods now available. This paper focuses on method descriptions, initial data, and operational issues from these two methods. A simple PM2.5 reconstruction using only sulfate and carbon is shown to be a useful diagnostic tool for instrument performance.

Paper #18, presented at the Air & Waste Management Association Visibility Specialty Conference on Regional and Global Perspectives on Haze: Causes, Consequences and Controversies. Asheville, NC, October 25-29, 2004.

INTRODUCTION

Regional haze in the MANE-VU domain is driven by a combination of transported aerosols from sources within and outside of the 12-state region. Determining the relative contribution of source regions to visibility degradation is a key task under the haze rule. A new network of sites was deployed during the summer of 2004 to assess this issue. The Rural Aerosol Intensive Network (RAIN) is coordinated by NESCAUM, but is a cooperative effort of MANE-VU member state air agencies. RAIN covers the region from western MD (near large sulfur sources in the Ohio river valley) through northwest CT (a “swing” site expected to have impact from a wide range of source locations and types) to Acadia National Park on the Maine coast -- the proverbial “end of the regional tailpipe” transport receptor site. The initial network consists of these three rural moderate elevation (700 to 2500 feet) sites, in a SW to NE line (Figure 1), all with detailed PM and visibility-related measurements. The network design includes highly time-resolved (1-2 h) aerosol mass, composition, and optical property measurements to provide enhanced insight into regional aerosol generation and source characterization, factors that drive short-term visibility, and aerosol model performance and evaluation.

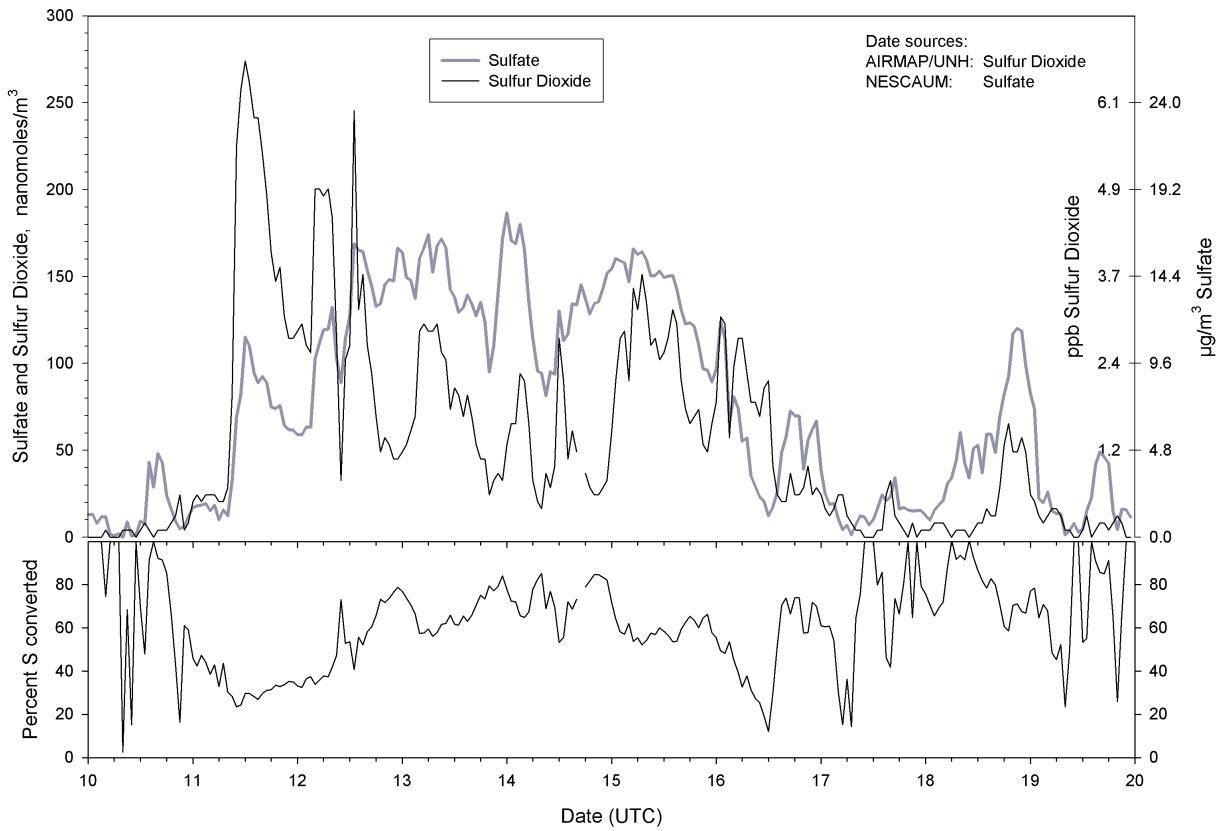
Figure 1. RAIN site locations.



Highly time-resolved aerosol data are at the core of this network, since they can provide dramatic insight into source influence and atmospheric and chemical processes (much of this information is lost when sampling on a daily time scale). An example of this is the hourly relationship between SO₂ and sulfate at the summit of Mt. Washington, NH (6300 ft.) during a major regional haze event in August 2002 (Figure 2). The left axis shows Sulfate and SO₂ in molar

units for direct comparison, and the right axis shows them in more commonly used units. The bottom plot is the percent S converted from SO₂ to sulfate. The onset of the event mid-day Coordinated Universal Time (UTC, or 7AM local time) on the 11th shows both sulfate and SO₂ rising rapidly over a few hours and then dropping somewhat. The percent S converted shows a relatively smooth rise during this same period, a much less dynamic signal. Over the four core days of the event, the percent converted gradually rises from about 25 to 75%, which implies a more aged air mass later in the event. There are many other useful temporal aspects of these data in this example that would be inaccessible from 24-hour duration samples. From a “sub-daily” short-term visibility perspective, factors such as the rapid changes in sulfate shown here combined with strong diurnal cycles in relative humidity can result in very large deviations across a day from average visual range. RAIN will provide both direct hourly measurement of visual range and most of the factors that drive it in the eastern U.S., which will provide opportunities to improve our understanding of the overall process.

Figure 2. Mt. Washington NH Summit, August 2002
Hourly Sulfate and Sulfur Dioxide



Recent advances in measurement technologies have made it practical to deploy robust methods for realtime sulfate and elemental/organic aerosol carbon that are both relatively straight forward to run and provide high quality data. The Sunset Laboratory field carbon analyzer and the new Thermo Electron Environmental model 5020 sulfate analyzer (based on a method developed by the lead author while at Harvard) are used at the RAIN sites; this is the first use of these new methods in routine ongoing state-run networks (the Mt. Washington 2002 hourly sulfate data is

from an early R&D version of the Harvard/Thermo Electron analyzer). These methods, combined with other more routine measurements such as IMPROVE aerosol, NGN-2 (wet) nephelometers, continuous PM2.5, trace SO₂, ozone, meteorology, and automated digital visibility cameras (CAMNET), make up the RAIN core monitoring lineup. The RAIN network design is an example of supplemental measurements at IMPROVE sites which help fill in the detailed temporal details of the physical, optical, and chemical features of regional haze. Components of this network could also serve as a template for the new rural "Type 2" NCORE EPA monitoring network design¹. Some of the RAIN sites have or will have additional related measurements, including "true" trace CO, NO_y, dry scattering (NGN-3a nephelometer), and other measurements. An example of how state agencies might use the data from RAIN sites in the context of assessing the influence of inter-state transport of pollutants is presented by Seybold et al.² in these proceedings.

As part of the "Technology Transfer" process of new measurement methods from research oriented sites to routine state/local agency deployment, one of the early tasks of RAIN has been to evaluate and optimize the carbon and sulfate aerosol method's operational parameters. One example of this optimization process is the wide range of choices on how the Sunset Laboratory carbon analyzer could be run. Numerous operational issues and options were identified prior to the start of the RAIN program. These include the magnitude of OC blanks (which could be a substantial amount relative to rural OC aerosol levels even with the OC sample stream denuder), and the option of a 2-hour cycle for "OC1-2-3-4" thermal fractions, which might be useful for OC source-type characterization especially on a time-resolved basis (and also is expected to give a reduction in the OC blank value). Yet to be determined is how the Sunset carbon analyzer (a TOT method) might be run to give a more IMPROVE-like EC/OC TOR measurement. We are working closely with Sunset Labs on these and other issues related to this method.

METHODS

Thermo Electron Environmental Sulfate Analyzer.

The Thermo Electron Environmental (Franklin MA) model 5020 SPA (Figure 3) is a new commercial product that measures ambient sulfate in a true continuous flow mode, in contrast to a collect and analyze sequence as used in other approaches^{3,4}. Conversion efficiency for the 5020 is high (essentially 100%) and is not dependent on other components of the aerosol's composition. The method is based on catalytic thermal reduction of sulfate to SO₂ at 1000° C; the resulting SO₂ is measured with enhanced high-sensitivity pulsed fluorescence techniques. This method is based on technology developed in 2001 at the Harvard School of Public Health (Boston MA)⁵; various early non-commercial research versions of this method have been used in

Figure 3. Thermo Electron Model 5020 Sulfate Analyzer



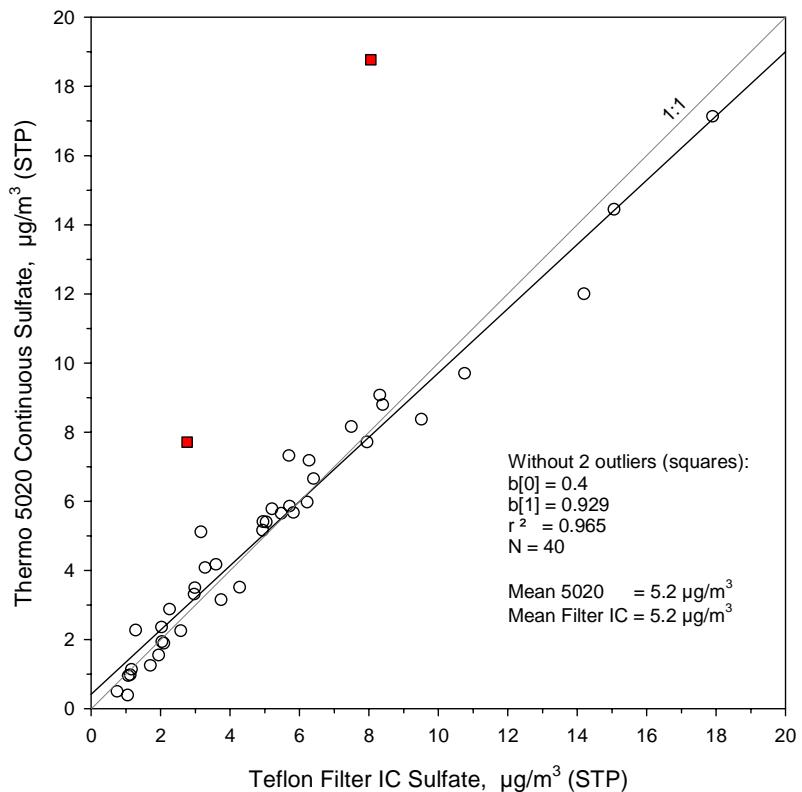
several of the US EPA Supersites, the EPRI SEARCH/ARIES program, and other studies^{6,7}. The system inlet used in the RAIN program is the Magee Scientific (Berkeley CA) BGI SCC 0.732 photometer cyclone. The analyzer sample inlet flow is 0.9 LPM, resulting in a 2.5 μm size cut according to the cyclone manufacturer. A long-life sodium carbonate-coated metal multi-annular acid gas denuder (Sunset Laboratory, Hillsborough NC) is used upstream to remove SO₂ prior to sampling. The system is auto-zeroed frequently using its own internal source consisting of the sample air matrix minus particles. This approach removes or minimizes potential interfering species. For the initial deployment in the RAIN program, the analyzer is run in a 15-minute auto-zero cycle, providing a 1-hour LOD of approximately 0.3 $\mu\text{g}/\text{m}^3$. For the data presented here, sample mode data are calculated at the end of each cycle by the analyzer, using both of the adjacent baseline measurements to maximize sensitivity. The pre-production system used to generate the data presented here has a small but consistent negative offset of 0.2 $\mu\text{g}/\text{m}^3$; that value is added back into the data during processing and validation steps for the RAIN sites. Product information on the commercial version of this method is at:

<http://www.thermo.com/com/cda/product/detail/1,1055,10119218,00.html>

This method was intensively evaluated by comparison of data from a pre-production version of the model 5020 analyzer at the St. Louis Supersite in East St. Louis, IL. Two collocated comparison techniques were used: six-hour Teflon filter samples with IC analysis, and an automated semi-continuous IC method.

Six-hour duration integrated samples were collected twice daily on 47 mm Nylon filters using a modified version of the Harvard-EPA Annular Denuder System (HEADS) which in this case included an impactor with 2.1 μm at 10 lpm, a sodium carbonate annular denuder, and a Nylon filter. The samples were extracted by sonication in MilliQ with 1.0 mM sodium bicarbonate and 4.0 mM sodium carbonate, and analyzed by ion chromatography. 42 data pairs were collected between July 21 and September 3, 2004. Figure 4 shows a scatterplot of these data; the regression line is the dark line and the 1:1 line is the grey line. Two outliers are not included in the regression results. The mean sulfate measured by both methods is

Figure 4. Thermo continuous sulfate vs. filter IC sulfate, St. Louis Supersite, July-Sept 2004



$5.2 \mu\text{g}/\text{m}^3$, and the R^2 is 0.965. These data demonstrate that the 5020 conversion efficiency is essentially unity.

A collocated comparison for hourly data was also performed at this site using a Particle-Into-Liquid Sampler (PILS), an automated wet collection ion chromatography method³ that has been shown to be comparable with traditional integrated filter sulfate samples. Hourly sulfate data from these two methods are shown in Figures 5 (a scatterplot of 13 day's data) and 6 (a detailed 2-day time-series). The two methods agree well numerically; for the March 19-31 period, the slope is 0.98 and the intercept is 0.0. The correlation on an hourly basis is also high; R^2 is 0.925 when four PILS "carryover" hours are removed, and 0.91 with all hours. Mean sulfate is $2.0 \mu\text{g}/\text{m}^3$ during this comparison period, lower than the June 2001 through May 2002 annual mean of 3.5 for this site; higher sulfate concentrations would presumably result in a higher correlation than reported here.

Figure 5. Hourly Thermo Electron 5020 vs. PILS sulfate,
E. St. Louis Supersite, March 19-31, 2004

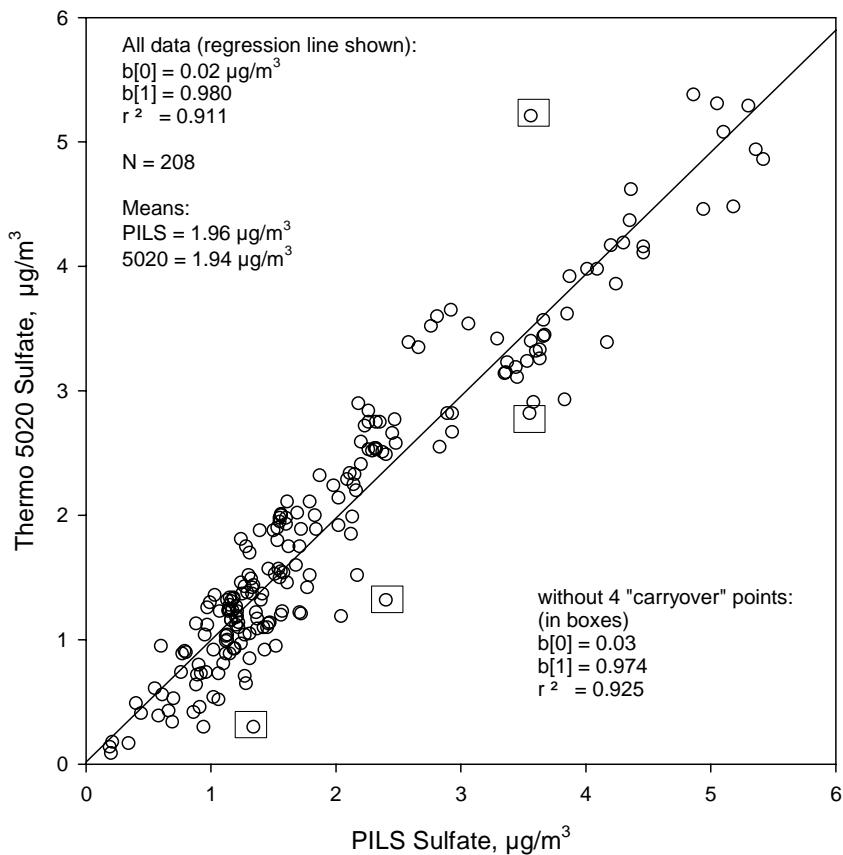
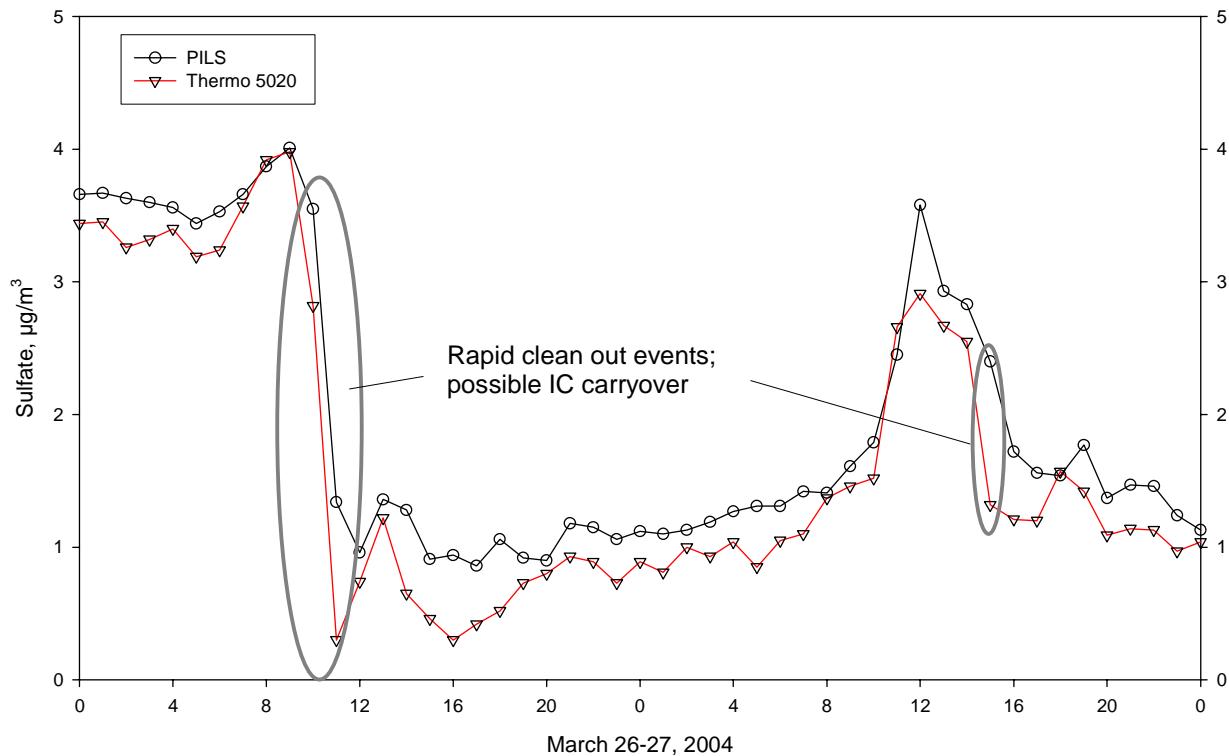


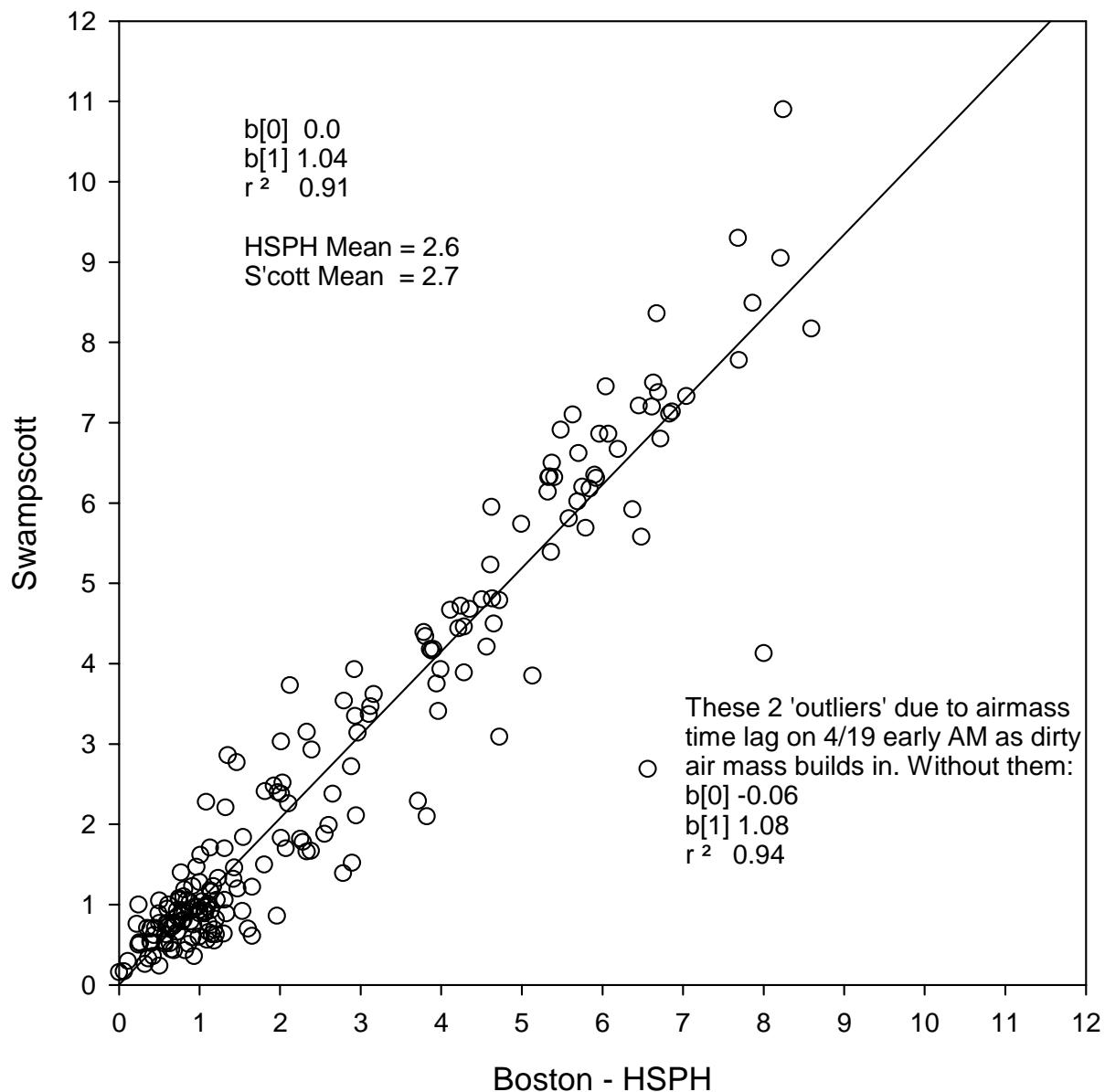
Figure 6 shows a two-day sequence with substantial dynamic range; time is local standard (CST). The two circled periods are evidence of apparent "carryover" of the PILS method, causing it to lag the true sulfate concentration after rapid clear-out events.

Figure 6. Example of PILS carryover (St. Louis Supersite)



The precision of the Thermo Electron 5020 sulfate analyzer has not been thoroughly evaluated, but an upper bound can be ascertained by comparing two pre-production systems that were run at different sites in the Boston area during April 2004. Figure 7 shows hourly data for eight days (April 16-23, 2004) for a site in Swampscott and Boston MA. The sites are 21.4 km apart and very different in nature; the Swampscott site is coastal suburban (17 km northeast of Boston, 160 meters north of the ocean) and frequently influenced by marine air masses, while HSPH is urban and 8 km inland. Despite these site differences and distance, the correlation is very good ($R^2 = 0.94$, higher than with PILS collocation). Two “outliers” were removed as shown; based on time-series analysis the large difference for these hours is due to a frontal boundary passage.

Figure 7. Swampscott vs. HSPH 1-hour sulfate, 16-24 April 2004.



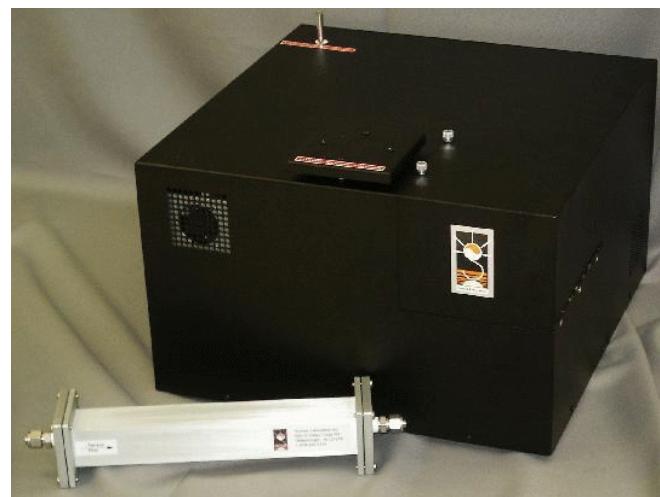
Operation

The service interval for the 5020 sulfate analyzer is 2-3 months for the denuder, inlet cleaning, leak tests, and SO₂ calibrations. The furnace core life is expected to be 6 months or more; to date we only have 3 months of experience with it. Overall, the system has run smoothly and with minimal effort at all three sites after initial installation was completed. Final validation of data relies on comparison with IMPROVE sulfate measurements, which are not available until 6 to 9 months later.

Sunset Labs Carbon Analyzer.

The version of the Sunset carbon analyzer (Figure 8) being run in RAIN is the new NDIR detector configuration, not the original FID method described and validated by Bae et al.⁸ The NDIR approach does not require any flammable gases, a major advantage both in safety and operational convenience over the FID version of this method. RAIN is running the method in the “long” mode, on a two-hour sample cycle. Compared to a one-hour cycle, this is expected to give a lower OC artifact and allows analysis for the “OC1-2-3-4” thermal fractions, whereas hourly sampling only gives a single OC value. These OC fractions may be useful as PM Source Signatures on this sub-daily time scale, but this is not evaluated in this paper. For RAIN data, we are using the optical EC (attenuation of laser transmission during sampling) for the simple EC/OC partitioning instead of the thermal EC data, since for these rural sites thermal EC is often below the methods LOD even with a 2-hour sample cycle. The optical EC data has been empirically scaled by the manufacturer to fit the thermal EC data response using a 2nd order polynomial to account for differences in EC attenuation as a function of loading on the filter.

Figure 8 Sunset Laboratories EC-OC Carbon Analyzer



OC blank values from this method were evaluated at the Frostburg site by using a pair of collocated analyzers to run “dynamic blanks” (normal sampler operation but with a Teflon filter upstream of the denuder) on both 1- and 2-hour cycles, but operational issues at that site during this early study period have made these data difficult to interpret. Product information on the method is at: <http://sunlab.com/CarbonAerosolField.html>

RESULTS

RAIN field operations were phased in during the spring of 2004, with valid data for most sites starting in late June, prior to the NEAQS intensive study in the region. One of the biggest challenges in a network like this is to be able to identify serious instrument or method problems in a timely manner. One near-realtime approach to evaluation of the data quality from these systems is to perform a mass reconstruction, comparing the major PM species to the continuous PM2.5 measurements (“measured” PM). Here we use only the carbon and sulfate data and some reasonable assumptions for other components of PM2.5, since during the summer in the eastern US there is minimal nitrate and crustal material contribution to PM2.5; that leaves carbon and sulfate as the dominant species. For the PM2.5 reconstructions presented here, we assume that sulfate is mostly neutralized (mass is sulfate ion times 1.3) and has modest water associated with it even after drying (add 20%), and use a rural aged OC mass conversion factor of 1.8 (no water factor is used for the OC). Based on limited experience to date with 2-hour cycles, an average

OC blank of $0.5 \mu\text{g}/\text{m}^3$ is subtracted before the OC mass multiplier is applied. These values are summed, and then multiplied by 1.1 to account for a generic crustal and nitrate mass contribution; both are expected to be minimal in the eastern US during the summer. This was done for all available valid data from early July to mid-August for all three sites. PM2.5 was measured with a 50° R&P (Albany NY) model 1400A TEOM® at Acadia NP and a Met One (Grants Pass, OR) model 1020 BAM (Beta Attenuation Monitor, with sample heater) at Mohawk Mt. and Frostburg MD. A correction based on historical data was applied to the R&P TEOM data to make it comparable on average to Federal Reference Method (FRM) PM2.5 data. No correction was applied to the Met One BAM data, in part because that method is generally comparable to the FRM and in part because it is a new site without any history to rely upon. Both of these methods control for but do not eliminate bound water as part of the PM2.5 measurement. Nitrate loss from the TEOM is not a concern during summer at Acadia NP, since nitrate concentrations are expected to be very low relative to the total PM2.5. Nitrate loss from the Met One BAM method is generally considered to be minimal.

Figures 9 and 10 show scatter plots of the results for the measured and reconstructed 2-hour mean PM2.5 for Acadia and Mohawk Mt CT; the reconstructed 2-hour PM2.5 is about 10 to 15% lower than the measured PM2.5 and is well correlated with the measured PM. The agreement and correlation are reasonable given both the noise in the methods and the assumptions used. There is some water associated with OC PM; including that and using an OC mass factor of 2.0 instead of 1.8 would also tend to improve the numerical agreement.

Figure 9. Reconstructed and measured PM, Acadia NP

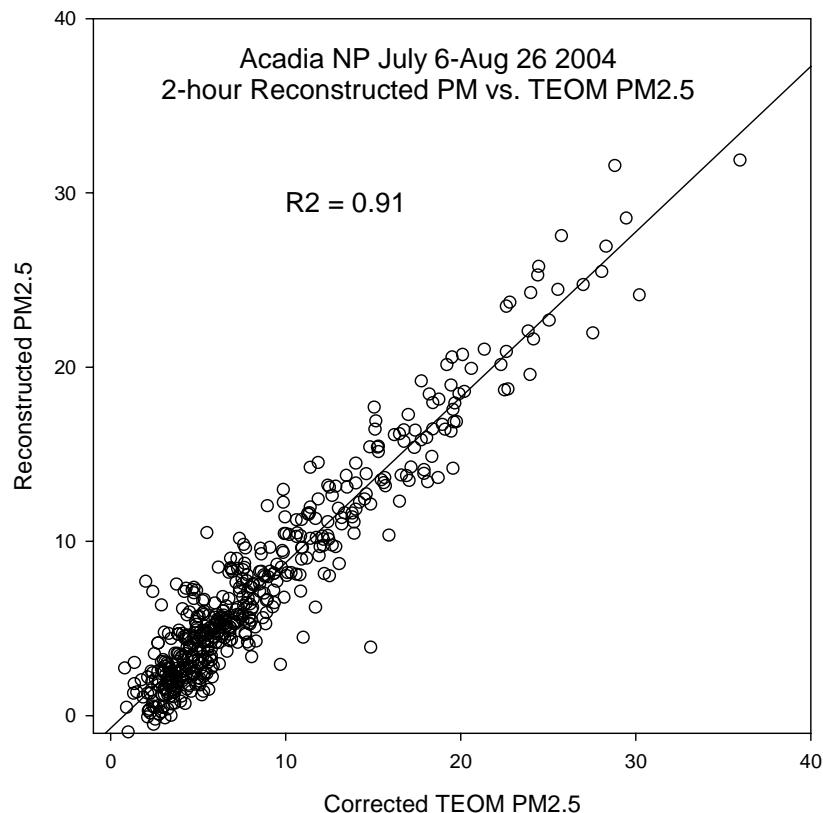
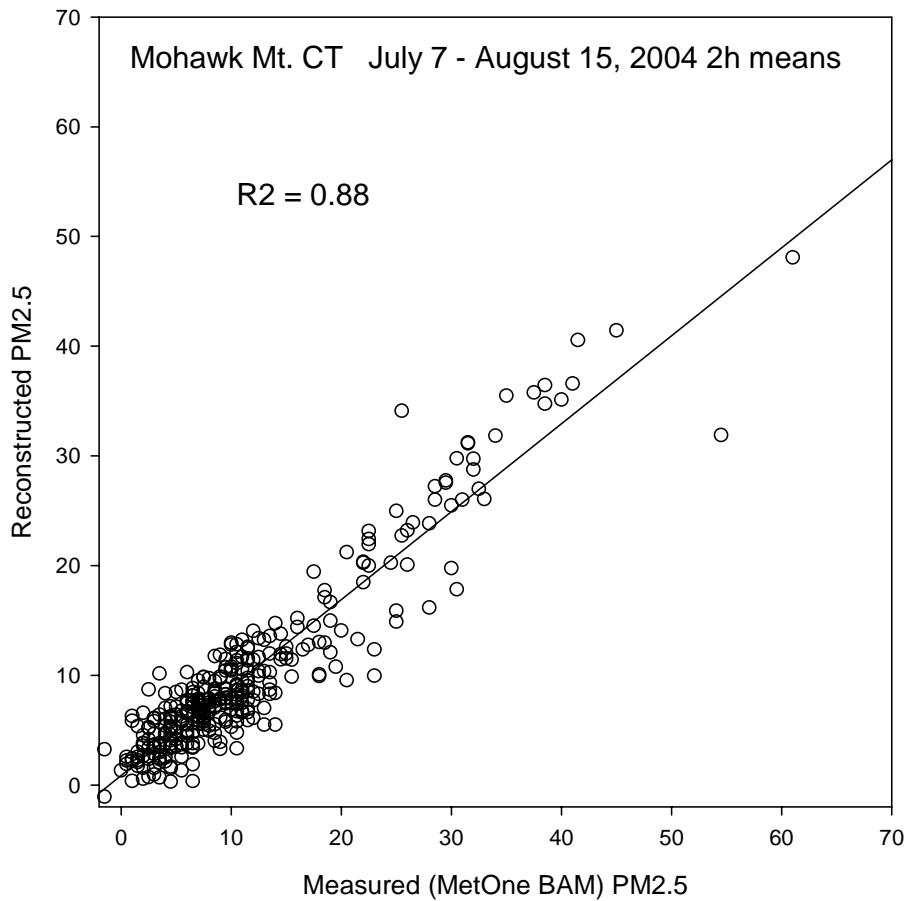
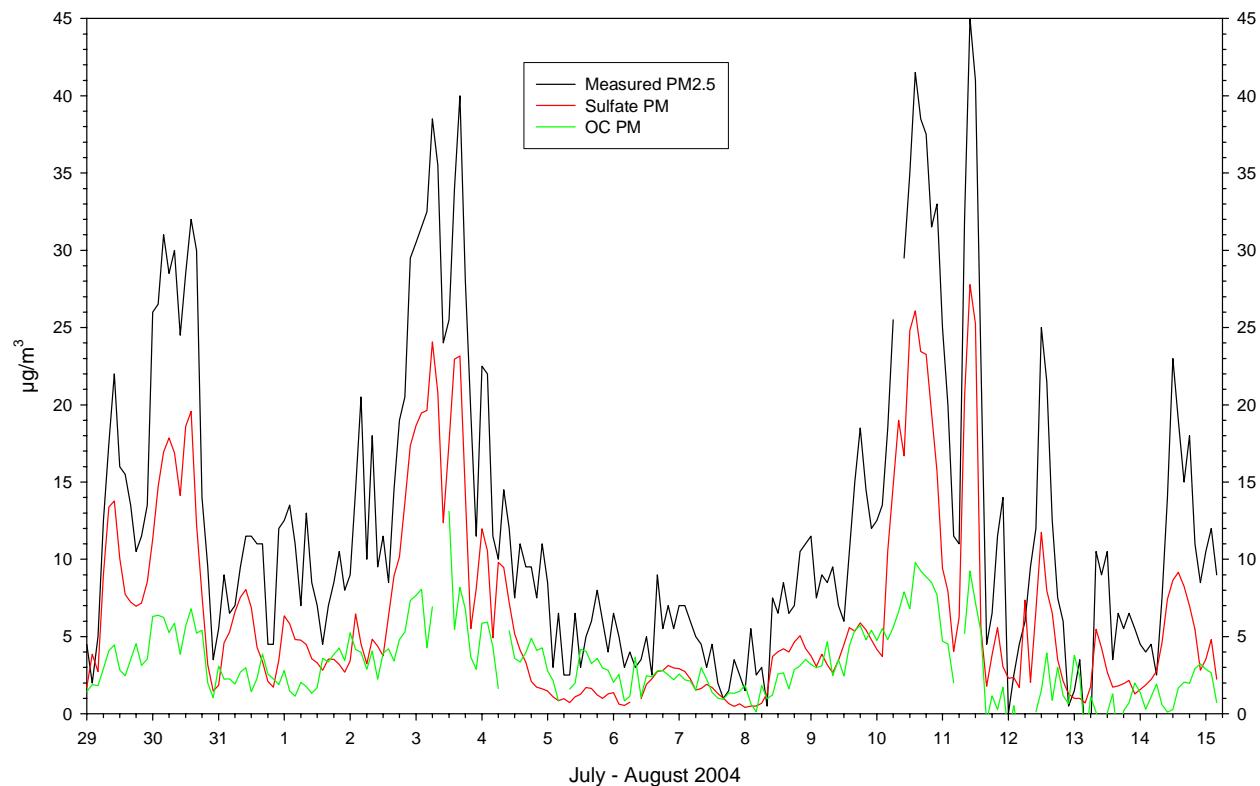


Figure 10. Reconstructed and measured PM, Mohawk Mt.



A time-series plot of the estimated mass attributed to sulfate and OC aerosol along with the measured PM2.5 (Met One BAM 1020) at Mohawk Mt. in northwest CT for a 17-day period is shown in Figure 11 (time is EST). Three multi-day events are evident where 1-hour PM2.5 exceeds 30 $\mu\text{g}/\text{m}^3$, with sulfate dominating the observed PM2.5 during those periods but not during other times. Sulfate shows much more dynamic range than the organic carbon aerosol at this rural site.

Figure 11. Mohawk Mt. CT 2-hour sulfate and organic carbon-related PM, and measured PM2.5



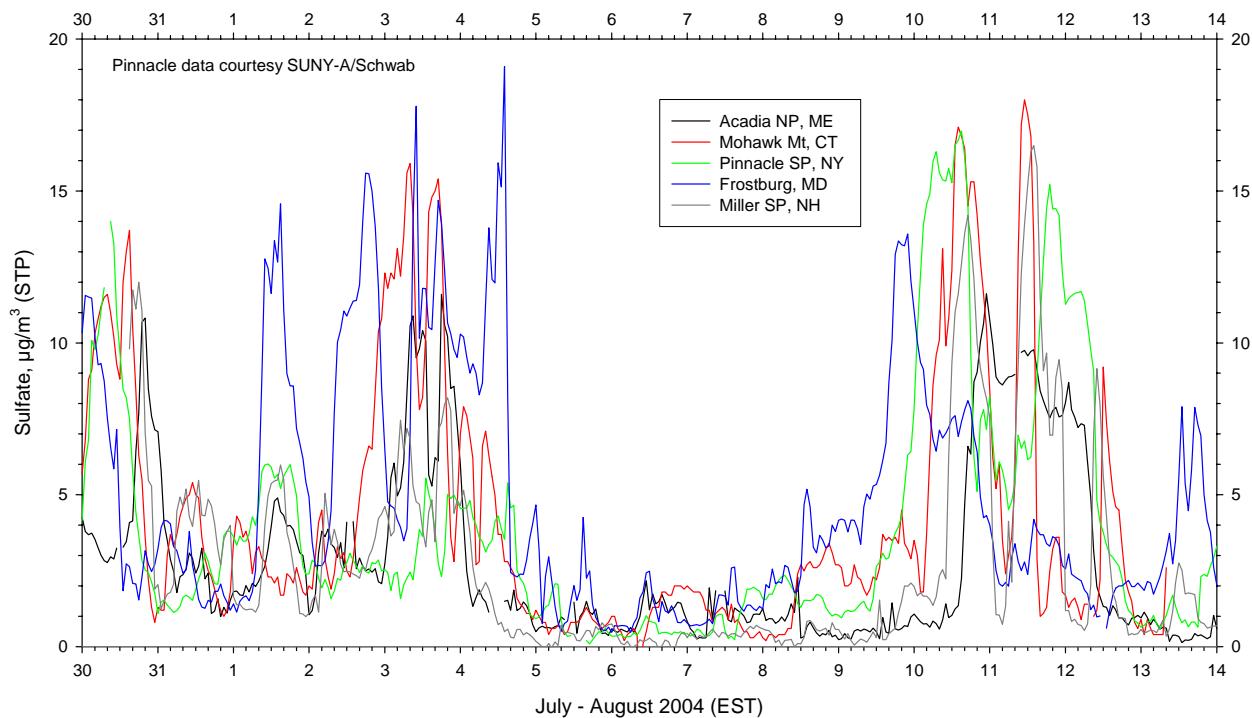
A similar mass reconstruction was done for the western MD site at Frostburg (Piney Run). The results for this site showed that reconstructed PM2.5 was substantially lower than the measured PM2.5, indicating that there were problems with data from one of the three methods used in the reconstruction: carbon, sulfate, or PM2.5; this review initiated corrective action for the carbon instrument installation at that site. Based on the initial experiences from this network, and the relative complexity of the Sunset carbon analyzer even in this NDIR configuration, we are exploring approaches to provide simple and independent real-time performance checks for the Sunset carbon method.

One option is to also deploy a Magee Scientific (Berkely CA) Aethalometer for BC; the optical EC and Aethalometer BC relationship should be reasonably consistent on a day-to-day basis (although different numerically because of the way the optical density data are processed); this approach covers most of the common failure modes of the Sunset method. A potential additional value to the Aethalometer 2-wavelength method in this network would be as a wood smoke indicator⁹. Another powerful diagnostic tool for determining proper operation of the Sunset method is the running of routine “dynamic blanks” and using the Sunset’s optical EC signal to assess the system for leaks. This parameter should be very close to zero (less than 50 ng/m³ for a 2-hour cycle mean). The thermal EC data can not be used for this test; its LOD is much higher than the optical EC LOD. The effective thermal OC LOD is several hundred ng/m³ or more because of the uncertainty and variability of the OC artifact, so it can not be used for this test.

Spatial Sulfate Assessment

In addition to the three RAIN sites, there were two additional pre-production Thermo model 5020 sulfate analyzers running during July and August 2004 in the Northeast US, at Pinnacle State Park in south-central NY (12 km SW of Corning) run by SUNY-Albany, and at Miller State Park in southwest NH (Pack Monadnock Mt.) run by NH-DES and NESCAUM. Figure 12 shows a time series plot of preliminary hourly sulfate data for all five sites. Large-scale synoptic patterns can be observed across this region. The period August 5 to 8 is relatively clean at all five sites, and a regional-scale event is indicated by elevated levels at all sites for August 2-4 and 10-12. There are substantial sub-daily dynamics at all sites. Changes in sulfate concentrations of an order of magnitude over a few hours are common, as are short (less than 12-hours) but large events (Mohawk Mt. on August 11th for example). The August 19-12 sequence also shows the progression of transport from SW to NE, starting with elevated sulfate at the Frostburg (MD) site on the 19th, continuing to the NY, CT, and NH sites on the 10th, and finally reaching Acadia NP (ME) on the 11th.

Figure 12. Five-site hourly sulfate, July 30 - August 13, 2004

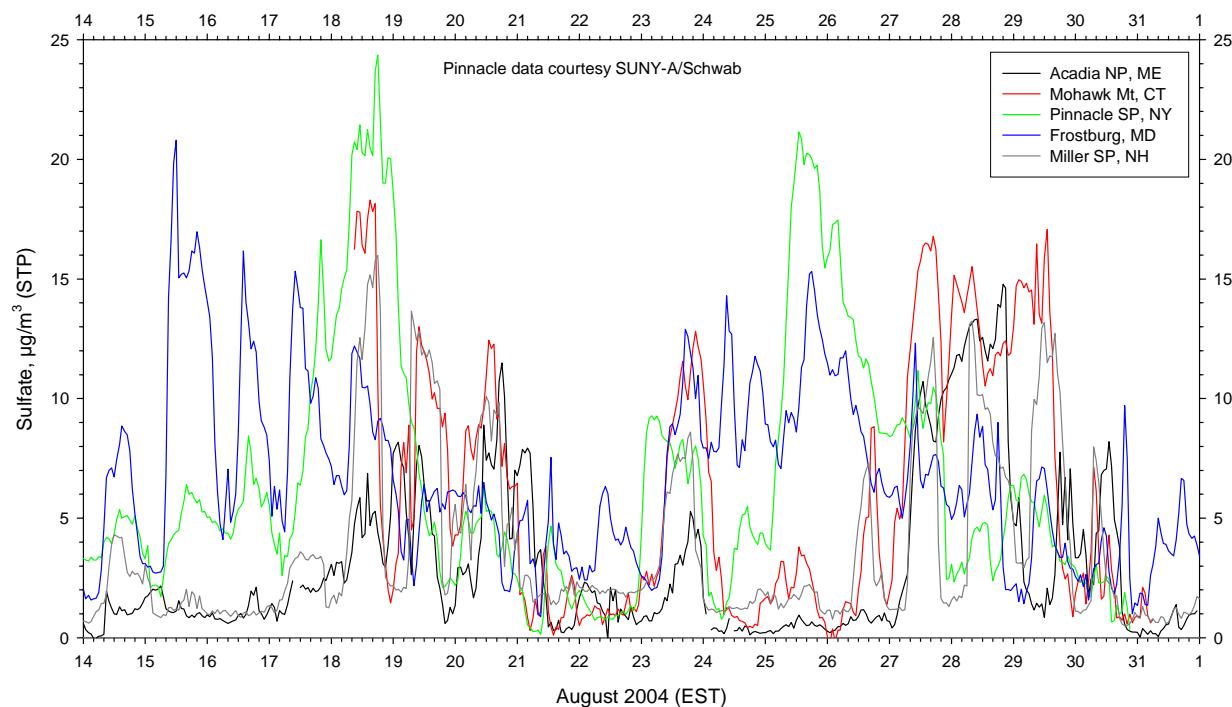


One of the more interesting observations of the continuous sulfate data from this period is the relative consistency of the maximum short-term (few hours) observed concentrations of sulfate. Despite the large spatial scale of these sites, all sites except Acadia (furthest from the large source regions) tend to exhibit a persistent upper limit of about 16 to 18 $\mu\text{g}/\text{m}^3$ sulfate. This is in contrast to the well documented gradient of average sulfate concentrations across this spatial scale¹⁰. One hypothesis that might explain this observation is that continued conversion of sulfur dioxide to sulfate approximately compensates for dilution and deposition of sulfate during event

periods. Although total S presumably decreases further away from the major SO₂ source areas in the Midwest, sulfate may not decrease as fast as SO₂.

During the second half of August 2004, this pattern was somewhat different, with 2 separate periods (August 18 and 25) where 1-hour sulfate peaks for the Pinnacle State Park (Addison NY) site were distinctly higher than the other four sites, as shown in Figure 13. The 1-hour value of 24 µg/m³ sulfate observed on the 18th was the maximum value across all sites all summer. Given the location of the large sulfur sources, the Pinnacle site might be expected to have some of the highest short-term sulfate concentrations in the region. It is far enough from the sources for substantial conversion to occur (SO₂ data are not yet available for this site), but close enough for dilution and deposition to be less dominant than at sites in New England. As with the first half of August, a large dynamic range over short time intervals is common. There are periods where the entire region has elevated sulfate (18-19, 27-28), and also periods where New England is decoupled from MD and NY (24-26).

Figure 13. Thermo 5020 hourly sulfate, August 14-31 2004.



Sulfur Phase Assessment.

One of the objectives of RAIN is to allow assessment of the phase of the sulfur at these rural transport-influenced sites. The extent to which S is present as sulfate can give some idea about the age of the polluted air mass; each site has both real-time SO₂ and sulfate measurements for this reason. An initial analysis of sulfur phase is presented here for the summer of 2004 for the two sites where SO₂ data were available: Frostburg, MD as near-source, and Acadia NP, ME as far-source. In order to compare S phase directly, the traditional units of $\mu\text{g}/\text{m}^3$ for sulfate and ppb (v/v) for SO₂ are both converted into nano-mole/m³. At STP (25°C and 1 atmosphere), 1 ppb SO₂ is 40.9 n-mole/m³, and 1 $\mu\text{g}/\text{m}^3$ sulfate is 10.4 n-mole/m³.

Figures 14 and 15 show SO₂ and sulfate as well as sulfate/(sulfate+SO₂) for the summer season at these two sites. The left axis is n-mole/m³ S, and traditional units are shown on the right axis. Note that the Y-Axis scales are not the same on these two plots; the Frostburg site has much higher levels of S. This is expected since it's much closer to the Ohio River valley, a large source region for sulfur emissions. For clarity, the S phase plot underneath the concentration data is limited to hours where S is greater than 20 n-mole/m³. Time is EST.

Figure 14. Frostburg MD sulfur phase hourly means, Summer 2004.

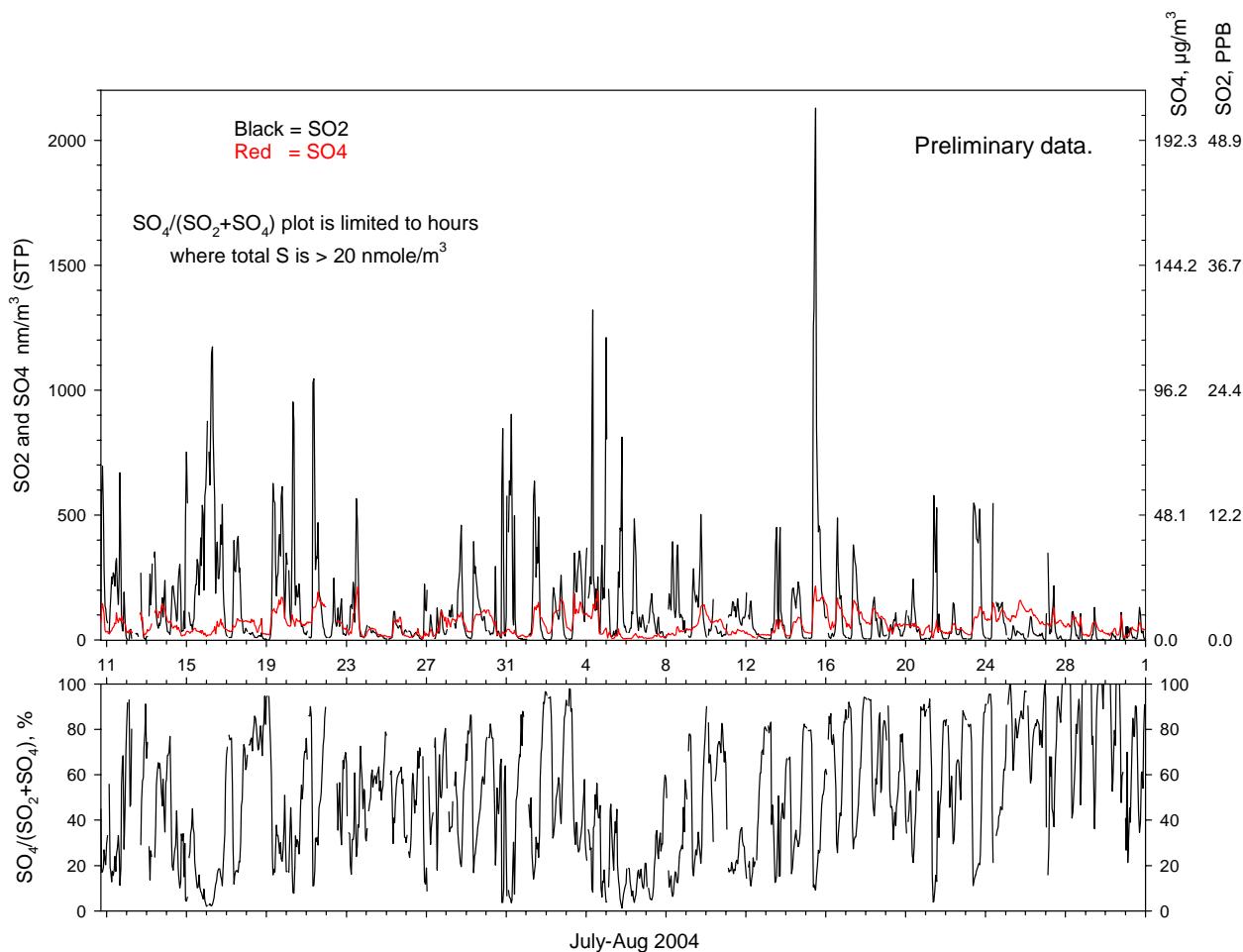
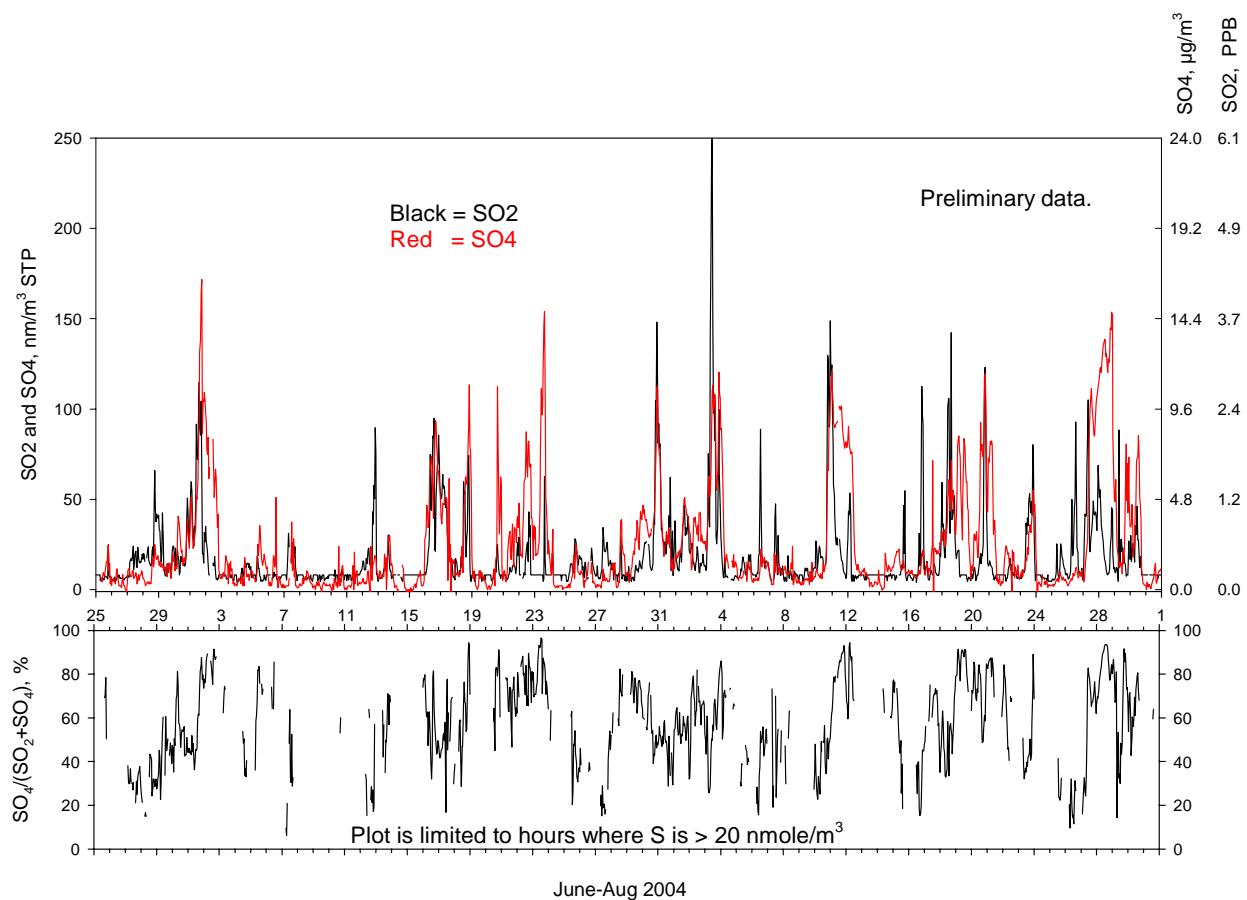


Figure 15. Acadia NP, Maine sulfur phase hourly means, Summer 2004

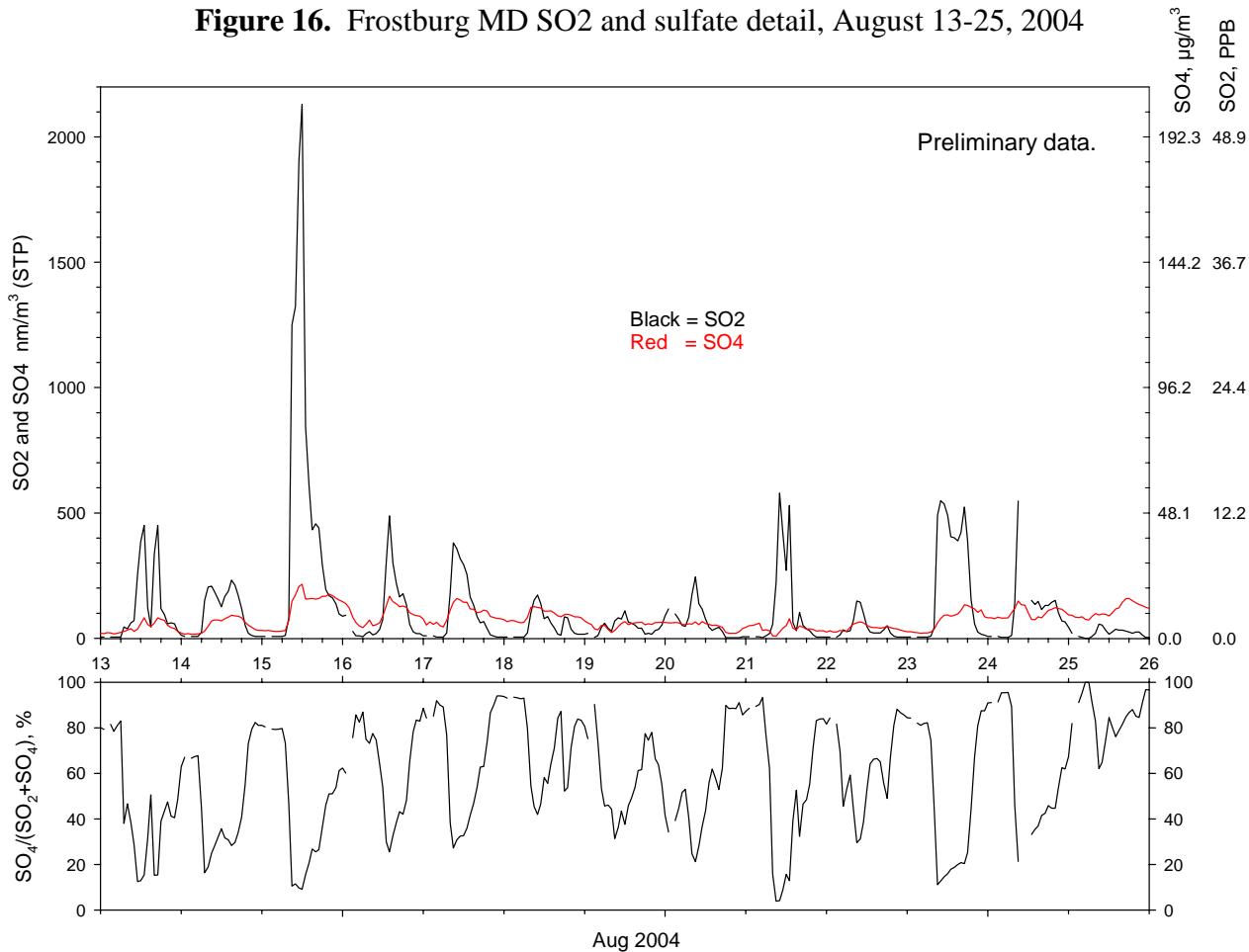


The maximum 1-hour observed SO₂ concentration at Frostburg is eight times higher than that at Acadia NP (52 vs. 6.3 ppb). For sulfate, that ratio is 1.2 (21 vs. 17 $\mu\text{g}/\text{m}^3$). For Frostburg, the mean SO₂ and sulfate are 116 and 61 n-mole/ m^3 respectively (percentage of S as sulfate=34). For Acadia NP those values are 18 and 24 n-mole/ m^3 and 57%. The lower concentrations and higher percentage of S as sulfate at Acadia relative to Frostburg is consistent with Acadia being much further from the major S source region than Frostburg.

One striking feature of the Frostburg SO₂ and S phase plot is a very strong diurnal component, with SO₂ dropping to very low levels during the night. Sulfate also shows a diurnal pattern, but generally does not drop as much or as fast during night-time hours as the SO₂. These features are also present in the Acadia data, but not as clearly. Figure 16 presents a 13-day excerpt of these data with more temporal detail (time is EST). The site elevation is 780 meters, so in the summer it would be expected to be within the boundary layer during the day and well coupled to relatively local SO₂ emission sources; the late-morning SO₂ spike is consistent with the height of the boundary layer growing past the site's elevation. At night the site is probably in the residual layer (above the boundary layer, but not in the free troposphere), cut off from "fresh" ground level sources but not from the previous day's accumulated pollution. The rapid drop in observed SO₂ concentrations nearly every evening might be explained by dry deposition;

although the site is at 780 meters, the surrounding terrain is only about 100 meters lower. Sulfate does not drop as much or as fast at night; this is consistent with large differences in the dry deposition rates for sulfate and SO₂ (the SO₂ rate is much larger). If this site were an isolated peak with the same elevation, the diurnal patterns in SO₂ and sulfate could be very different.

Figure 16. Frostburg MD SO₂ and sulfate detail, August 13-25, 2004



CONCLUSIONS

The Thermo 5020 sulfate analyzer performs well and requires minimal operational effort compared to other approaches for real-time sulfate measurements. The Sunset carbon analyzer is a more complex instrument to deploy and operate properly, even in its NDIR configuration. Initial data review based on a simple mass reconstruction indicates that data from the carbon analyzer is of reasonable quality during the summer of 2004 at two of the three RAIN sites. A rigorous evaluation of data quality for either method will not be possible for several months, when the collocated IMPROVE carbon and sulfate data for summer 2004 become available. The mass reconstruction approach is shown to be a useful tool for these sites to identify serious problems with these methods in near-real time.

A limited assessment at the Mohawk Mt. site suggests that sulfate has substantially more dynamic range than the organic carbon aerosol. Data from two additional continuous sulfate sites in the region are available for July-August 2004; with five sites, more detailed spatial and temporal patterns can be observed. All sites show substantial sub-daily variability in sulfate concentrations; changes of an order of magnitude over a few hours are common. Despite the large spatial scale, all sites except Acadia (furthest from the large source regions) often exhibit a surprisingly persistent upper limit of about 16 to 18 $\mu\text{g}/\text{m}^3$ sulfate for maximum short-term (few hours) observed concentrations of sulfate. The maximum short term concentration of sulfate was 24 $\mu\text{g}/\text{m}^3$ at the Pinnacle State Park (Addison NY) site. As expected given the proximity to source regions, mean SO₂ concentrations are higher at Frostburg than at Acadia NP (ratio=6.4), and the mean percentage of S as sulfate is lower (34 vs. 57%). The strong diurnal patterns for SO₂ and percentage of S as sulfate at the Frostburg site suggest that dry deposition may play a large role in removal of SO₂ at night at that site.

Future Work.

Met data (surface observations, back trajectories, profiler data) and other parameters such as NO_x or NO_y and ozone will be used to attempt to explain the spatial and sub-daily temporal features of the observed sulfate, SO₂, and aerosol carbon data. A longer term goal of RAIN is to enhance the network with other measurements and sites in future years. A NWS ASOS visibility sensor at a RAIN site would allow the large network of existing ASOS data to be “tethered” to visibility measurements we understand well. In the near future, we expect to make data from RAIN available in real-time to web data resources like FASTNET^{11,12} and AIRNow. Combining the intensive RAIN aerosol data with the extensive ASOS data via tools like FASTNET will provide for a much more detailed exploration of the temporal, spatial and compositional relationships between aerosol species and their associated optical effects.

Strong aerosol acidity, nitric acid, and ammonia are measurements that would be desirable on either an integrated or real-time basis at these sites. There are no continuous nitrate measurements in RAIN at this time, since available methods are not yet sufficiently robust, and nitrate is not (yet) usually a major PM factor at these sites. Measurements similar to those in RAIN done to the west and south of the MANE-VU domain (Ohio and Virginia for example) would greatly enhance our understanding of the impact of the large sulfur source region in and around the Ohio river valley on regional visibility.

ACKNOWLEDGMENTS

The RAIN program would not be possible without the ongoing support of the participating state air agencies in MD, CT, and ME, as well as the National Park Service, MANE-VU, and the U.S. EPA. The contributions of NH DES, SUNY-Albany, and the EPA/HSPH Boston PM-Center for continuous sulfate data are also acknowledged. Baseline operations (including the filter ion and PILS sampling) for the sulfate method validation work at the St. Louis – Midwest Supersite for this study period was funded by the Lake Michigan Air Directors Consortium (LADCO). The authors also acknowledge Ms. Catherine Reid and Ms. Andrea Clements for their assistance with the filter sulfate measurements and PILS sulfate measurements, respectively.

REFERENCES

1. US EPA. Final Draft of The National Ambient Air Monitoring Strategy, Chapter 4 (April 2004). <http://www.epa.gov/ttn/amtic/monstratdoc.html>
2. Seybold MG, Smith CD, Krask DJ, Woodman MF, Allen GA, Castro MS, McKnight JM (2004). "Monitoring Interstate Pollutant Transport from the Western Maryland Piney Run Site: Objectives, Design, and Demonstration." Paper # 48, these proceedings.
3. Weber RJ, Orsini D, Daun Y, Lee YN, Klotz PJ, Brechtel F (2001). "A Particle-into-Liquid Collector for Rapid Measurement of Aerosol Bulk Chemical Composition." *Aerosol Science and Technology* **35**: 718-727.
4. Stolzenburg M, Hering SV (2000). "A New Method for the Automated Measurement of Atmospheric Fine Particle Nitrate". *Environ. Sci. Technol.* **34**:907–914.
5. US Patent Application Publication # 20040082072, Allen et al., published April 29, 2004.
6. Drewnick F; Schwab JJ; Hogrefe O; Peters S; Husain L; Diamond D; Weber R; Demerjian KL (2003). "Intercomparison and evaluation of four semi-continuous PM_{2.5} sulfate instruments." *Atmos. Environ.*, **37**, 3335-3350.
7. Bairai ST, Tanner RL, Olszyna KJ, Valente, ML, Valente RJ (2004). "Continuous Measurement of Ambient Levels of PM_{2.5} Sulfate." AWMA Symposium on Air Quality Measurement Methods and Technology, April 2004.
8. Bae MS, Schauer JJ, DeMinter T, Turner JR, Smith D, Cary RA (2004). "Validation of a semi-continuous instrument for elemental carbon and organic carbon using a thermal-optical method". *Atmos. Environ.* **38**:2885-2893.
9. Allen GA, Babich P, Poirot RL (2004). "Evaluation of a New Approach for Real Time Assessment of Wood Smoke PM". Paper # 16 in these proceedings.
10. Malm WC, Schichtel BA, Pitchford ML, Ashbaugh LL, Eldred RA (2004). "Spatial and monthly trends in speciated fine particle concentration in the United States". *J. Geophys. Res.*, **109**, D03306.
11. FASTNET website and associated data, software tools and event catalog:
http://webapps.datafed.net/dvoy_services/dvoy_book.aspx?path=HOME/Projects/FASTNET
12. Poirot RL, Husar RB, Kleiman G, Kenski D. (2004). "Aerosol and Haze Observations during 2004 with the FASTNET Distributed Monitoring System". Paper # 93, these proceedings.