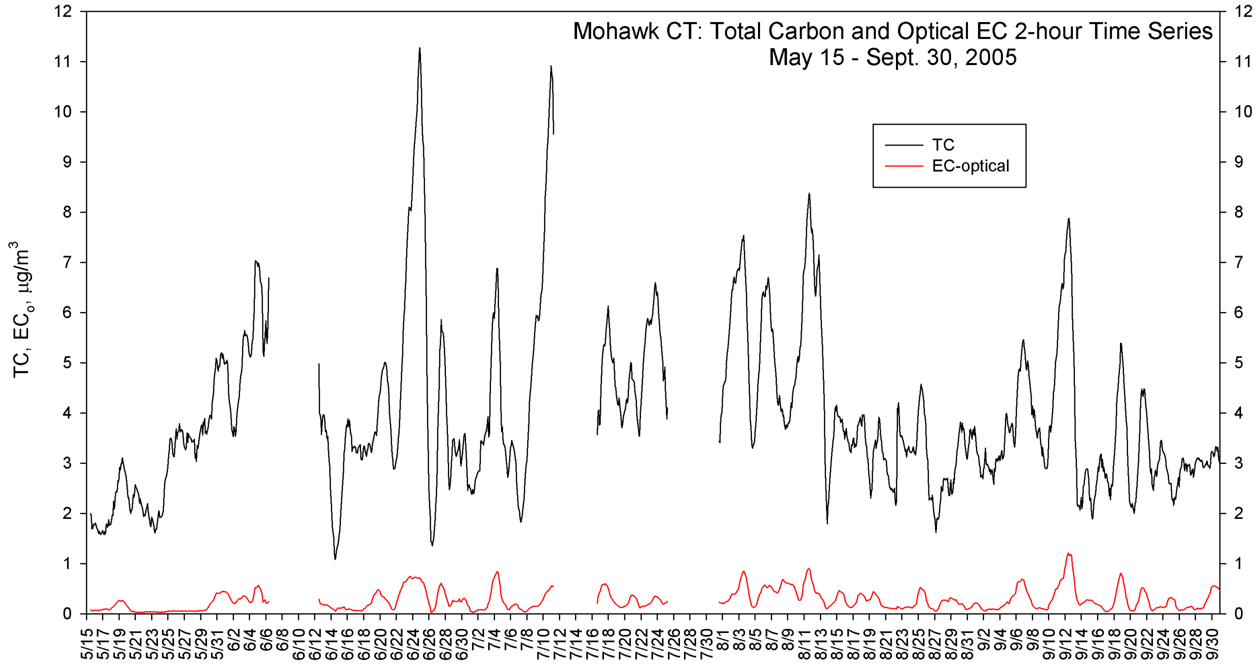
Semi-continuous aerosol carbon data from the MANE-VU RAIN program:

Assessment of data quality and data analysis approaches



Prepared by
NESCAUM
For the
Mid-Atlantic/Northeast Visibility Union Regional Planning Organization

February 22, 2010

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Acknowledgments

NESCAUM could not have completed this work without the IMPROVE Program and the long-term commitment of the National Park Service and other federal partners to maintain visibility monitoring networks and the VIEWS data system. The state air programs of MD, CT, and ME are acknowledged for funding and operation of the RAIN program sites. NESCAUM also acknowledges the funding for this work through U.S. EPA agreement number XA-97318101-4 to the Ozone Transport Commission in support of the MANE-VU Regional Planning Organization. NESCAUM is solely responsible for the content of this report and any errors it may contain.

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Executive Summary

This report represents the most recent effort to assess the data generated by semi-continuous elemental and organic carbon instruments run at the three RAIN (Rural Aerosol Intensive Network) sites. The data analysis presented here will be useful to improving our understanding of the dynamics of rural sub-daily and daily carbon aerosols in the MANE-VU domain. The data quality assessment will be used to further develop methods for data processing and validation of these complex data as well as refine field-site operational protocols, leading to more complete and higher quality data sets both retrospectively and in the future.

Over the past several years, NESCAUM - as a partner in the MANE-VU regional planning organization - has coordinated the operation of the RAIN program to better understand the sources of visibility impairment and the necessary steps to eliminate it. This technical memorandum provides an analysis of available 2006-2008 RAIN semi-continuous aerosol carbon data, including comparisons to co-located IMPROVE carbon data. In addition, issues with data quality, data capture, automated post-processing techniques, and the need for timely data screening are discussed. Recommendations for addressing each of these issues are provided.

The need to revisit the processing and validation of existing data from this method to generate a more complete and higher quality final data set for additional analysis is also discussed. An important factor in the timely review and screening of data to identify problems promptly is the availability in April 2009 of the "data masher" post-processing software. Although the data presented here have been processed using this software, the ability to quickly review recent data for problems was not available, resulting in substantial amounts of missing or invalid data.

An additional conclusion from this report is that analysis of the RAIN semi-continuous carbon data is limited, and that aspects such as temporal trends (seasonal or multi-year) and spatial gradients are better analyzed using existing IMPROVE carbon data sets that have denser spatial networks and longer time-series of data. Future RAIN data analysis should include other related pollutants such as semi-continuous fine particulate matter (PM2.5), sulfate, and ozone, as well as meteorological data.

The limited utility of these carbon data to identify and quantify the contribution of wood smoke (both wildfire and space heating sources) to regional carbonaceous aerosols is discussed, along with approaches that could be used to better assess this source in the future. For identification of transported (aged) wood smoke aerosol, the only quantitative marker is the ^{14}C isotope "new carbon" method. The use of Sunset carbon data with the DataFed CATT tools (incremental probability) may be worth investigating for identification of sources of organic carbon (OC) aerosols.

Finally, as sulfur emissions continue to trend downward in the eastern US, the relative importance of OC aerosol as a cause of visibility impairment will increase over time. OC may be the dominant aerosol species for visibility in the MANE-VU domain within the next ten years or so. It is therefore important to develop tools for measurement and assessment of OC aerosol and its sources as input to control and compliance programs for both PM and regional haze.

1. INTRODUCTION

1.1 Background

This report presents information intended to assist states in establishing reasonable progress goals and fulfilling their long-term emissions management strategies under the 1999 U.S. Environmental Protection Agency (U.S. EPA) "Regional Haze Rule" [64 Fed. Reg. 35714 (July 1, 1999)] for MANE-VU Class I areas. As part of the MANE-VU regional haze program, a network of sites with several different measurements of "real-time" fine particulate matter (PM2.5), its major chemically speciated components, and related criteria gases was established in 2004. The Rural Aerosol Intensive Network (RAIN) has three rural sites spanning the MANE-VU domain, from western Maryland to Acadia National Park in Maine. The RAIN network is described in detail in a NESCAUM MANE-VU technical memorandum from 2006: http://www.nescaum.org/documents/2006-05-memo8-rain.pdf/

The network background, design, methods, and site descriptions are included in this earlier report along with some limited preliminary data analysis; the reader should refer to this report to gain an understanding of the context of the assessments included in this report. Additional details on the Sunset Laboratories field carbon analyzer method and its performance are available in the references at the end of this report.

The main objectives of this report are:

a. Assess the quality of the Sunset RAIN Carbon Aerosol data using collocated 24-hour IMPROVE sample data. Discuss approaches to improve data capture and quality, both in terms of field operations and data processing and validation techniques and tools.

b. Review how this highly time-resolved can be used to provide information beyond that available from the existing third-day IMPROVE data with its longer sample record and denser network. Discuss the limitations of Sunset carbon data analysis without other parameters, and recommend what additional parameters would enhance future analysis.

The performance of and data from the Sunset Laboratory semi-continuous carbon analyzer are assessed in this report for a three year period (2006 - 2008, with some additional data from 2005). Data quality is evaluated by comparison of Sunset total carbon with data from collocated every third-day 24-hour duration IMPROVE samplers. Summary data analysis of 2-hour duration samples is performed to investigate how these highly time-resolved data may be used to better understand the possible sources and dynamics of aerosol carbon, primarily the organic carbon component. Trend, spatial, and seasonal analyses are not presented here, since data from the IMPROVE network are more useful for these kinds of analyses due to the much denser network and longer data record.

Limitations of the existing datasets are discussed, and suggestions for improving data quality and data capture for both existing and future Sunset carbon data are presented. Initial experiences with using the "data masher" program for data post-processing and validation are evaluated. The limitations encountered in analysis of the available data point to the need for integration of other data types to support the analysis of Sunset carbon data. These other data are essential to fully utilize the highly time-resolved data from this instrument.

2. Data validation and comparison with IMPROVE total carbon

2.1 Overview.

This chapter presents the results of comparison of total aerosol carbon (TC) between the Sunset analyzer and the IMPROVE collocated samples. The Sunset analyzer, like all semi-continuous aerosol instruments, can not be routinely calibrated in the field with known amounts of the actual aerosol being measured. Field calibrations are done by demonstration of proper operation of instrument sub-systems, such as the CO2 detector and sampler flow measurement checks. Dynamic field blanks are performed on a limited basis to identify additional possible instrument problems such as leaks.

Even with these operational checks, a routine and ongoing comparison with an independent method must be done to determine the validity and quality of the Sunset carbon data. The evaluation of collocated IMPROVE data is a level 2 (external consistency) validation step. This is an essential part of the data validation process, and must be done before any further use of the Sunset carbon data.

2.2 Total Carbon Linear Regressions.

2.2.1 Data Validation method

The comparison between the Sunset and IMPROVE measurements is done only for total carbon data, since the “split” between EC and OC is different and not consistent between the two thermal analysis methods. TC however should be the same between methods with the exception of the OC blank correction (there is no significant EC blank value in either method). TC as used here is the sum of reported EC and OC, where OC is “carbon as OC” without any correction for other components that make up the organic carbon aerosol mass. Unless otherwise noted, OC used in this report refers to “carbon as OC.”

The aerosol carbon method comparisons presented here use the blank corrected OC (“OCf”) plus EC (“ECf”) from IMPROVE (as reported in VIEWS), and the sum of EC and uncorrected OC from the Sunset instrument. Since over a long period (e.g., a year or more) the “true” OC blank value for both methods is essentially constant, this approach produces an estimate of the Sunset OC blank that is consistent with the OC blank correction that is applied to IMPROVE samples. The intercept of the linear regression of Sunset TC on IMPROVE TC is the “best estimate” of the Sunset OC blank value. The “dynamic” blank field tests also provide an estimate of the Sunset OC blank value, but are highly variable “spot checks” that are best used as field performance checks of the instrument, and not for generating an OC blank value for data reduction.

Because the intercept of the regression between the methods accounts for the effect of OC blank values of both methods, the slope represents the bias between the methods. The slope should be reasonably close to 1.0 since the TC analysis from both methods is expected to be comparable (carbonate carbon is not a significant issue here since a PM2.5 inlet size cut is used on both samplers). Finally, the regression correlation is an indication of stability of the methods over an extended (one or more year) period of time. The assumption made here is that the

IMPROVE TC carbon method is likely to be stable and reproducible over this time frame, and thus any substantial degradation in the correlation is likely due to problems with the Sunset carbon data.

The regression results can be used as a "big picture" look at data quality. If the regression results are reasonable, then the Sunset data can be considered to be useable, and the intercept value can be used for a Sunset OC blank correction. "Reasonable" means an intercept between 0.4 and 1.2 $\mu g/m^3$, a slope within 0.8 to 1.3, and an R2 of 0.8 or higher. For this report, regressions are usually done on a calendar year data period, since this should provide a large enough number of valid sample pairs (121 if all sample pairs are available) for a stable regression. For these data it is not unusual for the number of valid data pairs to be substantially less, mostly due to missing data from the Sunset method.

2.2.2 Generating "IMPROVE-like" OC data from the Sunset method data.

Once data quality criteria have been met, the regression results can be used to make the Sunset carbon data more comparable to IMPROVE carbon, at least for OC; the method differences are much larger for EC, so it is more difficult to make Sunset EC IMPROVE-like (this is why regressions are done on TC only). Since OC has a much larger impact on rural visibility than EC, the limitations with Sunset EC are not as important.

Since the blank offset for both IMPROVE and the Sunset method is only associated with OC, the Sunset OC data are first blank corrected by subtracting the regression intercept term. The resulting data are divided by the regression slope to yield a corrected "IMPROVE-like" OC value.

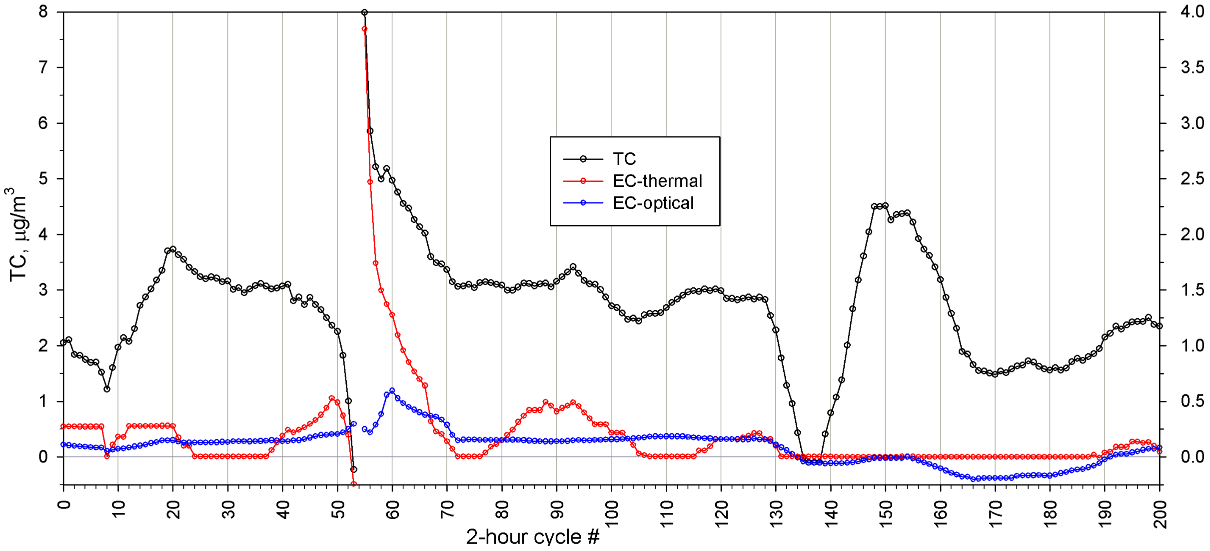
2.3 Total Carbon regression results

2.3.1 Data Processing and Screening

A recent effort in support of processing and validation of Sunset carbon analyzer data was the development of the "data masher" -- a program that reads in the output of the instrument's "RT-Calc" program ("results" cycle data files) and outputs a fully populated data file that includes data flagging and voiding based on numerous internal instrument parameters. The output also includes valid daily mean values for comparison with IMPROVE data. The Sunset data masher software was developed in 2009 by CT DEP, NESCAUM, and Jay Turner at Washington University in St. Louis, with funding from MANE-VU and CT DEP. This software and related documentation are available at:
ftp://airbeat.org/private/RAIN/Sunset-Carbon/

A year's worth of Sunset data can be processed by this program in a few minutes. While the output is reasonably clean, the data still need to be reviewed for problems that are not identified by the data masher. There are also cases where the existing version of the data masher can void data that may be valid even when a validation parameter is out of range -- e.g., some of the masher void criteria may be too strict. An example of periods of invalid data that were not detected by the masher is shown in Figure 1. This is a 400-hour time series from Mohawk Mountain., October13-30 2005. Based on TC, data from cycle 50 to 70 and cycle 129 to 147 are void or suspect, and need to be reviewed. Cases like this can also be used to inform revisions to the data masher to improve its automated data screening process.

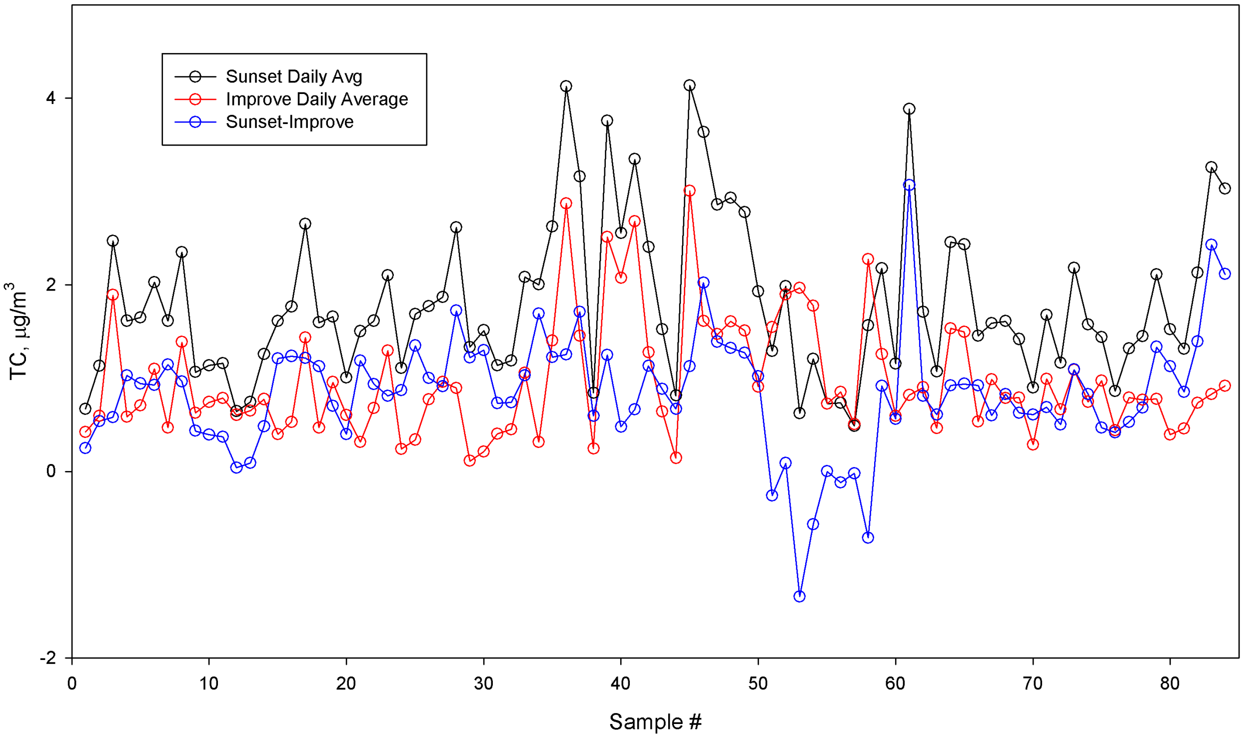
Figure 1. Example of invalid data that was not detected by existing screening criteria.



Note that the optical EC does not follow the thermal EC, especially in the period from cycle 50 to 60. Use of optical EC as a validation tool is discussed in more detail in section 2.5.2 of this report.

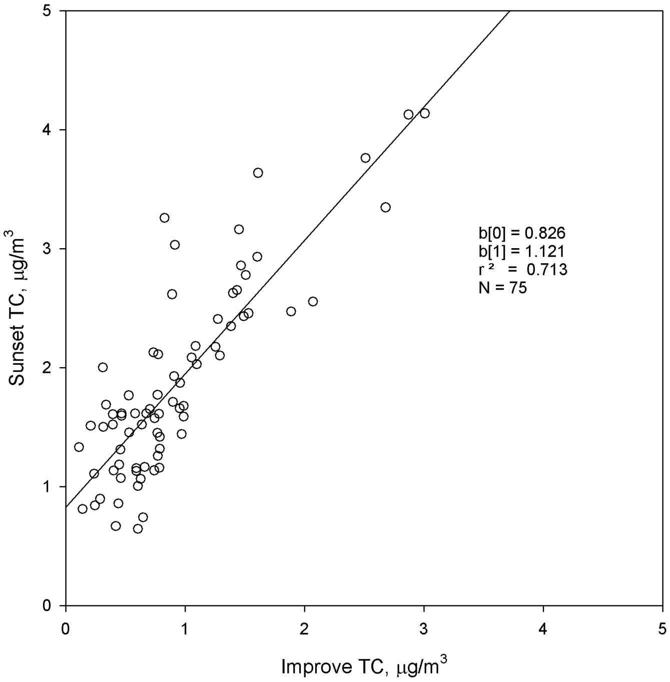
State agencies processed the data using the most recent version of RT-Calc (version 5.13) and the “official” release of the data masher (version 1.0c), and supplied the result to NESCAUM with varying degrees of additional review. These processed data were first reviewed for completeness. In some cases, the original valid output from the data masher was minimal - in one case only three sample pairs were available for a one-year period. Closer inspection of the Sunset data for this case showed that the data masher was voiding most of the data based on an internal instrument parameter that did not appear to effect the data quality substantially; in this case most of the year’s data was considered valid except for a 1-month period where the relationship between the two methods diverged from the usual pattern. Figure 2 shows a 1-year time series plot of these data.

Figure 2. Time series validation plot of Improve and Sunset TC



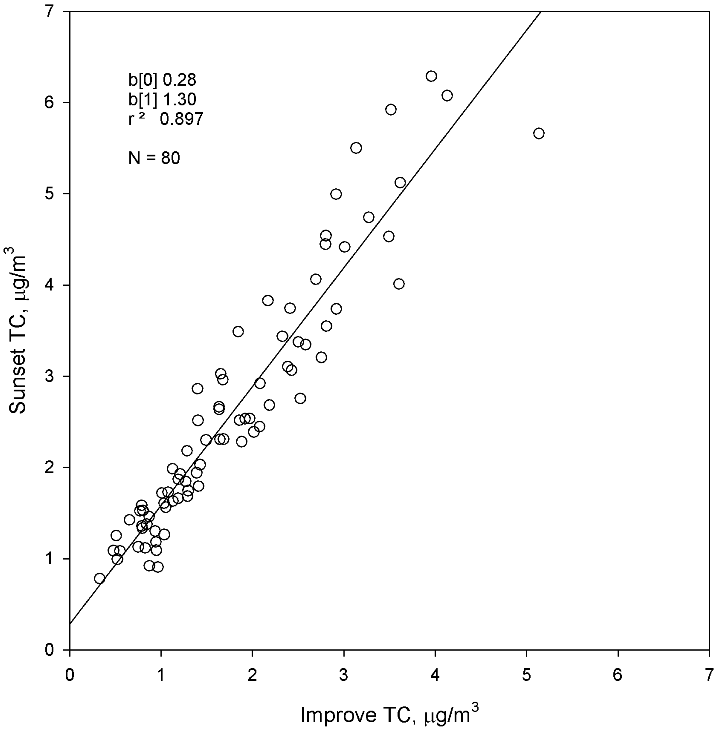
It is clear from the difference (blue line) that something happened to the data from sample #50 to 58, and again at sample 62. Temporal clusters of "different" data such as this are candidates for closer inspection to determine if there is some operational evidence of an instrument problem. In this case, the "sample volume" changed drastically for this period, confirming an operational problem with the Sunset analyzer. Removing these data increased the R2 from 0.45 to 0.71 and increased the slope from 0.90 to 1.12. The resulting regression and scatterplot are shown in Figure 3.

Figure 3. Acadia 2006 Sunset vs. Improve TC



TC regression results varied from site to site and from year to year within sites, indicating quality control issues either with the instrument operation and/or data validation and screening. The Sunset method is capable of good performance as assessed by IMPROVE TC comparison; an example of this is the data from Frostburg in 2007. The TC R^2 for that site-year is 0.90, as shown in Figure 4.

Figure 4. Frostburg 2007 Sunset vs. IMPROVE TC



The slope is 1.30, indicating that the Sunset TC is higher than IMPROVE. This is a plausible result given the post-sample handling of IMPROVE filters, which are not stored cold after exposure and during shipping. This may cause loss of semi-volatile organic carbon aerosol; any loss would vary depending on many factors including season and the composition of the collected sample. The Sunset samples are analyzed at the end of the 2-hour sample period. An additional difference is that the Sunset samples are collected with an upstream organic carbon vapor denuder while the IMPROVE samples do not have a denuder. All these sampling and handling differences can contribute to variable artifacts between the two methods that can be either positive or negative and may vary over time and across sites. Data from years before and after 2007 from Frostburg did not show as high a correlation for TC, indicating varying levels of Sunset data quality across time.

2.4. Data Capture.

The percent of possible data intervals that are valid over a specified time range is defined as the data capture percentage. The interval may vary from a day to a 3-month quarter to a year. It is accepted practice that at least 75% of possible samples be valid within an interval for that interval to be considered valid. For 2-hour cycle samples, 9 out of 12 must be valid for the day's value to be valid. This metric was used for validation of Sunset data against IMPROVE 24-hour samples.

Data capture as measured by a valid Sunset daily mean measurement varied widely both within and across sites. Because the design goal of the data masher was to void only data that were clearly invalid (data that might be valid but questionable are flagged but included), data capture as discussed here is from the output of the data masher. At one extreme, Acadia 2006 had four days of valid Sunset data for the entire year (much of the masher voided data has been determined to be valid based on data screening and comparison with IMPROVE). One of the best data capture site-years was Frostburg 2005, with 78% of possible days (286) being valid. If void hours were manually reviewed and restored as appropriate, the daily data capture would likely increase somewhat. Maintenance and dynamic zeros limits daily data capture to no more than approximately 90% under ideal conditions.

2.5 Issues with data quality and completeness.

The examples above make it clear that the field operation and data validation procedures in use are not adequate to consistently produce data of adequate quality and completeness. There are several steps that can be taking to minimize these problems. These primarily involve more timely data review using approaches that do not require IMPROVE data, since there is about a one-year lag for those data to become available. It must be noted here that as noted below, a key tool in data review is the "data masher" software. This software was not available until April 2009, and although the data reviewed in this report have been processed with the masher, the routine screening steps described below were not practical to perform on a routine basis without the masher.

2.5.1 Routine data screening.

Data should be "mashed" and screened frequently to identify instrument problems. The "raw" instrument data are usually processed into cycle data every few weeks by the user. The resulting "cycle" results file should be "mashed" immediately and the resulting data reviewed for problems. There are several levels of review (level 1 QC) that can be done based on this output.

A quick time series plot of cycle EC and OC data in a spreadsheet program can reveal many different problems, including excessive missing data, dynamic zero periods needing evaluation and removal, extreme "suspect" values, atypical relationships between EC and OC, and so on. Any data flagged or voided by the data masher should be investigated based on the reason for flag or void reported by the masher output file. If flags suggest problems with the instrument, corrective action can be taken in a timely manner, minimizing data loss.

2.5.2 Optical vs. Thermal EC screening.

Another useful QC check is to compare the thermal and optical EC at the cycle time-base level (2-hours) and with larger datasets, the daily level. Sunset optical EC is a surrogate measurement of soot based on the change in near-IR light transmission through the filter from the start to the end of the sample interval; this is very similar to the BC measurement made by the Aethalometer. The optical EC measurement is simpler since it only requires the flow to be correct; the thermal EC measurement is much more complex and therefore is subject to more failure modes. Thus the optical EC data can be used to detect problems with the thermal analysis

EC and OC data.

The 2-hour cycle thermal EC is often noisy for the low concentrations at rural sites, but the thermal-optical data comparison is still useful. At the daily (24-hour) level, the thermal EC noise is greatly reduced, and a much cleaner relationship between thermal and optical EC should exist. A simple scatterplot can be done that would detect operational problems. Figures 5, 6, and 7 show examples of optical vs. thermal EC scatterplots using 2-hour data. Figure 8 is an example of one year of daily (24-hour) data.

Figure 5. Mohawk 2-h EC, 2004-2008

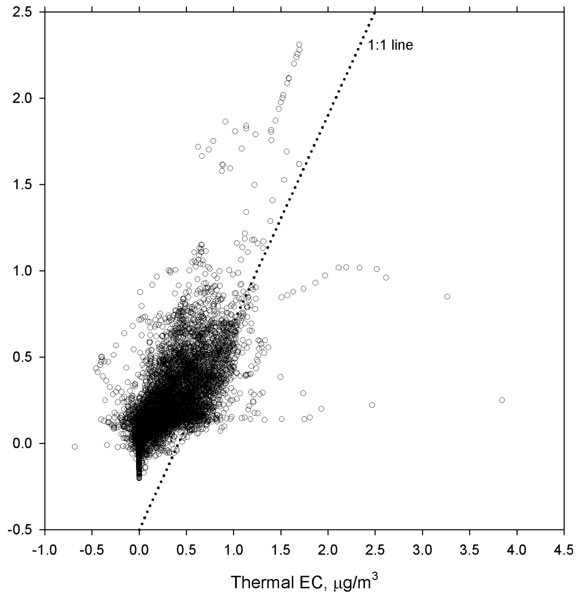


Figure 6. Acadia 06-08 warm season 2-h EC

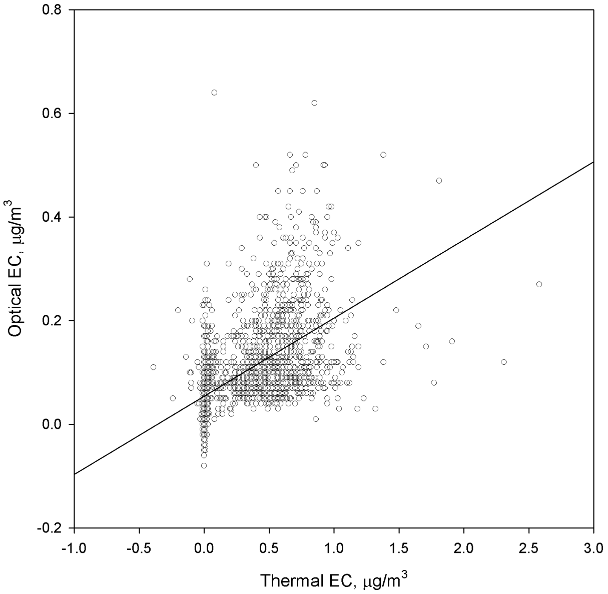


Figure 7. Frostburg 2-h EC, 2005-2007

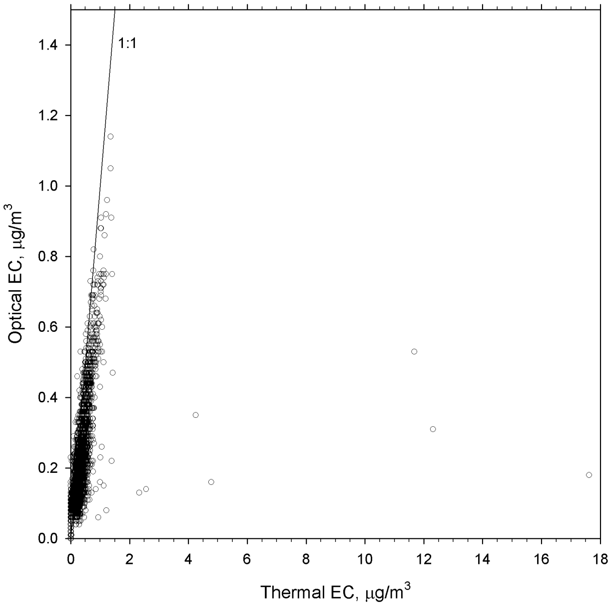
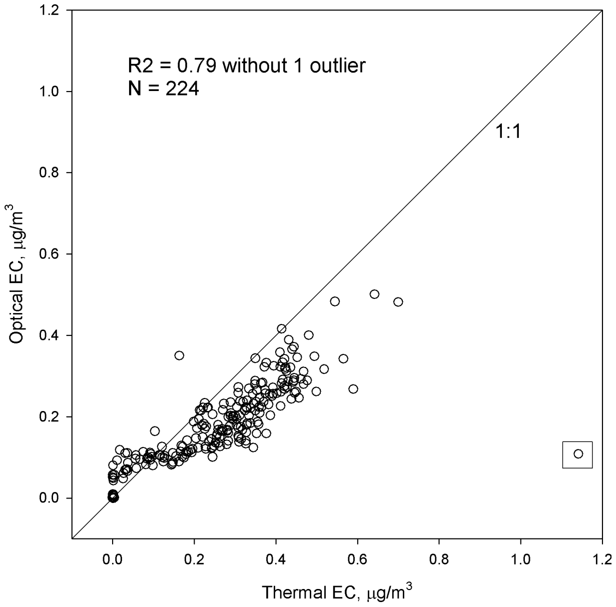


Figure 8. Frostburg 24-h EC, 2007



These examples show the utility of using optical vs. thermal EC for identification of suspect data. Time series plots (2-hour or daily) could be used to identify what time periods are likely to be invalid. In general, the optical and thermal EC should be in reasonable agreement and well correlated; the manufacturer has chosen an internal instrument optical EC conversion factor to match the thermal EC data at typical locations. Note that these scatterplots all show indications of 0 concentration cases that need further investigation. For example, the Acadia plot has a large cluster of thermal EC at 0 with optical EC ranging from -0.1 to 0.3 µg/m^3, and the Frostburg 24-hour plot shows a separate cluster of points where both EC values are 0.

3. Data Analysis.

3.1 Diurnal Patterns.

Diurnal plots are often an informative analysis method for highly time-resolved data; the time of day pattern is often useful in assessing different source contributions. EC at the RAIN sites is low compared to OC, in part because the sites are rural and in part due to the NIOSH method 5040 EC/OC split used by the Sunset analyzer. Thus the diurnal analysis presented here is either OC or TC, not EC.

Diurnal patterns can have day of week and seasonal differences. For OC, sources in cold weather months can be very different than warm weather. Because of the often limited data capture for this data set, diurnal plots are only split into two seasons: April through September ("warm," high solar radiation) and October through March ("cold," low solar radiation). Photochemical and biogenic organic carbon aerosols (along with transported wildfire smoke) would be expected to be more dominant in the warm months, with primary emissions such as wood smoke from space heating as well as mobile sources during cold months.

Figures 9, 10, and 11 are 2-season diurnal plots for the three RAIN sites. For each site, OC is higher in the warm season, while EC is not as variable. There is a notable lack of a diurnal pattern for both OC and EC. This might be explained by the rural regional scale of these sites, which were relatively free from local sources by design, but is still somewhat unexpected since mixing height varies with time of day. The lack of a summer daytime peak suggests local biogenic SOA does not make up a large fraction of OC aerosol at these sites, although enhanced vertical mixing may disperse the local SOA source.

Figure 9. Frostburg Diurnal OC and EC

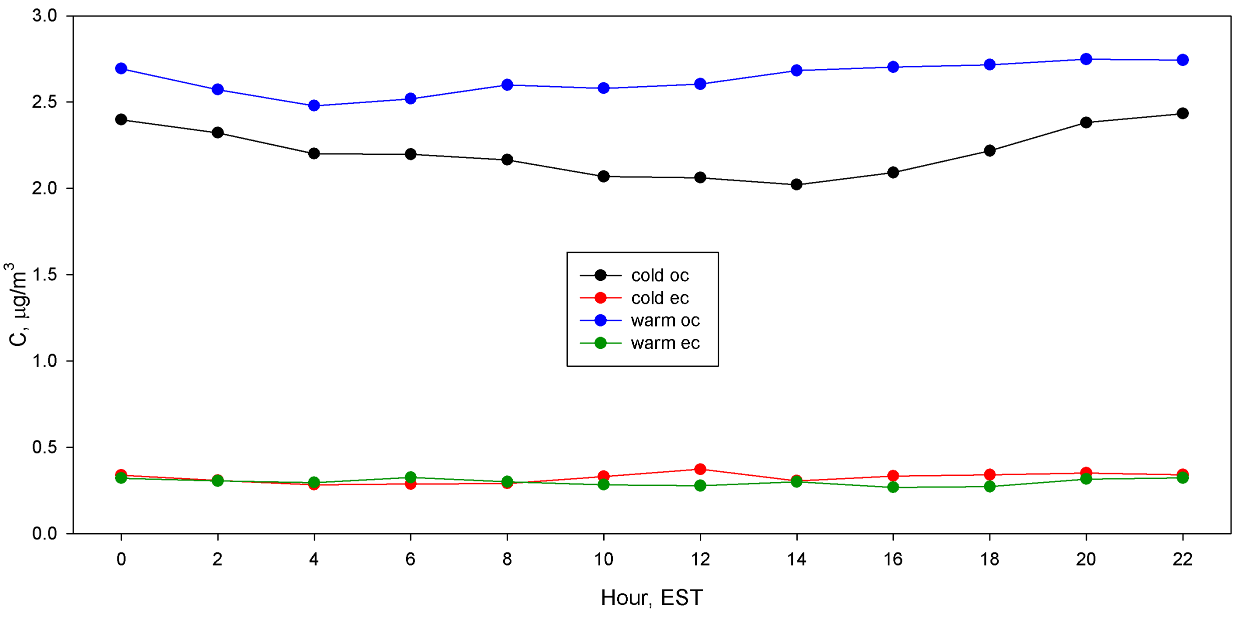


Figure 10. Mohawk Diurnal OC and EC

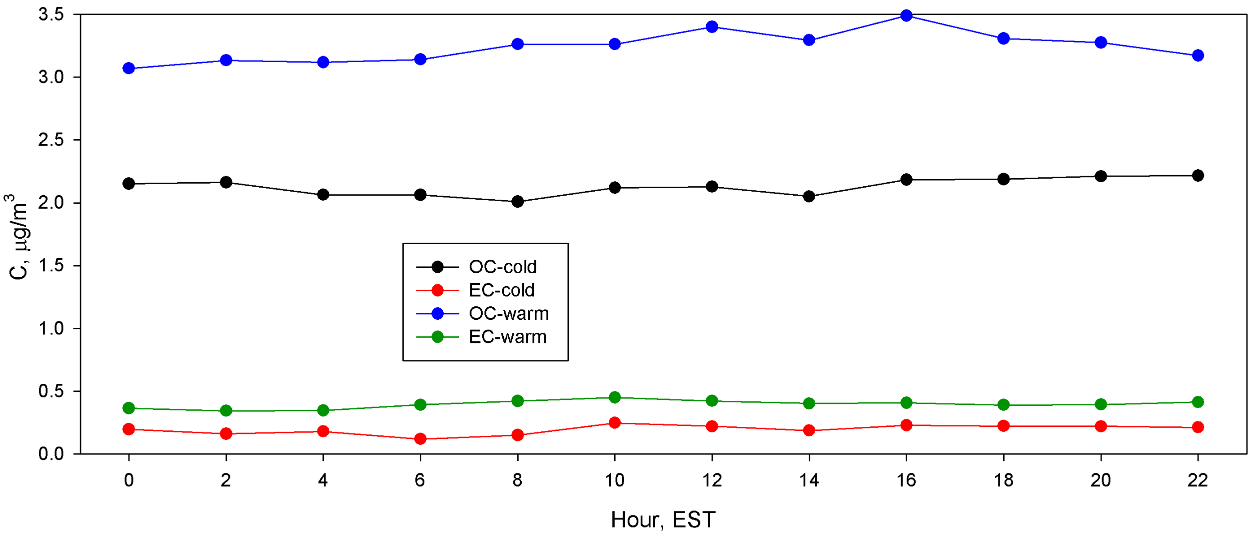
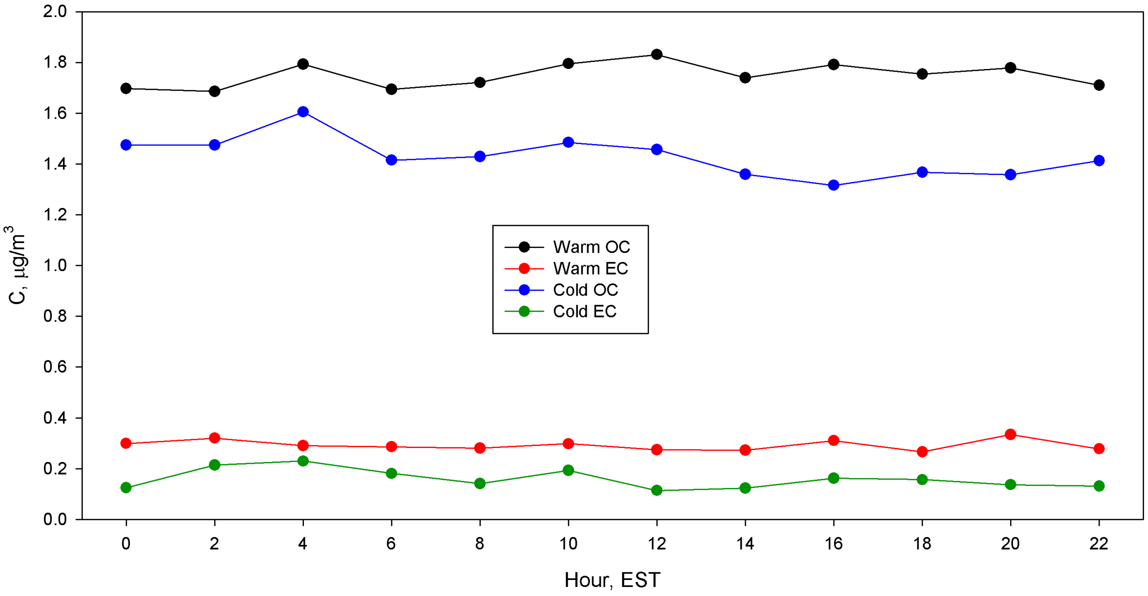


Figure 11. Acadia Diurnal OC and EC



The only suggestion of an OC source may be the modestly elevated Frostburg night concentrations. This is a typical pattern of local wood smoke, and Frostburg is the most likely of all three sites to have any impact from this source because of its proximity to population and lower relative height to surrounding terrain.

3.2 Distribution of 2-hour data.

Although the diurnal patterns show very little dynamic range, the 2-hour data are more variable. Figures 12, 13, and 14 are box plots of OC and EC distributions.

Figure 12. Frostburg OC-EC distribution

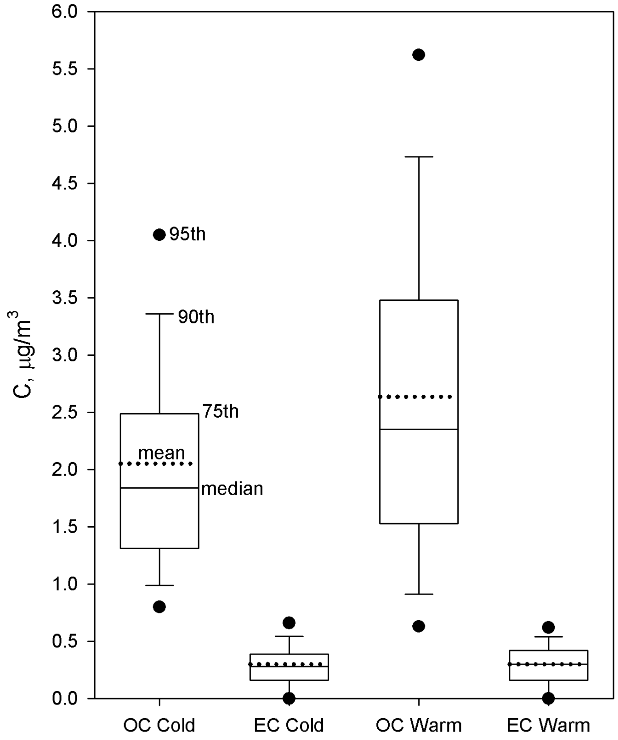


Figure 13. Mohawk OC-EC distribution

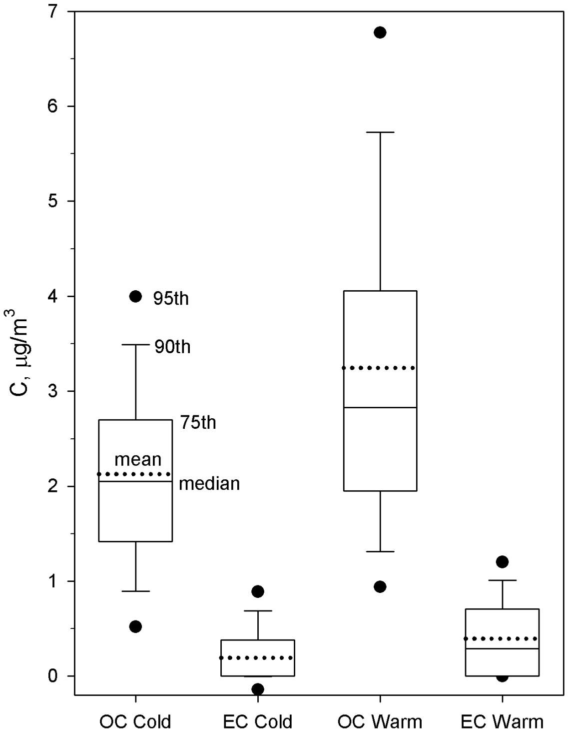
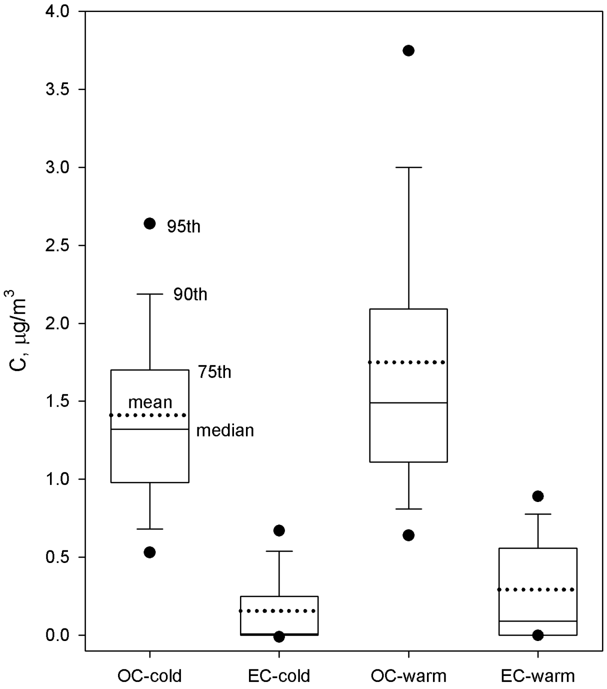


Figure 14. Acadia OC-EC distribution



The distribution of 2-hour OC is not highly skewed; winter OC at Mohawk and Acadia is reasonably normal. EC at Frostburg is normally distributed for both seasons, but is highly skewed at all other sites and seasons. This implies there is a persistent source near Frostburg but not at the other sites; Acadia and Mohawk EC are influenced more by occasional but large EC events.

4. Discussion.

4.1 Utility of Sunset OC-EC data for assessment of wood smoke

Without other relevant measurements, the OC-EC data from these sites are of very limited use for assessment of the contribution of wood smoke to the observed aerosol carbon concentrations. There is nothing in the data that is specific to wood smoke. In large events such as the 2002 Quebec fires or local winter valley wood smoke inversions, these data can provide additional detailed information, including the OC to EC ratio of a dominant source. However, the lower but more chronic wood smoke aerosol carbon can not usually be picked out as an "event"; it is masked by other carbon sources and meteorologically driven temporal variability

4.2 Other approaches to assessing wood smoke contribution to aerosol carbon

Several other methods have been used to apportion the amount of PM2.5 or carbon aerosol to wood smoke. Most are integrated filter-based measurements using various chemical markers. Non-soil fine mode potassium (K-NON) has been used mostly in the IMPROVE network; it can identify periods of substantial wood smoke impact, but not the more subtle and persistent non-event wood smoke contribution. K-NON data has been used with Sunset carbon data to identify and apportion wood smoke aerosol for distinct events (Liu, 2005).

More recently, levoglucosan has been widely used as a specific and sensitive wood smoke marker that is semi-quantitative. The Aethalometer "Delta-C" method has also been shown to be a robust wood smoke marker, with the advantage of high time resolution data. However any aerosol organic carbon marker is subject to photochemical degradation, reducing or removing the marker from transported wood smoke. Jimenez et al. (2009) show that after photochemical aging, organic aerosols from different sources become similar in chemical and physical properties (*see also* Andreae, 2009). Thus, both levoglucosan and Aethalometer Delta-C are likely to be limited to assessing local (previous night or same-day) wood smoke.

One method that can be used for apportioning "old" from "new" aerosol carbon even in a long-range transport scenario is the ^{14}C isotopic ratio approach (Jordan et al., 2006; Zheng et al., 2006; Schichtel et al., 2008, Fisseha et al., 2009). Carbon from fossil sources is depleted in ^{14}C compared to contemporary carbon. While there are non-wood combustion sources of "new" carbon such as meat cooking, trash incineration, and biogenic aerosols, the relative impact of these sources at rural eastern sites such as those in the RAIN program are presumably minor; biogenic aerosol is the only possible confounder, and only in warm weather months.

4.3 Utility of longer-term OC datasets for wood smoke source attribution

Another approach that can provide qualitative information on sources of OC is presented in the MANE-VU RAIN 2006 memorandum at:

http://www.nescaum.org/documents/2006-05-memo8-rain.pdf/

Chapter 3.3 discusses and evaluates some techniques for identification of wood smoke. The use of the DataFed CATT incremental probability method (CATT-IP) showed evidence of substantial summer transported wildfire wood smoke impact at Acadia. However, this approach needs a large data sample -- at least a decade of third-day IMPROVE samples.

The daily carbon data available from the Sunset instrument would reduce the time needed to use this approach to only a few years, assuming reasonable data capture. Refinements to this method could be investigated that make use of the sub-daily carbon data; daily metrics such as the 6-hour mid-day EC and OC means may provide enhanced insight into the influence of transported wildfire smoke or biogenic OC on regional OC concentrations.

For the biogenic OC case, one would not expect to see a strong directional influence for a ubiquitous source. For the Frostburg site, a directional indication towards large forested areas such as the Ozark or Blue Ridge mountains might be observed. Wildfire and back-trajectory data could be included in this analysis to exclude influence from summer wildfires, and thus focus on other sources of SOA.

CATT-IP has not yet been used on winter carbon aerosol data (Sunset or IMPROVE), but it may be useful in assessing wood smoke from wood-fired space heating sources.

4.4 Present and future role of OC in visibility impairment for the MANE-VU domain

Chapter 5 of the RAIN 2006 report noted above also includes a preliminary analysis of the relative impact of sulfate and OC on short-term (2-hour) visibility at Acadia from July 1, 2004 through March 31, 2005. For this data set, measured sulfate alone (with RH correction) predicted the variability in visual range as measured by the nephelometer as well as sulfate and OC, but under-predicted the numeric value. Adding in the Sunset OC to the reconstructed scattering improved the numeric agreement by 14%. Thus at Acadia for this time period, OC was a minor contributor to reduced visibility. Nitrate was not measured or included in this analysis, but is a negligible contributor to visibility degradation at Acadia. Given that Acadia has the lowest sulfate levels of any of the RAIN sites, these findings are likely to be valid at other rural MANE-VU locations.

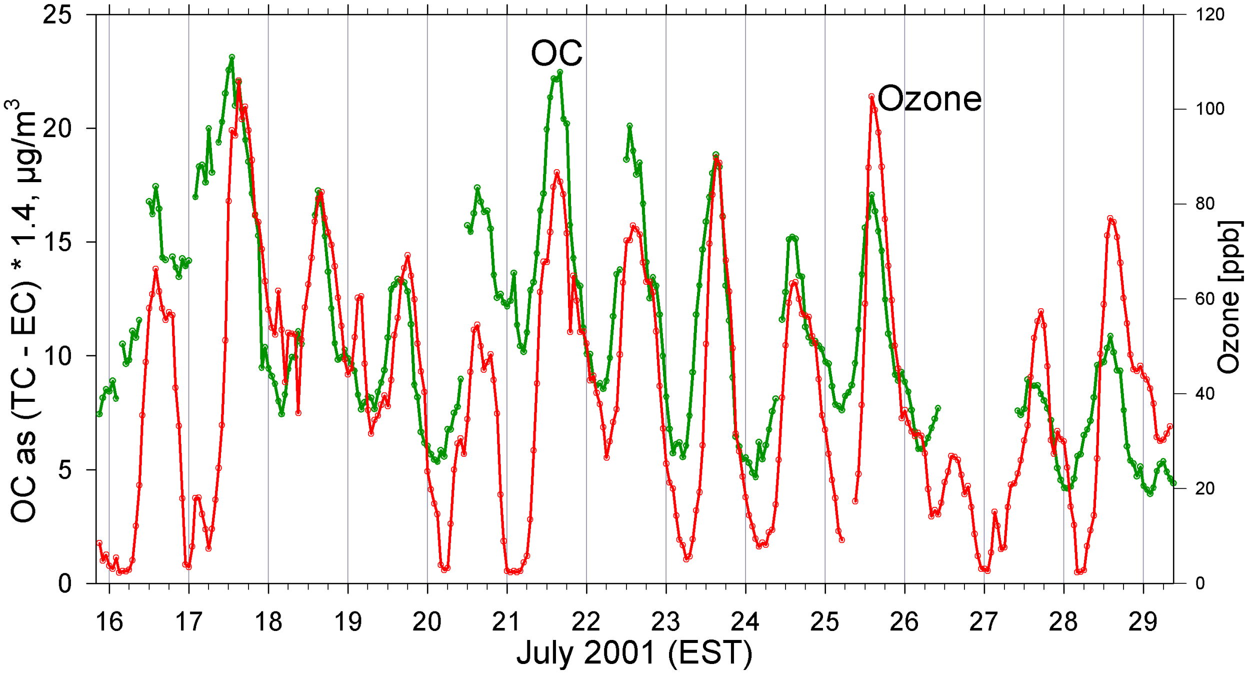
It is important to note that sulfate continues to trend downward due to numerous control programs on coal and oil-fired EGUs, and in the near future for lower-sulfur fuels as well. The pending revision to the SO2 primary NAAQS, with its source-oriented monitoring network and a relatively stringent 1-hour indicator, is expected to result in substantial additional non-compliance for source areas upwind of the MANE-VU domain. This will result in additional reductions in regional transport of SO2 and thus sulfate, but not for several years; the NAAQS process will not result in substantial SO2 source reductions until 2018 or later.

Similar reductions of aerosol OC are not expected, and although ammonium nitrate may trend upward with sulfur reductions, its impact on visibility in eastern rural areas is likely to remain small. Over time the relative contribution of OC to visibility impairment will increase substantially and eventually dominate visual range in the Mane-Vu domain, perhaps as soon as 2020. Thus it continues to be important to assess (and improve our ability to assess) the contribution of OC to visibility degradation. Identifying and quantifying major sources of aerosol OC will also become a more important component of development of control programs.

4.5 Urban vs. rural OC issues

This report has focused on rural organic carbon aerosol. It is important to note that the short-term dynamics and seasonal patterns of OC are likely to be different for urban-influenced sites, either in or just downwind of large urban areas. Fresh (local) mobile-source SOA is more abundant near urban areas, resulting in enhanced interactions between SOA and strong gas-phase oxidants such as ozone that do not occur with aged organics. A clear example of this process is shown in Figure 15, a two-week time-series plot of hourly ozone and Sunset OC from the NE-OPS site nine miles northeast of downtown Philadelphia.

Figure 15. Hourly OC and Ozone, Summer 2001, Northeast Philadelphia



Note that aerosol OC peaks are much higher than observed at RAIN rural sites, and occur at the same time as ozone every day. This makes sense given the role of oxidants in SOA formation. Of interest is the rapid drop in OC with the drop in ozone. The removal of ozone by deposition and titration in the early evening is well understood, but aerosol OC does not have these rapid removal mechanisms. The only plausible explanation for the rapid drop in OC concentration as ozone decreases is a phase change of the semi-volatile organic carbon (SVOC) aerosol back to gas phase. This suggests that a large fraction of the observed aerosol OC here is SVOC, and that ozone and related oxidants push gas-phase VOC into the aerosol phase; when oxidants are removed, the SVOC equilibration shifts, volatilizing aerosol OC.

4.6. Updates to the Sunset carbon method.

The RAIN program is now almost six years old, as are the original Sunset instruments. For those sites that have not had their carbon analyzer overhauled and updated, it is highly recommended to return it to the manufacturer for this work. A large number of improvements have been made in the method since early 2004, and many of these can be retrofitted to older instruments. The instruments can also benefit from a “mid-life” overhaul and tuneup. The cost of the overhaul and update varies depending on the condition of the instrument, but is approximately $5,000. It is strongly recommended that this be done.

Another consideration is the cycle time – 1- vs. 2-hour duration. When the network was originally deployed, there was no clear consensus as to which mode should be used. One consideration was minimizing the blank value; the increased aerosol loading using the 2-hour cycle might provide a lower OC blank and better sensitivity. The 2-hour cycle time also allows a multiple temperature OC analysis and pyrolysis correction for EC, using the NIOSH 5040 method. More recently the vendor has suggested that a “fast” EC-OC 1-hour cycle would provide the best quality OC data as well as provide the hourly data that are consistent with data from other “continuous” measurements. This 1-hour “RT-Quartz.par” mode includes a thermal EC analysis with pyrolysis, and is the default method for new instruments. The actual sample time for each hour is 47 minutes.

Another consideration is the addition of a daily “static blank” run. This is an analysis cycle without any sample collection, and can provide data about the instrument’s condition that is useful during data validation; the results should be 0 concentration (plus noise) for all measurements. Using the 1-hour EC-OC cycle described above, a real sample is collected during the same hour, but the sample duration is only ~30 minutes.

A review of these options will be done in conjunction with the vendor and other experienced users of this method. If a change in instrument configuration is made, it must be done in a coordinated manner across the network. CT DEP has been running additional Sunset instruments at non-rural sites, and EPA (OAQPS) is about to deploy a pilot network of this method at eight sites. It may be desirable to harmonize the method used for all routine Sunset carbon data.

5. Conclusions

The data capture and data quality from the RAIN Sunset aerosol carbon analyzer need improvement. For most site-years the percent of days with valid data is well under the generally considered acceptable value of 75%. The correlation with IMPROVE TC (an essential level two validation step) ranged from very good to moderate. For the sunset data to be useful (e.g., of reasonable overall quality), the R2 should be > 0.8; Sunset data sets with values substantially below this are of questionable value. In general, the slope and intercept regression values were reasonable. The intercept value is a good indication of the Sunset analyzer OC blank relative to IMPROVE blank correct OC data, and is more stable than the occasional "dynamic zero" blank estimates.

There are two primary areas where changes should be made to improve data quality and capture. First, data should be processed with the data masher and screened in a timely manner (every few weeks) to identify and correct problems quickly. This screening should include a comparison of thermal and optical EC, a valuable diagnostic tool that has not been effectively used. It must be noted that the data masher was not available until April 2009; thus the data analyzed here could not benefit from this screening process.

Second, the data masher itself may be responsible for some cases of invalid data; it may be too conservative in some of the instrument parameter void criteria it uses. In this case, it should be possible to revise how the masher validates data, and how it reports voided data (there may always be some cases where useable data are voided based on various parameters). Once appropriate changes are made to the data masher, it may be worth reprocessing those datasets that had a large number of data records voided (as opposed to data that are missing).

Analysis of the RAIN semi-continuous carbon data by itself is limited; aspects such as temporal trends (seasonal or multi-year) and spatial gradients are better analyzed using existing IMPROVE carbon data sets that have denser spatial networks and longer time-series of data. There was a surprising lack of warm or cold season diurnal variability in the OC data at all three sites. Distributions of 2-hour cycle data showed a slightly skewed distribution for OC and a highly skewed EC distribution. Future RAIN data analysis should include other related pollutants such as semi-continuous PM2.5, sulfate, and ozone, as well as meteorological data.

Use of the Sunset carbon data alone is of very limited value in assessing the contribution of wood smoke to PM. Levoglucosan or Aethalometer Delta-C could be used, but there is evidence that those methods are limited to "fresh" wood smoke and may not work for transported aged wood smoke. Carbon aerosol isotope ratio methods are the only robust tool for differentiating between old (fossil fuel) and new (biomass or biogenic) combustion aerosols. If data capture and quality are sufficient, applying the DataFed CATT incremental probability tools to Sunset data may provide enhanced insight into sources of OC.

As sulfur emissions continue to trend downward in the eastern US, the relative importance of OC aerosol as a cause of visibility impairment will increase over time. OC may be the dominant aerosol species for visibility in the MANE-VU domain within the next ten years or so. It is therefore important to develop tools for measurement and assessment of OC and its sources as input to control and compliance programs for both PM and regional haze.

Urban OC aerosol can be very different from the more aged and transported aerosol at the RAIN sites. An example of oxidant-driven conversion of "fresh" (mobile-source) SOA from gas to particle and back to gas phase is shown from Philadelphia in 2001. While this process may occur at the RAIN sites, it would be expected to be less frequent and not as distinct since the aerosol and its precursors are aged and less reactive.

The carbon analyzer instruments in the RAIN program are now six years old. An overhaul / update for this equipment should be done for those instruments that have not already gone thru this process. Many improvements in the method have been made and most can be implemented in the existing older hardware. This would be a modest investment that should result in better data quality and improved data capture, as well as extending the useful life of the instrument.

It is worth revisiting the analysis protocol used in RAIN. There are options that provide hourly data with the potential for improved sensitivity. The Sunset carbon analyzer is starting to be used in other routine monitoring networks, and an effort should be made to harmonize the operation of these instruments to insure that the data are comparable.

6. References

Abstracts for journal references below are available by using the DOI number at:
http://dx.doi.org/

RAIN Sunset analyzer field SOP:
ftp://airbeat.org/private/RAIN/SOPs/Sunset-OCEC_RAIN-SOP_Ver1.0.pdf

Sunset “Data Masher” post-processing software documentation:
ftp://airbeat.org/private/RAIN/Sunset-Carbon/SunsetCarbonMasher_Manual_1.0c.pdf

Method references:

http://www.sunlab.com/products-services/model-4-field-analyzer.html

Bae et al., 2007. Intercomparison of two different thermal-optical elemental carbons and optical black carbon during ABC-EAREX2005. Atmos. Environ., 41, 2791–2803, doi: 10.1016/j.atmosenv.2006.11.040

Bae et al., 2004. Validation of a semi-continuous instrument for elemental carbon and organic carbon using a thermal-optical method. Atmos. Environ., 38, 2885–2893, doi: 10.1016/j.atmosenv.2004.02.027

Bauer et al., 2009. “Characterization of the Sunset Semi-Continuous Carbon Aerosol Analyzer.” J. Air & Waste Manage. Assoc., 59:826–833, doi: 10.3155/1047-3289.59.7.826

Snyder and Schauer, 2007. “An Inter-Comparison of Two Black Carbon Aerosol Instruments and a Semi-Continuous Elemental Carbon Instrument in the Urban Environment.” Aerosol Science and Technology, 41:463–474, doi: 10.1080/02786820701222819

Other References:

Andreae, 2009. “ Perspective on Jimenez et al. - A New Look at Aging Aerosols.” Science, doi: 10.1126/science.1183158

Donahue et al., 2009. “Atmospheric organic particulate matter: From smoke to secondary organic aerosol.” Atmos. Environ., 43, 94–106, doi: 10.1016/j.atmosenv.2008.09.055

Fisseha et al., 2009. “Determination of primary and secondary sources of organic acids and carbonaceous aerosols using stable carbon isotopes”. AtmosEnviron 43: 431–437, doi: 10.1016/j.atmosenv.2008.08.041

Fraser et al., 2000. “Using Levoglucosan as a Molecular Marker for the Long-Range Transport of Biomass Combustion Aerosols.” EnvironSciTechnol, doi: 10.1021/es991229l

Jimenez et al., 2009. “Evolution of Organic Aerosols in the Atmosphere.” Science, doi: 10.1126/science.1180353

Jordan et al., 2006. “Radiocarbon determination of wood smoke contribution to air particulate

matter in Launceston, Tasmania." AtmosEnviron, 40, 2575–2582,
doi: 10.1016/j.atmosenv.2005.12.024

Liu et al., 2005. "Atmospheric Aerosol over Two Urban-Rural Pairs in the Southeastern United States: Chemical Composition and Possible Sources." AtmosEnviron,
doi: 10.1016/j.atmosenv.2005.03.048

NESCAUM (2006). "Regional Aerosol Intensive Network (RAIN): Preliminary Data Analysis".
http://www.nescaum.org/documents/2006-05-memo8-rain.pdf/
Northeast States for Coordinated Air Use Management, Boston, MA.

Puxbaum et al., 2007. "Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background." JGR,
doi: 10.1029/2006JD008114

Schichtel et al., 2008. "Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States." J. Geophys. Res., doi: 10.1029/2007JD008605

Simoneit et al., 1999. "A review of biomarker compounds as source indicators and tracers for air pollution." Environ. Sci. Poll.Res, doi: 10.1007/BF02987621

Sullivan et al., 2008. "A method for smoke marker measurements and its potential application for determining the contribution of biomass burning from wildfires and prescribed fires to ambient PM2.5 organic carbon." J. Geophys. Res., doi:10.1029/2008JD010216

Ward, 2009. "The Kalispell, Montana PM2.5 Source Apportionment Research Study,".
Report from The University of Montana – Missoula Center for Environmental Health Sciences,
http://www.deq.state.mt.us /AirQuality/docs/KalispellCMBReport2008_09.pdf

Zencak et al., 2007. "Quantification and radiocarbon source apportionment of black carbon in atmospheric aerosols using the CTO-375 method." Atmospheric Environment, 41, 7895–7906,
doi: 10.1016/j.atmosenv.2007.06.006

Zheng et al., 2006. "Spatial distribution of carbonaceous aerosol in the southeastern United States using molecular markers and carbon isotope data." J. Geophys. Res., 111, D10S06,
doi: 10.1029/2005JD006777