ASSISTANCE AGREEMENT QUARTERLY REPORT
for the reporting period January 13, 2002 through April 12, 2003

June 1, 2003

St. Louis - Midwest Particulate Matter (PM) Supersite Monitoring Program
EPA Assistance ID No. R-82805901-0

Work Progress and Status

Data Validation. Data validation on the St. Louis – Midwest Supersite "Year #1" (i.e. the measurement period funded under this cooperative agreement, April 2001 through May 2002) data streams has been a major focus of this quarter's activities. Quality assured data is submitted by the respective measurement PI's to the St. Louis – Midwest Supersite PI (Turner) for review. The data sets are subsequently forwarded to Desert Research Institute where they are imported into the DRI database which is set up for efficient exporting to the NARTSO data archive and Supersites program-wide relational database (as has been demonstrated by DRI submissions of the Fresno Supersite data). The status of the core data streams as of June 1, 2003 is summarized in the following table.

Data Stream	CY 2001 Data	Q1 CY 2002 Data	Q2 CY 2002 Data
Submission deadline to NARSTO archive and Supersites database	June 1, 2003	July 15, 2003	October 1, 2003
- criteria gases	submitted to DRI	submitted to DRI	submitted to DRI
- meteorology	submitted to DRI	submitted to DRI	submitted to DRI
- substrate mass (PM-1, -2.5, -10)	submitted to DRI	submitted to DRI	submitted to DRI
- substrate PM-2.5 ions	to DRI by 6/2/03	to DRI by 6/2/03	to DRI by 6/2/03
- substrate PM-2.5 EC & OC	to DRI by 6/2/03	to DRI by 6/2/03	to DRI by 6/2/03
- substrate PM-2.5 metals	see report text	see report text	to DRI by 10/1/03
- semicontinuous PM-2.5 mass	submitted to DRI	submitted to DRI	submitted to DRI
- semicontinuous PM-2.5 BC & UVC	submitted to DRI	submitted to DRI	submitted to DRI
- semicontinuous PM-2.5 sulfate	to DRI by 6/6/03	to DRI by 6/6/03	to DRI by 6/6/03
- semicontinuous PM-2.5 nitrate	to DRI by 6/15/03	to DRI by 6/15/03	to DRI by 6/15/03
- semicontinuous PM-2.5 EC & OC	to DRI by 6/2/03	to DRI by 6/2/03	to DRI by 6/2/03
- semicontinuous size distributions	to DRI by 6/6/03	to DRI by 6/2/03	to DRI by 6/2/03
- retrospective organics speciation	see report text	see report text	see report text
- retrospective hourly metals	see report text	see report text	to DRI by 10/1/03

Several data streams for the entire measurement period have already been submitted to DRI. Data for substrate PM-2.5 ions and their precursor gases has been validated by both Harvard and Washington University (WU) and will be submitted upon inserting the uncertainty estimates on June 2. Data for both substrate and semicontinuous EC and OC has been validated by both Wisconsin and WU and will be submitted upon reformatting the validation description codes on June 2. The size distributions data was validated by both Minnesota and WU; during the week of May 26, however, an error was found in the data processing algorithm and thus the data is being

reprocessed for submission by June 6 (DRI has already reviewed an example data set to ensure it can be efficiently imported into their database). Data for semicontinuous sulfate has been validated by Harvard and is currently being reviewed by WU; this review and the submission to DRI will be completed by June 6. Data for semicontinuous PM-2.5 nitrate is currently being validated by WU staff; the data analyst (who currently resides in California) will be on campus on June 11-12 to meet with the Supersites PI to finalize the data set for submission by June 15.

Chemical analysis for substrate metals was delayed to provide time for DRI to install their ICP-MS unit and develop and test suitable analysis protocols. Given the critical timing for data submissions, however, a decision will be made by June 6 by Turner in collaboration with DRI (Chow) and the Supersites Project Officer (Jones) concerning whether the ICP-MS analysis is tractable or XRF should be immediately programmed for the samples towards meeting the data submission obligations.

Finally, two data streams were programmed for retrospective analysis after the entire year of samples were collected. In both cases, the sample selection decisions were subsequently delayed to take advantage of opportunities to improve the quality and/or size of the data set. Sample collection for organics speciation was continued during Year 2 of the measurement program (funded via a grant through USEPA Region VII) and EPRI has provided funds to double the size of the sample set to be analyzed. Organics speciation for the two-year sampling period has recently been programmed for analysis and due to EPRI's leveraging 140 samples will be analyzed from the Year 1 measurement period; this represents a significant expansion beyond the 100 samples originally programmed through this cooperative agreement at the expense of a delay in the analysis timeline. The samples chosen from the Year 1 measurement program are being analyzed in chronological order to support incorporation into the databases as soon as possible. Sample collection for hourly metals continued until November 2002. To date chemical analysis has been conducted on twenty-one days of samples (25% of the funded number of samples). This data will be submitted to the DRI database by June 6. The remaining sixty days of samples to be programmed for analysis will be selected by June 4 (a conference call has been scheduled for this purpose) and analysis will be conducted in chronological order to again support incorporation into the databases as soon as possible. Turner will consult with the Supersites Project Officer during the week of June 2 concerning the status of these analyses and data submissions.

Personnel

There are no changes to the key personnel.

Expenditures

There are no adjustments to the project budget.

Quality Assurance

Data validation efforts were summarized in the "Work Progress and Status" section of this Quarterly Report.

Results

This quarterly report focuses on one of the several data analysis efforts currently underway. Preliminary results were presented by Hill, Goodwin and Turner at the 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (March-April 2003, Pittsburgh, PA). An abstract has been submitted for presentation of the subsequent analyses at the Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA).

Middle Scale Contributions to Ambient Black Carbon. A suite of analyses are being performed which capitalize on the extended time series afforded by the sustained two years of measurements at the East St. Louis (IL) core monitoring location. In this quarterly report, we summarize only one such effort - an analysis to characterize the various geographic scales of black carbon emissions as they impact the monitoring site. This is a particularly timely topic because: (1) selected health effects studies suggest there may be adverse impacts arising from the carbonaceous component of ambient aerosol (including "soot") and thus it is important to understand the zone of representation of monitoring sites used in those and future studies; and (2) instruments for semicontinuous measurement of aerosol black carbon are being deployed at several of the National Air Toxics Trends Monitoring Network sites and the data collected at high time resolution - indeed, higher time resolution than the reporting requirements for this network - can be exploited to gain insights into the nature of the emission sources impacting these sites.

Figure 1 summarizes the overarching motivation for this work. The zone of representation for a monitoring site depends on the various scales of influence for emission sources impacting that site. The observed behavior is likely specific to the parameter being measured due to differences in the spatial and temporal patterns of emissions and varying influences exerted by atmospheric processes (e.g., secondary formation). Figure 2 presents the classification scheme adopted by Watson and Chow (2001) for characterizing spatial scales of influence from emission sources. Our immediate interest is to separate the micro- and- middle-scale influences from the neighborhood- and urban-scale influences as the former will necessarily be site-specific and should be taken into consideration when interpreting data from a given monitoring site.

Figure 3 presents the two data streams initially used in our analysis. All measurements were conducted at the East St. Louis (IL) core monitoring location. Emphasis is placed on the aethalometer black carbon data stream due to its aforementioned relevance to health effects studies and the National Air Toxics Trends Monitoring Network. The second data stream - the "total aerosol length concentration" was included because it is a bulk aerosol property rather than

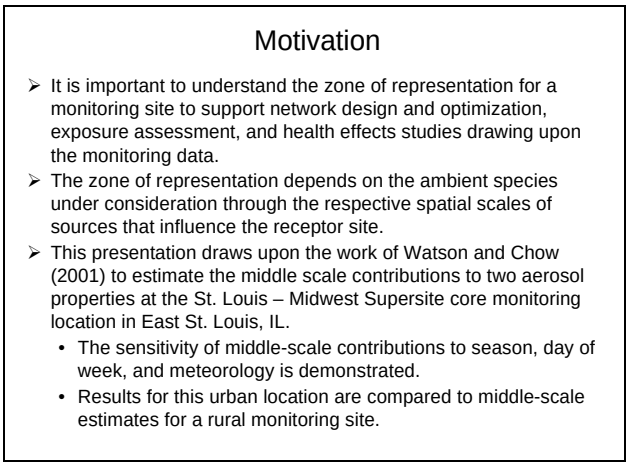

Figure 1.

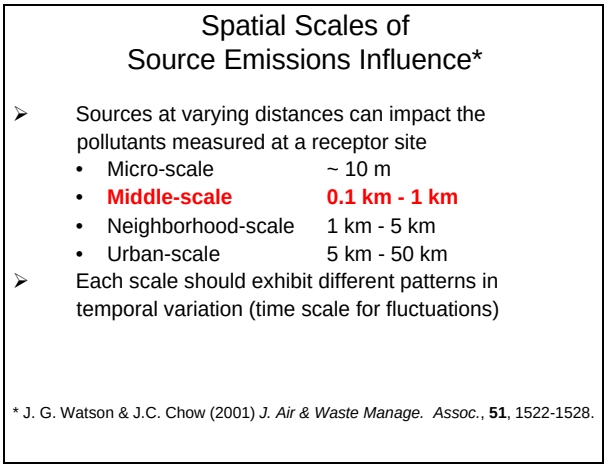

Figure 2.

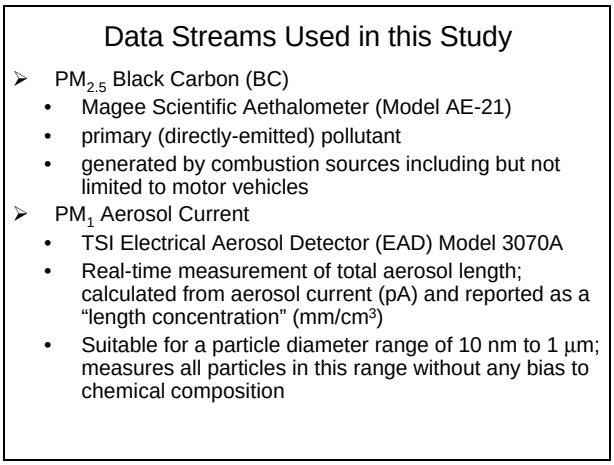

Figure 3.

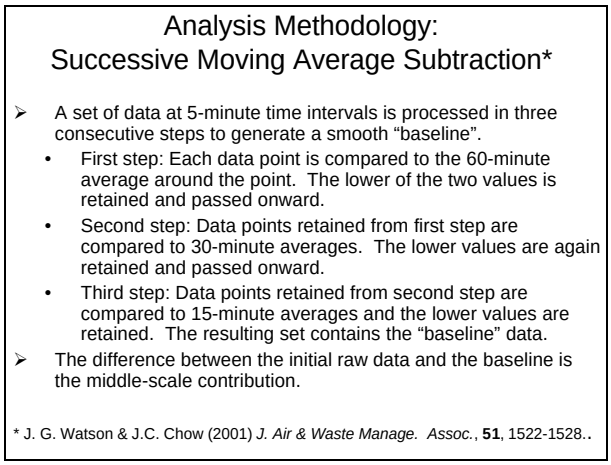

Figure 4.

a specific chemical component and thus we would expect a different response for this metric. Specifically, all particles will contribute to the total aerosol length concentration and thus we expect a damped response for middle scale contributions to this bulk aerosol parameter compared to those specific aerosol chemical components which have substantial middle scale influences (e.g., black carbon which originates from combustion sources including but not limited to motor vehicles).

The approach is to separate middle scale influences from influences occurring on larger spatial scales by taking advantage of the time scales for fluctuations in the measured response for a given aerosol parameter. The time scales for fluctuations from sources relatively far from the source should be damped out due to atmospheric dispersion. Watson and Chow (2001) present the rationale for this statement; we look at it in the following complementary - albeit perhaps somewhat different - manner. The time scale for fluctuations in the response from far-field sources will be damped by atmospheric dispersion because, in addition to plume spreading in the axial direction (i.e. the direction of the mean wind), the plume spreading in the horizontal

direction will render the response less sensitive to modest fluctuations in the wind direction. For micro- and middle-scale sources, there is relatively little transport time for dispersion; fluctuations can arise on these short time scales due to the transient nature of the sources (e.g., individual motor vehicles) or fluctuations in the wind direction causing the relatively narrow plume to hit-or-miss the site. Figure 4 (previous page) summarizes the analytical approach taken by Watson and Chow (2001) to isolate the middle scale contributions. They correctly state that the power of their approach resides in its simplicity (indeed, perhaps at the expense of robustness). **We are currently assessing the extent to which the proposed method does indeed capture the middle scale contributions, but in any case the approach is essentially a low pass filter which can be used to separate the ambient signal into components that fluctuate at relatively higher frequency and components that fluctuate at relatively lower frequency.** Note that high time resolution measurements (e.g., 5-minute time bases or finer) are needed for this analysis.

Figure 5 shows the application of this filtering technique to a single day of data. The red line is the black carbon concentration as measured at 5-minute time resolution. The green line is that portion of the black carbon assigned to the baseline (i.e. neighborhood- and urban-scales) while the yellow line is the black carbon concentration assigned to the middle scale[1] (or more generically, the black carbon with relatively short time scales for concentration fluctuations). The raw signal (red) exhibits several spikes of short time duration which are assigned to the middle scale (yellow). Dramatic middle scale events occur during the rush hour periods (0500-0800 CST and 1600-1800 CST) although numerous events also occur throughout the day. This pattern suggests the prevalence of vehicular emissions to the middle scale black carbon signal.

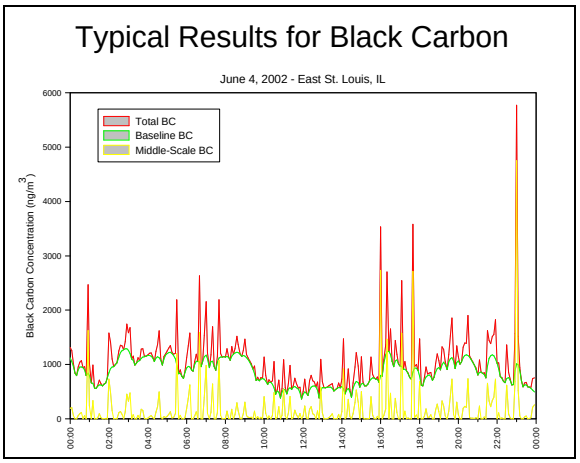

Figure 5.

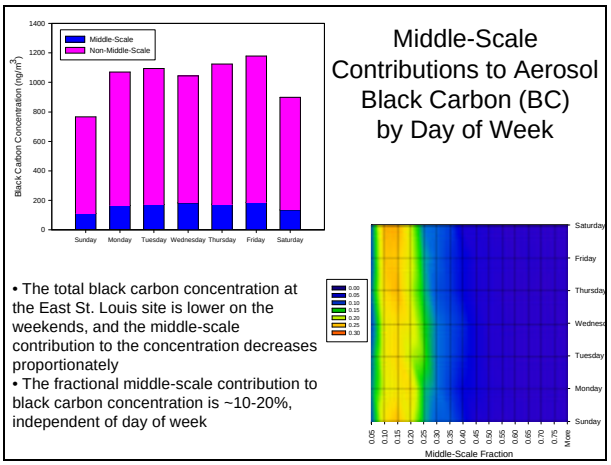

Figure 6.

[1] The microscale contributions - if significant for averaging periods of five minutes or longer - are presumably rolled into the middle scale contributions. We will investigate this assumption using an aethalometer black carbon data stream collected at one-minute time resolution. For the remainder of this report the term "middle scale" shall refer to middle scale and microscale contributions.

The baseline (green) exhibits a decrease starting about 0900 CST followed by a broad minimum until about 1600 CST. This is indicative of the period of increased ventilation as driven primarily by the growth in the mixing layer depth (and to some extent by increasing wind speed). The baseline/middle-scale split is an operational definition prescribed by the filtering technique; its quantitative robustness is debatable (e.g., note the local maxima in the baseline (green) coinciding with the peaks in the middle scale (yellow)) but the approach as currently implemented does at least semi-quantitatively apportion the total black carbon and, as described below, appears to be meaningful.

Using this framework, we have investigated the middle scale contribution to ambient black carbon and also the total aerosol length concentration using several parameters to stratify the data (e.g., season, day of week, hour, wind speed, wind direction). Several of these cases were presented at the PM2003 meeting, and in this quarterly report we focus on only a subset of these cases. Figure 6 (previous page) shows the middle scale and baseline (non-middle scale) contributions to the total black carbon concentration by day-of-week for an entire year of data (CY 2002). The upper-left plot shows that both the total and middle scale mean black carbon concentrations are lower on weekends than weekdays. The lower-right plot shows that the *frequency distribution of the fraction of black carbon apportioned to the middle scale* is insensitive to day of week (the color intensity along each horizontal line corresponding to a day of the week reflects the frequency distribution of the middle scale contribution specified on the y-axis). Figure 7 shows the same plots for the total aerosol length concentration. Middle scale contributions to total aerosol length concentration are lower than the middle contributions to the aerosol black carbon concentration and are also insensitive to day-of-week.

Figure 8 summarizes the analysis - including materials not shown in this quarterly report - at the time of the PM2003 presentation. We have subsequently continued this work to address several outstanding questions. In particular, we have been investigating the factors governing the observed weekday/weekend differences in the total black carbon concentration and middle scale black carbon concentration. Figure 9 shows diurnal profiles for the baseline and middle scale

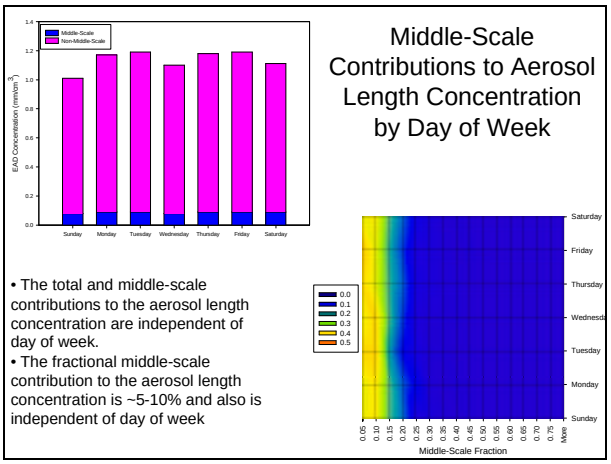

Figure 7.

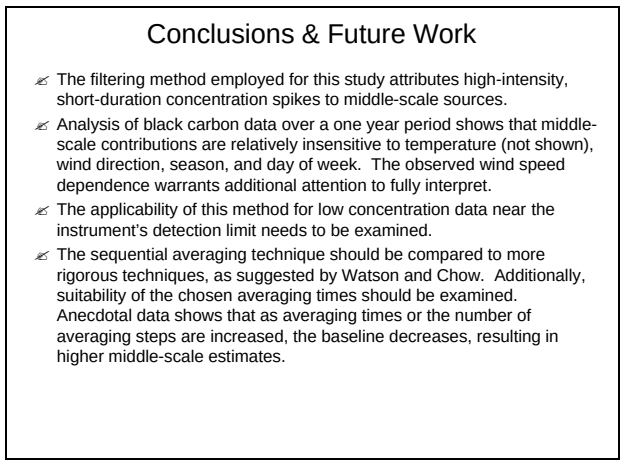

Figure 8.

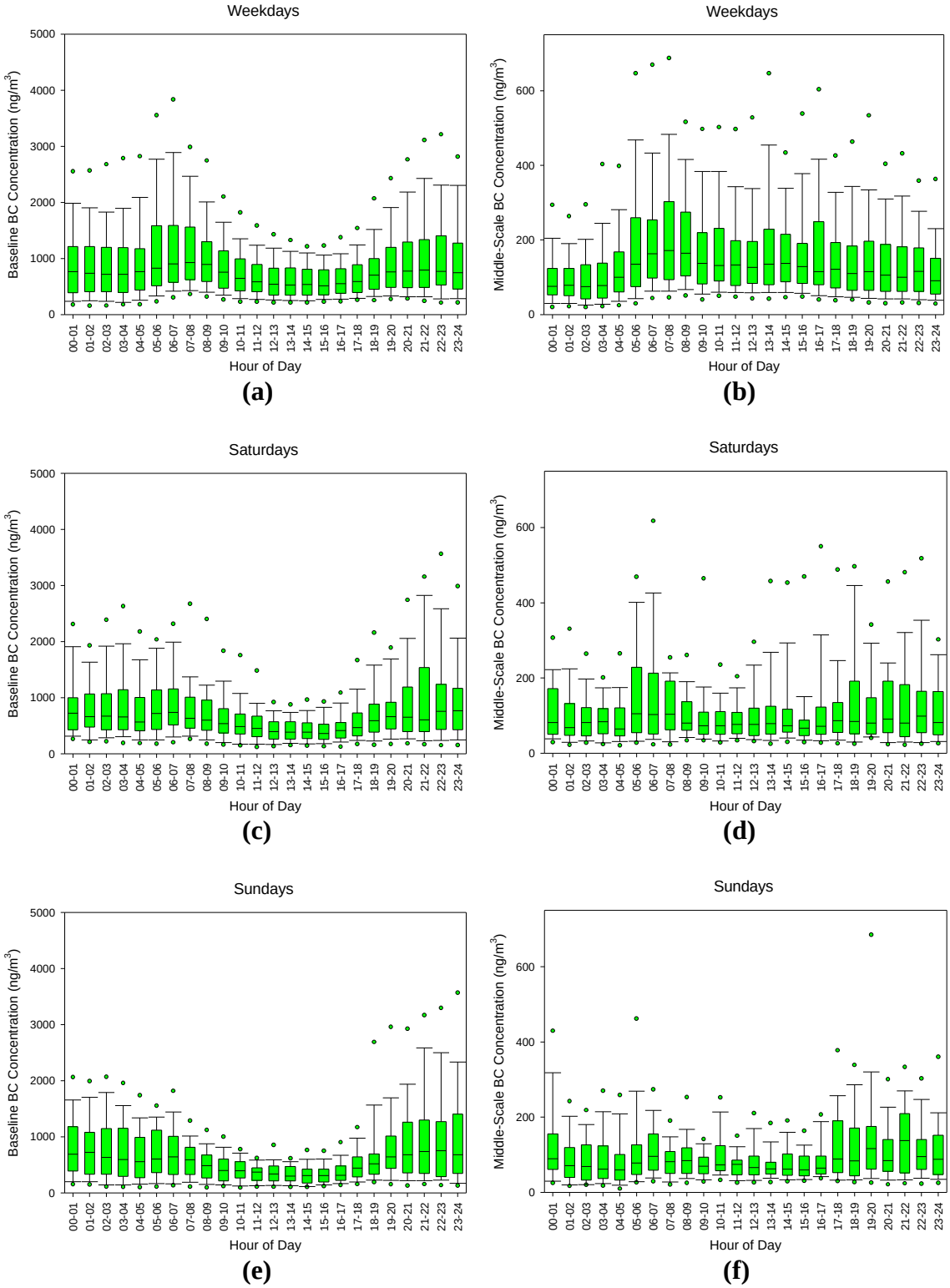
Weekdays
Baseline BC Concentration (ng/m3)
Hour of Day
(a)
Weekdays
Middle-Scale BC Concentration (ng/m3)
Hour of Day
(b)
Saturdays
Baseline BC Concentration (ng/m3)
Hour of Day
(c)
Saturdays
Middle-Scale BC Concentration (ng/m3)
Hour of Day
(d)
Sundays
Baseline BC Concentration (ng/m3)
Hour of Day
(e)
Sundays
Middle-Scale BC Concentration (ng/m3)
Hour of Day
(f)

Figure 9.

black carbon concentrations stratified by weekdays, Saturdays, and Sundays. The distributions arising from processing an entire year of data are shown for each hour as a box plot where the bottom, middle and top lines defining the box represent the 25^{th}, 50^{th} and 75^{th} percentiles, respectively, and the whiskers represent the 5^{th} and 95^{th} percentiles. Figure 9a shows that the weekday baseline black carbon concentration increases during morning rush hour and subsequently exhibits a mid-day minimum when the atmospheric ventilation is usually greatest. An evening rush hour peak is not discernible - likely because the emissions are diluted by atmospheric ventilation over the transport time scales relevant for neighborhood- and urban-scale influences - and the baseline black carbon concentration rises in the early evening upon the mixing layer collapsing and the onset of atmospheric stability. The trends for weekends are more difficult to elucidate, possibly due to the smaller data sets (this analysis will be repeated in the forthcoming months using a two full years of data - May 2001 through April 2003 - as doubling the data set will likely stabilize the distributions). Figure 9c suggests there might be a modest maximum in the baseline black carbon concentration during the morning rush hour period on Saturdays, while Figure 9e suggests there is no rush hour maximum in the baseline black carbon concentration on Sundays.

The middle scale black carbon concentrations behave quite differently compared to the baseline black carbon concentrations. The weekday middle scale black carbon concentration exhibits a morning rush hour peak but does not exhibit the strong influence of atmospheric ventilation observed in all the baseline black carbon concentration profiles. Indeed, the weekday middle scale black carbon concentrations are highest during the daytime hours and lowest during the nighttime hours, consistent with expected patterns in local activities which would emit black carbon (e.g., local vehicular traffic). Not only are the middle scale sources persistent throughout the daytime hours, they are not dramatically affected by the diurnal changes in atmospheric ventilation because the transport times between the source and the monitor are very short compared to the characteristic time for dispersion even under strongly ventilating conditions. Weekend middle scale black carbon concentrations have narrower hourly distributions with barely discernable elevated concentrations during rush hour on Saturday and no discernable elevation in concentration during rush hour on Sunday. Similar to the weekday middle scale black carbon diurnal profile, the weekend middle scale diurnal profiles do not exhibit the influence of atmospheric ventilation.

This analysis of diurnal profiles for the baseline (neighborhood- and urban-scale) black carbon and middle scale black carbon, stratified by day of week, provides significant insight into the nature and representativeness of the black carbon concentrations measured at the East St. Louis (IL) core monitoring site. Additional interpretation will be provided in subsequent quarterly reports.

In summary, analysis of the high time resolution aethalometer data can provide insights into the both the temporal and spatial nature of the emission sources impacting the black carbon concentration measured at a monitoring site. While additional work is needed to fully elucidate the strengths and weaknesses of the method as implemented, our preliminary results suggest there would be significant value in applying this methodology to aethalometer black carbon

measurements at other sites, including but not limited to the National Air Toxics Trends Monitoring Network. This endeavor would require cooperation from the participating monitoring agencies because there are currently no requirements for the high time resolution (i.e. 5-minute) data to be reported to USEPA.

Publications and Presentations

One oral presentation and nine poster presentations were made at the 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (April 2003, Pittsburgh, PA).

- "Overview of the Saint Louis – Midwest Supersite", J.R. Turner, et al.
- "A Spatio-Temporal Aerosol Climatologic Context for the Saint Louis – Midwest Supersite", S.A. Duthie, et al.
- "Middle Scale Source Contributions to High Time Resolution Particulate Matter Measurements at the Saint Louis – Midwest Supersite", J.S. Hill, et al.
- "New Insights into the Dynamics of Sources of Fine Particulate Matter Using Semicontinuous Chemical Speciation Samplers", J.J. Schauer, et al.
- "Highly Time-Resolved Measurements of Elemental Composition at the Baltimore, St. Louis, Pittsburgh, and Tampa Supersites Using the UM High-Frequency Aerosol Slurry Sampler: Unprecedented Resolution of the Sources of Primary Atmospheric Aerosol", J.M. Ondov, et al.
- "Particulate Matter Mass Concentration Measurements at the Saint Louis – Midwest Supersite", E.S. Simon, et al.
- "Diurnal Cycles and Sporadic Events in the Saint Louis Aerosol", W.H. White, et al.
- "Regional Ultrafine Particle Events Observed in St. Louis, MO", Q. Shi, et al.
- "Continuous Measurement of the Atmospheric Aerosol Size Distribution at the St. Louis – Midwest Supersite", H. Sakurai, et al.
- "Recent Advances in Our Understanding of Physical and Chemical Properties of Particulate Matter, P.H. McMurry

Quarterly Report Summary

See Attached