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

March 10, 2003

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

Work Progress and Status

1. *Routine Data Collection*. Core site (East St. Louis, IL) measurements under this cooperative agreement formally ceased on May 31, 2002. As described in the previous quarterly report, a majority of the measurement matrix has been sustained, however, under a separate agreement contract managed through USEPA Region VII (Michael Davis, Project Officer). These measurements leverage the work conducted under the original cooperative agreement by providing a longer time series for climatological assessments and health effects studies. In addition, under the USEPA Region VII contract the movable platform was deployed in rural northeast Kansas for the period September – December 2002 in support of CENRAP's efforts to characterize fine particulate matter and regional haze in the central United States.

2. *Retrospective Analysis for Speciated Organics*. The St. Louis - Midwest Supersite sampling strategy includes daily 24-hour integrated collection for $PM_{2.5}$ speciated organics analysis by extraction/GC-MS. Under the original cooperative agreement, funds were programmed to analyze 100 days of samples drawn from the nominally one-year field campaign. We recently received funding from EPRI to double the number of samples to by analyzed for $PM_{2.5}$ speciated organics, yielding a total of 200 days of samples over the nominally two-year field campaign covered under this cooperative agreement and the USEPA Region VII contract. The samples to be analyzed include: 120 samples corresponding to the 1-in-6 day national sampling schedule; an additional 27 samples to provide daily coverage for July 2001 (the Eastern Supersites Intensive study period); and 18 samples corresponding to three "focus weeks" being studied in detail by the St. Louis - Midwest Supersite Consortium. These three one-week periods represent a relatively broad spectrum of meteorological conditions and dynamic range for the aerosol bulk composition (June 22-28, 2001; November 7-13, 2001; March 19-25, 2002). An additional 35 samples can be programmed for analysis.

3. *Data Analysis Workshop*. The St. Louis – Midwest Supersite convened its third data analysis workshop on October 22, 2002. The meeting was attended by representatives from each institution in the St. Louis - Midwest Supersite Consortium, as well as representatives from USEPA Region VII, Missouri DNR, and the allied exposure and health effects studies (Harvard University School of Public Health, St. Louis University School of Public Health).

4. *Collaborations with Stakeholder Organizations*. The St. Louis - Midwest Supersite continues to expand its collaborations with LADCO and the Midwest RPO. As described in a previous quarterly report, the Midwest RPO has contracted Turner (St. Louis Supersite) and Pandis (Carnegie Mellon Supersite) to collaborate on a PM model development and validation effort project conducted by LADCO and Environ. The objective is to get PM modeling tools into the hands of State agencies over the next several months to support preliminary analyses for PM nonattainment and regional haze planning. Turner continues to participate in monthly conference calls, coordinates St. Louis Supersite data delivery and data interpretation, and participated in the Midwest RPO Modeling Review meeting (November 11-12, 2002) which examined in detail the state of the modeling effort. Turner and Duthie participated in the LADCO Monitoring Technology Review Meeting (October 30, 2002) and presented results for the St. Louis - Midwest Supersite experience with semicontinuous monitors.

Personnel

Dr. Warren White has moved from Washington University in St. Louis to the University of California, Davis. His role with the St. Louis – Midwest Supersite remains unchanged.

Expenditures

There are no adjustments to the project budget.

Quality Assurance

DRI has successfully tested their ability to upload data from their database to the NARSTO data archive. Thus, the St. Louis - Midwest Supersite measurement PIs have started to formally populate the DRI database to facilitate submissions to both the NARSTO data archive and Supersites programwide relational database. As described in the previous quarterly report, data for the entire twelve-month period has been validated for a suite of measurements; thus, our priority at this time is to aggressively populate the DRI database.

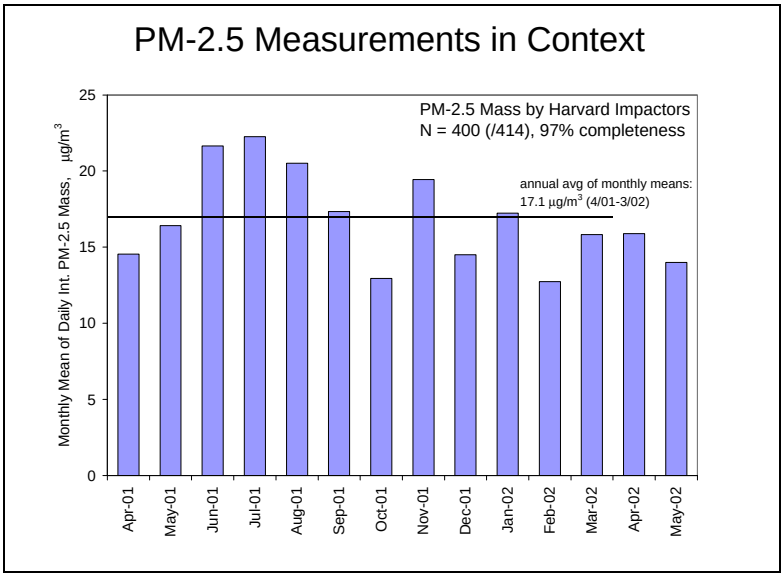
Results

In lieu of a detailed narrative on recent results, we have included excerpts from presentations at the A&WMA Symposium on Air Quality Measurement Methods and Technology (November 2002, San Francisco, CA) concerning $PM_{2.5}$ ion measurements, and from the Supersites PI Meeting (January 2003, Atlanta, GA) concerning diurnal profiles and sporadic events in the St. Louis aerosol.

A. $PM_{2.5}$ Ion Measurements at the St. Louis - Midwest Supersite

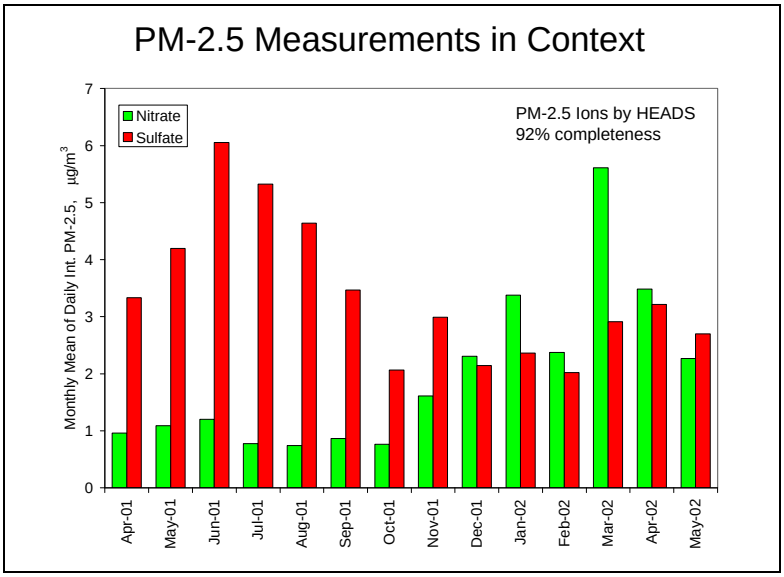
Figure A-1 shows the monthly mean $PM_{2.5}$ mass concentration constructed from daily 24-hour integrated sampling using Harvard Impactors (our *de facto* filter-based gravimetric mass method). The PM mass concentration is highest during the summer months with substantial month-to-month variation during the remainder of the year. The annual average of the monthly mean $PM_{2.5}$ mass concentrations is 17 $\mu g/m^3$ which is consistent with NAMS/SLAMS data collected at the East St. Louis site since inception of the $PM_{2.5}$ complicance monitoring network..

Figure A-1



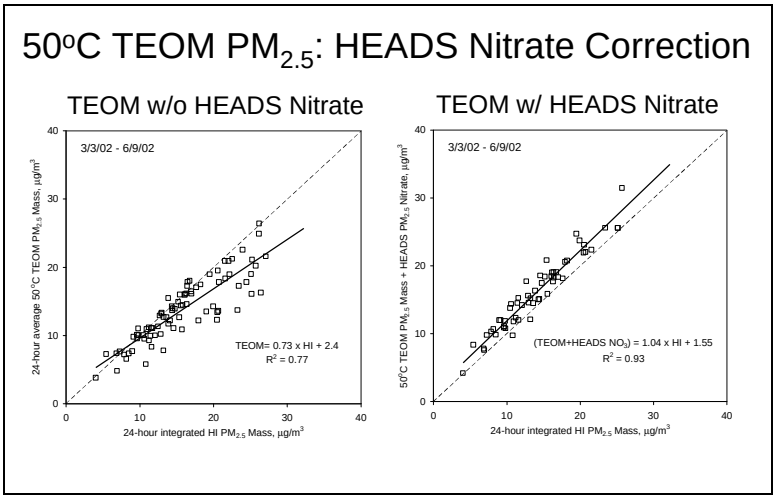
Monthly mean $PM_{2.5}$ sulfate and nitrate mass concentrations (from daily 24-hour integrated HEADS substrate measurements) show strong seasonal variation (Figure A-2). Sulfate is highest during the summer while nitrate is highest during the winter/spring period.

Figure A-2



It is well established that a TEOM operating at 50°C measures the nonvolatile component of ambient particulate matter. The left-hand plot in Figure A-3 is a scatter plot of daily-average $PM_{2.5}$ TEOM mass versus daily-integrated $PM_{2.5}$ filter mass (from Harvard Impactors) for the period March 3 - June 9, 2002. The data appears to be stratified into two groups - some data closely follows the 1:1 line while other data exhibits TEOM mass substantially lower than the filter mass. The right-hand plot in Figure A-3 shows the same plot with daily-integrated HEADS nitrate added to the daily-average TEOM mass. This nitrate correction to the data yields an improved coefficient of linear regression (R^2 = 0.93 versus 0.77), regression slope (1.04 versus 0.73) and regression intercept (1.6 versus 2.4 $\mu g/m^3$). Thus, it appears that nitrate loss from the TEOM can explain the difference between the TEOM and filter mass concentrations. The relatively-large intercept of 1.6 $\mu g/m^3$ might arise from nitrate loss from the filter measurements which are also sensitive to sampling artifacts.

Figure A-3



Multiple methods were used for semicontinuous measurement of $PM_{2.5}$ sulfate and nitrate at the St. Louis - Midwest Supersite. This summary focuses on comparisons to the substrate data obtained using HEADS.

Figure A-4

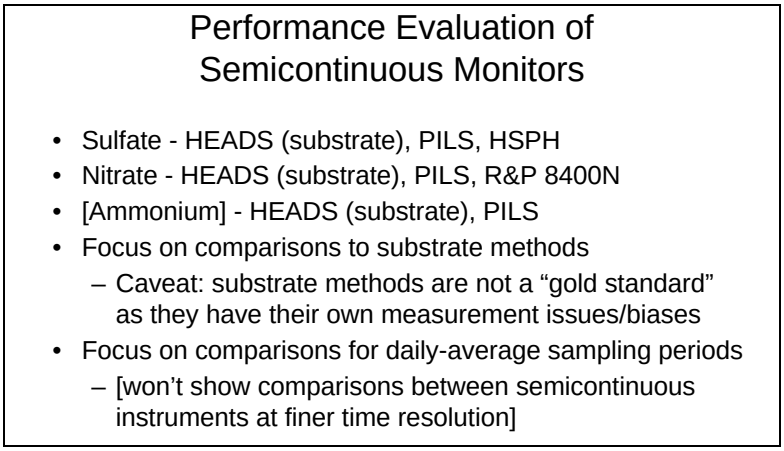


Figure A-5 shows daily-average $PM_{2.5}$ sulfate by the HSPH method versus daily-integrated $PM_{2.5}$ sulfate by the HEADS substrate method for three months during the study period. There is good agreement between these methods. For other cases (not shown), however, the HSPH sulfate data was high correlated with - but substantially lower than - the HEADS sulfate. We believe that the high-temperature converters used to convert PM sulfate to gaseous sulfur dioxide in the HSPH method lose their efficiency over time, as good agreement is restored after installing a new converter. We are currently documenting the time scale for the loss in converter efficiency.

Figure A-5

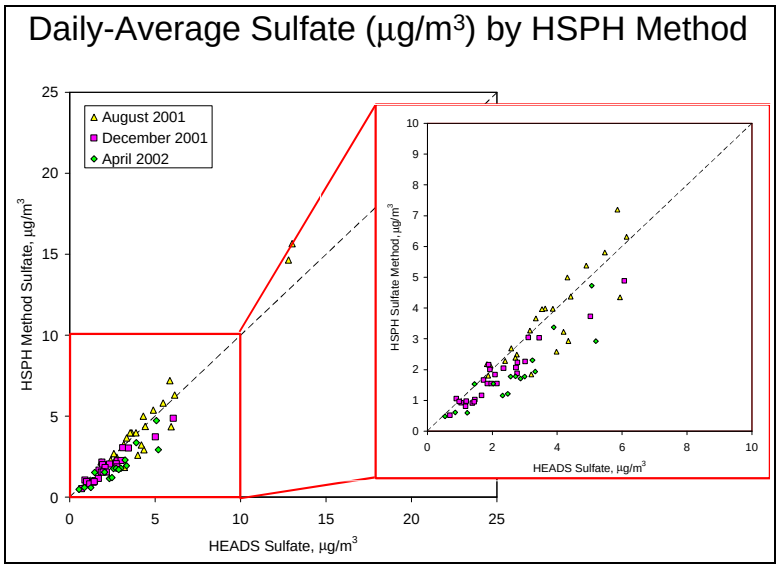
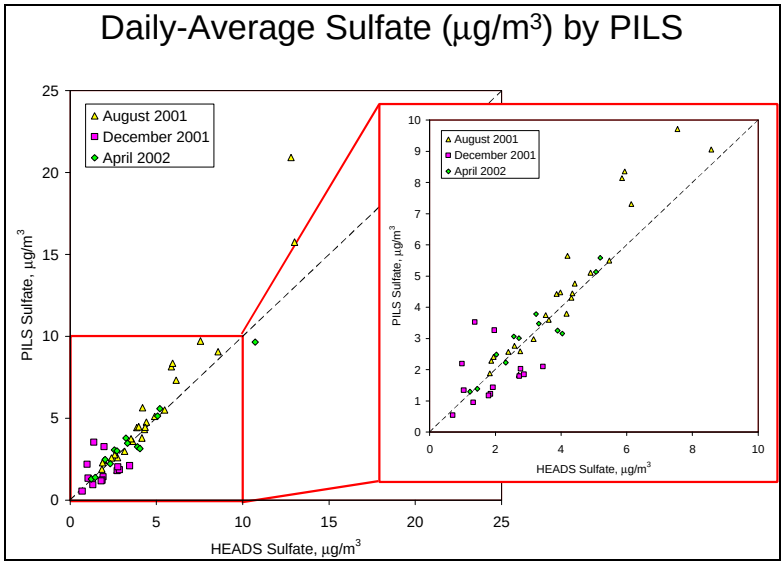


Figure A-6 shows daily-average $PM_{2.5}$ sulfate by the particle-into-liquid sampler (PILS) method versus daily-integrated $PM_{2.5}$ sulfate by the HEADS substrate method for same three months as the previous figure. Again, there is good agreement between these methods especially given that several hardware changes were implemented over the course of the one year study period (e.g., changes from sample loops to concentrator columns in the ion chromatographs) in an effort to resolve PM organic acids by PILS.

Figure A-6



PILS nitrate data also showed good agreement to HEADS substrate data for two of the three months presented in this summary (April 2003 data is being reprocessed). This is particularly satisfying given the dynamic range of ambient temperatures for St. Louis winters which requires extra precautions to avoid nitrate volatilization upon drawing the sample into the shelter housing the equipment. For example, over the period December 8, 2001 through January 8, 2002 the daily average ambient temperature ranged from -8°C to +8°C yet PILS and HEADS data tracked well throughout this period (Figure A-8).

Figure A-7

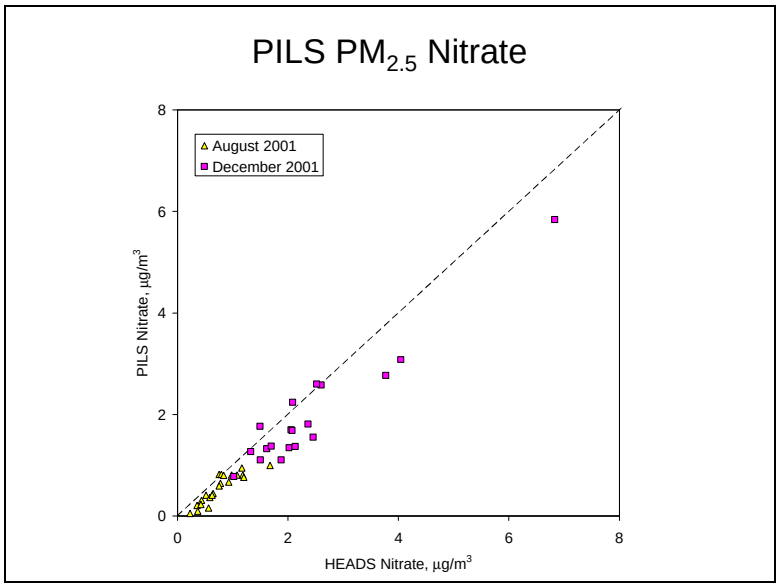
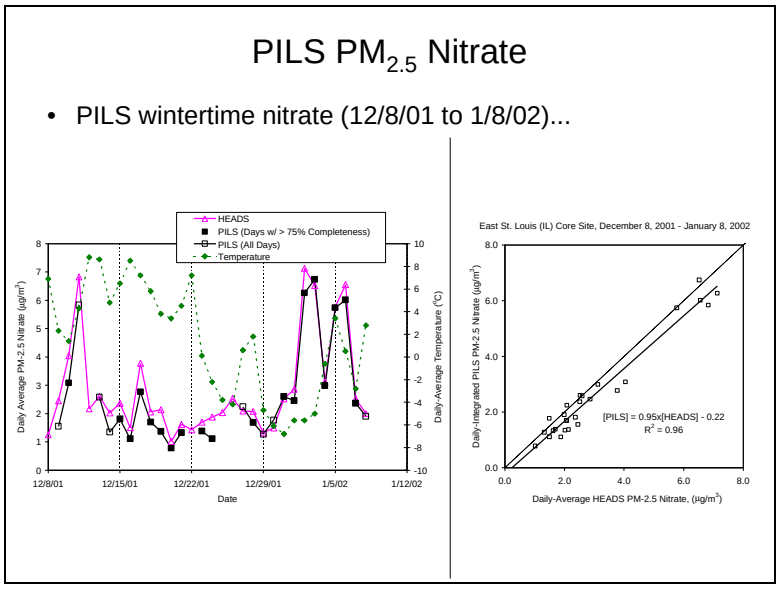
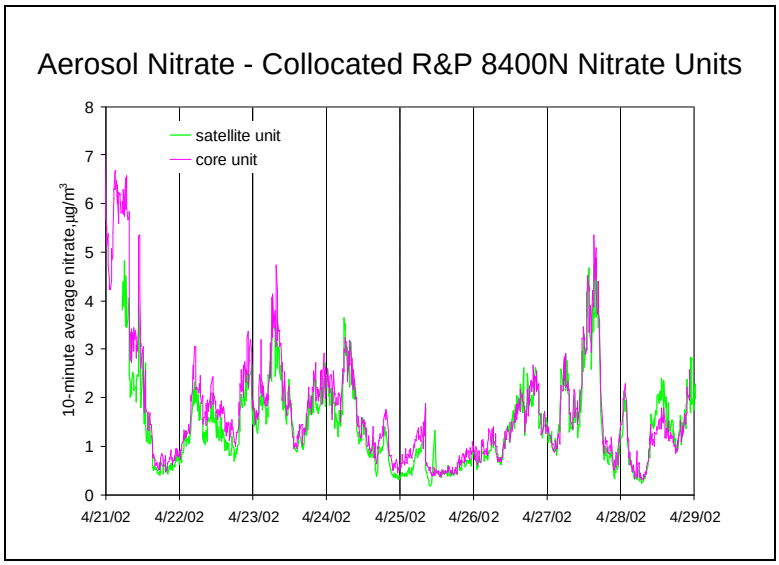


Figure A-8



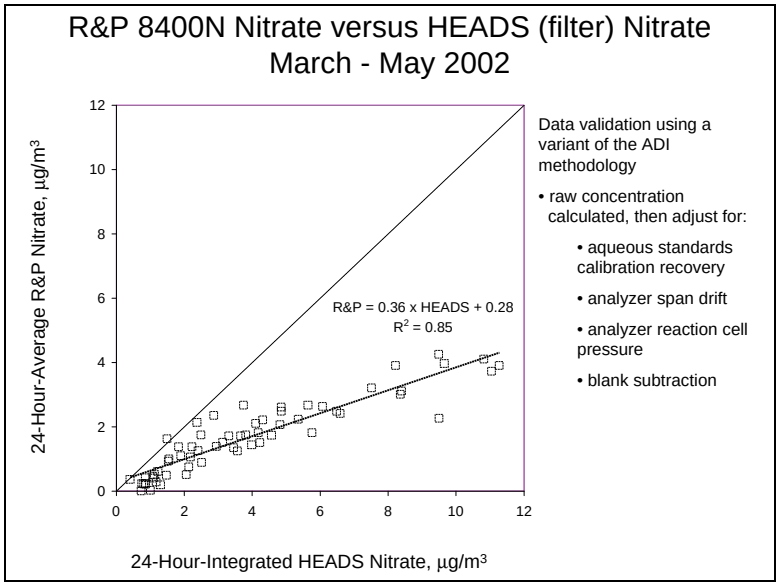
Semicontinuous $PM_{2.5}$ nitrate measurements with the R&P 8400N commenced in mid-December 2001. Measurements with collocated instruments showed tracked well as shown in Figure A-9.

Figure A-9



Comparisons to substrate nitrate showed a strong correlation but the R&P nitrate mass concentrations were substantially lower than the HEADS nitrate. Figure A-10 shows the agreement for a three-month period with a wide dynamic range for daily-integrated HEADS nitrate (0-12 µg/m^3). The reasons for this discrepancy are currently being investigated, including systematic performance evaluation tests on the R&P nitrate units used in the field campaign.

Figure A-10



B. Diurnal Cycles and Sporadic Events in the St. Louis Aerosol

The following slides are a preview of materials to be presented by W.H. White, et al., at the 2003 AAAR PM Meeting (April 2003, Pittsburgh, PA).

Semicontinuous (e.g., hourly) data for PM mass and composition display a variety of behaviors. Figure B-1 shows one week of hourly data for $PM_{2.5}$ sulfate by two methods (HSPH and PILS, Figure B-1a), $PM_{2.5}$ mass by collocated Andersen CAMMS (designated "core" and "sat", Figure B-1b) and $PM_{2.5}$ organic carbon by the Sunset field analyzer (Figure B-1b). For the sulfate time series, the first 2-3 days featured relatively low concentrations with irregular fluctuations. These were followed by three days of much higher baseline sulfate concentrations, capped by regular early-afternoon peaks. This episode ended with an abrupt return to lower and more stable concentrations.

The sulfate behavior is broadly indicative of synoptic scale climatology driving a *multi-day* episodic event. A much different pattern was observed in the organic carbon time series over the same period, with the most interesting feature occurring on a much shorter time scale. On the morning of June 24, there was a five-hour OC event with hourly organic carbon (carbon only, not an assumed organic mass) concentrations of order 40-60 $\mu g/m^3$, accounting for about half of the 80-120 $\mu g/m^3$ hourly $PM_{2.5}$ total mass concentration. This *within-day* sporadic event likely arises from a nearby source of primary emissions. The time series of $PM_{2.5}$ total mass shows the impact of both multi-day episode and within-day event.

The behaviors exhibited in Figure B-1 for $PM_{2.5}$ mass and its major components raise several questions concerning the representativeness of average diurnal profiles. Figure B-2 sets forth one such question - whether there are features in long hourly time series that cannot be recovered from routine 24-hour filter sampling, even when it is supplemented by limited-duration studies at higher time resolution to characterize “representative” diurnal behavior. This is an issue faced immediately by health researchers seeking to model individual exposures based on existing large-scale particle monitoring networks. Related questions concern the frequency of sporadic events like the sulfate episode and OC peak of Figure B-1, and their relative importance as contributors to total dose and health risk (the “episodicity” of exposures).

To assess the adequacy of daily-average data, we need other indices that capture intra-day variations in exposure. Familiar candidates include the daily maximum 1-hour (or n-hour) concentration, or the range or standard deviation of the 24 hourly concentrations. After some experimenting, we have come instead to quantify intra-day variability in terms of a "peak ratio": this is defined as the day’s highest running 4-hour concentration divided by the average concentration during the remaining 20 hours, with the 4-hour period of integration representing a compromise between time resolution and sensitivity to micro-scale events. Peak ratios are dimensionless, and measure the *relative* “peakiness” of a diurnal cycle, independent of the day’s overall concentration levels. The following table illustrates the relationship of the peak ratio to the fraction of a day’s integrated dose contributed by the peak 4 hours.

% of daily-integrated mass attributed to the 4-hour peak period	$\frac{\text{(avg of 4 highest hrs)}}{\text{(avg of other 20 hrs)}}$
17%	1.0
25%	1.7
50%	5.0
67%	10.0

Figure B-3 shows the peakiness for $PM_{2.5}$ sulfate as a function of the daily-average $PM_{2.5}$ sulfate concentration. The data generally fall within an envelope of decreasing peakiness with increasing daily-average concentration. Peak ratios as high as 3 were observed only when 24-hour concentrations were under 3 $\mu g/m^3$. Peak ratios were below 2 (meaning that the peak 4-hour period contributed less than 30% of the total day's sulfate) whenever 24-hour concentrations were above 8 $\mu g/m^3$, as in the 3-day episode shown in Figure B-1. In other words, high 24-hour sulfate values were delivered by the sustained high concentrations characteristic of conditions favoring regional-scale accumulation, not by the transient peaks characteristic of local emissions or well-defined plumes.

$PM_{2.5}$ elemental carbon (EC) exhibits substantially different behavior, in Figure B-4. Peak ratios were generally higher, exceeding the plotting limit of 10 on the three days indicated by triangles. Moreover, there is no decrease in peakiness with increasing concentration; the highest 24-hour concentration was associated with off-scale peak ratios. Short term concentration spikes are what we expect from a primary pollutant with local sources; indeed, the extreme 24-hour concentration and peak ratio noted in the previous sentence resulted from an industrial accident a few kilometers away.

The behavior of $PM_{2.5}$ organic carbon (OC), in Figure B-5, is qualitatively similar to that of EC. Peak ratios are somewhat more moderate, as might be expected in a species with secondary as well as primary sources. The June 24 event seen in Figure B-1 yielded the point in the upper-right-hand corner; the fact that this point is rather isolated establishes that event as having been anomalous rather than representative.

Figure B-6 shows the peakiness for $PM_{2.5}$ total mass. Total mass is less peaky than the major PM components, because the dynamics of peakiness in the major components (e.g., sulfate, nitrate, carbon) are largely uncoupled. That is, the peakiness contributed by one PM component can be compensated for in the total mass by the out-of-phase contributions of other, uncoupled species.

In summary, Figures B-3 through B-6 demonstrate one approach to a climatology of aerosol behavior, characterizing the frequency and magnitude of concentration excursions occurring on subdaily time scales. This exploration is continuing, with other metrics and summary formats under examination.

Figure B-1a

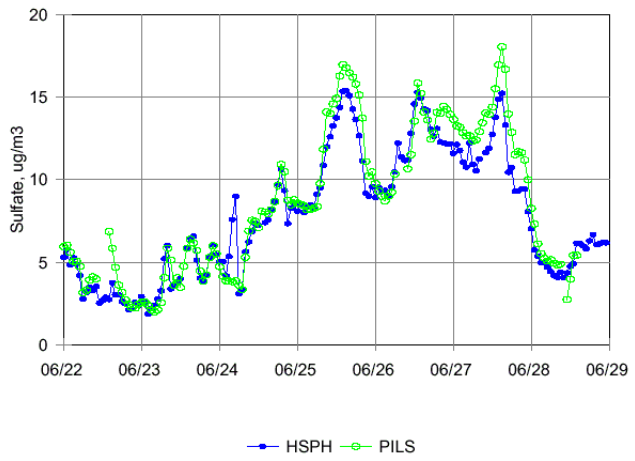


Figure B-1b

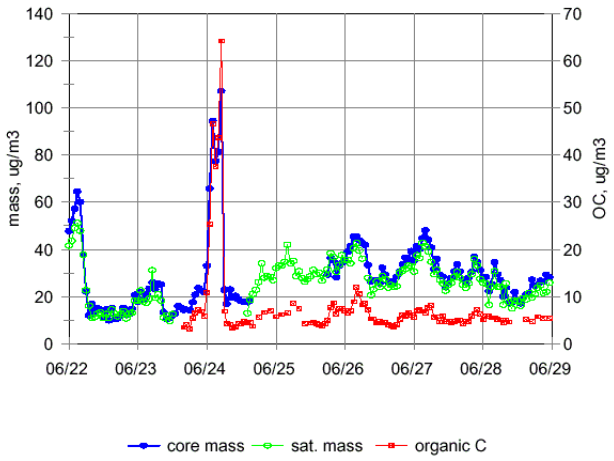


Figure B-2

$[X]_{1h}(day,hour) \sim [X]_{24h}(day) \cdot \{[X]_{study}(hour)/[X]_{study}\}$?

or

Do hourly measurements over an extended period give us anything we can't get from long-term 24h sampling and short-term diurnal studies?

Figure B-3

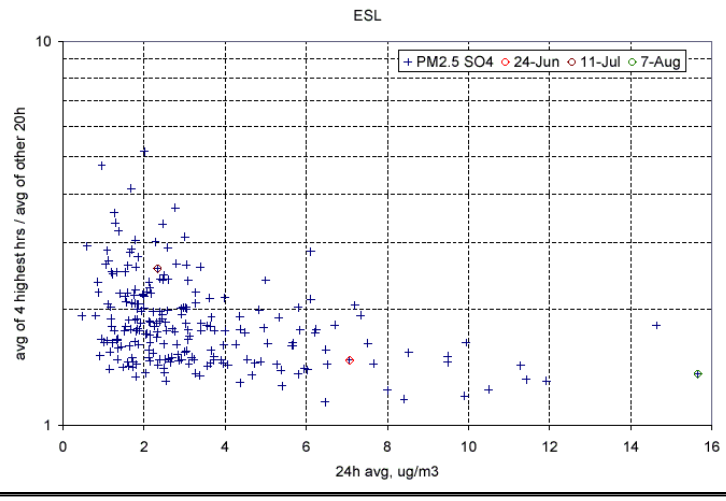


Figure B-4

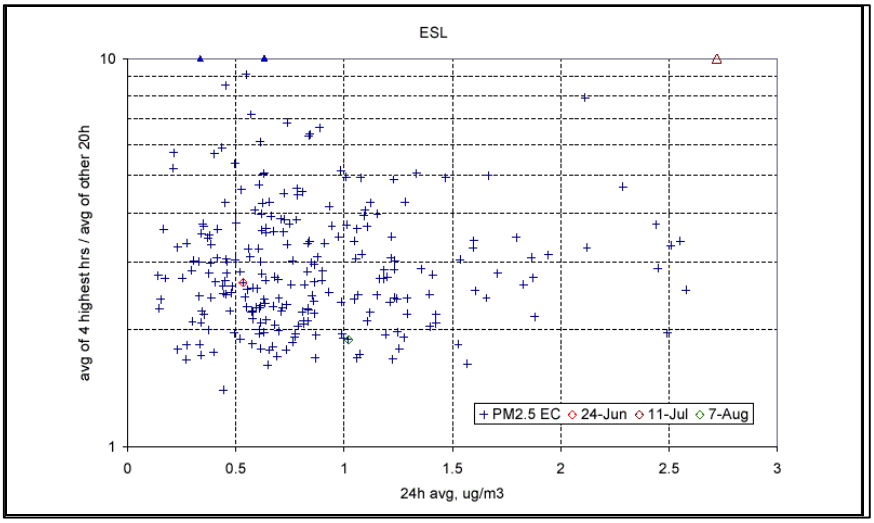


Figure B-5

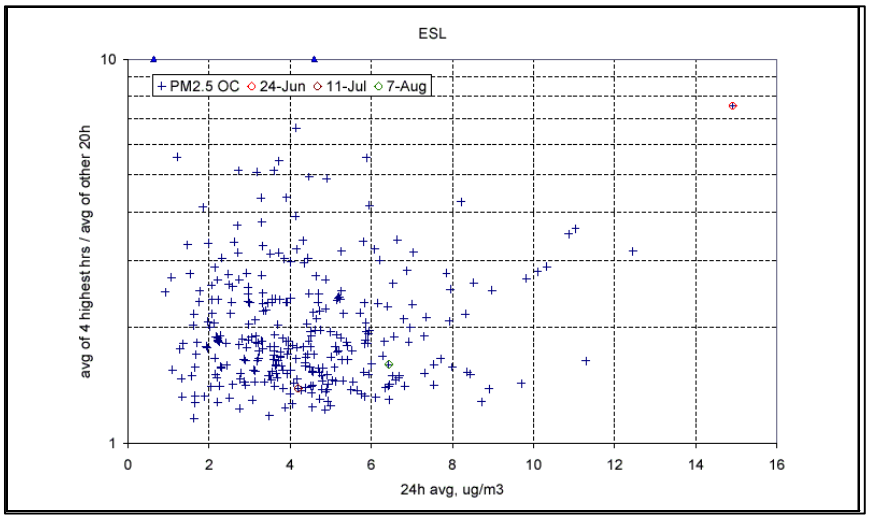
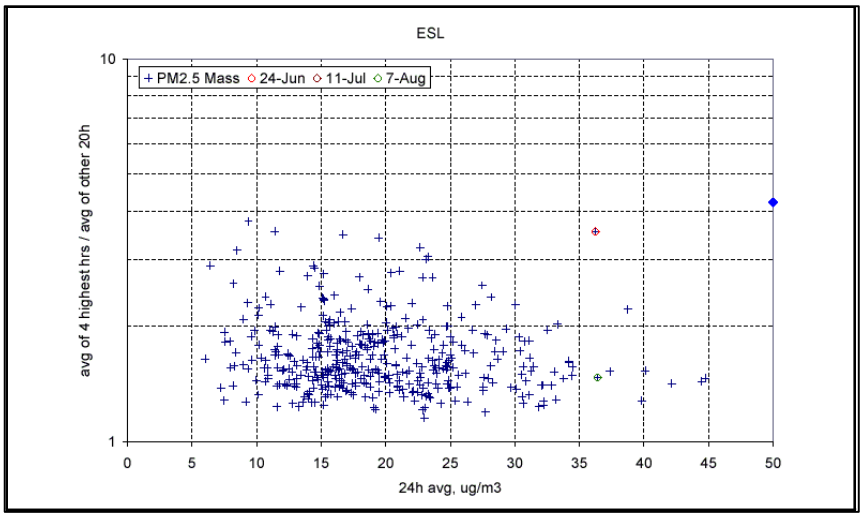


Figure B-6



Armed with some sense of the day-to-day variability in particle species' diurnal behavior, we next turn our attention to the regularities in their diurnal cycles. The following figures show diurnal cycles observed in the hourly $PM_{2.5}$ data from East St. Louis (IL) during the study to date. Each figure summarizes hourly concentrations for one particular species. The green curve shows the mean concentration of that species at each hour, averaged over all days with 24 valid hours of data. The light green vertical bars indicate ± one sample standard deviation. The gray and red curves also show mean concentrations of the same species at each hour, but are averaged over subsets of all days, selected as indicated in the figure legends.

Figures B-7 and B-8 show the mean diurnal cycles of $PM_{2.5}$ on all days and on days with high 24-hour sulfate or OC concentrations. Figure B-7 employs all days with complete data for both $PM_{2.5}$ and OC, while Figure B-8 employs all days with complete data for both $PM_{2.5}$ and sulfate. Differences in data recovery rates between the OC and sulfate instruments yield different numbers of days (N) in the two figures. The data used to construct the gray curve in Figure B-7 are from the 58 days with 24h-average OC concentrations in the top 20%, and those used for the red curve in Figure B-7 are from the 51 days with 24h-average sulfate concentrations in the top 20%.

The mean diurnal behavior of $PM_{2.5}$ suggests the influence of local surface-layer emissions and the daily cycle of atmospheric ventilation on hourly concentrations in East St. Louis. These factors can be inferred from the observed rise in concentrations in the late afternoon and evening as convection weakens, winds diminish, and local emissions accumulate in an increasingly shallow layer of air, reaching their peak concentrations in the hours before dawn and the return of convection and advection. The same mean behavior is observed on OC-rich and sulfate-rich days, the logarithmic plots in Figures B-7 and B-8 showing that hourly $PM_{2.5}$ concentrations were simply higher by a near-constant multiple throughout the day. The scaling strategy suggested in Figure B-2 may thus be adequate in some applications.

A different situation is illustrated by Figures B-9 through B-11, which show data from the University of Minnesota PSD system. Each of these figures shows particle number concentrations from one of three different size ranges. As before, mean diurnal cycles are shown for all days with 24 hours of valid data, and for selected days. In this application, the selected days are those with 24h-average concentrations of CO or SO_2 in the top 20%, as indicators of differing source mixes. The smallest particles exhibit a mid-morning peak that is enhanced on high-SO_2 days but indifferent to high-CO days. The largest particles, in contrast, follow a $PM_{2.5}$–like cycle that exhibits an early-evening peak and enhanced overnight concentrations on high-CO days but is indifferent to high-SO_2 days. The intermediate (0.1-1.0 μm) particles show intermediate behavior, with both a mid-morning peak on high-SO_2 days and an early-evening peak on high-CO days.

Although the plots in Figures B-9 through B-11 are linear rather than logarithmic, it is not hard to see that the diurnal profiles averaged over different subsets of days are not simply multiples of each other. In this application, therefore, the scaling strategy of Figure B-2 fails to capture an essential feature of the hourly data.

Figure B-7

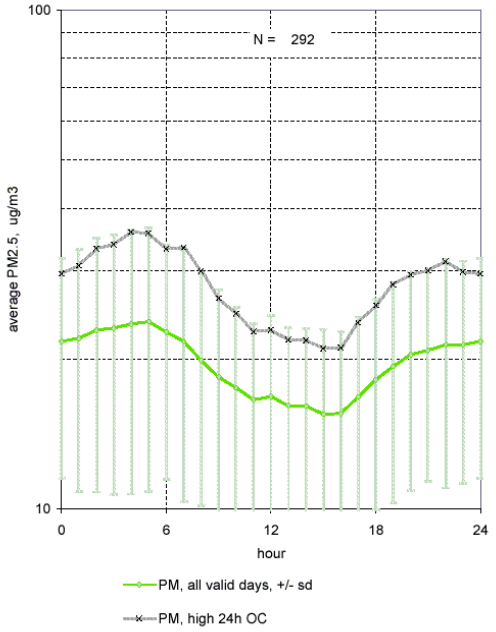


Figure B-8

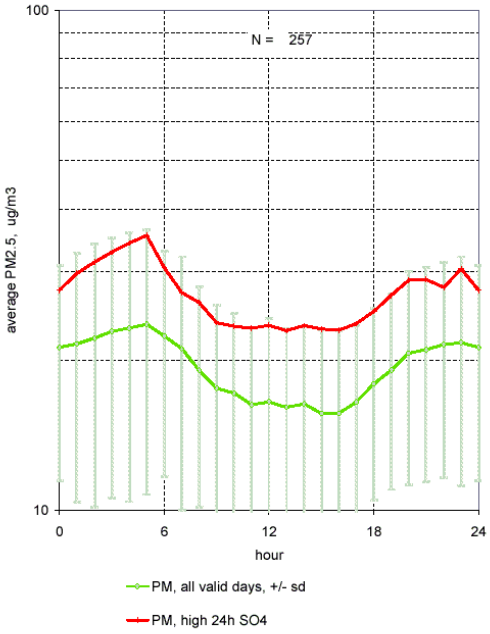


Figure B-9

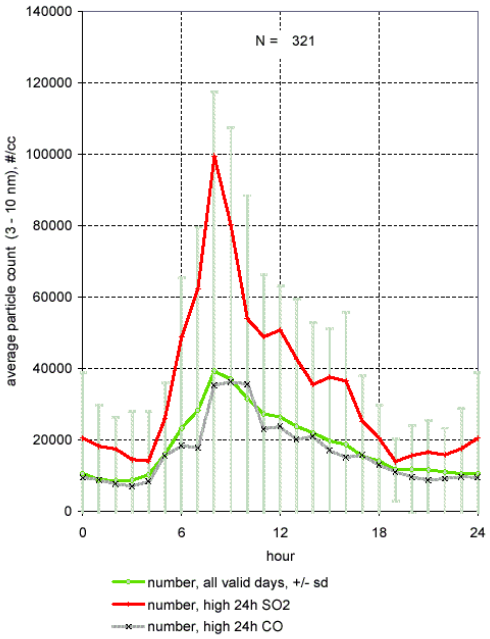


Figure B-10

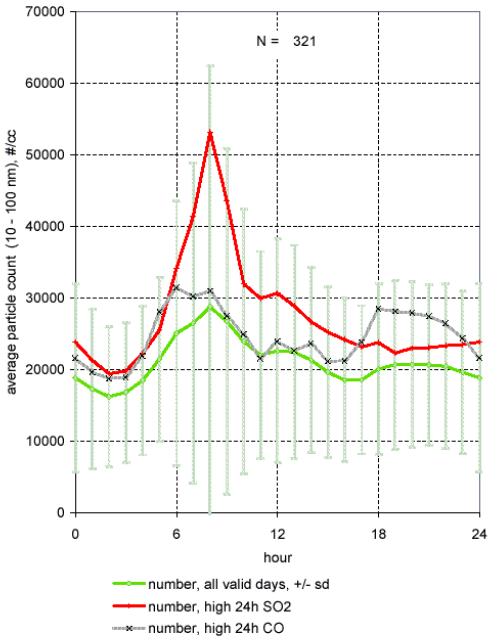
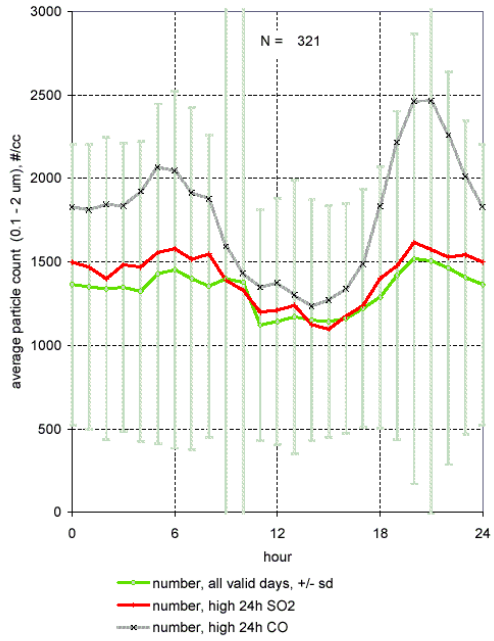


Figure B-11



Planned Activities for the Forthcoming Quarter

For the 13th project quarter will focus almost exclusively on data validation and submission to the DRI database for subsequent submittal to the NARSTO data archive and Supersites programwide relational database. Extensive data analysis and interpretation is also underway, and we anticipate our first manuscript submissions to occur during the 13th project quarter.

Publications and Presentations

One (1) paper was presented at the A&WMA Symposium on Air Quality Measurement Methods and Technology (November 2002, San Francisco, CA)

- "$PM_{2.5}$ Ion Measurements at the St. Louis – Midwest Supersite", J.R. Turner, M.N.S. Yu and S.A. Duthie.

Ten (10) abstracts have been accepted for presentation 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