Assistance Agreement Quarterly Report Summary: 10th Quarter

Date of Report: July 15, 2002

Agreement No: R82806301

Title: **Baltimore Supersite: Highly Time and Size Resolved Concentrations of Urban PM2.5 and its Constituents for Resolution of Sources and Immune Responses**

Investigators: **J. M. Ondov**, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD; **T. J. Buckley,** School of Hygiene and Public Health, Johns-Hopkins University, Baltimore, MD; **P. K. Hopke**, Clarkson University, Potsdam, NY; **M. B. Parlange**, Johns-Hopkins University, Baltimore, MD; **W. F. Rogge**, Department of Civil and Environmental Engineering, Florida International University, Miami, Florida; **K. S. Squibb**, Department of Pathology, University of Maryland at Baltimore; and **A. S. Wexler**, University of California, Davis, CA

Institution: Department of Chemistry and Biochemistry, University of Maryland, College Park, MD

Research Category: Particulate Matter Supersites Program

Project Period: January 15, 2000 to December 31, 2003

Objectives of Research: Our primary objectives are to I) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques; ii) provide important information on the potential for health effects of particles from specific sources and generic types of sources, iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, v) provide support to existing exposure and epidemiologic studies to achieve enhanced evaluation of health outcome-pollutant and -source relationships, and vi) test the specific hypothesis listed in our proposal.

ACTIVITIES

During the 10th report period the following activities were performed.

1. Continued operation of the Ponca St. Site with full instrumentation
2. Two-day PI's data meeting.
3. Preparation of Abstracts for National Meetings
4. Initiation of July Intensive.
5. Baltimore Supersite Data Base Loading and Data Flagging

Additional information on these activities is presented below..

STATUS

Supersite Instrument operation. We continue to operate all instruments at Ponca St., our main Supersite. These are as follows:

1. RSMSIII - single particle mass spectrometer
2. High-Frequency Aerosol Slurry Samplers - Separate instruments are deployed for metals and cytokine assays, both at 30 min time resolution.
3. Scanning Mobility Particle Sizer (SMPS) - 9 to 450 nm, every 5 minutes
4. Aerodynamic Particle Sizer (APS) - 500 nm to 20 : m, every 5 minutes
5. 30-degree TEOM for 30 min aerosol mass concentrations
6. R&P 8400N Nitrate Monitor - 10 min particulate nitrate
7. Harvard/Edgerton Sulfate instrument - 30 min sulfate concentrations
8. Sunset Labs EC/OC - hourly
9. Meteorological station: Wind speed (two heights) and direction, Temperature, Relative Humidity, solar insolation, and rain.
10. Lidar (1 in 6 days, daily during the July Intensive campaign; lidar measurements were made at Homewood on April 16, 24, 30, May 6, 14, 16, 22; June 12, 23, and 29. Daily measurements were made at Ponca St. in July.
11. 3-D sonic anemometer has be restored to the site
12. Speciation and FRM sampling - daily during July intensive, 1 in 3 days otherwise.
13. UM Fine Particle Sampler, every other day, using the SEAS PM inlet.

In addition, the Maryland Department of Environment (MDE) is operating the following:

14. VOC by online GC
15. Ozone, NO, NO2, and CO
16. Speciation and FRM sampling at Essex (1 in 3 days)

Additionally, we recently installed a 10-stage MicroOrifice Impactor and two Radiance Research Integrating Nephelometers (one was installed inside the trailer where air is cooled to ambient indoor conditions, and the other was installed on the roof where air aspirated at ambient outdoor conditions.) The MOI was deployed to The nephelometers permit estimation of bscat and visual range. The MOI will provide samples for elemental analysis and cytokine assays in an attempt to ascertain information on fresh vs aged (and generally larger) aerosol particles.

Collaborations. In addition to the measurements listed above, colleagues from the University of Maryland Chesapeake Biological Laboratory have been collecting aerosol particles in 24 - hr filter and Berner Impactor samplers for PAH analyses to compliment the our time-resolved measurements. Seimi-continuous gas phase ammonia measurements have also been made in two campaigns during the summer. The group is also collecting a limited number of air canister samples for VOC analysis by GC MS to be performed by MDE.

PROGRESS SUMMARY/ACCOMPLISHMENTS

July Data Meeting

On July 2nd and 3rd, we held a meeting for principle Investigators and other interested parties to present and discuss preliminary findings, as well as to discuss strategies for future presentations and publications. Presentations were made on the full range of instruments deployed, including Lidar, Single Particle Mass Spectrometer, SEAS, commercial semicontinuous instruments, speciation and FRM samplers, and particle spectrometers. In addition, CBL made presentations on the semicontinuous ammonia and Berner Impactor measurements. Analysis methodology for SEAS were presented as were methods for cytokine assays. Presentations were also made on the status of the Baltimore Supersite database and on requirements for submitting data to the NARSTO archive. Lastly, findings of the MARCH Atlantic, JHU health effects, and E.H. Pechan/DOT projects were presented.

Descriptions of measurements and data collected were presented for FMC, Clifton, and Ponca St. In addition to description of the methods, plots of data were shown to help the various investigators get a sense of the data. The FMC and Clifton Park data have been described in previous progress reports. Therefore, herein, some highlights of the findings for Ponca st. are described. Review of the FMC data lead to the decision to analyze several more days of samples collected there. One particularly important observation was that we readily observed the plume from the Gould St. Power plant at FMC and did so at precisely the expected wind angle. This is important as it shows that transport vectors derived from wind angles measured at the site are true over the distance of 4 or 5 km; at least for north westerly winds. We had feared that land/water circulations and interference from terrain elevations might alter the movement of plumes aloft.

SMPS and NO/NOx data. These data are highly informative and capture what appears to be a major component affecting air quality in Baltimore, i..e, motor vehicle traffic. Preliminary analysis of SMPS data reveals that on weekdays elevated nuclei (i.e., 20 to 80 nm) particle concentrations often occur between 3:00 and 6:00 AM, between 6:00 and 9:00 AM, and again in the late afternoon/early evening in accordance with local rush-hour traffic patterns. Sometimes very small nuclei particles are elevated around mid-day as shown in Figure 1, where we show data for Saturday, Feb 16,

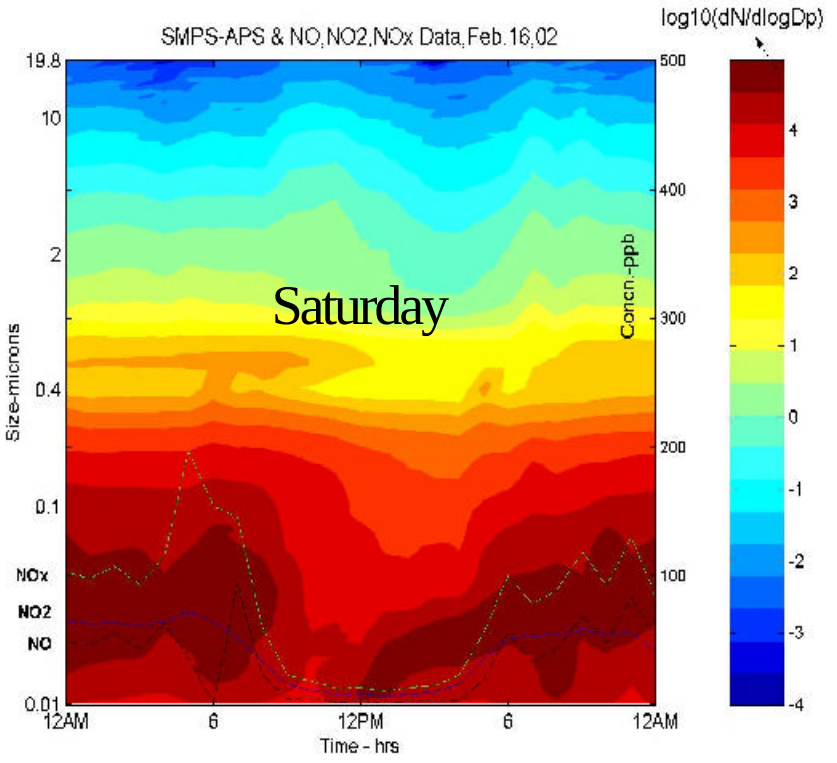

Figure 1. Size spectra of aerosol particles collected at Ponca st. show elevated concentrations corresponding to Nox in the early morning and afternoons/evenings.

2002, i.e., a day when local traffic volume is much less than on weekdays. As shown, the 20-80 nm events coincide with high NO concentrations and the start of morning MTA bus operations at their facility in close proximity and west-south west of the site. The 10-nm midday events do not and are likely to be secondary aerosol nucleation events. Spectra for week days show a similar but more distinct pattern of high particle concentrations between 6:00 and 9:00 AM and somewhat elevated concentrations in the afternoon. Friday particle elevations were seen to begin earlier in the afternoon than other those for weekdays examined. Wind direction, NO (also NO_2 and O_3), hourly particulate EC/OC (Sunset Labs semicontinuous monitor), VOC (online GC), and SMPS data will be used to classify diesel emission events. These data will later be combined with 30 minute metals and limited 3-hr detailed organic compound analyses to extract a diesel emission source profile, suitable at least, for the MTA bus fleet, and to identify potentially useful, new, intrinsic tracers for this source.

Nitrate/NO/NOx data. At all of the sites, nitrate concentrations were highly elevated during nighttime periods when relative humidity was elevated, especially, RH in excess of 90% where much liquid water is undoubtably present on the particles - so much so that they are probably droplets. Clearly, the equilibrium between particulate nitrate and ammonia/nitric acid dissociation products is suppressed at lower nighttime temperatures, but when RH is elevated ammonium nitrate dissolves and ionizes, preventing its escape into the gas phase. In addition, both nitric acid and ammonia are highly soluble in water, so these species that might otherwise be present in the atmosphere as gases tend to be efficiently scavenged. Shown in Figure 3 are Clifton Park data where nitrate elevations were observed at around 6:00 AM in August, 2001.

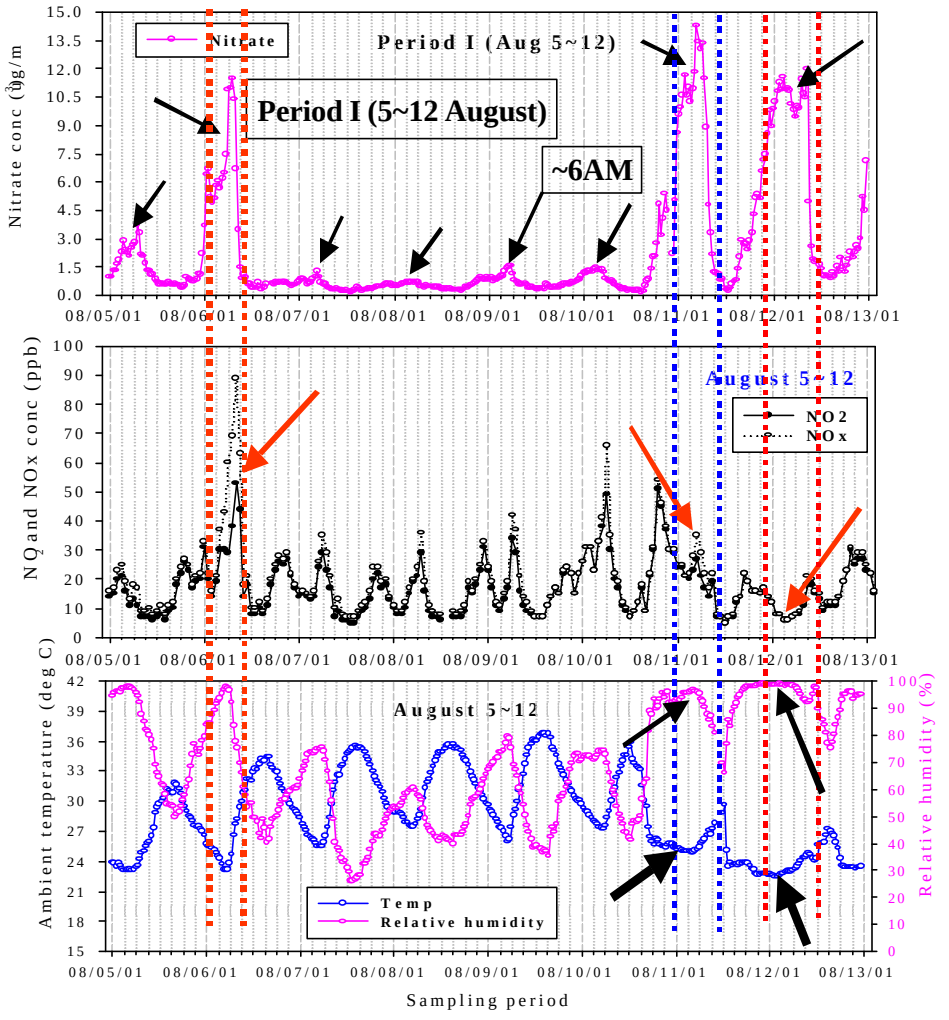

Figure 3. Particulate nitrate, NO2 and Nox, and T and RH (top, center, and bottom panels) measured at Clifton Park.

Cytokine Studies. Epidemiological evidence suggests that human mortality and morbidity

are associated with exposure to fine particulate matter (PM2.5), which is a highly complex and variable mixture of inorganic ions, elemental carbon, organic compounds, trace elements, and water. We therefore hypothesized that urban $PM_{2.5}$ would be biologically active in an *in vitro* assay system that we developed using a human airway epithelial cell line (A549) and a mouse cell line of monocytic origin (RAW 264.7). To test this hypothesis, we exposed A549 or RAW 264.7 cells to fine particulate matter collected over time intervals as short as 1 hour with a recently developed high frequency semi-continuous aerosol sampler. Both A549 and RAW cells responded to exposure to SEAS particles collected from the FMC location by production of the pro-inflammatory cytokines IL-6 and TNF-a as well as to the chemokines IL-8 and MCP-1, respectively, in a manner that varied with time. We hypothesized that endotoxin, a component of Gram-negative bacterial cell walls, might be responsible for the observed biological activity. To test this hypothesis, we exposed A549 or RAW 264.7 cells to SEAS particles as before, with the addition of the antibiotic Polymyxin B (20 mg/ml). Cytokine/chemokine production was reduced by less than 50% for samples collected at most time periods, indicating that endotoxin is not the sole biologically active component of the SEAS particles. Exposure of A549 cells and RAW 264.7 cells to 0.4 mM $ZnCl_2$ and purified endotoxin (2.5-50 ng/ml) from Escherichia coli resulted in strikingly different cytokine profiles between these two cell types, thus pointing to a specific role for different components of $PM_{2.5}$, especially metals, in the local immune response following lung exposure to fine particulate matter.

Cytokine Slurry sample storage tests. Results of tests to determine the effect of immediate vs delayed freezing of slurry samples on the results of cytokine assays suggest that bacterial growth, as measured by endotoxin concentrations, is observed when samples are allowed to remain in the fraction collector for 24 or 48 hrs before transferring them to the freezer. Although it is not feasible to freeze all samples immediately, samples are now being transferred to freezer storage within 24 hours. Batches of samples collected recently have been stored within 12 hours. This protocol was deemed to be adequate, as endotoxin concentrations were relatively low compared to concentrations shown to cause measurable responses in the cytokine assays.

July Intensive Campaign

Our planned intensive sampling campaign was begun on the 1st of July. In addition to the normal measurements, Speciation measurements at the Ponca St. and Essex sites were increased from 1 in 3 days to daily. As noted above, we added the MOI for the July intensive, but the most notable addition was the initiation of sequential Filter/PUF sampler collections at about 600 LPM at 3 hr intervals, on July 12th. The Filter and PUF samples will be analyzed by Wolfgang Rogge's group using GC-MS. To our knowledge this is the first time highly time resolved sampling has been attempted for a large range of semivolatile organic species. The Filter/PUF sampling was initiated later due to problems with the EC/OC analyzer which kept this instrument from operating normally.

Canadian Smoke Episode

Smoke from the Canadian forest fires was observed between July 7th and 9th. The smoke plume aloft was evident in vertical LIDAR scans and PM2.5 concentrations in excess of 200 : g/m3 were recorded. During this event EC and OC both exceeded 70 : g/m3 (see Figure 4). We are evaluating data from the various other instruments and plan a publication describing this event. Analyses of

SEAS metals and cytokine slurry samples are planned for this period.

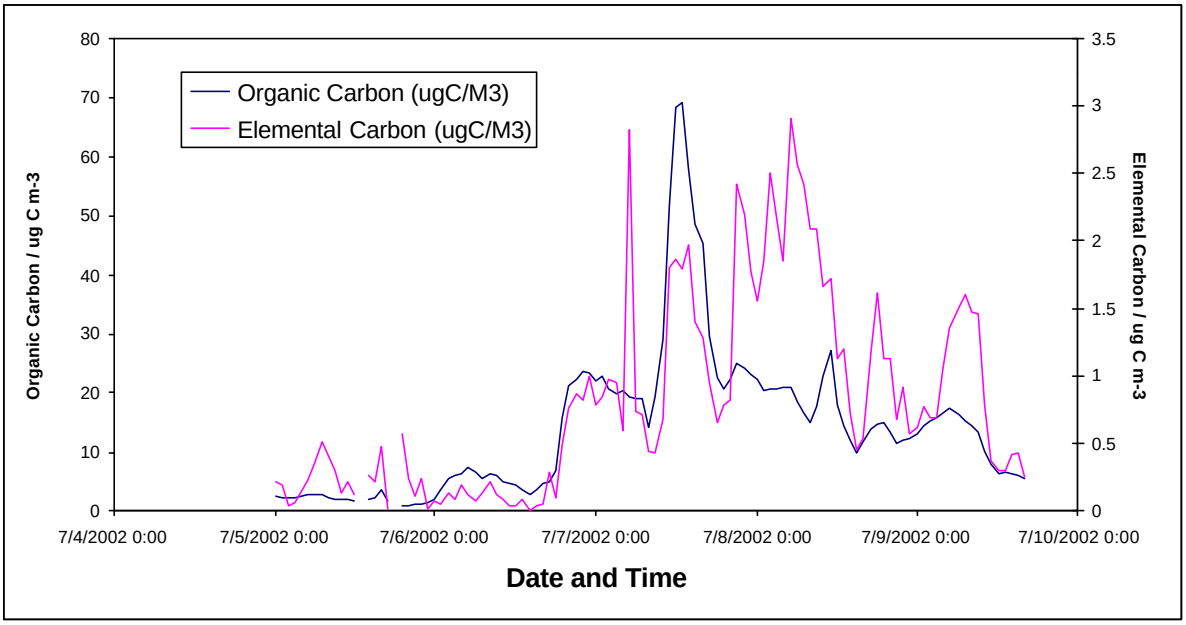

Figure 4. Organic and Elemental Carbon Concentrations before and during the Canadian smoke event observed at Ponca St.

Single Particle MS

Single particle mass spectra were obtained throughout the second quarter with the RSMS-3 instrument. For the sampling period between 4/1/02 and 6/19/02, only positive ion spectra were recorded. On 6/20/02, the negative ion detector was installed and simultaneous positive/negative ions have been collected since that time. Single particle measurements were performed in the following manner: a complete sample cycle was performed every two hours except for maintenance and repair periods. During an individual sample cycle, measurements were made sequentially for 9 particle sizes between 45 and 1240 nm diameter (aerodynamic). For each size, the measurement period ended after 10 minutes or the acquisition of 30 particle mass spectra, whichever came first. Typically, 40 minutes were required to cycle through the 9 particle sizes for the ambient particle concentrations present during this time period.

Maximum number of particle hits: 240 particles/interval or 2880 particles/day
Typical number of particle hits: 1500-2200 particles/day
Total particle hits between 4/1 and 6/30: 93,174
Fraction of time lost to maintenance and repair: 33%
(Fraction of time lost since July 1 is running at 10%, so we have been able to significantly increase reliability over time.)

Data Analysis. Figure 6 is a plot of number of particles with non-zero signal intensity vs. mass-

to-charge ratio for April and May 2002. Most particles contain at least some nitrate and EC/OC. In addition, many metals can be identified; several, but not all, are indicated in the figure.

Figure 7 shows how single particle data can be related to meteorological data using manganese as an example. The top left figure is a plot of dN/d[log(d_p)] vs. particle size for particles containing manganese averaged over April and May 2002. The distribution is bimodal with maxima at ca. 150 and 770 nm. Other metals also show a bimodal behavior, and for many the larger diameter mode exhibits a greater number density than the smaller diameter mode. The top right figure is a plot of dN/d[log(d_p)] vs. time-of-day for particles containing manganese averaged over April and May 2002. Emissions are fairly constant during the daytime, suggesting an industrial source. The bottom figure is a plot of dN/d[log(d_p)] vs. wind direction for particles containing manganese averaged over April and May 2002. This plot may be correlated with specific emission sources near the sampling site. (Important note: The values of dN/d[log(d_p)] in this figure are for detectedparticles only must be divided by the instrument detection efficiency (approximately 10^{-5}) to obtain the true number concentration.)

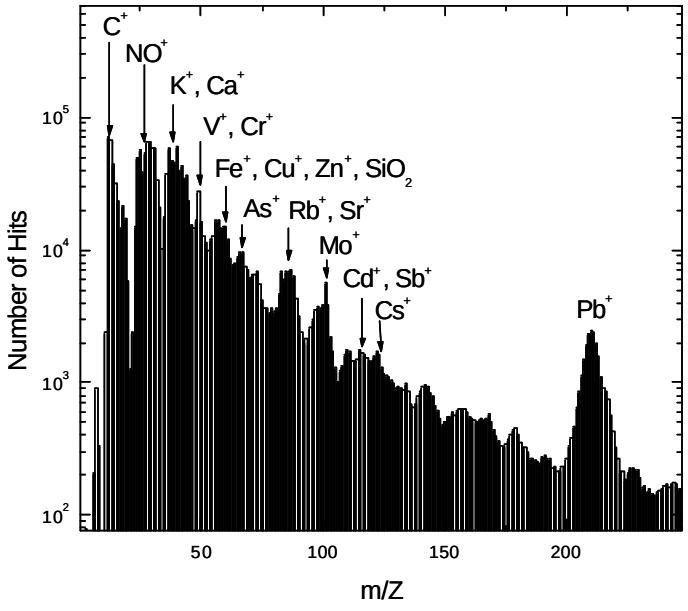

Figure 5. Mass frequency spectrum of single particles analyzed at Ponca St.

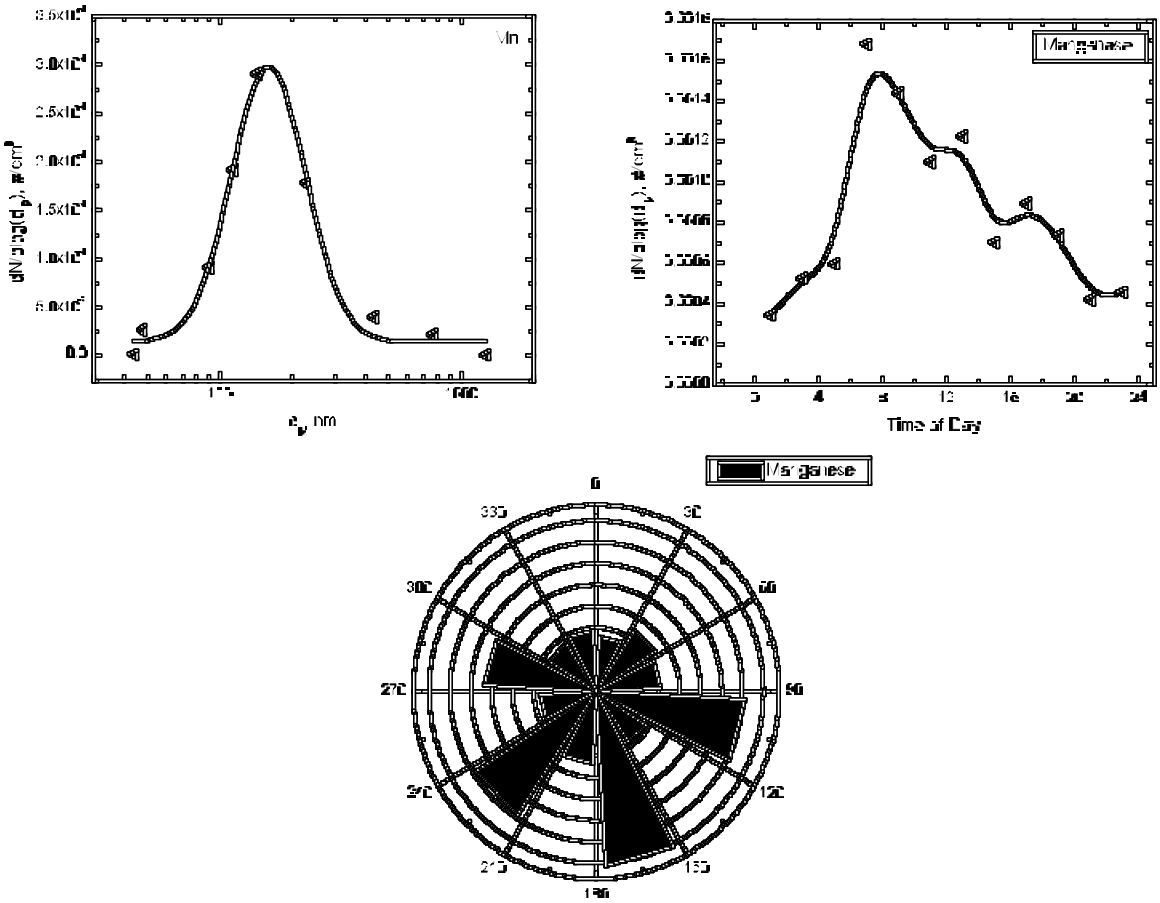

Figure 6. Mass vs particle size spectra for particles containing Mn observed at Ponca st.

Meteorological Data, 4/15/2002 to 7/15/2002

Data were sampled continuously during the entire time period. Plots of data are available online at http://www.jhu.edu/~dogee/mbp/supersite2001/.
Instruments used are as follows:

Instrument	Measured Variables	Completeness of Data	Non-functionality, reason
Rain Gage	Rain [mm] @ 1 Hz	98%	4/22/02 20:30 – 4/23/02 12:00 operator error 5/3/02 00:00 – 10:30 operator error 5/9/02 11:00 – 24:00 operator error
Cup anemometer 1	Magnitude of horizontal wind vector [m/s] @ 1 Hz		
Pyranometer	Solar Radiation [W/m^2] @ 1Hz		
Cup anemometer 2	Magnitude of horizontal wind vector [m/s] @ 1 Hz		
Wind Vane	Azimuth angle of wind vector [^o]; standard deviation of wind angle \sigma_{\theta} [^o]		
Vaissala Temperature and Humidity Probe	Temperature [^o C] and relative humidity [%] @ 1 Hz		
CSAT 3-D Sonic anemometer	Velocities u,v,w [m/s], potential temperature [^o C] @ 20 Hz; friction velocity u_* [m/s], Monin Obukhov Length L [m], sensible heat flux H [W/m^2]	51%	5/3/02 00:00 – 10:30 operator error 5/9/02 11:00 – 24:00 operator error 5/13/02 09:30 – 5/15/02 17:30 storm 5/24/02 00:00 – 06:00 power outage 6/4/02 18:00 – 8/4/02

With respect to data quality all sensors functioned well (within errors specified by the manufacturer) for all times except the missing periods mentioned in the table. To assure high data quality, the cup anemometers were calibrated on 6/5/2002 in the JHU wind tunnel. The sonic anemometer as well as the vaisala temperature humidity probe was calibrated in June by the manufacturer. Solar radiation, mean wind speeds, temperature and humidity showed the expected diurnal variations. Moreover, turbulence parameters such as atmospheric stability and friction velocity showed corresponding behavior.

Baltimore Supersite Relational Database (BSSRDB)
The BSSRDB now contains all data collected prior to August 15th, except for Single Particle MS, speciation and FRM monitor, SEAS elemental analysis, and cytokine data.

Data Flagging. We have devised and begun implementation of two types of procedures to "flag"data loaded into the BSSRDB. The first is an instrument parameter file processor, which scans the parameters captured in the data stream of each of our instruments and flags the data as good, questionable, correctable, questionable and correctable, or bad, based on instrument status

codes, expected data range, and criteria specific to each instrument. For example, when the values of the reaction cell Pressure deviate from 5 inches of Hg, the correctable flag is assigned. When the sampling cell compartment temperature differs from the ambient outside temperature by more than 4^{o}C, the correctable flag is also set, in anticipation of future corrections factors to be applied. The second is a web based application that permits flagging of data based on operator log information. The instrument operator provides a table of date/times of non "good" data or the unique data ID number. The information in the table are then loaded to the web-based operator flagging application by the data manager. These applications and protocols permit rapid flagging of data and minimization of flagging errors.

Nitrate Data Reduction. Correction factors for Reaction cell pressure have been developed and we are reexamining the data reduction algorithm to permit recalculation of Nitrate data from the R&P 8400N monitor. Corrections to data in the BSSRDB are being made only by the Data Manager after approval from the PI and review by instrument operators using a specially developed application.

Publications/Presentations/meetings

Y.C. Chang, J. P. Pancras[1], J. M. Ondov, RESOLUTION OF PRIMARY PARTICLE PLUMES FROM INDIVIDUAL POWER PLANTS WITH THE UNIVERSITY OF MARYLAND HIGH-FREQUENCY AEROSOL SLURRY SAMPLER. To be presented at the European Aerosol Society Meeting, September 2002, Taiwan.

Seung S. Park, Patrick Pancras, Yu Chen Chang, Dawn H. Cation, and S. Gazula, John M. Ondov, INVESTIGATION OF SOURCES WITH HIGHLY TIME-RESOLVED AEROSOL AT THE BALTIMORE SUPERSITE USING POSITIVE MATRIX FACTORIZATION. To be presented at the Winter meeting of the American Association for Aerosol Research, Charleston, NC, October 2002.

R Mitkus, K Squibb, J Powell, D. H. Catino, and J Ondov. IN VITRO ASSAY OF THE BIOLOGICAL ACTIVITY OF $PM_{2.5}$ AND ITS COMPONENTS COLLECTED BY A HIGH FREQUENCY AEROSOL SAMPLER AT AN URBAN SUPERSITE. To be presented at the Winter meeting of the American Association for Aerosol Research, Charleston, NC, October 2002.

Wolfgang F Rogge*, Orhan Sevimoglu and Anna Bernardo-Bricker. ORGANIC PM2.5 AT THE BALTIMORE PM SUPERSITE: DIURNAL VARIATION WITH A RESOLUTION OF THREE HOURS. To be presented at the Winter meeting of the American Association for Aerosol Research, Charleston, NC, October 2002.

David Harrison*, Narayanan Nair, Seung Shik Park, J. Patrick Pancras, Sarala Gazula, and John M. Ondov. RESOLUTION OF A MUNICIPAL DIESEL EMISSION COMPONENT AT THE BALTIMORE SUPERSITE FROM HIGHLY TIME- and COMPOSITIONALLY-RESOLVED AEROSOL AND GAS MEASUREMENTS. To be presented at the Winter meeting of the American Association for Aerosol Research, Charleston, NC, October 2002

J. M. Ondov, HIGHLY TIME AND SIZE RESOLVED CONCENTRATIONS OF URBAN PM2.5 AND ITS CONSTITUENTS FOR RESOLUTION OF SOURCES AND IMMUNE RESPONSES: HIGHLIGHTS OF RESULTS FROM THE BALTIMORE SUPERSITE PROJECT. To be presented at the Winter meeting of the American Association for Aerosol Research, Charleston, NC, October 2002

Future Activities.

1. We will continue to hold weekly PI teleconferences as needed.
2. SEAS: Test have been devised to I) determine intercomparability of colocated SEAS instrument; and ii) to determine collection efficiency relative to an integrated filter based method with an identical (PM1.25 inlet) are being implemented.

3. We will continue operating the Baltimore Supersite until November 30th, 2002. The July intensive will continue until August 15th, to permit maximum overlap between data collected by the various instruments. A final full scale intensive campaign will be conducted in November, 2002.