

## Assistance Agreement Quarterly Report Summary: 14<sup>th</sup> Quarter

**Date of Report:** August 1, 2003

**Agreement No:** R82806301

**Title:** **Baltimore Supersite: Highly Time and Size Resolved Concentrations of Urban PM<sub>2.5</sub> and its Constituents for Resolution of Sources and Immune Responses**

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**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 AND FUTURE PLANS

During the 14th report period the following activities were performed.

1. Data collected during the Mini-intensive in February have been reduced, flagged, and loaded into the Baltimore Supersite Relational Database (BSSDB). Completion of Level II verification is anticipated in the next quarter, to the degree possible.

2. All data collected in 2001 (Clifton and FMC sites) have been submitted to the NARSTO archive. First quarter 2002 data will be submitted in the next week.
3. We have provided log-in IDs and passwords to all BSS PIs and have established an FTP site for the exchange of outlines for manuscripts, abstracts, and publications.
4. An Investigator's data meeting was held at the University of Maryland, College Park on June 18<sup>th</sup> and 19<sup>th</sup>, and was attended by the BSS PIs as well as by representatives of the JHU-EPRI Baltimore health effects study and by members of the UMCP Meteorology Department.
5. We have submitted the following publications during the second quarter of 2003:

Highly-time resolved particulate nitrate measurements at the Baltimore Supersite, by Harrison, D., Park, S. S., Ondov, J. M., Buckley, T., Kim, S. R., Jayanty, R. K. M., submitted to Atmospheric Environment.

Atmospheric boundary layer structure as observed during a haze event due to forest fire smoke, by M. Pahlow, J. Kleissl, M. B. Parlange, J. M. Ondov and D. Harrison Submitted to Boundary Layer Meteorology.

Aerosol optical characterization by nephelometer and lidar during the Baltimore PM Supersite, 4 - 12 July 2002, by M. Adam, M. Pahlow, V. A. Kovalev, J. M. Ondov, M. B. Parlange, submitted to JGR Atmospheres.

Tolocka, M. P., Lake, D. A., Johnston, M. V., Wexler, A. S. Number concentrations of fine and ultrafine particles containing metals, submitted to Atmos. Environ.

6. 30-min slurry sample analyses for metals and cytokines continue.
7. Detailed meteorological summaries for major events identified during 2002 are being prepared.
8. All data, except pending off-line analyses and LIDAR data, have been loaded into the BSSDB.
9. Synchrotron XRF analyses results have been received for August 7-14 2001. Concentrations of 27 elements were reported at 30 minute intervals for 8 size ranges.

### **LIDAR DATA**

Johns-Hopkins students are working to transfer the LIDAR data to the Narsto archive. A webpage structure ([http://www.jhu.edu/~dogee/mbp/supersite2001/lidar\\_data.htm](http://www.jhu.edu/~dogee/mbp/supersite2001/lidar_data.htm)) has been constructed and sent to NARSTO for validation. Mixing heights have been derived for about half of the LIDAR data. In addition to the Narsto work, the research is underway to the determination of the aerosol vertical extinction coefficient from the LIDAR data, in connection with the ground level measurements of the PM<sub>2.5</sub>, Nitrate, Sulphate, EC/OC and aerosol scattering coefficient.

### **METEOROLOGICAL SUMMARIES:**

Table 1 contains a list of high PM events observed during the BSS study in 2002. Detailed

meteorological descriptions for each of these events are being prepared and made available at <http://www.jhu.edu/~dogee/mbp/supersite2001/metsummary/summary.htm>. A chronological description of one of the episodes is presented below as an example.

**Table 1 List of high PM events during 2002**

Days (EST in 2002)	Features	24-hr PM <sub>2.5</sub> ug/m <sup>3</sup>	Lidar	3D- sonic anemom eter
4/17 - 4/18	Nitrate transient, high EC, OC	no TEOM	no	yes
6/10 - 6/11	High nitrate peak (~11 mg/m <sup>3</sup> ) in the morning of June 11 due to high RH High sulfate peaks (13~15 mg/m <sup>3</sup> ) in the afternoon of both June 10 & 11 due to high ozone	no TEOM	no	no
6/24 0900h - 6/26 0600h	High sulfate peak (~ 28 ug/m <sup>3</sup> ) over the period with high Ozone	on TEOM	no	no
7/2 0900h - 7/3 0700h	High sulfate peak (~25 ug/m <sup>3</sup> ) over the period with high Ozone	no TEOM	7/3	no
7/6 1900h - 7/9 1900h	Canadian Smoke: very high OC, high sulfate peak (~18 ug/m <sup>3</sup> ) for 7/9 1000h-1500h due to high ozone	7/6 29.1 7/7 85.6 7/8 55.6 7/9 44.0 event: 64.8	7/6, 7/7, 7/8, 7/9	no
7/15	Nitrate transient		yes	no
7/18 0230h - 7/19 2200h	High sulfate peak (~24 ug/m <sup>3</sup> )	7/18 51.5 7/19 47.1 event: 51.5	7/18	no
8/12 0900h - 8/14 1500h	High sulfate (24 ug/m <sup>3</sup> ) & OC and high Ozone (possibly secondary OC produced in the afternoon)	8/12 39.5 8/13 57.1 8/14 37.8 event: 51.9	8/12, 8/13, 8/14	yes
10/3 1700h - 10/4 1400h	ECOC, nitrate, sulfate peak at nighttime of October 3 observed	10/3 37.3 10/4 39.5 event: 43.9	no	yes

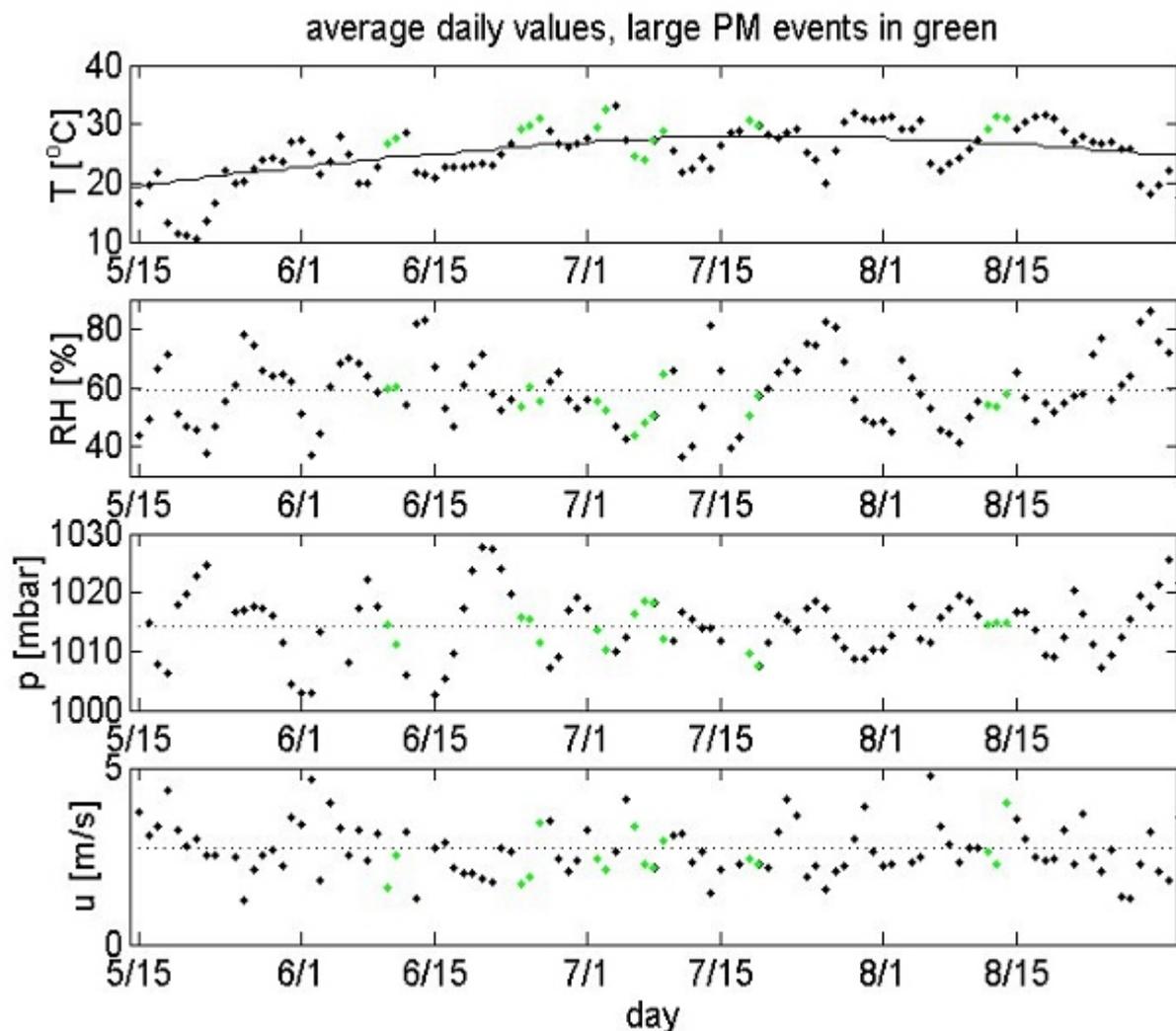
11/20 - 11/21	Nitrate, ECOC transient		no	yes
11/29	OC transient		no	yes

### Overview of Meteorological Data

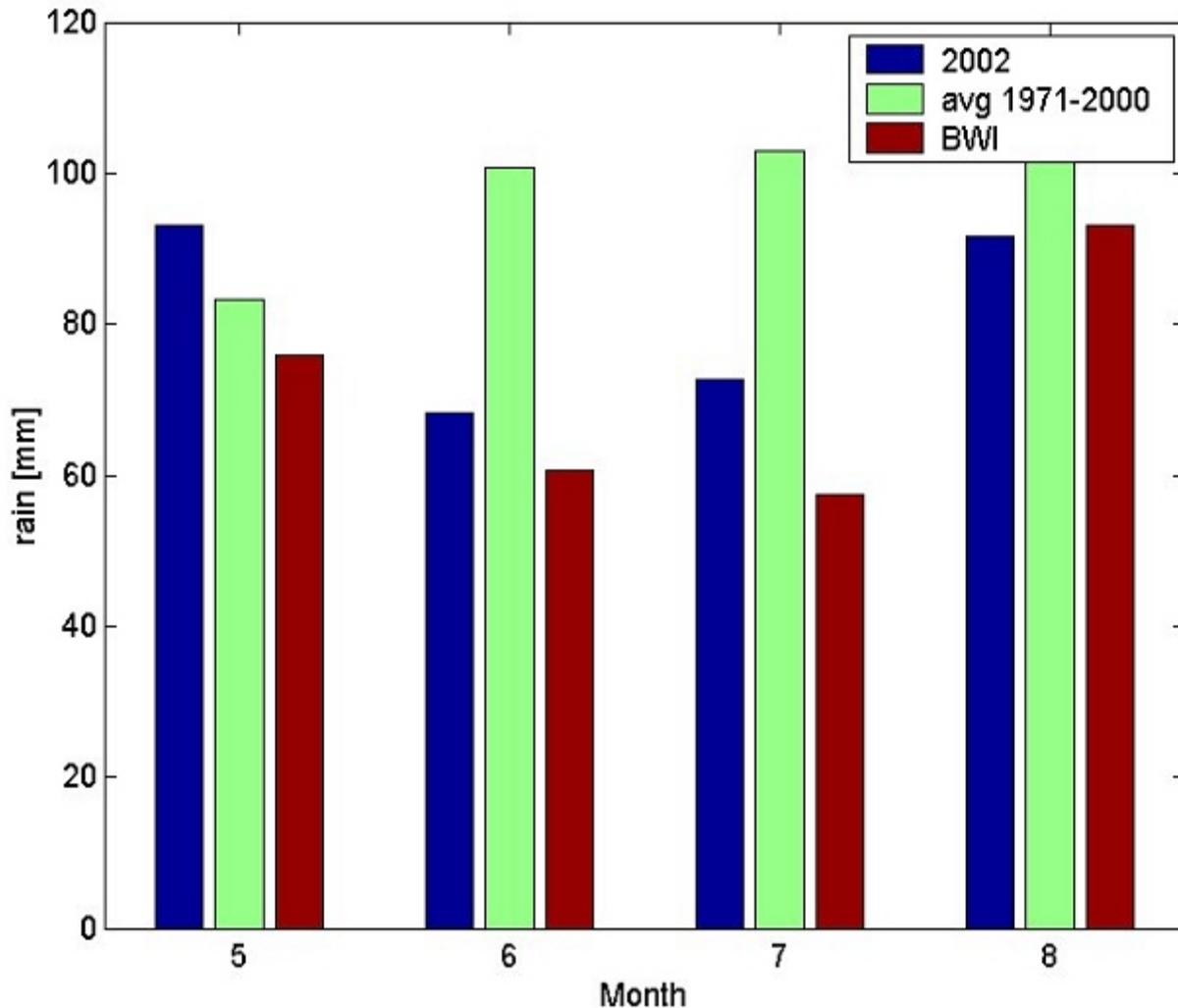
The first figure below shows temperature, relative humidity, pressure and velocity as daily averages. The days with high PM are marked in green. In the temperature plot the line shows the 1971-2001 climate average, the dotted lines in subplots 2,3,4 shows the 3 month average value for the Baltimore supersite (BSS) measurements. The second figure shows the rain measured at BSS compared to rain measured at BWI weather station and the 30 year average.

Clearly, June and July 2002 were dry. Precipitation was about 30% below the 30 year average. Rainfall at BSS and BWI are comparable, but there is ~ 10% more precipitation at BSS. August was more wet but still more than 10% below the 30 year average. From the first figure one can conclude:

- large PM events occur preferably on hot days. except for the canadian forestfire episode on 7/6-7/9 all average daily temperatures are 2 - 5 °C higher than the climate average. During the forest



fire episode the extremely large pollution led to a strong reduction in solar radiation which caused a lower peak daytime temperature.



- the relative humidity is for most events around the 3 month average
- pressure is for most events around the 3 month average. it is usually decreasing during the event which means that the end of an event is often associated with the approach of a lower pressure system (clouds, cold front).
- the wind speed is below average for most events. The last day of the event or the day after often shows wind speeds well above the average (6/12, 6/26, 7/9, 8/14)

**Chronological Description of June 10-11 event.** High sulfate concentrations develop after 6/10/2002 00h and reaches peaks of  $\sim 13 \text{ ug/m}^3$  on 6/10 14h and 6/11 12h (double peak). Sulfate

drops after 6/11 18h and more sharply between 6/12 8h and 12h. Nitrate is low until 6/11 03h and peaks at  $3\text{ug/m}^3$  on 6/11 05-10h and remains elevated until 6/12 9h. OC is constant at  $\sim 6\text{ug/m}^3$  until 6/11 6h and peaks at  $10\text{ug/m}^3$  between 6/11 9h and 6/12 9h. EC peaks together with OC 6/11 6h at  $2\text{ug/m}^3$  and remains elevated until 6/11 9h. The  $\text{O}_3$  concentrations on 6/9, 6/10, and 6/11 are elevated with peaks at  $\sim 100\text{ppb}$  and reduce on 6/12 to a peak of  $75\text{ppb}$ . Ozone in midatlantic region. CO is low 6/11 15h - 6/12 03h but reaches a sharp peak synchronized with EC and Nitrate on 6/11 06h and remains on background levels after 6/11 15h.  $\text{NO}_x$  behaves similar as CO with a peak of  $150\text{ppb}$  due to high NO. MODIS visible satellite pictures show hazy conditions over the chesapeake bay region on 6/10 1015h EST.

**Meteorology: Synoptic Scale.** A weak cold front approaches BSS on 6/9/2002 19h EST. It becomes stationary on 6/10 7h and moves slightly northward over NJ, PE as a weak warm front on 6/11 7h. It becomes stationary again over southern NY and then gains strength and moves south as a cold front on 6/12 19h. An Appalachian lee trough, characteristic for weather conditions with high Ozone events, is diagnosed on 6/11 from 7h until 24h.

There are scattered reports of haze in the Baltimore area on 6/10 and more widespread haze on 6/11. On 6/10 upper air pressure at 850 mbar levels is high over Kentucky, at 500 mbar a ridge is observed to the west. On 6/11 a ridge at 850mbar reaches from AL to MD's eastern shore, the 500 mbar ridge remains in place to the west. Visibility at BWI drops below 16km at on 6/10 18h and reaches a minimum of 3 km on 6/11 0430h. The soundings at IAD on 6/11 show a residual mixed layer and eastward flow throughout the boundary layer with a strong cap at 660mbar.

The HYSPLIT backtrajectories show Northerly flow on 6/10 00h shifting to Easterly/local (distance  $< 500\text{ km}$ ) flow on 6/10 06h until 6/10 00h when winds turn back to Northerly and then Northeasterly on 6/11 12h. This wind direction with predominantly local flow persists until 6/12 07h, when strong Easterly winds (500km in 12 h) and later strong Northeasterly winds go along with the end of the pollution episode.

**Meteorology: Conditions at BSS.** Relative humidity was on normal levels, with peaks and lows of 80% and 40%, respectively. Temperature increased steadily from June 9 onwards and reached highs of  $30^\circ\text{C}$  and  $34^\circ\text{C}$  on June 10&11, respectively (the 30-day average peak temperature is  $27^\circ\text{C}$ ). June 12 started very hot with the ambient temperature  $>30^\circ\text{C}$  at 09h, but the approaching cold front caused a drop of  $5^\circ\text{C}$  at 16h. Atmospheric pressure was constant at  $\sim 1013\text{ mbar}$  from 6/9 18h - 6/11 09h, but decreases thereon and reaches a minimum of  $1003\text{ mbar}$  with the passage of the cold front 6/12 15h.

There was no precipitation at BSS from 6/7 - 6/13. Cloud cover during 6/10 and 6/11 was no more than 1/8, but full cloud cover is observed with the passage of the cold front. The lower peak in solar radiation on 6/10 compared to 6/9 might be caused by light absorption by aerosols.\

Local wind directions oscillate around Northerly flow on 6/9, 6/10, and 6/11. During 6/12 winds turned easterly. A period of weak winds starts 6/10 9h and a calm episode follows 6/10 22h - 6/11 5h. A short period of stronger winds ( $5\text{ m/s}$ ) 6/11 17h-19h and a longer period of strong winds on 6/12 6h follow. The passage of the cold front goes along with very strong winds ( $>6\text{ m/s}$ ) on 6/12 17h.

In conclusion, a period of weak winds coincides with a build up in sulfate during 6/10. The peaks

in EC, CO, NO<sub>x</sub> follow directly on a period of calm winds on 6/10 22h - 6/11 5h. The strong drop in aerosol concentration happens 12h before the passage of a cold front which is preceded by stronger winds and a shift in wind direction to Easterly. The Appalachian lee trough is analyzed on 6/11 and hot weather with no rain support air pollution during the entire event

**SEAS:** Three hundred additional samples, representing all valid samples collected at Ponca St. between 19th and 26th of November 2002, have been analyzed since the last reporting period. In order to have a continuous time-series data set, SEAS samples have been split and the second halves were frozen for biological assays during the periods where only one SEAS was sampling. Atmospheric elemental concentration data obtained from SEAS have been entered into the BSSDB along with the appropriate analytical flags. Level II validation is pending. Analysis and comparison of 24-hr filter-based PM<sub>1.2</sub> vs. SEAS data are to be completed during the next project period. Several hundred additional samples from the July 2002 intensive have been selected for Metals and Cytokine analyses and are being processed. This will take several months. Choosing which samples to analyze depends on which other data we have and requires time-consuming checks of records for all instruments.

#### **PROGRESS ON BIOASSAY OF SEAS SAMPLES**

In vitro test procedures for measuring the bioactivity of SEAS samples have been established. Effect measurements analyzed for each sample include cytotoxicity (measured by alamar blue reduction), endotoxin concentration, and alterations in cytokine release (MCP-1 and IL-8 for A549 cell assays and TNF $\alpha$  and IL-6 for RAW264.7 cell assays). Assays have been run on complete daily sets of SEAS samples from the FMC site and for two days (July 17<sup>th</sup> and 18<sup>th</sup>) from the Ponca Street site. Additional studies have been conducted using standard PM samples (NIST 1648 and NIST interim PM<sub>2.5</sub>), lipopolysaccharide (LPS) and one metal ion, zinc (Zn) to support interpretation of our results.

**SEQUENTIAL ORGANIC SAMPLER DATA:** Approximately 2 weeks worth of samples and blanks (139 filters and 139 PUFs) have been extracted for analyses Florida International University. Approximately 5 days worth of these (220 PUF, Filter, and Blank) samples have been analyzed for approximately 100 compounds. A substantial number of Blank filters and PUFs need to be analyzed. Thus averages can't be developed for the entire intensive period before they can be applied to the sample data. Therefore, we are awaiting completion of analyses of the entire intensive period before the data will be released for loading into BSSDB and submission to NARSTO. We've completed selection of the remaining samples for GCMS analyses. These include 25 samples collected in February 2003, when we conducted a mini-intensive to obtain true Winter data.

**OTHER DATA:** The following data sets need to be loaded into BSSDB: SEAS Cytokine response data (not yet existent), Organic Compound analysis data, Drum impactor synchrotron XRF data (not yet received), and VOC canister data.

## MULTIVARIATE DATA ANALYSIS

During this quarter, Clarkson has developed an initial trial multilinear engine script for implementing the data analysis model in which data obtained on different time interval samples are analyzed. Customary multivariate techniques (PCA, PMF) cannot utilize the full information content of data sets measured under multiple timing schedules. It would be necessary to somehow transform the data to one timing schedule. Either, the high-resolution data would need to be averaged over the averaging intervals of the slowest data, typically 24 hours, or the low-resolution data would have to be interpolated for the short time periods of the fast measurements. Averaging would lose all of the valuable high-resolution information. On the other hand, interpolation is based on an invalid assumption of temporal smoothness of sources. As an example, in a land-breeze/sea-breeze situation, both sea-related and land-related aerosols typically arrive to the receptor site during 12 hours. Interpolation would ignore this cyclic pattern and attribute similar amounts of concentration to all 24 hours of the sampling period. In this way, it would be impossible to correctly deduce the proper connections between the 24-hour interpolated aerosol data and high-resolution (e.g., hourly) concentration data displaying the true short term patterns (e.g. Se in a plume from a coal-fired power plant). Such examples of high short term variations in Se have been observed at the Baltimore supersite.

The new modeling approach proposes a solution to the problem caused by multiple timing schedules. The essential idea is that different data may occur with different averaging levels in different sections of the model. More importantly, the unknown quantities to be determined are present in different sections of the model in different averaging levels. Each individual equation in the model approximates one data value (concentration) as a linear combination of unknown concentrations (= factors) describing the sources. Each data value is preferentially used in its original timing schedule. No interpolation of original data is needed. Averaging is only used for high-resolution data if such data is needed in an equation that otherwise contains low-resolution data only.

The previous example is continued in order to illustrate the concept in more detail. The apparent temporal behavior of the power plant source is one unknown factor in the model. In the hourly time domain, this source is described by the hourly values  $g_{dh,p}$ , where the subscript  $p$  identifies the power plant source among all sources. The subscripts  $d$  and  $h$  denote day and hour, respectively. In the 24-hour domain, the same source is described by the 24-hour values  $g_{d,p}$ . The customary factor analytic (bilinear) equations in the two different time frames are then

$$x_{dh,j} = \sum_{p=1}^P g_{dh,p} f_{jp} + e_{dh,j} \quad (1)$$

for the hourly time frame and

$$x_{d,j} = \sum_{p=1}^P g_{d,p} f_{jp} + e_{d,j} \quad (2)$$

for the 24-hour time frame. The coefficients (factor elements)  $f_{jp}$  represent concentrations of element/compound  $j$  in the emission profile of source  $p$ . For the hourly data, equation (1) will be used:  $x_{dh,j}$  (where  $j$  corresponds to any of hourly species emitted by the power plant like Se)

denotes the concentration measured at hour  $h$  on day  $d$ . For 24-hour data, the second equation (2) applies. Then  $x_{d,j}$  denotes any of the concentration measured on day  $d$  with 24-h averaging.

Equations (1) and (2) need to be complemented by equations that connect the different versions of the unknown factors:

$$g_{d,p} = \sum_{h=1}^{24} g_{dh,p} / 24 \quad (3)$$

Developing efficient algorithms for solving these equations might be a very laborious task. However, the present work will be based on the well-established program Multilinear Engine (ME-2), that contains tools for handling these kinds of equations. By using this program, one does not need to be concerned with the practical solution of these equations. It suffices to specify the equations by using the formalism provided. Then the engine part of the program automatically and efficiently determines the least squares solution of the specified equations.

We are currently testing this model with simulated data and will begin applying it to the Baltimore Supersite data during the next quarter. Initially we will be limited to the semicontinuous measurements including nitrate, sulfate, OC and EC along with the 24 hour speciation network data. The semicontinuous measurements will be averaged to 1 hour intervals so that the initial problem contains only two time intervals. Subsequently more complex models will be developed, particularly after the SEAS data become available.

Future Plans. Initial trials of the multiple time interval data analysis model will be made. As with any new modeling effort, we will need to carefully explore the interaction of the data point weights, the degree of regularization, and extent of the longest time interval data on the quality of the resulting source resolution.

We hope to have the data available for the single particle mass spectrometry calibration modeling during this next quarter and to begin to organize those data to permit the calibration modeling to be done later this year.

We will also be exploring further the relationships between the continuous and the integrated measurements of nitrate, sulfate, and OC/EC using multivariate calibration methods.

### **SUPERSITES RELATIONAL DATABASE**

During this quarter, we have continued to collect data from the NARSTO archive and from various data suppliers. In concert with EPA personnel, we have contacted all of the Supersite PIs and the collaborating measurement programs to obtain their data. We have now substantially increased the total quantity of data in the archive. In particular, we have obtained the data from AIRMAP, TVA, SEARCH, ASACA, and Fall Line. We have most of the Supersite data from summer 2001, but we have yet to receive any data from St. Louis. We also have not received much data from the fourth quarter of 2001, and thus, we continue to request data from the suppliers.

We are well underway in the data analysis task needed for the database design. Table creation has begun and the web site now has an ID request page and information for data suppliers. It also has skeleton pages for other (but not all) functions.

**Future Plans.** We have essentially completed the data classification scheme. We are working with the database programming subcontractor to produce a classification routine by which the data can be processed and made available for archiving in the relational database. We continue to move toward the establishment and availability of the database so it is available on or about October 1, 2003.

#### **ASSESSMENT OF NITRATE MEASUREMENTS AT PONCA ST.**

Nitrate content of airborne particles were measured at 10-min intervals at the Baltimore Supersite, Ponca St. location in east Baltimore, from February 14 through November 30, 2002, using the R&P 8400N semicontinuous nitrate monitor to determine its contribution to fine-particle aerosol mass concentrations. Comparison with 24-hr filter based nitrate measurements made concurrently using the U.S. Environmental Protection Agency's Speciation monitoring and analysis protocol, revealed a discrepancy of 33% between the 24-hr averages derived from the two methods, for most of the 9.5 month study period, after all corrections, including conversion efficiency measured with pipetted  $\text{KNO}_3$  standards, span-gas audit results, and Reaction Cell Pressure deviations. This suggests that the 8400N conversion efficiency for nitrate in Baltimore was 68%. The uncertainties (precision) in individual 10-min measurements, estimated from measured parameters, averaged 8.7% and ranged from 6.3 to 23%, excluding uncertainty encompassing dissociation losses. Uncertainties in 24-hr averages of the 10-min measurements were generally larger (median of 9.1%) owing to added uncertainty associated with missing/invalid values. The detection limit for 24-hr averaged concentrations, (defined as the value where the measured concentration is twice its uncertainty) was typically  $0.17 \mu\text{g}/\text{m}^3$  during the study. That for the 10-min measurements was typically  $0.24 \mu\text{g}/\text{m}^3$  (also after slope correction to achieve agreement with 24-hr speciation measurements). Regression slopes were statistically equivalent for all months except February and October (an outlier not understood) averaged 1.33 and intercepts were generally small and insignificant. Good agreement between the 24-hr data sets was achieved after the mean regression slope were applied to the 10-minute data, for these months. In February, when flat flash strips were used and instrument compartment ( $T_{\text{comp}}$ ) - outdoor ambient temperature differences were often severe, i.e., conditions favoring loss of ammonium nitrate by dissociation equilibrium, the regression slope was statistically larger than the average for the remaining months, and unlike that for the other months, the intercept was positive and significant. A nonlinear least squares model incorporating terms to account for dissociation losses was used to investigate the potential error in 10-minute nitrate Measurements at Ponca St. nitrate data from the instrument in an effort to determine the level of confidence in which short-term excursions in nitrate concentrations may be reliably identified. Results suggest that the largest errors in measured nitrate concentrations resulting from dissociation losses occur when concentrations are near the detection limit, instrument-outdoor temperature differences were large, and ambient RH low (<40%), i.e., conditions which most frequently and severely occurred in February and March. In February, dissociation losses as

large as  $1.65 \mu\text{g}/\text{m}^3$  (100 % of the slope-corrected measured value) may have occurred and such losses were predicted to be >30% in 63.5% of the 10-min measurements for that month. However, model predictions for the other months, when new ridged-flash strips were used, suggest that dissociation losses were much less significant, at most 57% of the slope-corrected measurement and <15% in 72% of the 10-min measurement (87% were <30%). For the other months, predicted losses were <15% for >95% of the measurements. Our experience suggests that the semicontinuous monitor can produce reliable 10-minute concentrations when instrument-outdoor differences are kept small, an independent measurement is used to correct the data, and are improved when grooved flash strips are used.

**Future Plans.** We are preparing a manuscript characterizing transient nitrate concentration excursions and discussing their influence on PM<sub>2.5</sub> concentrations in Baltimore.

### **CHARACTERIZATION OF NITRATE WITH RSMSIII**

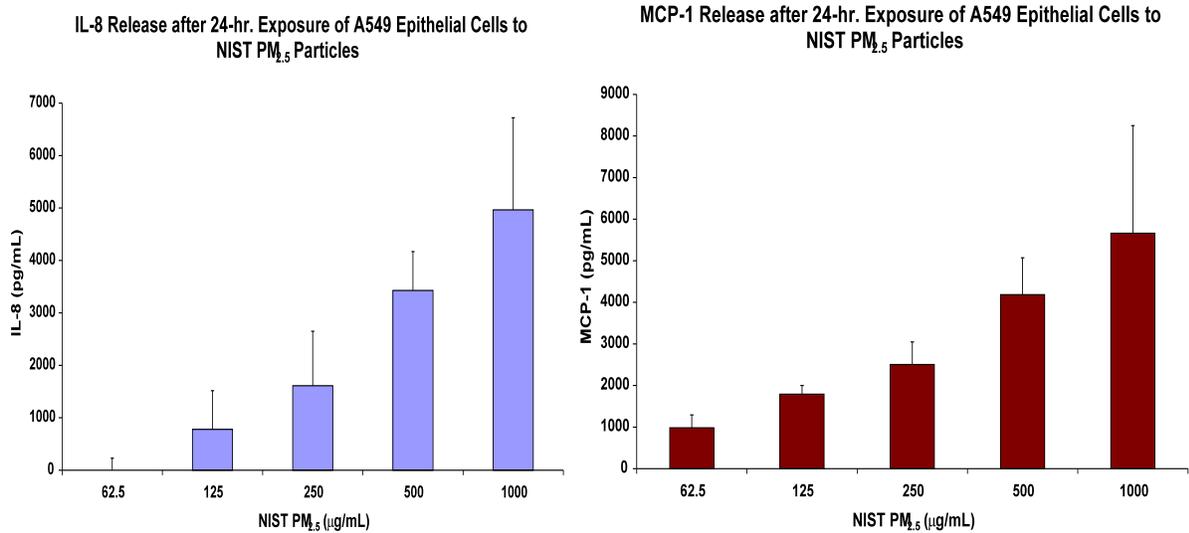
Ambient particles in Baltimore, Maryland were characterized from April through November 2002 using the real-time single particle mass spectrometer, RSMS III. Nitrate containing particles were selected on the basis of a signal at  $m/z$  30 in the positive ion mass spectrum above a threshold value. These spectra were subsequently analyzed by the fast adaptive neural network algorithm Art2-a to distinguish nominally “pure” nitrate particles from internally mixed particles containing nitrate. Examination of these data revealed ultrafine particle events of two types: a large burst of nominally “pure” nitrate particles in the 50-90 nm size range, and a smaller (and less frequent) burst of “pure” particles in the 50-90 nm size range that grew to 110-220 nm with time. Coincident with both of these events was an increase in the number of mixed composition particles containing nitrate, suggesting that they were formed by condensation of ammonium nitrate onto pre-existing particles. Meteorological variables, particle number concentrations and continuous nitrate mass measurements were compared to the single particle data. Number and mass concentrations estimated from RSMS III correlated well with similar measurements with other techniques. Ultrafine nitrate particle events were observed during periods of low temperature and high relative humidity as expected from ammonium nitrate equilibrium considerations. During these events, the partitioning of ammonium nitrate to the particle phase strongly influenced the particle number concentration as well as the chemical composition.

### **CYTOKINE ASSAY**

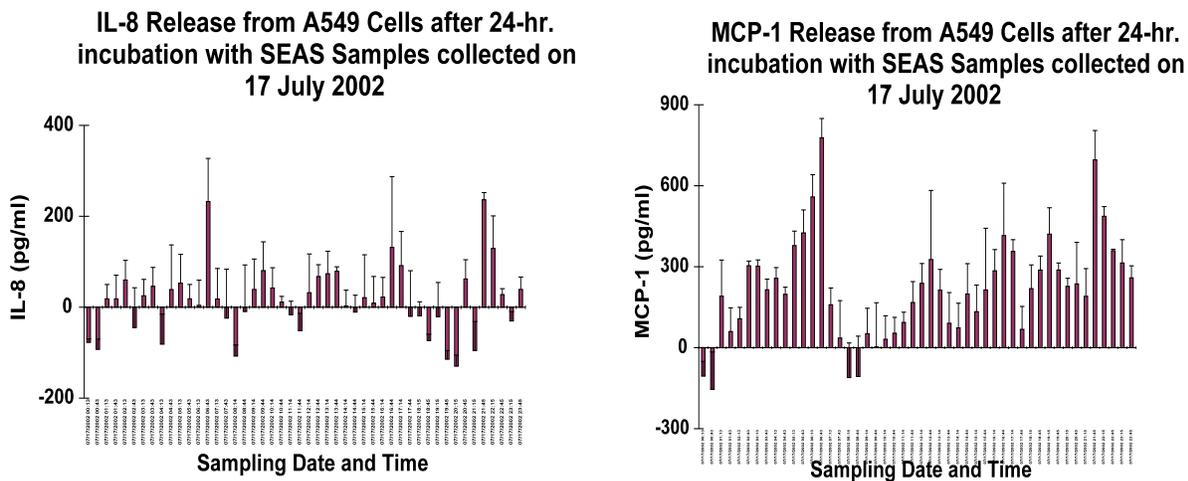
**Baltimore ambient PM<sub>2.5</sub> modulates cytokine and chemokine responses.** Studies to date have demonstrated that both standard NIST PM samples and Baltimore ambient PM<sub>2.5</sub> samples collected from the EPA Supersite Program Ponca Street site in downtown Baltimore alter the release of cytokines from cultured cells. A549 airway epithelial cells cultured with NIST PM 1648 and interim NIST PM<sub>2.5</sub> particles release increased amounts of IL-8 and MCP-1 compared to controls in a dose dependent manner (Fig. 1 and 2). Similar results were obtained with NIST PM1648 particle exposures (Mitkus et al., 2003a).

In similar experiments, PM<sub>2.5</sub> samples collected at 30 minute intervals by the semi-continuous aerosol sampler (SEAS) at the Ponca Street site in downtown Baltimore also stimulated release

of MCP-1 and IL-8 at most time points (Fig. 3 and 4), although some particle samples showed an inhibition of the basal release of these cytokines compared to non-exposed cells (Mitkus et al., 2003b). This hypothesis that this inhibition is due to PM<sub>2.5</sub>-associated metal ions is supported by *in vitro* studies in which MCP-1 release by A549 cells exposed to 25 to 400 μM ZnCl<sub>2</sub> was inhibited in a dose response fashion, while IL-8 release was increased (Mitkus et. al., 2003c). Such an effect of PM-bound Zn in the airways would alter the normal pulmonary inflammatory response to infectious organisms.

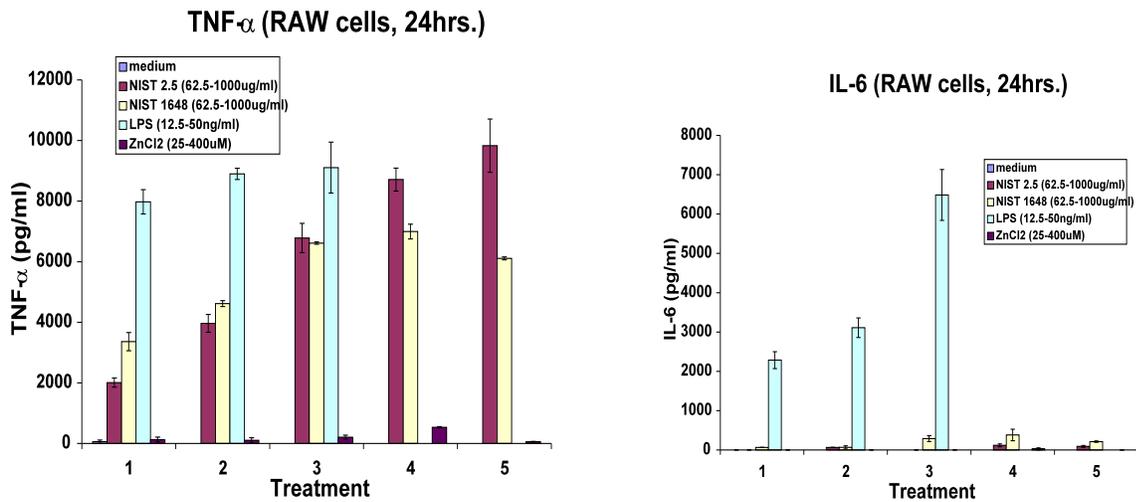


Figures 1 and 2. Release of IL-8 and MCP-1 from A549 epithelial cells in response to interim NIST PM<sub>2.5</sub> samples.

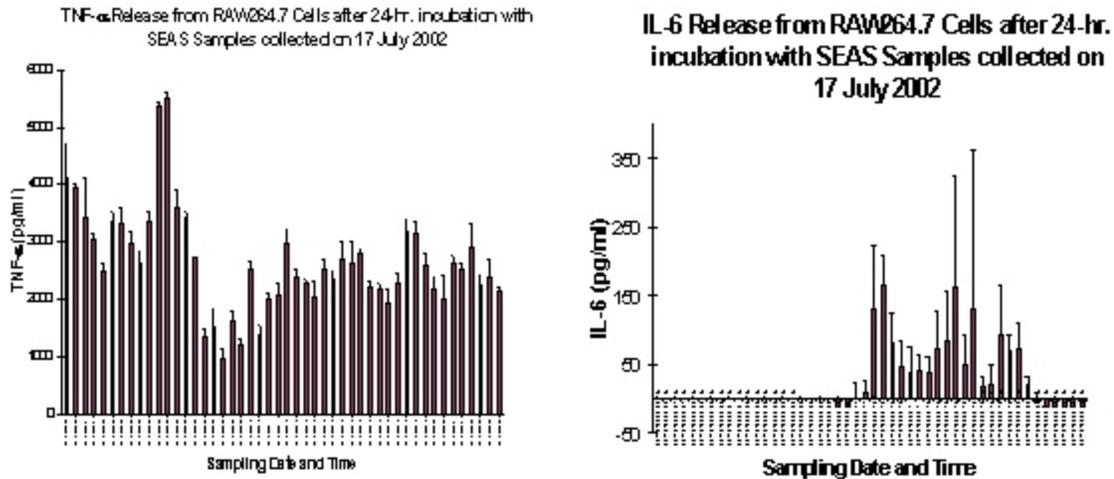


Figures 3 and 4. Release of IL-8 and MCP-1 from A549 epithelial cells in response to SEAS samples collected at the Baltimore Supersite.

Results from our studies have also shown a stimulatory effect of urban PM and endotoxin on TNF $\alpha$  and IL-6 release (Fig. 5-6). In a dose response fashion, RAW264.7 cells exposed to NIST PM 1648 and NIST PM<sub>2.5</sub> release increased amounts of TNF $\alpha$  and IL-6. Although this macrophage cell line minimally was responsive to ZnCl<sub>2</sub>, we observed the expected, strong response to LPS exposure. RAW264.7 cells exposed SEAS PM<sub>2.5</sub> samples collected from Baltimore, MD also stimulated an increased release of TNF $\alpha$  and IL-6 that varied depending upon the time of day of the collection of the samples (Fig. 7-8) (Mitkus et al., 2003b).



Figures 5 and 6. Release of TNF- $\alpha$  and IL-6 from RAW264.7 cells in response to interim NIST PM<sub>2.5</sub> samples.



Figures 7 and 8. Release of TNF- $\alpha$  and IL-6 from RAW264.7 cells in response to SEAS samples collected at the Baltimore Supersite.

These data suggest that components of urban PM<sub>2.5</sub> alter pulmonary immune cell response in either a stimulatory or inhibitory manner, depending upon the composition of the particles. They also indicate that endotoxin carried into the lung by its association with PM<sub>2.5</sub> may stimulate resident alveolar macrophage, causing local inflammation through the release of these inflammatory cytokines.

**Ambient PM-endotoxin levels vary at different times of the day.** Endotoxin levels were analyzed in ambient air PM<sub>2.5</sub> samples collected using the semi-continuous elements in aerosol system (SEAS) sampler at the FMC Corporation site situated to the south of downtown Baltimore. Continuous samples were collected at 30-minute intervals over a 22-hour period and analyzed for endotoxin (Figure x.). During this 22-hour period endotoxin levels ranged from 0.2 ng to 137 ng per sample and showed evidence of rising and falling endotoxin levels at different times of the day. Over the 22 hour sample period an average of 9.4 ng/m<sup>3</sup> of endotoxin was measured. This compares to 5-10 ng/m<sup>3</sup> in the occupation studies.

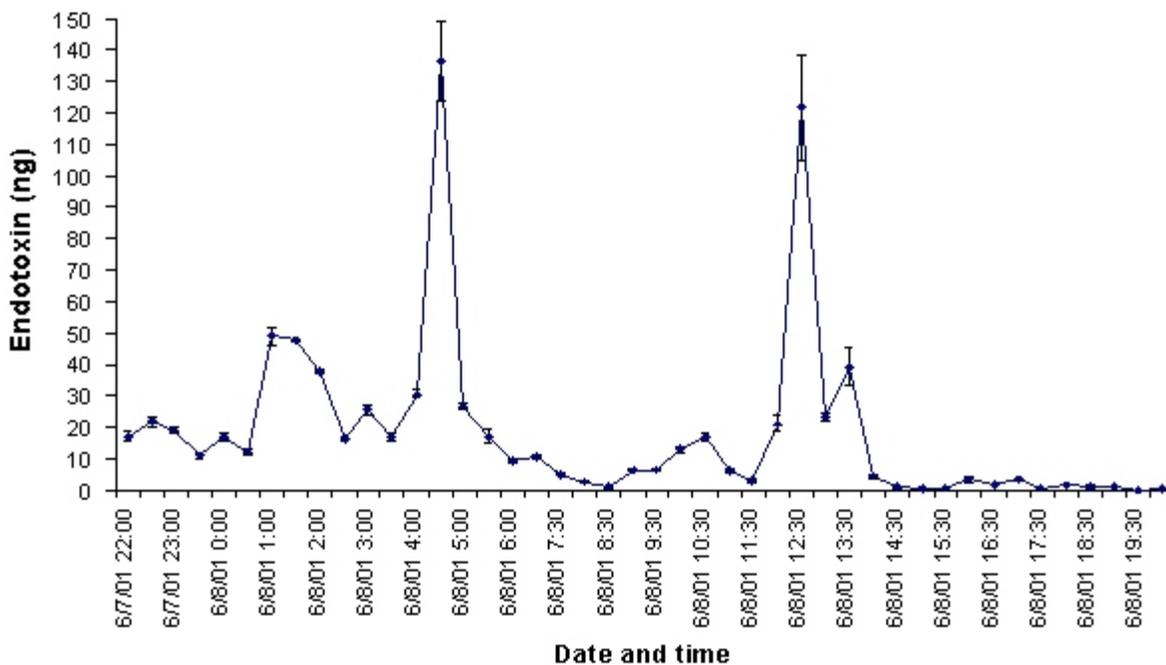


Figure 10. Endotoxin (ng) levels detected in 30-minute continuous SEAS samples collected at the FMC Corporation site.

## FILTER/PUF ANALYSES FOR ORGANIC COMPOUNDS

### Sample work up

For the summer intensive sampling period of 2002, a total of 139 filter/PUF samples were extracted and their extracts (278 separate filter and PUF extracts) processed on the GC/MS. In total, more than 500 mass spectrometric chromatograms have been generated, not counting standard GC/MS runs. So far about 25 filter/PUF pairs have been extracted for the Winter

intensive. Of the samples extracts processed on the GC/MS, about 8 sampling days worth of sample data have been analyzed and the data interpretation is completed to roughly 75%. The reminder 6 days worth of data interpretation is completed to about 40%. At the last Supersite meeting in Baltimore in June, first detailed results were presented for 8 continuous sampling days.

### Short Overview about First Results for the Summer Intensive

The data generated here during this Supersite study are the first of its kind in terms of time resolution. Ambient concentrations for individual organic compounds that are associated with fine particulate matter are available with a 3-hour interval, allowing us to investigate diurnal variations. Before, such detailed time resolution was only available for gaseous air pollutants.

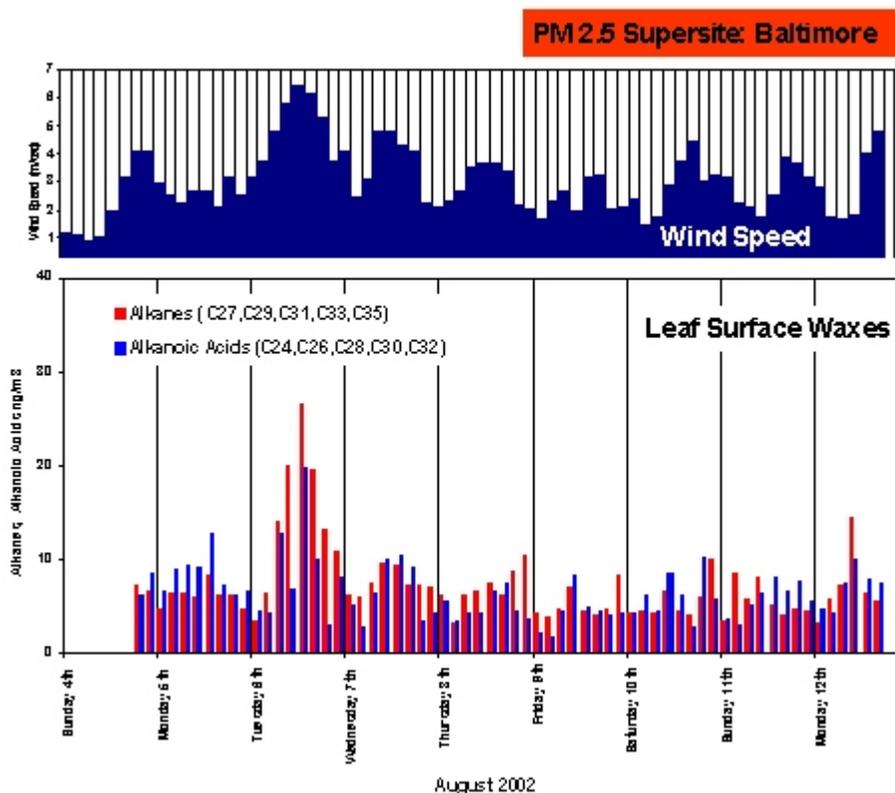
Due to the long-distance, regional, and local contributions of fine particulate matter to the Baltimore atmosphere, a repeating daily cycling of particle-bound organic compounds is not expected as is often seen for ozone, a mainly locally formed pollutant that has an expressed day and night-time cycle.

Following, are some highlights of the data presented at the June meeting.

**Leaf Surface Abrasion Products.** We know from our previous studies that leaf surface waxy layers are made up of fine wax-type protrusions of micron and sub-micron dimensions that are released to the atmosphere by

wind and weather and the rubbing motions of the leaves against each other.

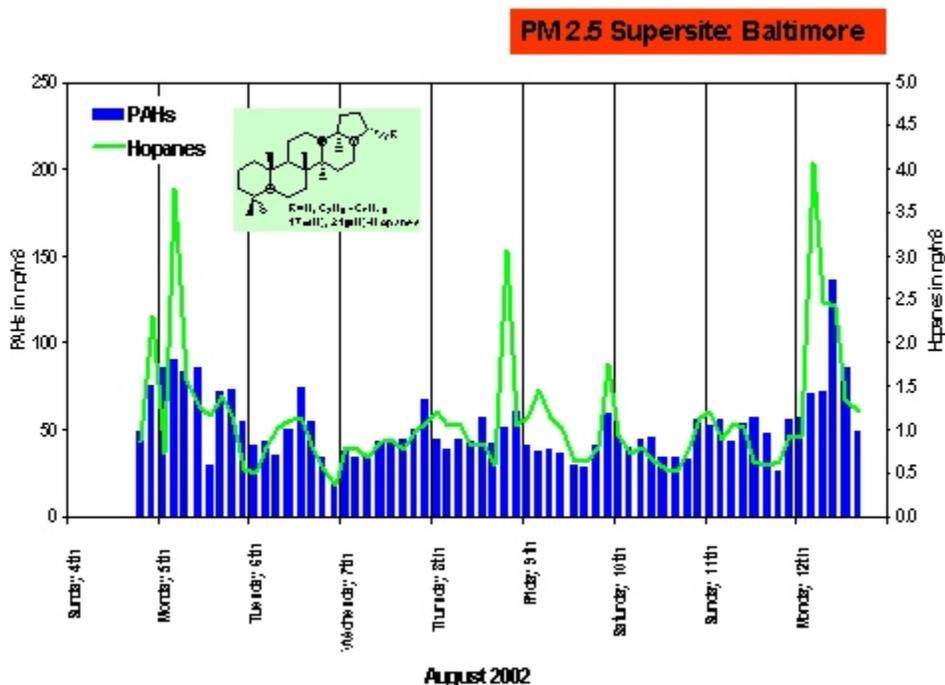
Below, the 3-hourly wind speed is plotted against the atmospheric concentrations for odd-carbon-number n-alkanes (C27, C29, C31, C31, C35) and even-carbon-



numbered n-alkanoic acids (C24, C26, C28, C30, C32), the predominant waxy aliphatic compounds found in leaf surface waxes. It can be seen that indeed the ambient concentration of these leaf surface wax constituents increases with the wind speed, more or less independent of the wind direction.

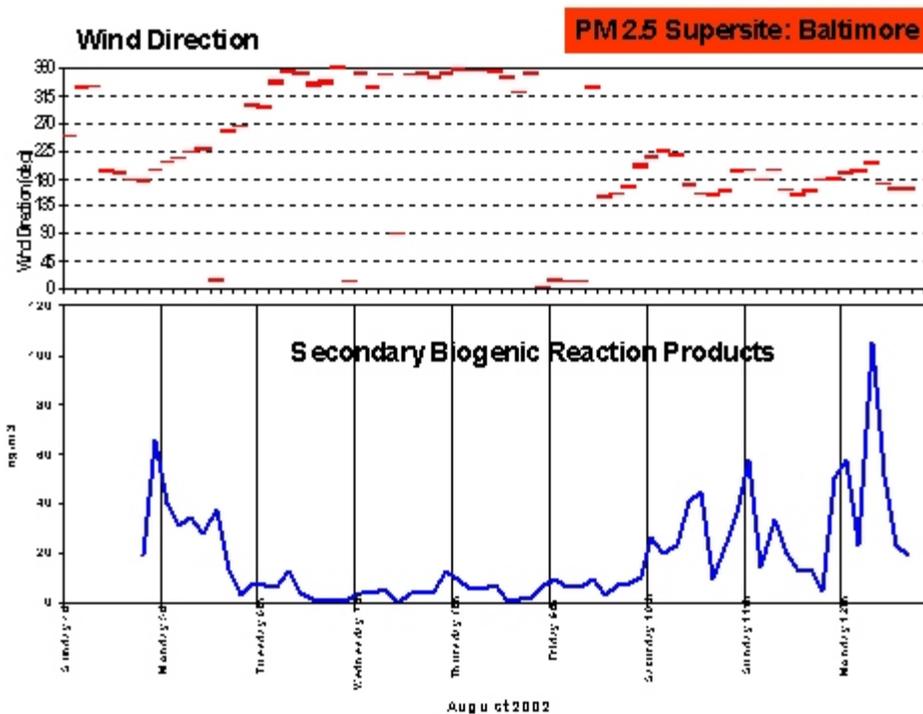
**Ambient Concentration of Fossil Fuel Combustion Marker: Hopanes.** Hopanoids, in their original form, were synthesized millions of years ago by bacteria and algae. During the crude oil maturation, hopanoids are converted to hopanes via deoxygenation and saturation reactions. Originally associated with lubricant oil, these hopanes are suitable markers for the release of vehicular exhaust from diesel and gasoline powered vehicles. Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion. The figure below depicts ambient total hopanes concentration versus total PAH concentration. More or less, the ambient concentration distributions for hopanes and PAHs are very similar, indicating that vehicular emissions also have a substantial impact on the ambient PAHs concentrations.

Ambient concentrations for hopanes, as well as PAHs, do not show a diurnally repeating cycling. This indicates that the mixing of local, regional, and long range transported emissions; together with the variations in wind direction and wind speed drastically modify the diurnal ambient concentration patterns caused only by local vehicular emissions.



**Biogenic Reaction Products from  $\alpha$ - and  $\beta$ -pinene: Nopinone, Norpinonic Acid, and cis-Pinonic Acid.** The ambient concentration of the sum of three biogenic atmospheric reaction products is shown below. In addition, a 3-hourly averaged wind direction plot is provided as well. Elevated concentrations have been measured for these biogenic reaction products whenever

the wind blows from the South, from Washington, D.C. Not shown here are the measured ambient ozone concentrations that show a similar concentration profile with elevated concentrations with southern wind directions



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- Markus Pahlow, Jan Kleissl, Marc B. Parlange, John M. Ondov and David Harrison. Atmospheric boundary layer structure as observed during a haze event due to forest fire smoke, Submitted to *Boundary Layer Meteorology*.
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## **PRESENTATIONS/MEETINGS**

### **INTERNATIONAL SOCIETY OF EXPOSURE**

Sapkota, A.; Symons, J.M.; Kleissl, J.; Wang, L.; Parlange, M.; Ondov, J.; Buckley, T.J.; The Impact of Canadian Forest Fires on Air Pollution in Baltimore City: A Case Study of Long-range Pollutant Transport. 13th Annual Conference International Society of Exposure Analysis. Stresa Italy, 2003.

### **NEOPS Data Summary Meeting, May 12, 13, 2003**

Ondov, J. M., (2003) Highlights of findings from the Baltimore Supersite Project. NEOPS Data Summary Meeting, May 12-13, Pennsylvania State University.

### **AAAS Meeting, Anaheim, October, 2003**

Ondov, J. M., Pancras, J. P., Park, S. S., Poor, N., Turner, J. R., Yu, M., Lipsky, E., Weitkamp, E., Robinson, A. (2003) PM emission rates from highly time-resolved ambient concentration measurements. To be presented at the October meeting of the American Society for Aerosol Research, San Diego.

Park, S. S., Harrison, D., Ondov, J. M. (2003) Seasonal and shorter-term variations in atmospheric nitrate in Baltimore. To be presented at the October meeting of the American Society for Aerosol Research, San Diego.

Park, S. S., Ondov, J. M., Harrison, D. H., Nair, P. V. (2003). Short-term and seasonal behavior of PM<sub>2.5</sub>, Nitrate, Sulfate, and EC/OC at the Baltimore Supersite in 2002. To be presented at the October meeting of the American Society for Aerosol Research, San Diego.

### **NARSTO Emissions Inventory Workshop**

Ondov, J. M., Poor, N. (2003) Emission Inventory Development through highly-time-resolved ambient sampling. NARSTO Workshop on Innovative Methods for Emission-Inventory Development and Evaluation, University of Texas, Austin; October 14-17, 2003.

### **AGS Meeting, San Francisco, December, 2002**

Adam, M., Pahlow, M., Ondov, J., Thomas, M., Parlange, M. (2002) Atmospheric boundary layer extinction coefficient from the 2001/2002 Baltimore PM Supersite experiments. Presented at the Fall meeting of the American Geophysical Society, Dec. 6-

7, San Francisco. Poster: A52C-0125

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- . SONG, X.-H., Hopke, P. K., Paatero, P., Ondov, J. M., Kidwell, C. B. (2002). Source Identification by a Multilinear Receptor Model Using Highly Time Resolved Chemical Composition and Wind Data. Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
- . Ondov, J. M. (2002) Highly Time and Size Resolved Concentrations of Urban Pm<sub>2.5</sub> and its Constituents for Resolution of Sources and Immune Responses: Highlights of Results from the Baltimore Supersite Project." Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
- . Harrison, D., Nair, N., Park, S. S., Pancras, J. P., Gazula, S., Ondov, J. M. (2002) Resolution of a Municipal Diesel Emission Component at the Baltimore Supersite from Highly Time- and Compositionally-resolved Aerosol and Gas. Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
- . Mitkus R., Squibb<sup>1</sup>, K., Powell, J., Catino, D. H., Ondov, J. M. (2002). In Vitro Assay of the Biological Activity of Pm<sub>2.5</sub> and its Components Collected by a High Frequency Aerosol Sampler at an Urban Supersite. Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
- . Park, S. S., Pancras, P., Chang, Y. C., Catino, D. H., Gazula, S., Ondov, J. M. Seung S. Park, Patrick Pancras, Yu Chen Chang, Dawn H. Cation, and S. (2002) Investigation of Sources with Highly Time-resolved Aerosol at the Baltimore Supersite Using Positive Matrix Factorization Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
- . Pancras, J. P., Gazula, S., Park, S. S., Ondov, J. M., Stevens, R. K. (2002) Elemental and Inorganic Analysis of Highly-time-resolved Aerosol Constituents in the Tampa Bay Regional Atmospheric Chemistry Experiment (BRACE) Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
- . Park, S. S., Pancras, J. P., Gazula, S., Ondov, J. M. (2002) Sources of Elemental Aerosol Constituents in Pittsburgh Using Positive Matrix Factorization of Highly Time-resolved Data To be presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
- . Wolfgang F. Rogge, Orhan Sevimoglu, Anna Bernardo-Bricker, Yu Chen Chang, David Harrison Organic PM<sub>2.5</sub> at the Baltimore PM Supersite: Diurnal Variation with a

Resolution of Three Hours. Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

Markus Pahlow, Jan Kleissl, Marc B. Parlange, John M. Ondov and David Harrison, "Characteristics of the Atmospheric Boundary Layer as observed During the Baltimore PM Supersite Experiment" Presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

### **EGS-AGU, 2003**

Adam, M.; Pahlow, M.; Kovalev, V.; Ondov, J.; Balin, I.; Simeonov, V.; van den Bergh, H.; Parlange, M. Determination of the Vertical Extinction Coefficient Profile in the Atmospheric Boundary Layer and the Free Troposphere" To be presented at EGS-AGU, 6-12 April 2003, Nice, France

Mariana Adam, Markus Pahlow, Marc Parlange, John Ondov, "Atmospheric Boundary Layer characterization during the Baltimore PM Supersite - July 2002" AAAR, 31 March - 4 April 2003, Pittsburgh, PA  
P11-16

### **Society of Toxicology Meeting, March 2003**

R Mitkus, J Powell, M Akkerman and K Squibb. Differential Immunological Response of Two Airway Cell Types to Zinc (Zn), an Active Component of Urban Particulate Matter (PM). To be presented at the Society of Toxicology annual meeting, March 9-13, 2003.

### **AAAR Meeting, March 2003**

R. Mitkus, J. Powell, M. Akkerman, J. Ondov and K. Squibb. Cytokine responses elicited by PM<sub>2.5</sub> SEAS samples collected at the Baltimore Supersite during a 2002 intensive study. To be presented at the AAAR meeting in Pittsburg, PA, March, 2003.

Mitkus, R.J., Powell, J., Zeisler, R., Akkerman, M. and Squibb, K. Comparison of the biological activity of NIST interim reference material for PM<sub>2.5</sub> with NIST standard reference material 1648 for urban particulate matter. PM AAAR 2003 meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health," Pittsburgh, PA., March 31-April 4, 2003

Shauer, J. J., Baie, M. S., Turner, J. R., White, W. .H., Koutrakis, P., Ondov, J. M., Pancras, J. P. (2003) New Insights into the dynamics of Sources of Fine Particulate Matter Using semi-continuous Chemical Speciation Samplers. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium on PM and Human Health, March, Pittsburgh.

Turner, J. R., Allen, G., Bahadori, Chow, J. C, Hansen, D. A., Husar, R. B., Koutrakis, P., McMurry, P. H., Ondov, J. M., Schauer, J. J., Watson, J. G., Weber, R. J. White, W. H., (2003). Overview of the Saint Louis Midwest Supersite. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium on PM and Human Health, March, Pittsburgh.

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Ondov, J. M., Buckley, T. J., Hopke, P. K., Johnston, M. V. Parlange, M., Rogge, W., Squibb, K. S., Wexler, A. S. (2003). The Baltimore Supersite Project: Highly Time and Size Resolved Concentrations of Urban PM<sub>2.5</sub> and its Constituents for Resolution of Immune Responses. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium on PM and Human Health, March, Pittsburgh.

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Ondov, J. M., Pancras, J. P., Gazula, S., Yu, M. N. S., Turner, J., Robinson, A., Pandis, S., Stevens, R. K., Poor (2003). 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. Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium on PM and Human Health, March, Pittsburgh.

Emily Wietkamp, Eric Lipsky, Allen Robinson, Natalie Anderson, Heather Leifeste, R. Subramanian, Juan Cabada-Amaya, Andrey Khlystov, Charles Stanier, Leonard Lucas, Satoshi Takahama, Beth Wittig, Cliff Davidson,, Spyros Pandis, Andrea Polidori, Ho-Jin Lim, Barbara Turpin, Patrick Pancras, John Ondov (2003) Fenceline sampling adjacent to a large coke production facility in Pittsburgh, PA Presented at the Association of Aerosol Research meeting, Particulate Matter: Atmospheric Sciences, Exposure, and the Fourth Colloquium on PM and Human Health, March, Pittsburgh.

