

## **Assistance Agreement Quarterly Report: 4<sup>th</sup> Quarter**

**Date of Report:** December 30, 2000

**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.

### **Progress Summary/Accomplishments**

We continue to hold weekly PI teleconferences on an as-needed basis. We conducted our second External Science Advisory Committee Teleconference on December 4<sup>th</sup>, 2000. This encompassed a thorough review of the project including substantive discussion of project changes which are outlined in

Appendix A. We have participated in the McMurry teleconferences on aerosol measurements (especially concerned with the issue of relative humidity during sampling) and in the recent Eastern Supersites conference call organized by Dr. Paul Solomon. Professor Hopke continues to participate in regularly scheduled teleconferences regarding harmonization of AQ across the Supersites and has begun work on the project QAPP. Professor's Rogge and Ondov have participated (Rogge, regularly) in the teleconferences on organic analysis methods.

**Project Changes.** The following changes were discussed during the ESAC teleconference of 12/4/00: Organic sample analysis strategy; Laboratory-only analysis of SEAS samples by GFAAZ; and reallocation of resources for intensive sampling campaigns. Summaries of these are given in Appendix A.

**LIDAR.** Some preliminary measurements were made with the JHU three-wavelength LIDAR from the Homewood campus. The instrument was returned to the manufacturer, however, to diagnose and repair a possible laser malfunction. JHU is developing an algorithm to determine the atmospheric boundary layer (or mixing layer) height from LIDAR data. Three different methods are currently being evaluated, namely the contour method, the one-sided derivative approach and the standard deviation method. Data taken with the JHU LIDAR for a very convective atmosphere has been used to determine the accuracy of those methods. The results are very satisfactory. Not only the average height of the ABL has been determined with good accuracy, but also the shape of the top of the ABL almost resembled the actual shape with its strong undulations. JHU is also development a new method for the inversion of the LIDAR equation. A new method to invert the LIDAR equation has been tested with experimental data. The method furnishes the LIDAR constant as well as the extinction coefficient and the backscatter coefficient profiles. The method proved to be very stable. Currently, further improvement of this method ("two-angle method") is underway.

**SEAS Improvements.** [We continue making improvements to the University of Maryland Semicontinuous Elemental Analysis system \(SEAS\). Specifically, we have completed additional testing of the SEAS steam injector, condensor and virtual impactor modules.](#) Extensive modifications to the steam injection system provide slurry volumes proportional to the concentration of the ambient aerosol. In previous versions of the SEAS the amount of steam injected into the system to achieve a fixed supersaturation of 1.8 has been controlled using the temperature of the major flow after the virtual impactor and ambient relative humidity. Test measurements with a TSI APS 3022 have shown, that a relative humidity of at least 93 % is necessary to provide the target aerosol droplet distribution at the virtual impactor. The amount of water vapor necessary to achieve this relative humidity is modified by the ambient aerosol particle number concentration and by the temperature difference between the SEAS (operated at fixed temperatures) and the ambient air. Furthermore, the amount of steam injected into the system must be kept as low as possible to avoid the formation of droplets without aerosol due to homogeneous nucleation. A second rH sensor has, therefore, been added to measure the relative humidity of the major flow of the virtual impactor. The target supersaturation is now adjusted by the SEAS software every 30 minutes (i.e. after each individual sample) to maintain a relative humidity of 95 % rH at the virtual impactor. With these modifications we get:

- a) A relative humidity of  $95 \pm 2$  % rH at the virtual impactor.

- b) No slurry from filtered air (i.e. no homogeneous nucleation).
- c) A slurry volume proportional to a particle number concentration for ambient air.

The virtual impactor of the SEAS has been operated previously at 5 % minor flow rate resulting in a cutoff diameter  $d_{50}$  of 1.7  $\mu\text{m}$ . Measurements with fluorescent PSL particles and with the APS have shown that the cutoff diameter can be shifted down to 0.7  $\mu\text{m}$  using a minor flow of 15 % of the total flow rate. This decrease of the cutoff diameter results in an improved collection efficiency for aerosol droplets created by condensational growth of ambient aerosol particles by the SEAS. Due to this modification the collection efficiency for hydrophobic PLS (0.089  $\mu\text{m}$  – 1  $\mu\text{m}$ ) has increased from 38 % to 70 %. (Note that hydrophobic PSL particles are a worst case simulation. Hydrophobic particles contribute only 20% to 30% to the ambient aerosol particles. Thus the collection efficiency for “real” ambient particles is larger than 90 %)

As described in the previous report, we have decided to move instrument control from the CR23X data logger platform to a LabView-driven PC. The control programs are now written, new input and output PC boards were installed, and the system was tested. The SEAS has been operated successfully for a test period of three weeks without downtime to software problems.

**Single Particle MS.** Dr. Tony Wexler and colleagues tested the new instrument design at Houston, and achieved 75% operational efficiency. They have incorporated Philip Hopke’s particle classification algorithm in the instrument computer and successfully tested it at Houston. Almost all of the long-lead time parts have arrived, and most of the rest are scheduled to arrive in the next two weeks. The only items that are not scheduled for delivery yet are the turbo pumps. Dr. Wexler was to accept them next week but canceled delivery because he is able to reduce power consumption of the instrument with a different turbo pump configuration. They plan on finalizing that order next week. Version 1 of the data acquisition software was completed and tested at the Houston supersite. Version 2 of the software, with complete laser control, is underway and the first tests have been completed successfully. A new nozzle design has been built. Pressure tests show that they will be able to reduce power consumption below their original estimates if the nozzle is able to transmit particles successfully. Those tests will occur soon.

**Cytokine Assays.** Two cell lines, RAW 264.7 mouse macrophage cells and A549 human lung epithelial cells (from ATCC) are being used to determine the response of these cells to *in vitro* exposures to urban air particulate matter samples. The purpose of this work is to establish a sensitive bioassay of the “immunoreactivity” of air particles that can be used as a predictor of health effects in air monitoring studies. The release of cytokines (IL-6, IL-8, GM-CSF and TNF $\alpha$ ) in response to exposure to standard particles (SRM 1648 and SRM 1649a) and urban air particles collected from Baltimore and Atlanta are being measured in both cell types to determine whether they respond similarly, and to the sensitivity of their response. Results indicate the macrophage do not release measurable levels of IL-6 and TNF $\alpha$  in response to particle exposure, while the A549 cell response was measurable by the standard ELISA assays. At this time, it appears that the A549 cells will be the better cell line to use for the bioassay, however studies are underway to determine whether priming of the macrophage by pretreatment with INF-gamma will increase the macrophage response. **Other Equipment.** We have decided to build our own

systems for collection of high-volume aerosol samples for detailed organic compound analysis and UMCP/FIU have arrived at a sampler design. We have assembled specifications for a data server computer to store the supersite data. The machine will initially have a RAID 5 array of five 72GB drives and will have capacity for another five 72 GB (or larger next year) hard drives.

**Laboratory Trailers.** We have prepared detailed specifications for purchase of our two laboratory trailers and have obtained some initial bids. The least expensive to date is more than we think we need to pay and we are negotiating with another vendor.

**Website:** Our Static Web site has been placed on line at: [www.chem.umd.edu/supersite](http://www.chem.umd.edu/supersite)  
Color maps of the Baltimore Region have been prepared in ARCVIEW and loaded onto our website. The maps show major PM emission sources (obtained from the EPA AIRS data base), metals emissionsources (TRI data), and estimates of emissions as well as the location of our sampling sites and key streets. Recently, we've added a site plan for the supersite at Clifton Park; our position papers on the RH issue and allocation of intensive resources; the efficiency curve for the UMCP all glass inlet impactor; SEAS data taken at College Park, MD, showing resolution of sources; and a 2-D scan showing relative particle concentration data showing traffic pollution over Baltimore streets. Various instrument SOPs are also located on the website (see below).

**SOPs/QAPP.** Hopke and Ondov have completed the draft version of the Quality Assurance Project Plan. SOPs/RPs for SEAS, aerosol slurry collections for cytokine assays, Lidar, and single particle Mass spectrometry have been completed. SOPs/Research Protocols for the Climet, SMPS, TEOM SEAS Chemistry, Bioassay, and RSMS (single particle mass spectrometry) are on our website.

**Site Permission and Preparation.** Dr. Ondov met with Tom Jeanette of the Baltimore Parks Department and we have received permission for access to this site. A detailed site plan was drawn up (see our website) and this was submitted to BG&E. Drs. Ondov and Tuch met with BG&E and finalized power requirements for the Clifton Park site. A 1000 A at 240 V service will be installed with separate meters feeding NIST, MDE, and the UMCP supersite trailers.

**Coordination with MDE and neighboring states.** We have had several communications with MDE about the Clifton Park site; i.e., power and site layout of trailers. In addition we have been in contact with Ted Erdman (Region III Chief) and Michael Zuvich (Pennsylvania Dept. of Environmental Protection) to discuss the allocation and scheduling of speciation samplers and what measurements these will provide. Ted Erdman has indicated that Speciation Measurements will encompass the following: PM mass and elements by XRF on Teflon filters; ions (sulfate, total nitrate, ammonium, sodium, and potassium) by ion chromatography on Nylon filters; and EC/OC and carbon species as determined via thermal-optical analysis of quartz filters.

Previously, Drs. Ondov and Tuch met with several Maryland MDE representatives and Rolf Zeisler from NIST to discuss resource allocations and power requirements at the Clifton Park Supersite. Victor Guide from EPA Region III also attended. Pending written authorization from Region III, MDE agreed to move

their PAMS site to Clifton Park for the duration of the Supersite Project. PAMS measurements include VOC canister collections during the ozone season, as well as semicontinuous chromatographic VOC measurements. MDE agreed to provide the requested FRM, Speciation, and continuous mass monitoring equipment. These systems will be operated on a 1 in 3 day basis (every day during intensive sampling campaigns) by UMCP and MDE personnel. Subsequently, Ted Erdman has provided authorization by email for the purchase of two sets of speciation samplers, analysis of samples, and purchase of a continuous PM<sub>2.5</sub> monitor. We are now engaged in discussions with Region III, MDE, and PA regarding the possibility and desirability of having funds provided to upgrade MDE's and PA's 50°C TEOM samplers to operational capability at 30°C. Washington, DC, uses a CAMMS unit at their McMillan Reservoir site, and has no TEOMs anywhere. Thus, we support MDE's desire to purchase a CAMMS for deployment at our supersite in Baltimore.

**Personnel Changes.** Dr. Patrick Pancras arrived on November 1<sup>st</sup> and has begun assuming project analytical duties. Dr. Yu-Chen Chang will join the UMCP Supersite Team on January 16<sup>th</sup>, 2001. Dr. Wexler has moved to UC Davis and will finish work on the Single Particle Mass spectrometer there. Dr. Johnston will continue instrument development activities at the University of Delaware.

**Publications/Presentations/meetings:**

No publications have yet been prepared. Dr. Ondov visited Professor Thomas Cahill's laboratory at UC Davis and also visited the Berkeley Synchrotron XRF facility during the week of December 4<sup>th</sup>, 2000. The purpose was to assess applicability to the Baltimore Supersite Project and obtain information needed for the QAPP and analytical SOP.

**Future Activities:**

1. We will continue to hold weekly PI teleconferences as needed.
2. Dr. Ondov will visit Professor Philip Hopke to investigate applications of factor analysis models to SEAS data already collected at College Park, MD.
3. We will attend Supersite coordination meetings.
4. Additional Instruments to be purchased include: Continuous Sulfate monitor (R&P estimates that these will be ready to ship in January, 2001); Drum impactors (we are working with Dr. Thomas Cahill on this); and our high-volume organic sampler. We expect to write a purchase order for these by the end of January, 2001.
5. The Baltimore Supersite project will initiate its 12-month field study on or about 1 May, 2001.

**Supplemental Keywords:** Single Particle Mass Spectrometry, ROS, Cytokine, Receptor Modeling

## APPENDIX A: PROJECT CHANGES

### 1. Intensive campaigns

Primary purpose:	i) gather source profiles, ii) support JHU exposure/epi studies
Original Proposal:	two (winter/summer) 45-day intensives at urban industrial site
Revised Proposal:	one 30-day intensive at urban industrial site; two 30-day intensives at urban supersite
Reasons:	Dubious advantage to winter campaign at industrial Allows for short-term Filter/PUF, 8-stage RTI, and daily FRM sampling at urban site; Continues to Support JHU exposure/Epi studies Moving intensive up to May gives i) benefit of source profile information in selecting samples for retrospective analyses and Need move equipment only once Allows for intensives at urban supersite (Clifton Park) for comparison/coordination with other Eastern SSs in July intensive

### 2. Organic Sampling Strategy

Original Proposal:	Five 24-hr samples/month @ 113 LPM, separate Filter/PUF analyses Consecutive 1 to 2 hr samples/@ 500 LPM; retrospectively analyze 90 separate Filter/PUF samples. Collect/analyze a few denuder/Filter/PUF samples; Analyze a few Bulk PM <sub>2.5</sub> samples
Purpose:	Explore nature of organic compounds present Provide data for source attribution (We originally intended to obtain annual mean concentrations)
Problem:	Original Proposal provides too few samples to effectively use advanced statistical analyses. It provides data for transition periods (non winter and non summer months) but these are not judged to be terribly useful.
Revised Proposal:	Five consecutive 24-hr samples @113 LPM for two months (i.e., during intensives), extract and analyze Filter/PUF samples together. Collect consecutive 3-hr samples @500 LPM during 2 intensives. Analyze 104 combined Filter/PUF samples (13 days worth per intensive + blanks.

Collect/analyze denuder/Filter/PUF and Bulk PM samples as specified above.

### 3. SEAS

Decline to field GFAAZ at sites. Little advantage. Creates QC/QA inconsistency between near-real time and retrospective analyses, Can process more samples for complete suite of elements at UMCP lab., allows better support of Pittsburgh and St. Louis Supesites. Could consider fielding GFAAZ near end of field project.

Inlet size cut: We are considering PM1.2 inlet. RE: removal of coarse dust component for improving source resolution and improved analytical efficiency. Have sharp-cut glass 1.2  $\mu$ m cyclone available. Final decision will be made after the new SPMS inlet is calibrated and tested.