

## QUARTERLY PROGRESS REPORT

**Cooperative Agreement Number** R 82806101-0

**Date of report:** March 15, 2002

**Title:** The Pittsburgh PM Supersite Program: A Multidisciplinary Consortium for Atmospheric Aerosol Research

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**Institution:** Carnegie Mellon University

**Project Period:** November 16, 2001 – February 15, 2002

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**Objectives:** Characterization of the atmospheric aerosol in the Pittsburgh region; development and evaluation of current and next generation atmospheric aerosol monitoring techniques; quantification of the impact of the various sources to the PM concentrations in the area; elucidation of the links between PM characteristics and their health impacts; study of the responses of the PM characteristics to changes in emissions.

**Work Status:** Baseline ambient monitoring in the central site was continued during November and December (including Christmas day) and the second intensive sampling campaign (ESP02) took place between January 2 and 22, 2002. During the intensive period, Carnegie Mellon University personnel also collected samples at satellite sites in Lawrenceville and Hazelwood neighborhoods of Pittsburgh, and Florence, PA and Greensburg PA. These samplers are part of the EPA speciation network. An additional site in Athens, OH satellite site was operated during this project period by

our Ohio University collaborators. Twenty-four hour samples are collected at this site on a 1 in 6 day schedule during the baseline period and on an everyday schedule during the intensive. The intensive sampling proceeded without any significant problems.

## **Some Highlights**

### *1. Instrumentation Development-RSMS-III*

A major focus of our work during this period was the continued development of the single particle mass spectrometer. The single particle instrument operated by UC Davis and the University of Delaware is the only instrument in the world capable of analyzing and sizing individual particles over the size range from 20 nm to 2 microns. The experiment in Pittsburgh is the first time anyone has a) operated a single particle instrument continuously for this length of time and b) done so remotely. The instrument has been very reliable although occasional hands-on maintenance is needed.

Since start up, data have been collected with the RSMS-III on more than 150 days. We record up to 30 spectra for each of 9 particle sizes starting at 1:00 AM each day on a three-hour cycle, but we limit time spent on each orifice to 10 minutes. Each scan then records the composition of up to 270 particles. The three-hour cycle means that 8 scans are run per day for a total of up to 2160 particles per day. We have been averaging about 2000 particle hits per day.

Operation of the instrument during extremely cold weather showed that the mechanical pumps could not operate under the extreme cold temperatures outdoors. This resulted in a loss of vacuum, which then caused the micro-channel plate detectors to arc, which then caused the A/D converters to fail. Permanent fixes have been installed to limit the possibility of this happening again: 1) the pumps have been enclosed in an insulated box with a temperature controlled fan so that they will no longer be subject to extreme outdoor temperatures, 2) the high voltage power supplies are controlled by the pressure sensors so that they are cut off if the pressure in the mass spectrometer rises too high, 3) the high voltage power supplies are also cut off if the power fails so that when the power comes back on, they must be manually reset when the mass spec pressure returns to normal,

and 4) the A/D converters are now operated with 1 Mohm internal resistance and a 50 ohm terminator is used to protect them from over voltages.

Another RSMS-III operational issue we have been working on is the laser. The laser is often the source of system down time, but a) employing injection gas, in a gas cabinet, and b) purging the laser light path with nitrogen gas to limit UV induced oxidation of the optics have limited laser-related problems. Precision alignment of the laser with the aerosol particle beam has also permitted us to use lower laser energies, resulting in longer laser lifetimes. Finally, the LabView software that operates the instrument has been improved over time to better manage the laser and better assess the acquisition of valid spectra.

## 2. Semi-Continuous Measurements of VOCs

In collaboration with researchers at the University of California at Berkeley an in situ instrument was used to measure gas phase organic compounds at the main site from the beginning of January through the middle of February. The instrument will also be deployed for one month during the upcoming summer, and potentially for the fall intensive. The Berkeley Hydrocarbon Instrument is a two channel in-situ gas chromatograph designed for automated operation in the field. The first channel, with a standard flame ionization detector (FID) and a porous layer open tube (PLOT) capillary column, measures light hydrocarbons (VOCs -- alkanes, alkenes, and alkynes for C2 through C5), while the second channel, with a mass selective detector (mass spectrometer) and a DB-wax column measures selected oxygenated organics (OVOCs -- alcohols, aldehydes and ketones) and halogenated compounds. Air samples are preconcentrated in a cold trap attached to a thermoelectric cooler (TEC), which requires no cryogen, facilitating remote operation. With this preconcentration, most compounds can be measured with at or below one part per trillion by volume (pptv) in a 20 minute sample. Typically, samples are collected for 20 minutes during each hour and analyzed hourly. The measured compounds include species that are emitted primarily from several anthropogenic sources as well as from several natural sources, which can be fingerprinted by subjecting the dataset to a multivariate factor analysis. Furthermore, many of the

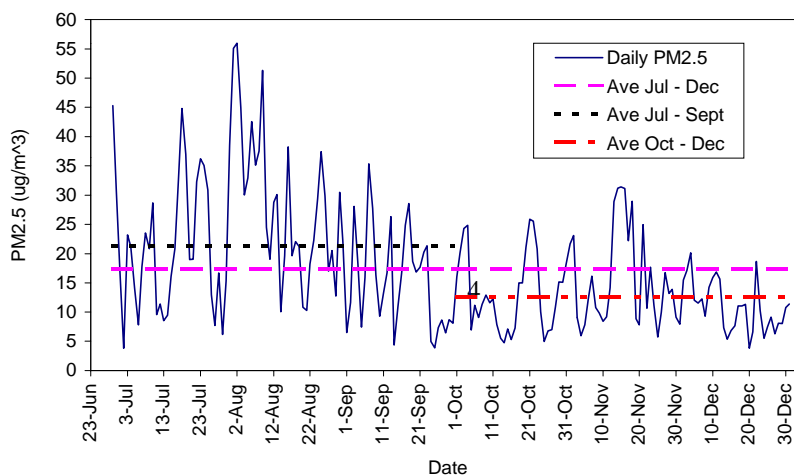
OVOCs are secondary compounds produced by photochemical activity in the atmosphere, so their measurement constrains the photochemical oxidation rate.

### 3. Source Characterization:

The PAQS team has begun negotiations to obtain access to a number of sources in the Pittsburgh region. We have obtained preliminary approval to sample in the Squirrel Hill Tunnel (a tunnel on Interstate 376 located ~ 2 miles from the central monitoring site) and the Bellefield Boiler (a coal-fired steam generator located ~ 0.5 miles from the central monitoring site). We have requested permission to conduct fence line monitoring at two Allegheny County monitoring sites – North Braddock and Lincoln. These sites are located next to a large steel mill and a large coke production facility and both experience significantly higher PM levels than other monitoring sites operated by the county. With advanced instrumentation we should be able to obtain reasonable fingerprints from these sources. We have identified one potential opportunity to participate in an effort to characterize emissions from a coal-fired utility boiler. This is an area that we continue to work on. Initial plans were also made to collect dust samples from various locations around Pittsburgh, and to collect a composite sample of the biomass that is representative of that found in Southwestern PA.

### **Preliminary Results and Discussion**

Figure 1 shows a time series of daily PM<sub>2.5</sub> mass measured at the central monitoring site with an FRM from June 30, 2001 through December 31, 2001. The average daily concentration of PM<sub>2.5</sub> was 17.4 µg/m<sup>3</sup> during this period. The data indicate a strong seasonal variation in both PM<sub>2.5</sub> levels and composition within Pittsburgh. PM<sub>2.5</sub> levels were higher in the summer, with an average level of 21.3 µg/m<sup>3</sup> during July, August and September. Levels were lower in the fall and winter,



with an average level of  $12.6 \mu\text{g}/\text{m}^3$  during October, November and December. The mass data illustrate how the PM levels in Pittsburgh vary in an episodic fashion.

Figure 1. Daily  $\text{PM}_{2.5}$  mass measured with an FRM for June 30 through December 30, 2001.

Figures 2-3 summarize the chemical composition of the  $\text{PM}_{2.5}$ . Figure 2 shows the average  $\text{PM}_{2.5}$  composition for the period from July 1, 2001 through the middle of January 2002. This average includes data from 182 days. The average  $\text{PM}_{2.5}$  mass across all of these days is  $17.2 \mu\text{g}/\text{m}^3$ . The major components of this  $\text{PM}_{2.5}$  mass include sulfate (mass 37% of total mass) and organic material (30% of total mass). On a study-to-date average basis, 10% of the mass is unaccounted for and is reported as missing. Unaccounted for mass is defined as the difference between the  $\text{PM}_{2.5}$  mass measured with an FRM and sum of the individual chemical components.

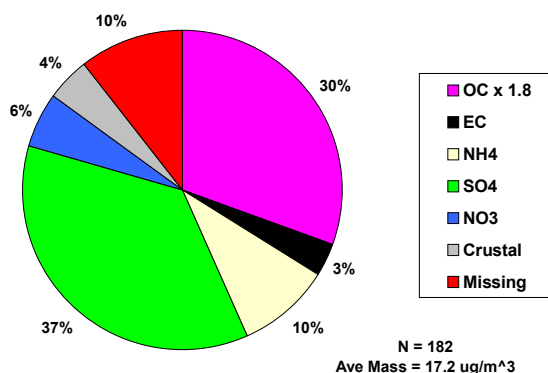


Figure 2. Average chemical composition of  $\text{PM}_{2.5}$  for PAQS study through the mid-January 2002. “Missing” indicates the differences between the mass measured with the FRM and the sum of the chemical components.

Figure 3 shows composition data on a monthly average basis. The total height of each bar represents the average mass measured during the indicated month. Each bar has been broken down to indicate the levels of the different components for a given month. Again the major chemical components are sulfate and organic material. The data also suggest nitrate contributes a significant component of the  $\text{PM}_{2.5}$  mass in the winter. The average  $\text{PM}_{2.5}$  level during the first part of the winter (December and half of January) of 2001 was  $10 \mu\text{g}/\text{m}^3$  with the major components being sulfate (27% of total mass) and organic material (36% of total mass), and nitrate (19% of total mass). The higher levels of  $\text{PM}_{2.5}$  in the summer are primarily due to elevated formation of

secondary organic aerosol and higher conversion rates of sulfur dioxide to sulfate. The appearance of significant nitrate levels during the winter is due to a combination of lower temperatures and lower sulfate levels.

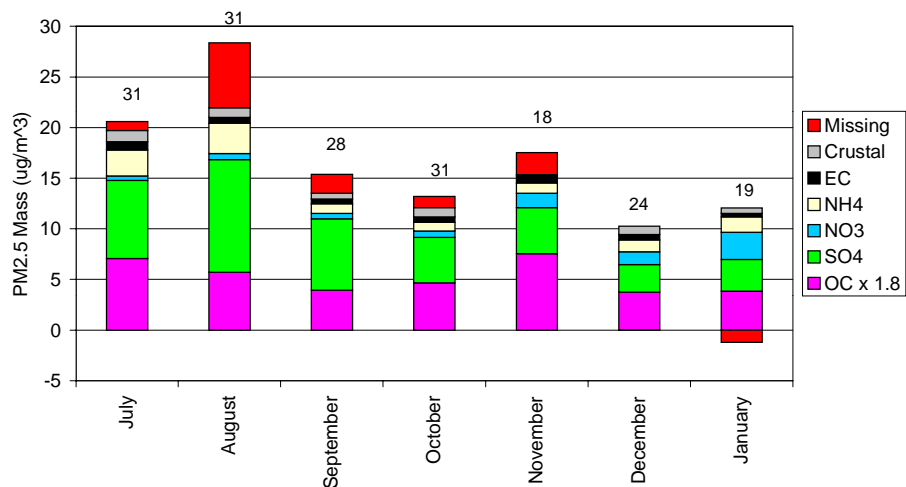
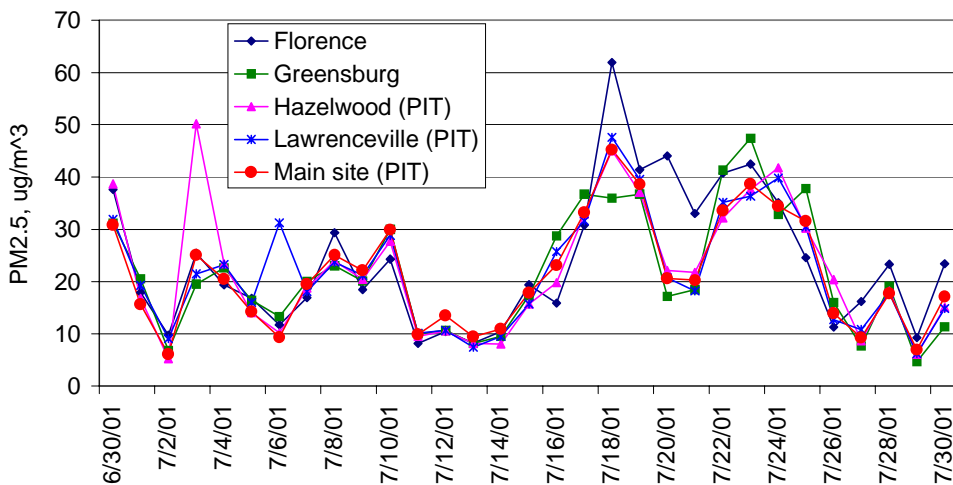


Figure 3. Monthly average mass and chemical composition of  $PM_{2.5}$ . The height of each bar represents the total mass measured for that period using an FRM. The numbers above each bar indicate the number of days from that month included in the average. Missing indicates the differences between the mass measured with the FRM and the sum of the chemical components.

Figure 3 also examines the mass balance between the measured  $PM_{2.5}$  mass and the sum of chemical components on a monthly basis. For the period of July through November, the mass measured with the FRM was greater than the sum of the chemical components. We are currently investigating whether or not this “extra mass” measured by the FRM is water retained on the Teflon filters. The preliminary data for January suggest that sum of the chemical components is greater than the mass measured with the FRM. A potential explanation for this is volatilization of the nitrate aerosol from the FRM samples.

By comparing how concentrations change at sites within Pittsburgh and at satellite sites much further from Pittsburgh, it is possible to identify the relative importance of local sources. For example, Figure 4 shows 24-hour average airborne concentrations of  $PM_{2.5}$  mass determined gravimetrically using Teflon filters at five monitoring sites during the summer 01 intensive. The

sites include the main monitoring station next to CMU campus, as well as Lawrenceville, Hazelwood, Florence and Greensburg. Lawrenceville and Hazelwood are located within a few kilometers of the main site, both in heavily populated areas of the city with considerable automobile traffic. The Florence site is located about 50 kilometers west of the main site in a rural area with no nearby sources. The Greensburg site is about 50 kilometers east of the main site in a suburban area, close to a heavily traveled road but otherwise in an area of only moderate traffic with fewer stationary sources than in the city. Concentrations track each other well among these five sites, with



similar levels at the two rural sites (Florence and Greensburg) and at the three urban sites. This suggests that PM<sub>2.5</sub> mass at all five sites is determined mostly by the same sources, namely regional sources upwind of this area.

Figure 4. Time series of PM<sub>2.5</sub> mass measured at the central monitoring site and 4 satellite sites.

A similar finding is seen for airborne PM<sub>2.5</sub> sulfate, shown in Figure 5. In fact, the points at the five sites show closer agreement for sulfate than for PM<sub>2.5</sub> mass, suggesting that sulfate is influenced to a greater extent by regional sources upwind. This is a reasonable observation; since sulfate is known to be primarily a secondary pollutant that is influenced by sulfur emissions at least several hours transport time upwind. These emissions are mostly SO<sub>2</sub>. PM<sub>2.5</sub> mass, although containing a large fraction of sulfate, also contains other chemical species (nitrate, black carbon) that have significant local components in the city of Pittsburgh.

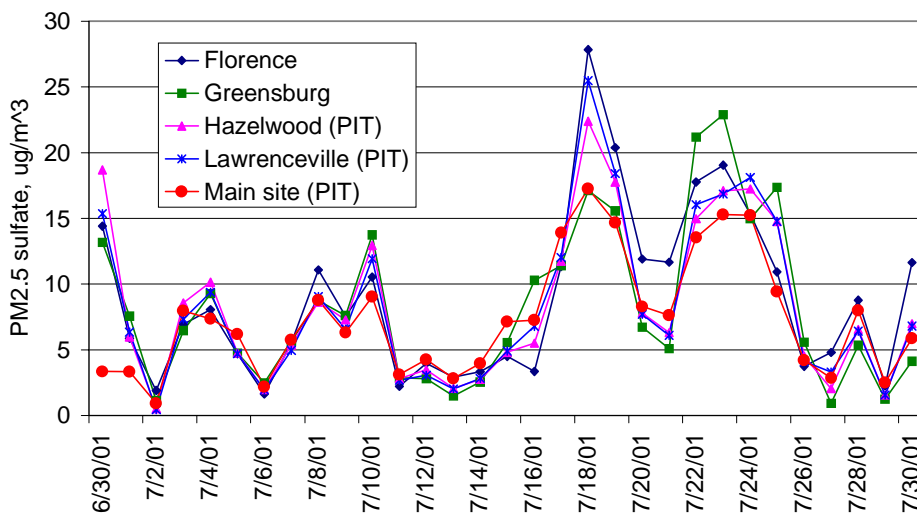


Figure 5. Time series of PM<sub>2.5</sub> sulfate measured at the central monitoring site and 4 satellite sites.

### Nucleation and Ultrafine Particles

The total particle number concentration and ultrafine particles at the central monitoring site appear to be dominated by nucleation bursts. The nucleation bursts vary in intensity from weak increases in the ultrafine and nuclei mode particle counts to very intense events which increase the overall number concentration from typically less than 20,000 per cm<sup>3</sup> to over 100,000 per cm<sup>3</sup> in a few hours. Figure 6 shows measurements of particle number concentration with time of a nucleation burst using Scanning Mobility Particle Sizers (SMPS).

Evidence of nucleation bursts can be seen on approximately 50% of the days. Figure 7 compares the diurnal pattern of total particle number concentration for days with and without nucleation events. The frequency and intensity of these nucleation bursts make them the single biggest factor in determining the number concentration of particles at the sampling site in Schenley Park, followed by traffic intensity, other local combustion, and regional transport as contributing factors.

In February of 2002, an additional SMPS system was brought online at Florence, Pennsylvania, approximately 45 km upwind of Pittsburgh in a rural area. The preliminary results from the Florence site suggest that the nucleation events are regional, and therefore will influence particle



counts and size distributions at least throughout Western Pennsylvania and may be in an even wider area.

A major challenge of the PAQS is to determine the chemistry and meteorology that govern these nucleation bursts. Nucleation events are most common on sunny days with low levels of preexisting aerosol. Other variables that appear to play a role are temperature, ozone, and  $\text{SO}_2$ . Viable theories to be considered include sulfuric acid-water nucleation, sulfuric acid-water-ammonia nucleation, and secondary organics. Data was tested against a theoretical nucleation and growth model for sulfuric acid-water nucleation which showed that gas-phase sulfuric acid production and condensation rates are probably too low to account for the observed nucleation.

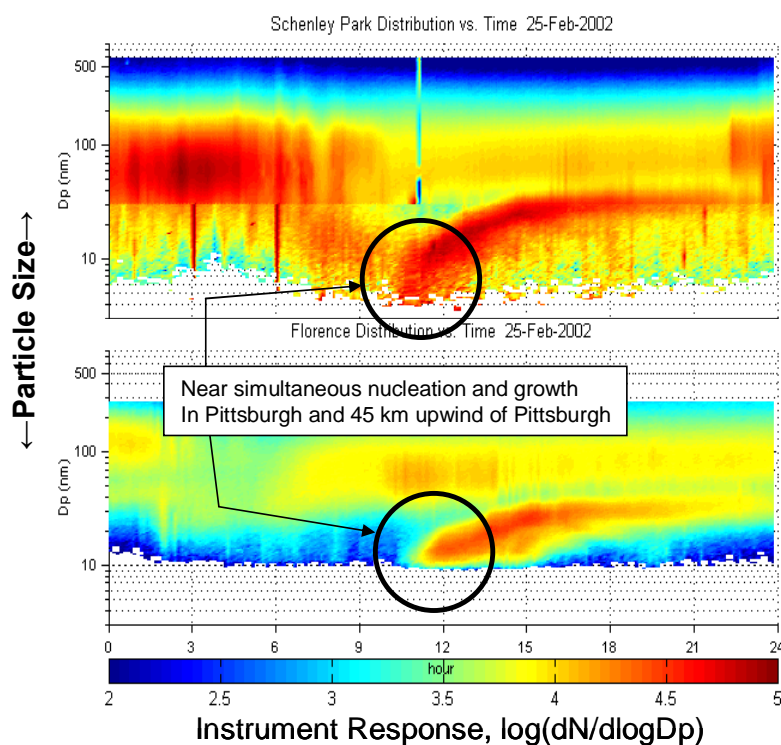


Figure 6. Comparison of measurements for February 25 from the Schenley Park (urban) site and Florence, PA (upwind, rural). The simultaneous nucleation at both sites has been seen several times since the Florence monitor was brought online in February.

The question will continue to be addressed by including the suite of gas-phase, meteorological, and particle-phase measurements being conducted at the Schenley Park and satellite sites such as 10-minute average sulfate, nitrate, and carbonaceous concentrations, 1-hour averaged inorganic

speciation, and 4-hour averaged organic carbon and elemental carbon speciation. Data from a size-segregated single-particle mass spectrometer operated by the University of California at Davis will also be included. Finally, hourly VOC concentrations measured by the University of California at Berkeley for selected portions of the study will be analyzed with respect to nucleation.

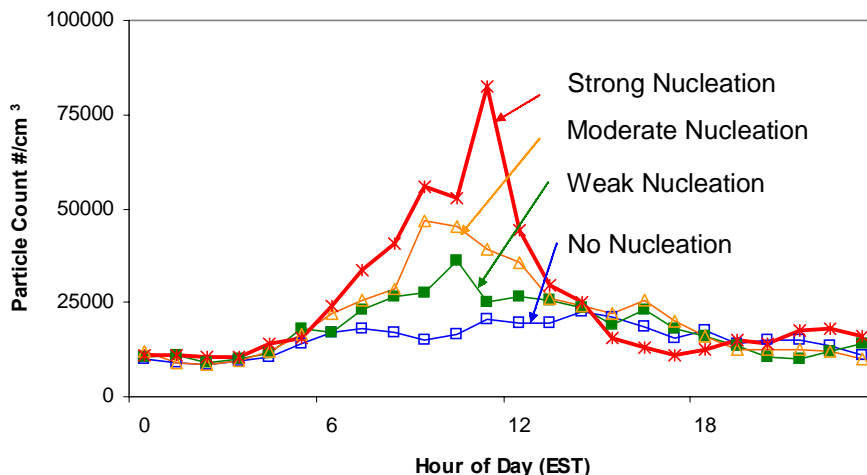


Figure 7. Total particle number concentration as a function of time of day for strong, moderate, weak, and no nucleation cases. Data is for the Schenley Park sampling station during July.

**Changes in Key Personnel Involved in the Project:** None.

**Expenditures to Date:** During the first two years of the project the Supersite team has used approximately all the budget for the corresponding period.

**Planned Activity for the Subsequent Reporting Period:** Major activities planned for the next quarter of the project include:

- Continuation of the baseline measurements
- March “nucleation” mini-intensive. Combination of the University of Southern California (Costas Sioutas) ultrafine particle concentrator with the single particle mass spectrometer to study the chemical composition of 20 nm particles during nucleation events.

- April mini-intensive for the “calibration” of the single particle mass spectrometer
- Continued analysis of the collected samples by the CMU team and its collaborators.
- Design of the source sampling and characterization experiments
- QA/QC of the July intensive data. Submission of the data files to EPA.

**Supplemental Key Words:** Airborne particulate matter, aerosol, size distribution, ultrafine, fine and coarse particles, atmospheric chemistry, source-receptor, measurement error, study design, epidemiology, regional modeling, source/receptor analysis, Pittsburgh, Ohio River Valley, Western Pennsylvania, photochemistry, meteorology, trajectory modeling, peroxides.

**Relevant Web Sites:** [homer.cheme.cmu.edu](http://homer.cheme.cmu.edu)