QUARTERLY PROGRESS REPORT

Cooperative Agreement Number R 82806101-0

Date of report: February 15, 2003

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

Principal Investigators: Spyros Pandis, Cliff Davidson, and Allen Robinson

Institution: Carnegie Mellon University

Project Period: September 16, 2002 - December 15, 2002

Investigators: Spyros Pandis, Cliff Davidson, Allen Robinson, Neil Donahue, Andrey Khlystov (*Carnegie Mellon Univ*.), Anthony Wexler (UC Davis), Murray Johnston (*Univ. of Delaware*), Wolfgang Rogge (*Florida Intern. Univ*.), Mark Hernandez, Joze Jimenez (*Univ. of Colorado*), Jeff Collett (*Colorado State Univ*.), Susanne Hering (*Aerosol Dynamics*), Jonathan Kahl (*Univ. Wisconsin*), Barbara Turpin (*Rutgers Univ*.), Bruce Doddridge, John Ondov, Steven Buckley (*Univ. of Maryland*), *RJ Lee, Inc.,* Kevin Crist (*Ohio University*), Delbert Eatough (*Brigham Young University*), Urs Baltensperger (*Paul Scherrer Inst*.), Phil Hopke (Clarkson U.), Jonathan Samet (*Johns Hopkins*), Allen Goldstein (UC Berkeley), Doug Worsnop (Aerodyne), William Aljoe (*DOE-NETL*).

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: The ambient sampling phase (Phase II) of the Pittsburgh Air Quality Study was succesfully completed in the end of September 2002. Approximately sixteen months of data were collected, including three intensive sampling periods (July 2001, January 2002, and July 2002) and several special experiments (instrument intercomparison, nucleation, etc). We are currently in the third phase of the study (Source Characterization) with measurements in one of the biggest coke facilities in North America and in the Squirrel Hill tunnel in Pittsburgh. The sampling station was removed from Schenley Park in November 2002. Several instruments were moved to the roof of the CMU Business School

and continue to operate providing "background" measurements for the source studies. In parallel the PAQS team is analyzing the collected data and is testing the hypotheses that have motivated the study.

The analysis of the collected samples during PAQS is proceeding according to schedule. We have finished the analysis of the major inorganic ions (CMU Speciation Sampler, PC-BOSS), the OC and EC (three CMU samplers and PC-BOSS), the mass concentrations (FRM, Dichotomous Sampler, and MOUDI impactor). The results of the continuous instruments have been corrected. Most of the data from the single particle spectrometer has been analyzed and processed. There is a small backlog only for the analysis of the metals, the bio-aerosols, and the organic speciation (because of the labor-intensive nature of the analysis). Most of the data have been loaded to the PAQS database and are currently undergoing QA/QC. The data are in the NARSTO format. A series of datafiles have been submitted to the NARSTO archive and the EPA Supersites relational database.

The analysis of the data is underway. The PAQS team submitted 6 papers to the first PM Supersites special issue in Aerosol Science and Technology. The papers have been reviewed and are currently revised. We are planning to submit 13 more papers to the second special issue in Atmospheric Environment in the end of February. Tentative titles are given in the end of this report. The PAQS team contributed four papers to the PM Supersite session in the Fall 2002 meeting of the American Geophysical Union. Details are provided in the publications and presentations section.

We completed the characterization of a major coke facility and the local transportation emissions. The emissions of the coke facility were characterized using fence monitoring techniques. The use of fast response instruments (SMPS-size distributions, semi-continuous OC/EC, semi-continuous metals, semi-continuous inorganic ions, gas-phase analyzers) allowed us to derive the composition and size distribution fingerprint of the source. The single particle mass spectrometer identified a class of particles that appears to be unique to this source. This exciting finding may allow us to identify in the ambient dataset single particles that came from the coke facility. The concentrations of gas and particulate phase pollutants in the Squirrel Hill tunnel in Pittsburgh were monitored for approximately one month. Measurements included major inorganic ions, OC and EC,

organic speciation, metals and crustal elements, single particle mass spectra, and a full suite of gas-phase measurements. Three periods were investigated: the morning rush hour dominated by automobile emissions, the nighttime traffic dominated by diesel truck emissions, and the daytime period. Traffic information (number of automobiles, trucks, average speed) and carbon dioxide concentrations in the tunnel were measured and will be used for the analysis of the results.

Results: The main findings of the PAQS papers submitted to the first PM Supersites special issue are summarized below.

The EC tracer method is applied to a series of measurements by different carbonaceous aerosol samplers in the Pittsburgh Air Quality Study (PAQS) in order to estimate the concentration of secondary organic aerosol. High-resolution measurements (2-6 hrs) and daily averaged concentrations were collected during the summer 2001 intensive (July 1 to August 4, 2001) and are used for the analysis. The various samplers used during PAQS show differences in the measured concentrations of OC and EC due to the different sampling artifacts and sampling periods. A systematic approach for the separation of periods where SOA contributes significantly to the ambient OC levels from the periods where organic and elemental carbon concentrations are dominated by primary emissions is proposed. Ozone is used as indicator of photochemical activity to identify periods of probable secondary organic aerosol production in the area. Gaseous tracers of combustion sources (CO, NO, and NO_x) are used to identify periods where most of the OC is primary. Periods dominated by primary emissions are used to establish the relationship between primary OC and EC, a tracer for primary combustion-generated carbon for the different sets of measurements for July 2001. Around 35% of the organic carbon concentration in Western Pennsylvania during July of 2001 is estimated to be secondary in origin. **(Cabada et al., AS&T, 2003)**

During the Pittsburgh Air Quality Study (PAQS) aerosol size distributions between 3 nm and 680 nm were measured between July 2001 and June 2002. These distributions have been analyzed to assess the importance of nucleation as a source of ultra-fine particles in Pittsburgh and the surrounding areas. The analysis shows nucleation on 50% of the study days and regional-scale formation of ultra-fine particles on 30% of the days. Nucleation occurred during all seasons, but was most frequent in fall and spring, and least

frequent in winter. Regional nucleation was most common on sunny days with below average $PM_{2.5}$ concentrations. Local nucleation events were usually associated with elevated SO_2 concentrations. The observed nucleation events ranged from weak events with only a slight increase in the particle number to relatively intense events with increases of total particles counts between 50,000 cm^{-3} up to 150,000 cm^{-3}. Averaging all days of the study, days with nucleation events had number concentrations peaking at around noon at about 45,000 cm^{-3}. This is compared to work days without nucleation when the daily maximum was at 8 AM at 23,000 cm^{-3} and to weekends without nucleation when the daily maximum was at noon at 16,000 cm^{-3}. 24-hour average number concentrations were approximately 40% higher on days with nucleation compared to those without. Nucleation was typically observed starting around 9 AM EST, although the start of nucleation events was later in winter and earlier in summer. The nucleation events are fairly well correlated with the product of [UV intensity times SO_2 concentration], and also depend on the effective area available for condensation. This indicates that H_2SO_4 is a component of the new particles. Published correlations for nucleation by binary H_2SO_4-H_2O can not explain the observed nucleation frequency and intensity, suggesting that an additional component (perhaps ammonia) is participating in the particle formation. **(Stanier et al., AS&T, 2003a)**

Hygroscopic growth of atmospheric particles affects a number of environmentally important aerosol properties. Due to the hysteresis exhibited by the aerosol hygroscopic growth, the physical state of particles and the amount of aerosol water is uncertain within a wide range of relative humidity found in the troposphere, leading to uncertainties in optical and chemical properties of the aerosol. Here we report the design and tests of an automated system (Dry Ambient Aerosol Size Spectrometer, DAASS) that was built to assess the amount of aerosol water at given atmospheric conditions. The system consists of two Scanning Mobility Particle Sizers (SMPS) and an Aerodynamic Particle Sizer (APS) that measure the aerosol size distribution between 5 nm and 10 μm in diameter. The inlets of the instruments and their sheath air lines are equipped with computer controlled valves that direct air through Nafion dryers or bypass them. The Nafion dry the air stream to below 30% RH at which point ambient particles are expected to lose most or all water and thus be virtually dry. The switch between the dried and the ambient conditions occurs

every 7 minutes and is synchronized with the scan times of the aerosol spectrometers. In this way the system measures alternatively dried (below 30% RH) and ambient aerosol size distributions. A comparison of the ambient RH and the dried RH size distributions and the corresponding integrated volume concentrations provides a measure of the physical state of particles and the amount of aerosol water. **(Stanier et al., AS&T, 2003b)**

A simple algorithm was developed to combine electrical mobility and aerodynamic size distribution data into a single distribution. This algorithm was tested during July 2001 with the Pittsburgh Air Quality Study by comparing size distributions measured using an SMPS-APS combination with simultaneous measurements using a MOUDI cascade impactor and $PM_{2.5}$ mass concentration measurements using a TEOM. The algorithm provides results that agree with both the impactor and TEOM measurements. As a result of this comparison, the ambient aerosol in Pittsburgh in July 2001 was found to have density of 1.5±0.3 g cm^{-3} and, on average, shape factor of 1.2. **(Khlystov et al., AS&T, 2003)**

The Positive Matrix Factorization (PMF) method was applied to the particle size distribution data acquired during the Pittsburgh Air Quality Study (PAQS) from July 2001 to August 2001. After removing those days with nucleation events, a total of 1632 samples each with 165 even-sized intervals from 0.003 to 2.5 micrometers were obtained from Scanning Mobility Particle Spectrometer (SMPS) and Aerodynamic Particle Sizer (APS). The temporal resolution was 15 minutes. The values of each set of five consecutive size bins were summed to produce 33 new size channels. The size distributions of particle number as well as volume were analyzed with a bilinear model. Three kinds of information were used to identify the sources: the number and volume size distributions associated with the factors, the time frequency properties of the contribution of each source (Fourier analysis of source contribution values) and the correlation of the contribution values with the gas-phase data. Through these analyses, the sources were assigned as secondary aerosol, stationary combustion, grown particles and remote traffic, local traffic, and sparse nucleation, in order of increasing number concentration contributions. Conditional probability function (CPF) analysis was performed for each source so as to ascertain the likely directions in which the sources were located **(Zhou et al., AS&T, 2003)**.

Publications:

1. J. C. Cabada, S. N. Pandis, and A. L. Robinson (2002) Sources of atmospheric particulate matter in Pittsburgh, Pennsylvania, JAWMA, 52, 732-741.
2. C. O. Stanier, A. Khlystov, and S. N. Pandis (2002) Chemical processes and long-range transport of aerosols: Insights from the Pittsburgh Air Quality Study, in *Long Range Transport of Air Pollution,* Kluwer.
3. Subramanian R., A. Y. Khlystov, J. C. Cabada-Amaya, and A. L. Robinson (2003) Sampling artifacts during measurement of ambient carbonaceous aerosol, *Aerosol Sci. Technol.,* (submitted).
4. Cabada J. C., S. N. Pandis, A. L. Robinson, R. Subramanian, A. Polidori, and B. Turpin (2003) Estimating the secondary organic aerosol contribution to PM2.5 using the EC tracer method, *Aerosol Sci. Technol.,* (submitted).
5. Stanier C. O., A. Y. Khlystov, and S. N. Pandis (2003a) Nucleation events during the Pittsburgh Air Quality Study: Description and relation to key meteorological, gas phase, and aerosol parameters, *Aerosol Sci. Technol.,* (submitted).
6. Stanier C. O., A. Khlystov, W. R. Chan, M. Mandiro, and S. N. Pandis (2003b) A method for the in-situ measurement of aerosol water content of ambient aerosols: The Dry Ambient Aerosol Size Spectrometer (DAASS), *Aerosol Sci. Technol.*, (submitted).
7. A Khlystov, C. O. Stanier, and S. N. Pandis (2003) Aerosol size distribution measurements from 3 nm to 10 μm: Instrument performance and particle properties, *Aerosol Sci. Technol.,* (submitted).
8. Zhou L. and P. Hopke (2003) The Advanced Factor Analysis on Pittsburgh particle size distribution data, *Aerosol Sci. Technol.,* (submitted).
9. Rees S. L., A. L. Robinson, A. Khlystov, C. O. Stanier, and S. N. Pandis (2003) The PM2.5 Federal Reference Method (FRM) and the chemical mass balance for fine particulate matter, *Aerosol Sci. Technol.,* (in preparation).
10. Wittig B., A. Y. Khlystov, S. Takahama, S. N. Pandis, S. Hering, B. Kirby, and C. Davidson (2003) Semi-continuous PM2.5 inorganic composition measurements during the Pittsburgh Air Quality Study, *Atmos. Environ.* (submitted).

11. Subramanian R. , A. Y. Khlystov, B. J. Turpin, A. L. Robinson (2003) Measurement of Ambient Carbonaceous Aerosols During the Pittsburgh Air Quality Study, *Atmos. Environ.* (in preparation).
12. Khlystov A. Y., C. O. Stanier, and S. N. Pandis (2003) In-situ continuous PM water concentrations measurements, *Atmos. Environ*., (in preparation).
13. Stanier C. O., A. Y. Khlystov, and S. N. Pandis (2003) Aerosol size distribution climatology, *Atmos. Environ.* (in preparation).
14. Cabada J. C., S. Rees, S. Takahama, A. Y. Khlystov, W. Tang, C. Davidson, and S. N. Pandis (2003) Aerosol size-composition distributions during PAQS, *Atmos. Environ.*, (in preparation).
15. Vayenas D., S. Takahama, and S. N. Pandis (2003) Formation and removal of ammonium nitrate and its precursors: System responses to emission changes, *Atmos. Environ.*, (in preparation).
16. Takahama S., D. Vayenas, S. N. Pandis, and C. Davidson (2003) Evaluating the aerosol equibrium assumption in an urban area in the Northeastern US, *Atmos. Environ.*, (in preparation).
17. Eatough D. and C. Davidson (2003) Meteorological influence on, and diurnal patterns in ambient fine particulate chemical composition at two sampling sites in metropolitan Pittsburgh: A 2001 intensive summer study, *Atmos. Environ.*, (in preparation).
18. Eatough D. and C. Davidson (2003) Source apportionment of $PM_{2.5}$, organic material and sulfate during the July 2001 summer intensive, *Atmos. Environ.*, (in preparation).
19. Gaffney J. et al. (2003) Natural radionuclides in fine aerosols in Pittsburgh, *Atmos. Environ.*, (in preparation).
20. Rogge W. et al. (2003) Organic PM2.5 at the Pittsburgh Supersite: Regional versus local concentrations and seasonal variations, *Atmos. Environ.*, (in preparation).
21. Cabada J. C., A. Khlystov, B. Wittig, and S. N. Pandis (2003) Fine particle light scattering reconstruction and measurements at PAQS, *Atmos. Environ.* (in preparation).

Presentations:

1. "Investigation of nucleation bursts in the Pittsburgh air quality study", 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (C. O. Stanier, A. Y. Khlystov, and S. N. Pandis).
2. "Monitoring of water content of ambient aerosol during the Pittsburgh Air Quality Study" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (A. Y. Khlystov, C. O. Stanier, D. Vayenas, and S. N. Pandis).
3. Performance of the Aerodynamic Particle Sizer 3320 during the Pittsburgh Air Quality Study (PAQS)" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (A. Khlystov, C. Stanier, and S. N. Pandis).
4. "Sulfate-ammonia-nitric acid interactions in an urban area" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (S. Takahama, A. Khlystov, B. Wittig, S. V. Hering, C. Davidson, A. Robinson, and S. N. Pandis).
5. "Sampling artifacts during measurement of ambient carbonaceous aerosol" 6th International Aerosol Conference, Taipei, Taiwan, September 2002 (R. Subramanian, A. Y. Khlystov, J. C. Cabada, S. N. Pandis, and A. L. Robinson).
6. "Formation and properties of regional aerosol: Some insights from the Pittsburgh Air Quality Study", NASA-GSFC, Greenbelt MD, May 2002,(C. Stanier, A. Khlystov, S. Rees, J. Cabada, A. Robinson, C. Davidson, and S. N. Pandis)
7. "Seasonal composition of PM2.5 and performance of the Federal Reference Method in Pittsburgh", PM2.5 and Electric Power Generation, Pittsburgh, April 2002 (S. L. Rees, S. Takahama, A. L. Robinson, A. Khlystov, and S. N. Pandis).
8. "Continuous measurements of ammonia, sulfate, and nitrate in Pittsburgh: Implications for PM2.5 control strategies", PM2.5 and Electric Power Generation, Pittsburgh, April 2002 (B. Wittig, A. Khlystov, S. Takahama, C. Davidson, A. Robinson, S. Hering, and S. N. Pandis).
9. "The contribution of long-range transport and secondary organic aerosol to PM2.5 in Pittsburgh", PM2.5 and Electric Power Generation, Pittsburgh, April 2002 (J. C. Cabada, R. Subramanian, S. N. Pandis, A. L. Robinson, W. Tang, N. J. Anderson, T. Raymond, and C. I. Davidson).

10. "The Dry-Ambient Size Spectrometer: A new technique for the automatic on-line measurement of the atmospheric aerosol water size distribution", Annual Meeting of American Geophysical Union, San Francisco, December 2001 (A. Khlystov, C. O. Stanier, S. N. Pandis).
11. "The July 2001 intensive of the Pittsburgh Air Quality Study", Annual Meeting of AAAR, Portland, Oregon, October 2001 (C. I. Davidson, A. L. Robinson, and A. Khlystov, S. N. Pandis).
12. "Sources of atmospheric carbonaceous particulate matter in Pittsburgh", Annual Meeting of AAAR, Portland, Oregon, October 2001 (J. Cabada, S. N. Pandis and A. L. Robinson).
13. "Automated measurements of dry and wet ambient aerosol distributions", Annual Meeting of AAAR, Portland, Oregon, October 2001 (A. Y. Klhystov, W. R. Chan, C. O. Stanier, M. Mandiro, and S. N. Pandis)
14. "Continuous measurements of ammonia and ammonium in ambient air", Annual Meeting of AAAR, Portland, Oregon, October 2001 (A. Khlystov, J. Sauser, R. Otjes, and S. N. Pandis).
15. The contribution of secondary organic aerosol to PM2.5 concentrations in Pittsburgh, AGU Fall Meeting 2002, San Francisco CA Dec. 2002 (J. C. Cabada, S. N. Pandis, A. L. Robinson, R. Subramanian, A. Polidori, and B. Turpin).
16. Preliminary results from the Pittsburgh Air Quality Study, AGU Fall Meeting 2002, San Francisco CA Dec. 2002 (S. N. Pandis, C. I. Davidson, A. L. Robinson, and A. Y. Khlystov)
17. Monitoring of water content of ambient aerosol during the Pittsburgh Air Quality Study, AGU Fall Meeting 2002, San Francisco CA Dec. 2002 (A. Y. Khlystov, C. O. Stanier, D. Vayenas, and S. N. Pandis)
18. Investigation of nucleation bursts during the Pittsburgh Air Quality Study, AGU Fall Meeting 2002, San Francisco CA Dec. 2002 (C. O. Stanier, A. Y. Klhystov, B. Wittig, S. N. Pandis, Y. Zhou, K. Bein, A. S. Wexler, C. Misra, and C. Sioutas)

Changes in Key Personnel Involved in the Project: None

Expenditures to Date: During the first eleven quarters of the project the Supersite team has used the entire budget for the corresponding period.

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

- Continued analysis of the collected samples by the CMU team and its collaborators.
- Preparation and submission of papers for the second PM Supersite special issue in Atmospheric Environment.
- Continuation of the source sampling and characterization experiments
- Modeling of the July 2001 intensive using a three dimensional chemical transport model (PMCAMx).
- QA/QC of the 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