QUARTERLY PROGRESS REPORT

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

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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: After the end of the July 2001 intensive measurement period (ESP01) the Supersite measurements returned to the baseline measurement schedule. This baseline schedule has been significantly enhanced compared to the original plan including 38 out of the 47 intensive period measurements (please see our August 2001 report for details). The next intensive is planned for January 2002.

The PAQS team participated in the data analysis meeting of all Supersites in RTP (November 2001) and presented some of the most interesting results so far. A brief summary of these findings follows.

The measured aerosol components (sulfate, nitrate, ammonium, sodium, organics, black carbon, crustal elements) can explain on average 90% of the measured $PM_{2.5}$ mass concentration for July and August. However, significant discrepancies were observed during the days of the highest $PM_{2.5}$ concentrations. During these days the FRM $PM_{2.5}$ exceeded the sum of the concentrations of the major components by as much as 40%. The excellent agreement among the three mass concentration measurements (FRM, Dichot, 30^{o}C TEOM) in the Supersite and the additional two $PM_{2.5}$ mass concentration measurements in Pittsburgh indicate that these differences are real and cannot be explained by experimental errors. Our hypothesis is that the additional mass is water associated with ammonium bisulfate during these periods. This hypothesis is tested using a variety of tools (both additional measurements and theory).

The frequency of nucleation events (formation of ultrafine particles by gas-to-particle conversion) increased significantly in the fall. During October we observed approximately two such events per week. Analysis of these events indicates that they occur when there is significant sunlight, the temperature exceeds 5^{o}C, and the $PM_{2.5}$ concentration is less than 20 $\mu g\ m^{-3}$. We have two hypotheses to explain these events: nucleation of sulfuric acid/ammonium/water particles or nucleation of organics. A set of experiments using the ultrafine particle concentrator of the Sioutas group (Los Angeles Supersite) and the single particle mass spectrometer are planned for the spring to test these hypotheses. An additional SMPS system will also be installed in the Florence site (50 miles from the Central Site) to investigate the spatial extent of these events.

The performance of the continuous instruments (R&P sulfate, R&P nitrate, Sunset continuous OC/EC, 30^{o}C TEOM with dryer, CMU steam sampler) was very good during the summer and early fall months. During these two seasons and for the $PM_{2.5}$ composition in Pittsburgh their results appear to be in good agreement with the traditional filter measurements.

The $PM_{2.5}$ concentration and composition measurements in the four satellite sites indicate that the regional contribution dominated $PM_{2.5}$ in Pittsburgh during July 2001. Practically all the

sulfate, and 80% or more of the organic particulate matter was transported to Pittsburgh. The city was responsible (on average) for half of the elemental carbon and nitrate concentrations. The local contributions became more important during the few stagnation periods, but on average long range transport was the most important source. This resulted in negligible concentration differences among the three sites in Pittsburgh ensuring that the Supersite measurements are representative of the average composition in the metropolitan area.

The continuous measurements of the aerosol liquid water content (using the CMU Dry/Ambient Aerosol Spectrometer, DAAS) showed that the ambient particles in Pittsburgh have significant aerosol water even at RH as low as 20%. Theoretical analysis of the results shows that some of the particles are wet and some are solid when the RH is between 20 and 70%. A Tandem Differential Mobility Analyzer will be used next summer to quantify these effects.

The semi-continuous metal concentration measurements of the Ondov group illustrated the short-term effect of local sources on the measured PM2.5 concentrations. These measurements are currently used by Hopke and his team to identify local sources affecting occasionally the central site and also for the quantitative apportionment of the measured primary $PM_{2.5}$.

The speciation of the organic aerosol by the Rogge group shows that a variety of compounds, as expected, are present in the Pittsburgh aerosol including C12-C34 alkanes, C7-C32 alkanoic acids, C16 and C18 alkenoic acids, several aliphatic dicarboxylic acids, several aromatic polycarboxylic acids, furanones, alkylcyclohexanes, PAHs, etc. A number of tracer compounds have been quantified including levoglucosan, cholesterol, benzothiazole, pinonic acid, etc. The analysis of these samples continues.

Use of the elemental carbon concentrations as a tracer for the primary organic carbon concentration, suggests that for July 2001 roughly one third of the measured organic particulate matter was of secondary origin. For specific days the secondary organic aerosol varied from practically zero to more than 60% of the total organic aerosol levels.

The continuous nitric acid and nitrate measurements showed that most of the atmospheric nitrate exists in the gas phase during the daytime in the summer. The removal of nitric acid by dry deposition is quite fast and the overall nitrate concentrations remain low. During the night

almost of the available nitrate moves to the particulate phase and its removal is slowed down. Additional nitrate is produced during the night by the reaction of NO_2 and O_3. The transfer of nitrate between the gas and the particulate phases as well as the dependence of its lifetime on this partitioning are currently investigated using a number of modeling approaches. Our hypothesis is that these interactions will have a strong effect on the efficiency of future SO_2 and NO_x emission controls.

The single particle mass spectrometer has been operating in the central site since the end of September. The fall results indicate the presence of several particle groups that can be used for the source apportionment of $PM_{2.5}$. A mini-intensive study is currently planned for the winter to "calibrate" this instrument, and to translate its semi-quantitative results to actual size/composition distributions.

Changes in Key Personnel Involved in the Project: Prof. Allen Goldstein and his team from the University of California in Berkeley have been added to the team. They will measure VOC concentrations (including oxygenates) every hour during the winter intensives as well as during selected periods in the spring and summer of 2002.

Expenditures to Date: During the first twenty one months 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 eighth quarter of the project include:

- Winter intensive measurement period in the first three weeks of January
- Continuation of the baseline measurements
- Continued analysis of the collected samples by the CMU team and its collaborators.
- PAQS data analysis and synthesis meeting in December
- Design of the source sampling and characterization experiments
- QA/QC of the July intensive data. Preparation of the data files for submission 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