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RELATIONSHIPS: THE ROLE OF COAL-FIRED  
POWER PLANTS

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## Executive Summary

This report describes the technical progress made on the Pittsburgh Air Quality Study during the period of February through July of 2001. The major effort during this period involved the set-up and initiation of the ambient monitoring campaign. The central sampling station next to the Carnegie Mellon University in Scheleny Park was completed. Baseline measurements began on June 1, 2001, and the first intensive sampling period occurred between June 30, 2001 and August 3, 2001. Data were collected at both the central site and a set of satellite sites surrounding Pittsburgh.

Preliminary examination of the data has been initiated. This report presents results of PM-2.5 mass and chemical composition measured on a 24-hr basis for the July intensive period. The average PM-2.5 concentration at the central monitoring site for the July intensive was  $23 \mu\text{g}/\text{m}^3$ . The variation in PM-2.5 levels indicates that a wide range of atmospheric conditions occurred during the month of July, and, therefore, the data will be useful for evaluating the performance of air quality models over a range of conditions. During July, the major chemical components of the PM-2.5 mass are sulfate and organic material. Elemental carbon and nitrate only contribute a small part of the PM-2.5 mass on a 24-hr average basis.

Comparing the measured PM-2.5 mass and the sum of the chemical components indicates problems with the mass balance. The total measured mass tends to be larger than the sum of the major chemical components at high PM levels, and smaller than the sum of the components at low PM levels. There are many potential explanations for the observed discrepancies; however, preliminary data suggests that water may be source of the mass balance discrepancy at high PM levels.

## Activity 1. Project Management

During this project period, subcontracts were negotiated and set-up between Carnegie Mellon University and the principle subcontractors: University of Maryland College Park, University of California at Davis, University of Delaware, Clarkson University, Ohio University, Brigham Young University, and Rutgers University. Subcontracts have not yet been set up with RJ Lee Group and the University of California at Davis due to insufficient funds.

## Activity 2. Ambient Monitoring

The purpose of this activity is to create an extensive database of ambient PM measurements for source apportionment, examination of aerosol processes, and air quality model development and evaluation. During this project period, a sampling station next to the Carnegie Mellon University in Scheleny Park was completed. This station houses the central monitoring site for the project. Baseline measurements were on June 1, 2001, and are scheduled to continue through October 2002. The first intensive was also conducted during this project period, the intensive started on June 30, 2001 and ended on August 3, 2001. As part of the EPA PM-2.5 speciation network, samples were also collected at satellite sites in Lawrenceville and Hazelwood neighborhoods of Pittsburgh, and Florence, PA and Greensburg PA. Carnegie Mellon University collected daily samples at each of these satellite sites during July intensive period. The Athens OH satellite site was operated by Ohio University during this project period as part of the DOE Upper Ohio River Valley Project. Support for this site is scheduled to be transferred over to the Pittsburgh Air Quality Study in August of 2001.

### *Preliminary Results*

This section presents some *preliminary* results from the July intensive sampling period to provide an overview of the atmospheric conditions during this period. The July intensive is a particularly important period of the investigation because it involved the coordination of a large number of research projects across the Eastern United States to collect a large data set for model evaluation.

A more thorough examination of the data collected during July including testing of hypotheses described in the proposal is currently underway and will be presented in subsequent progress reports. Preliminary validation has been performed on the data presented here, such as the application of calibration factors and the elimination of problem data associated with instrument malfunction. Further validation is currently underway.

Figure 1 presents daily PM-2.5 mass at the central sampling site measured using the Federal Reference Method (FRM). The average PM-2.5 concentration at the central monitoring site for the July intensive was  $23 \mu\text{g}/\text{m}^3$ . The variation in PM-2.5 levels indicates that a wide range of atmospheric conditions occurred during the month of July,

and, therefore, that the data will be useful for evaluating the performance of air quality models over a range of conditions.

Also shown on Figure 1 are 24-hour averages of the major chemical components of PM-2.5 measured at the central site. Data are shown for sulfate, nitrate, ammonium, organic carbon, and elemental carbon. The organic carbon data are the total mass of the organic material determined by multiplying the measured organic carbon mass by a factor of 2. The factor of 2 is an estimate of the contribution of H, N, O, and S to the total mass of the organic material (Turpin and Lim 2001). The data for the metal concentrations of the PM-2.5 were not available in time to include in this report; however, metals typically make up only a small fraction of the total PM-2.5 mass.

The data in Figure 1 indicate that during the summertime the major chemical components of the PM-2.5 mass are sulfate and organic material. Elemental carbon and nitrate only contribute a small part of the PM-2.5 mass on a 24-hr average basis.

The data shown in Figure 1 allow examination of the PM-2.5 mass balance -- whether or not the sum of the measured chemical components is equal to the PM-2.5 mass measured using the FRM. This is one of the hypotheses to be examined by the project. The data indicate a correlation between the FRM mass and the sum of the chemical components; however, the FRM mass tends to be larger than the sum of the major chemical components at high PM levels, and smaller than the sum of the components at low PM levels. This trend is clearly shown in Figure 2, which presents a plot of the ratio of PM-2.5 mass measured with the FRM to the sum of the major chemical components.

There are many potential explanations for the discrepancy between the FRM and the measured chemical composition shown in Figure 2. When the FRM mass is less than the sum of the components the difference could be due to loss of semi-volatile material (e.g. nitrate or organic material) from the FRM sample, which might occur during the 24-hr equilibration procedure before gravimetric analysis. Another potential explanation is a positive sampling artifact that causes one of the composition measurements to overestimate the levels of a particular component. For example, it is well documented that there can be a substantial positive artifact of organic material caused by the adsorption of organic vapors onto a quartz fiber filter (Turpin, Saxena et al. 2000). When the FRM mass is greater than the sum of the components, the difference could be due to missing component in the mass balance. As previously stated, the mass balance does not include the metal components of the PM-2.5; however, it is unlikely that metals will contribute enough mass to close the mass balance. For example, the data on 8/3/01 indicate 15  $\mu\text{g}/\text{m}^3$  of missing mass from the sum of the chemical components. A more likely explanation to the missing mass is water, which is supposed to be removed from the sample before gravimetric analysis by the equilibration procedure specified in the FRM. Data are available to examine each of these potential explanations.

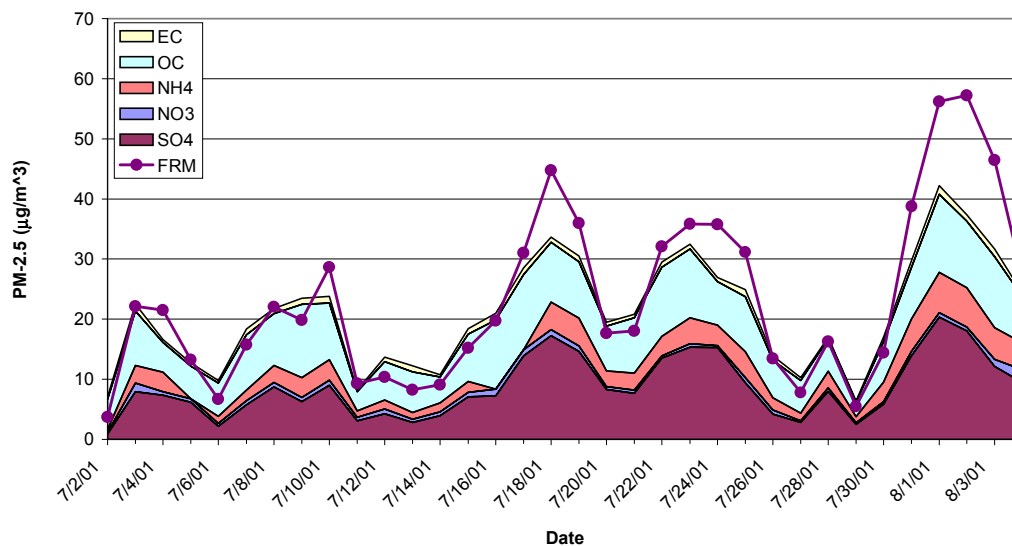


Figure 1. The PM-2.5 mass measured with the FRM and the major chemical components of the PM-2.5 at the central monitoring site during the July intensive sampling period.

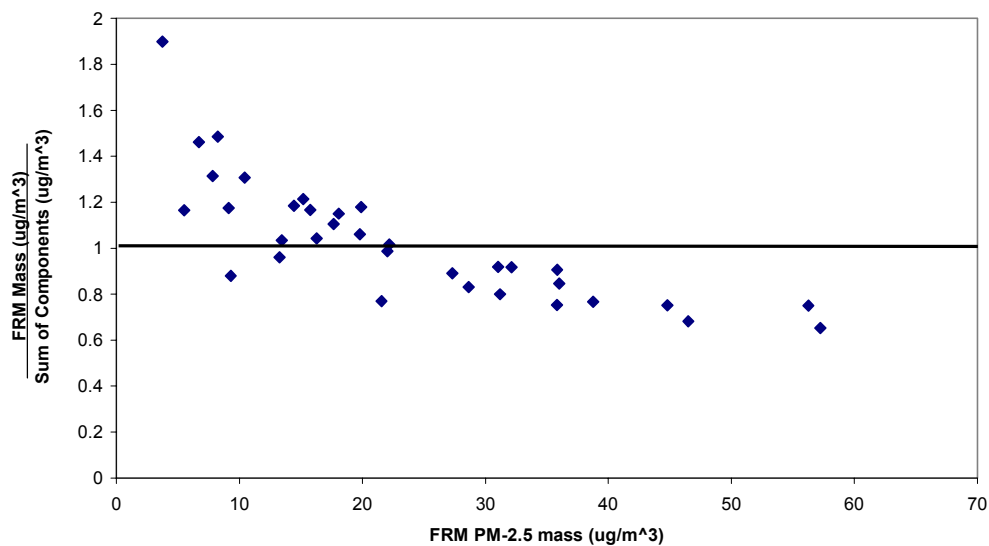


Figure 2. Ratio of PM-2.5 mass measured with the FRM to the sum of the major chemical components of the PM-2.5 as a function of the measured PM-2.5 mass. A value of 1 indicates that the closure of the mass balance – that the sum of the individual component species is equal to the total mass.

We now examine the issue of whether or not water is potential source of some of mass balance problems, to illustrate how the data from other measurements will be used to examine this mass balance question. Instrumentation at the central site has been set up to measure the wet and dry particle size distribution. These measurements allow the calculation of the total wet and dry particle volume. Preliminary results from these measurements are shown in Figure 3, which presents a time series of wet and dry particle volume for the July intensive sampling period. Large differences in between wet and dry volume indicate the aerosol includes significant water – the data indicate that at times, such as the period around July 18, as much as 50% of the aerosol mass is water. These periods typically occur with high relative humidity. Comparing the results in Figure 3 with the time series of PM-2.5 mass shown in Figure 1 indicates that the periods of high water content appear correlated with the unexplained peaks in the PM-2.5 mass measured with the FRM.

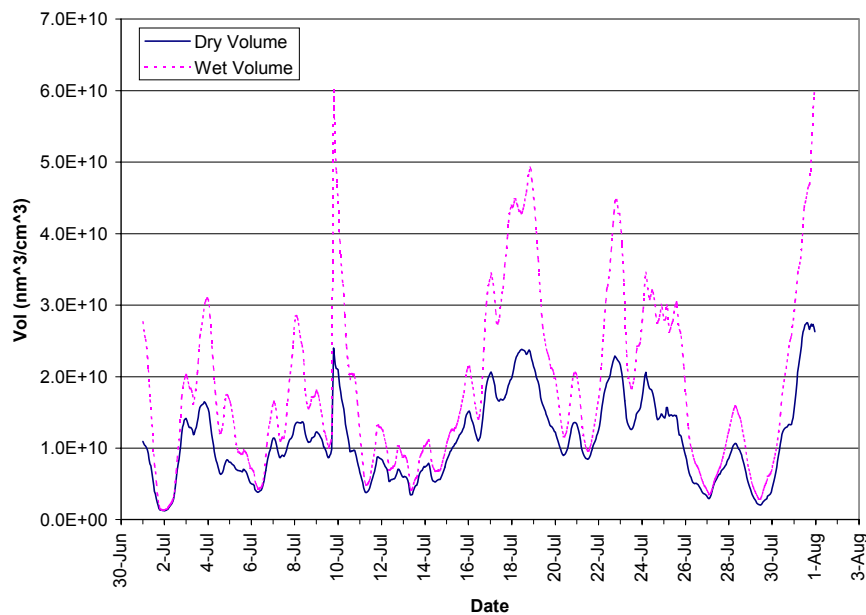


Figure 3. Time series of the measured wet and dry aerosol volume during the July intensive sampling period.

## Ambient Monitoring Activity

### *Activity 2.1 PM Size Distributions*

Carnegie Mellon University is operating an instrument that measures wet and dry PM size distribution from 3 nm to 20  $\mu\text{m}$ . Three wet and three dry distributions are measured each hour. This sampler will be operating during the entire ambient sampling period.



### *Activity 2.2 Size-resolved PM Mass and Composition*

During the baseline-sampling period, Carnegie Mellon University made daily 24-hr measurements of size-resolved PM mass using Micro-Orifice Uniform Deposit Impactors (MOUDI). During the July intensive sampling period, Carnegie Mellon University made daily 24-hr measurements of size-resolved PM mass and chemical composition (OC/EC and major ions) using Micro-Orifice Uniform Deposit Impactors (MOUDI). During the intensive two impactors were operated: one with aluminum foils to determine OC/EC via thermal analysis and another with Teflon filters for determination of mass and ions via ion chromatography.

### *Activity 2.3 Advanced Characterization of PM<sub>2.5</sub> Chemical Composition*

**Activity 2.3.1 Sampling Artifacts:** Brigham Young University installed the PC-BOSS diffusion denuder sampler at the central monitoring site. This sampler was operated during the July intensive collecting 5 samples per day to examine loss of semivolatile organics from particles during sampling. In addition, analyses will be conducted for sulfate, nitrate, ammonium, and acidity.

**Activity 2.3.2 Organic Aerosol Characterization:** During the intensive period, Rutgers University collected size-resolved samples using Hering Low Pressure Impactor on Zinc Selenide substrates for analysis with Fourier Transform Infrared Spectroscopy (FTIR). These size resolved samples were collected on a 1 in 3 day frequency. Rutgers University also collected daily 24-hr high volume samples for analysis of organic mass, functional groups and carbon by polarity. These high volume samples are being collected throughout the entire measurement period.

### *Activity 2.4 Continuous and Semi-Continuous PM Composition*

**Activity 2.4.1 In situ OC/EC:** Rutgers University installed a Sunset Laboratory *in-situ* semi-continuous OC and EC analyzer at the central monitoring site. The analyzer is based on the thermal-optical technique to characterize organic aerosol. The analyzer will be deployed at the central site throughout the monitoring period. The sampler is providing OC/EC data with a 2-4 hour time resolution, depending on atmospheric loading.

**Activity 2.4.2 Semi-continuous elements.** The University of Maryland operated a SEAS sampler at the central site during the intensive period. Samples were collected with a 15 minute time resolution to provide highly time-resolved data for 18 metals species (As, Cu, Mn, Ni, Cr, Cd, Se, Ag, Pb, Al, Fe, Zn, Ca, Bi, V, Ti, Be, and Ba).

### *Activity 2.5 Single Particle Characterization*

**Activity 2.5.1 Single Particle Mass Spectroscopy.**

Due to technical problems, The University of California at Davis and the University of Delaware did not operate the single particle mass spectrometer at the site during this project period.

**Activity 2.5.2 Laser-Induced Breakdown Spectroscopy (LIBS).** The University of Maryland measured the elemental composition of single particles in the atmosphere by Laser-Induced Breakdown Spectroscopy (LIBS) during the intensive period.

**Activity 2.5.3 CCSEM analysis.** During the intensive period, Carnegie Mellon University collected samples on polycarbonate filters for analysis by the RJ Lee Group using computer controlled scanning electron microscopy (CCSEM). Twenty-four hour PM-2.5 and PM-10 samples were collected on polycarbonate filters on alternating days during July.

#### *Activity 2.6 Aerosol Optical Properties*

Carnegie Mellon University measured the aerosol scattering coefficient using an integrating nephelometer. The visual range will also be measured during the measurement periods and additional observations will be collected from the airports in the area and archived. Pictures (in electronic form) of the area surrounding the supersite were periodically taken for the calculation of the visual range and documentation of the prevailing conditions.

### **Activity 3. Source Characterization**

#### *Activity 3.1 Emissions and Activity Survey*

Traffic activity data for the Pittsburgh region were collected by for the project.

#### *Activity 3.2 Source Sampling*

As per project schedule, no work was performed on this activity this project period.

### **Activity 4. Source Apportionment**

As per project schedule, no work was performed on this activity during this project period.

### **Activity 5. Three-Dimensional Deterministic Modeling**

As per project schedule, no work was performed on this activity during this project period.

### **Activity 6. Hypotheses testing:**

As per project schedule, no work was performed on this activity during this project period.

### **Activity 6. Reporting**

Required project reports were prepared and submitted during this project period.

### **References**

Turpin, B. J. and H. J. Lim (2001). "Species contributions to PM<sub>2.5</sub> mass concentrations: Revisiting common assumptions for estimating organic mass." Aerosol Science and Technology **35**(1): 602-610.

Turpin, B. J., P. Saxena, et al. (2000). "Measuring and simulating particulate organics in the atmosphere: problems and prospects." Atmospheric Environment **34**(18): 2983-3013.

### **Presentations and Publications**

Kane, D.; Frost, K.; Johnston, M.V. "Enhancing the Ablation Efficiency of Particles for Aerosol Mass Spectrometry", Presented at the American Society for Mass Spectrometry Annual Conference on Mass Spectrometry and Allied Topics, Chicago, IL, May 2001.

Pandis, S.N.; Davidson, C.I.; Robinson A.L. Khlystov A.Y. "Preliminary Results of the July 2001 Intensive of the Pittsburgh Air Quality Study" Accepted for presentation at the 20th Annual Conference of the American Association for Aerosol Research, October 15-19, 2001, Portland OR.

Cabada, J.C.; Pandis S.N.; Robinson, A.L. "Sources of Atmospheric Carbonaceous Particulate Matter in Pittsburgh, Pennsylvania", Accepted for presentation at the 20th Annual Conference of the American Association for Aerosol Research, October 15-19, 2001, Portland OR.

Khlystov A.Y.; Wan-Yu R.; Stanier C.O.; Mandiro M; Pandis, S.N. "Automated Measurements of Dry and Wet Ambient Aerosol Size Distributions" Accepted for presentation at the 20th Annual Conference of the American Association for Aerosol Research, October 15-19, 2001, Portland OR.

Khlystov A.Y.; Sauser, J.; Pandis, S.N.; Otjes, R.P. "Continuous Measurements of Ammonia and Ammonium in Ambient Air" Accepted for presentation at the 20th Annual Conference of the American Association for Aerosol Research, October 15-19, 2001, Portland OR.

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Conference of the American Association for Aerosol Research, October 15-19, 2001, Portland OR.

Kane, D.; Johnston, M.V. "Coating Ambient Ultrafine Particles for Enhanced Detection of Sulfates by Aerosol Mass Spectrometry" Accepted for presentation at the 20th Annual Conference of the American Association for Aerosol Research, October 15-19, 2001, Portland OR.

Cabada, J.C.; Pandis S.N.; Robinson, A.L. "Sources of Atmospheric Carbonaceous Particulate Matter in Pittsburgh, Pennsylvania", submitted to the Journal of the Air & Waste Management Association.