PROJECT TITLE:	Atmospheric Aerosol Source-Receptor Relationships: The Role Of Coal-Fired Power Plants
DOE AWARD #:	DE-FC26-01NT41017
REPORT:	Semi-Annual Technical Progress Report
REPORTING PERIOD:	August 1, 2001 – January 31, 2002
ISSUED:	March 2002
SUBMITTED TO:	US Department of Energy National Energy Technology Laboratory P.O. Box 10940 626 Cochrans Mill Rd Pittsburgh, PA 15236-0940 Attn: Bill Aljoe
PREPARED BY:	Carnegie Mellon University 5000 Forbes Ave Pittsburgh, PA 15213
PIs:	Allen L. Robinson, Spyros N. Pandis, Cliff I. Davidson (412) 268 – 3657; (412) 268 – 3348 (fax) e-mail: alr@andrew.cmu.edu

DISCLAIMER

ABSTRACT

This report describes the technical progress made on the Pittsburgh Air Quality Study (PAQS) during the period of August 2001 through January of 2002. The major activity during this project period was the continuation of the ambient monitoring effort. Work also progressed on organizing the upcoming source characterization effort, and there was continued development of several three-dimensional air quality models. The first PAQS data analysis workshop for the project was held at Carnegie Mellon in December 2001.

Two new instruments were added to site during this project period: a single particle mass spectrometer and an in situ VOC instrument. The single particle mass spectrometer has been deployed since the middle of September and has collected more than 150 days of data. The VOC instrument was only deployed during the intensive sampling period. Several instruments experienced operational issues during this project period. The overall data recovery rate for the project has been high.

The average daily concentration of $PM_{2.5}$ was 17.4 $\mu g/m^3$ during this period. The data indicate a strong seasonal variation in both $PM_{2.5}$ levels and composition. $PM_{2.5}$ levels are higher in the summer, with an average level of 21.3 $\mu g/m^3$ during July, August and September. Levels were lower in the fall and winter, with an average level of 12.6 $\mu g/m^3$ during October, November and December. The major chemical components of the $PM_{2.5}$ are sulfate and organic material throughout the year, with nitrate making a significant contribution during the winter. For the period of July through November, the mass measured with the FRM was greater than the sum of chemical components. We are currently investigating whether or not this "extra mass" measured by the FRM is water retained on the Teflon filters.

Comparison of data collected at satellite sites and the central site indicate that there was relatively little spatial variation in the $PM_{2.5}$ levels around Pittsburgh during July 2001. This suggests that $PM_{2.5}$ was determined mostly by the same sources, namely regional sources upwind of the study area. The total particle number concentration and ultrafine particle levels at the central monitoring site appear dominated by nucleation bursts. Evidence of nucleation bursts can be seen on approximately 50% of the days. 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.

TABLE OF CONTENTS

LIST OF FIGURES

INTRODUCTION

This is the second semi-annual report of the "Pittsburgh Air Quality Project" (PAQS) funded by the U.S. Department of Energy's National Energy Technology Laboratory under DOE Cooperative Agreement No. DE-FC26-01NT41017 to Carnegie Mellon University. This work is also supported by the US EPA through the Supersites program. In this three-year project, Carnegie Mellon University will conduct detailed studies of the ambient particulate matter in the Pittsburgh, PA metropolitan area. The work includes ambient monitoring, source characterization, and modeling (statistical and deterministic) for source apportionment. The major objectives of the project include:

- To achieve advanced characterization of the PM in the Pittsburgh region. Measurements include the PM size, surface, volume, and mass distribution; chemical composition as a function of size and on a single particle basis; temporal and spatial variability.
- To obtain accurate current fingerprints of the major primary PM sources in the Pittsburgh region using traditional filter-based sampling and state-of-the-art techniques such as dilution sampling and single particle analysis using mass spectroscopy and LIBS.
- To estimate the impact of the various sources (transportation, power plants, natural, etc.) on the PM concentrations in the area using both statistical and deterministic models.
- To quantify the responses of the PM characteristics to changes in these emissions in support of the emission control decision making in the area.
- To develop and evaluate current and next generation aerosol monitoring techniques for both regulatory applications and for determination of source-receptor relationships.

SUMMARY OF TECHNICAL PROGRESS

This section provides an overview of the progress made on the various project activities. This project period the majority of the effort went into activity 2 ambient monitoring; more limited effort was spent planning the upcoming source characterization effort and in the continued development of three-dimensional air quality models.

Activity 1. Project Management

During this project period the first data analysis workshop was held to review data from the Summer 01 intensive sampling period and to coordinate future work. The workshop was held on December 13 and 14 at Carnegie Mellon University. Personnel from Carnegie Mellon University also participated in the EPA Supersites data workshop held on November 13 and 14 in Research Triangle Park, NC.

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, evaluation of instrumentation, and air quality model development and evaluation. Ambient measurements were conducted throughout this project period. The second intensive sampling period occurred between January 2 and 22, 2002. Baseline measurements were made during the rest of this project period. During the intensive period, Carnegie Mellon University personnel also collected samples at satellite sites in the Lawrenceville and Hazelwood neighborhoods of Pittsburgh, and Florence, PA and Greensburg, PA. These samplers are part of the EPA speciation network. The Athens, OH satellite site was operated during this project period by Ohio University. Twenty-four hour samples were collected at this site on a 1 in 6 day schedule during the baseline period and on an everyday schedule during the intensive. Table 1 summarizes the list of measurements and sampling frequency during this project period.

Activity 3. Source Characterization

Activity 3.1 Emissions and Activity Survey

Emission inventory data from the Allegheny County Health Department and EPA were used this project period to identify the classes of major stationary sources in the Pittsburgh region. This information is being used to help finalize the target list of critical sources. The major categories of stationary sources are coal based power, coke production, and steel.

We are also continuing our effort to compile existing emissions data for the region. An emissions inventory of primary organic PM emissions has been assembled. This effort will be expanded to assemble a primary organic inventory for the region. We also continue to work on assembling fingerprints for important sources in the region. RJ Lee Group identified a large source apportionment study conducted around Wheeling, WV in the middle of the 1990s. This effort measured fingerprints from steel, coke and other large industrial facilities in the area. Traffic activity data for the Pittsburgh region were collected during this project period.

Activity 3.2 Source Sampling

During this reporting period, preparations were continued for the source sampling effort. In August, emission measurements were made using the Combustion and Environmental Research Facility (CERF) at NETL with the Carnegie Mellon University Dilution Sampler. As part of this effort, the Buckley group pulled a slipstream off of the sampler for characterization by Laser Induced Breakdown Spectroscopy (LIBS). This was the first time we tried to couple the dilution sampler to an advanced single particle instrument.

We have 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.

Activity 4. Source Apportionment

The plans for source apportionment were discussed at the PAQS data analysis workshop in December. We decided to conduct an initial statistical analysis of the data to help plan the source characterization study. Preliminary data from the Summer 01 intensive sampling period was sent in February 2002 to Clarkson University to initiate this effort.

Activity 5. Three-Dimensional Deterministic Modeling

During this reporting period the CMU modeling team has continued the development of the aerosol modeling tools, incorporated them in 2 three-dimensional chemical transport models (URM and CAMx-AERO), and evaluated them against available data sets. The Trajectory-Grid (T-G) approach has been incorporated in the CMU Hybrid Aerosol Module and the results have been compared to the currently used approach (Adams method in the LSODE package) in a one-dimensional Lagrangian trajectory model. The performance of the T-G method was excellent, decreasing the CPU cost by an order of magnitude without sacrificing any accuracy. The CMU aerosol modules (Equilibrium, Dynamics-MADM, and Hybrid) have been added to CAMx and have been used to simulate a 1995 pollution episode in Southern California. The performance of the model was very good both in terms of accuracy and computational efficiency. We are currently setting up the models for simulations in the Eastern United States domain using meteorological and emissions fields from the NARSTO 1995 campaigns. After this testing we will focus on the simulations for the July 2001 intensive (ESP01).

EXPERIMENTAL

Ambient measurements were conducted throughout this project period. The second intensive sampling period occurred between January 2 and 22, 2002. Baseline measurements were made during the rest of this project period. 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. The Athens, OH satellite site was operated during this project period by Ohio University. Twenty-four hour samples were collected at this site on a 1 in 6 day schedule during the baseline period and on an everyday schedule during the intensive. Table 1 summarizes the list of measurements and sampling frequency during this project period. Major equipment additions and operational issues that occurred this project period are discussed briefly below.

Single Particle Mass Spectrometer

In September, the University of California at David and University of Delaware brought on-line the single particle mass spectrometer RSMS-III to measure the particle-by-particle size and composition over the size range from 20 nm to 2 microns. RSMS-III can analyze for a wide range of compounds and compound classes including a) speciation of inorganics such as metals and metal oxides, refractory crustal materials such as silicon dioxide, and electrolytes such as sulfates and nitrates, b) speciation of aromatic organic compounds, and c) distinguishing elemental from organic carbon. The new features of this instrument include measurement of positive and negative ion spectra created from each particle and automated operation.

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, although this is not unexpected considering the complexity of the instrument.

Since start up, data have been collected with 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.

A major failure occurred in RSMS-III in late December and early January. The mechanical pumps could not operate under the extreme cold temperatures outdoors. This resulted in a loss of vacuum, which then caused the microchannel 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 cold 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 1Mohm 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.

In situ VOC

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 up coming 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.

Other instrument issues

Several instruments experienced breakdowns and other operational issues during this project period. This is not unexpected because many of these instruments are one of a kind currently under development. The overall data recovery rate for the project is high.

The *in situ* carbon analyzer was down from the beginning of September through the middle of October. The problems with the instrument were identified during routine QA/QC checks performed in early September and included failure of the methanator and some electronic issues. PAQS personnel from Rutgers University and Carnegie Mellon University worked with Sunset Laboratories to fix these problems. The long downtime was due in part to challenges getting parts because of the events on September 11.

The ADI carbon analyzer performed unreliably during the initial stages of the study. Personnel from Aerosol Dynamics worked on the instrument in December when they were in Pittsburgh for the data workshop. The problems were due to a combination of low carbon levels in Pittsburgh and flow balance issues. This instrument relies on a balance of flows across the sampling cell for sample collection and sample transport to the detector. The instrument flow configuration drifted after initial setup such that the cross flow rate was too high and prevented the flashed sample from being measured by the CO2 Licor detector. The averaging time of the instrument was increased for 30 minutes to improve instrument performance. The instrument has performed well since these changes were made.

Several of the API gas monitors have experienced major failures. The O_3 analyzer sample/reference valve developed a leak requiring installation of a replacement valve. The NOx analyzer developed a leak in the dry airline, requiring replacement of the nafion dryer and the flowmeter board. This analyzer also required two replacement pumps. The SO_2 analyzer developed a leak in the manifold, requiring rerouting of lines in the instrument.

We continue to work with the Aerodynamic Particle Sizer Spectrometer (APS 3320). There have been two types of problems: 1) overestimation of particle number/volume above about 2 μm due to false counts; 2) intermittent major overestimation of the number/volume in the full size range as was evident from comparisons with the SMPS and TEOM. The second problem began occurring on cold nights and intensified as the weather got colder. The unit was shipped back to TSI where a fault in T-compensation of the photo detector was found. As the unit was serviced at TSI for problem #2, we decided to simultaneously upgrade the electronics and the optical chamber of the APS which should solve problem #1.

Starting in early October, the steam sampler began experiencing problems with SO_2 causing a positive artifact that interferes with its sulfate measurements. The solution to this problem is to add a denuder to the inlet line to remove the SO_2 gas – this is how instruments such as the R&P 8400 eliminate the possibility of SO_2 artifacts. We have not added a denuder to the current steam sampler becase adding a denuder would eliminate the gas data (HNO3, HNO2, NH3, HCl) that we measure with the steam sampler. We have two other instruments measuring sulfate at the site so the lack of sulfate data from the steam sampler is not a major issue. We are building a second steam sampler that will include a denuder in the inlet line so that we will have simultaneous measurements of $PM_{2.5}$+gas and $PM_{2.5}$ with two steam samplers. $PM_{2.5}$ sulfate will then be measured with the steam sampler that has a denuder on the inlet line.

The epiphaniometer began having problems around 9/20/01. After about 1.5 months of trying to fix it in Pittsburgh, the unit was shipped back to Switzerland for repair.

The University of Maryland (semi-continuous metals and Laser Induced Breakdown Spectroscopy) did not participate in the January intensive as originally planned. Instead, they will make measurements during a special two-week study planned at the end of March 2002 to obtain data to calibrate the single particle mass spectrometer.

RESULTS AND DISCUSSION

In this section we provide an overview of the PM levels during this study period. We then describe four preliminary findings: 1) a comparison of the measured $PM_{2.5}$ mass and the sum of the chemical components to examine the $PM_{2.5}$ mass balance; 2) a comparison of the PM levels and composition at the different monitoring sites to evaluate the regional contribution to $PM_{2.5}$ in Pittsburgh; 3) an evaluation of the performance of advanced semi-continuous instruments based on comparison with standard filter pack measurements; and 4) evidence of new particle formation and the contribution of nucleation to the ultrafine aerosol.

Figure 1 shows a time series of daily $PM_{2.5}$ mass measured at the central monitoring site with an FRM from June 30, 2001 through December 31, 2001. The average daily concentration of $PM_{2.5}$ was 17.4 $\mu g/m^3$ during this period. The data indicate a strong seasonal variation in both $PM_{2.5}$ levels and composition within Pittsburgh. $PM_{2.5}$ levels are higher in the summer, with an average level of 21.3 $\mu g/m^3$ during July, August and September. Levels were lower in the fall and winter, with an average level of 12.6 $\mu g/m^3$ during October, November and December. The mass data illustrate how the PM levels in Pittsburgh vary in an episodic fashion.

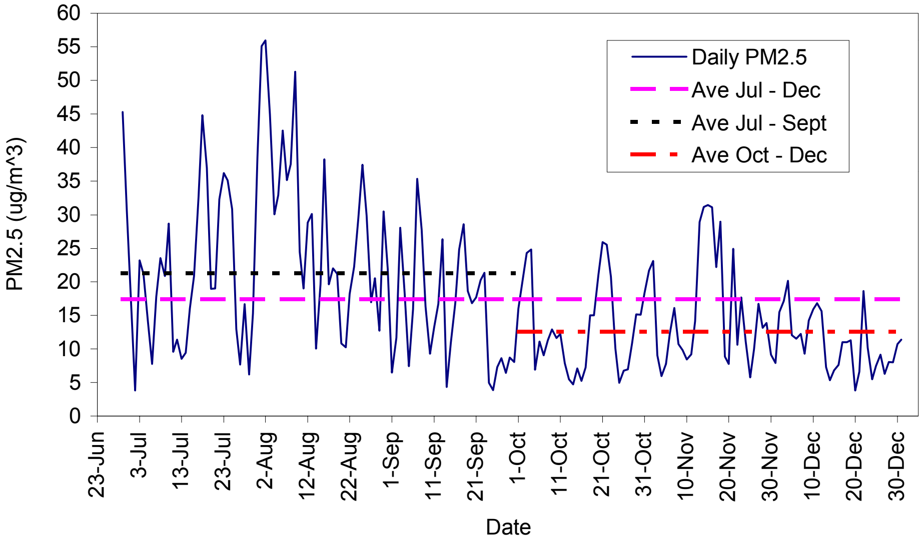


Figure 1. Daily $PM_{2.5}$ mass measured with an FRM for June 30 through December 30, 2001.

Figures 2-3 summarize the chemical composition of the $PM_{2.5}$. Figure 2 shows the average $PM_{2.5}$ composition for the period from July 1, 2001 through the middle of January 2002. This average includes data from 182 days. The average $PM_{2.5}$ mass across all of these days is 17.2 $\mu g/m^3$. The major components of this $PM_{2.5}$ 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 $PM_{2.5}$ mass measured with an FRM and sum of the individual chemical components.

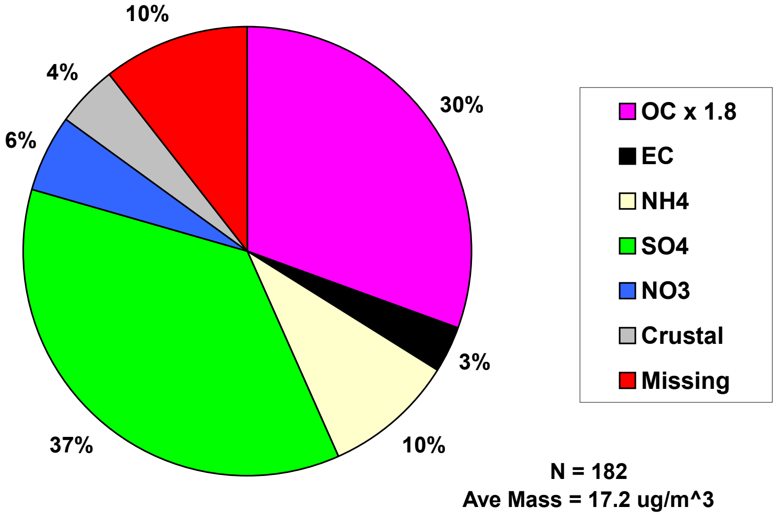


Figure 2. Average chemical composition of $PM_{2.5}$ for study through the mid-January 2002. "Missing" indicates the differences between the mass measured with the FRM and the sum of the chemical components.

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 $PM_{2.5}$ mass in the winter. The average $PM_{2.5}$ level during the first part of the winter (December and half of January) of 2001 was 10 $\mu g/m^3$ 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 $PM_{2.5}$ 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.

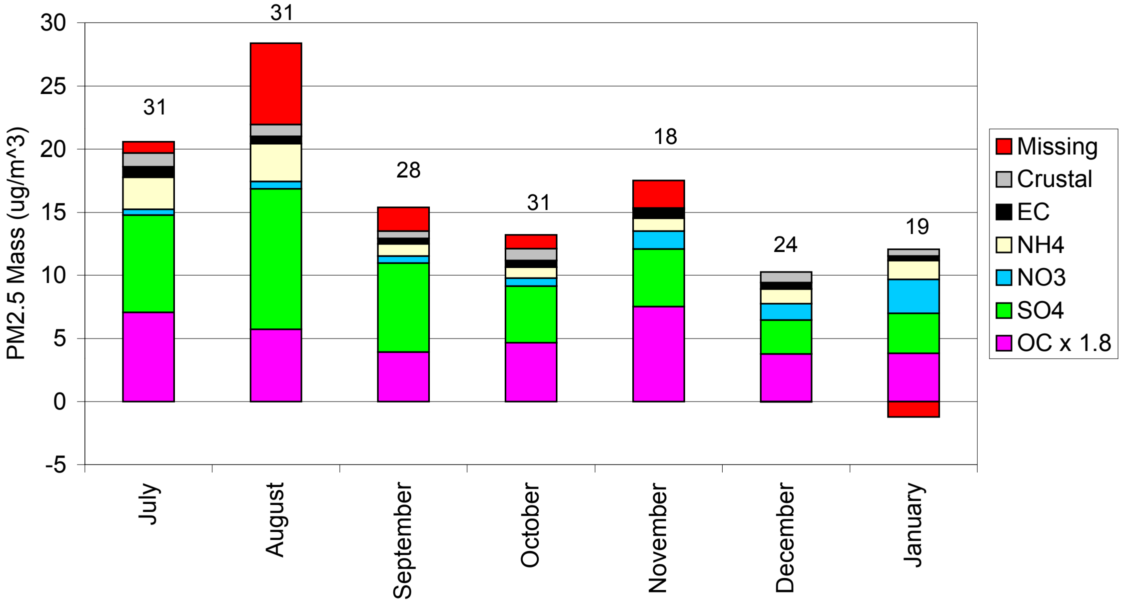


Figure 3. Monthly average mass and chemical composition of $PM_{2.5}$. The height of each bar represents the total mass measured for that period using an FRM. The numbers above each bar indicate the number of days from that month included in the average. Missing indicates the differences between the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

Evidence of the Regional Contribution

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.

The $PM_{2.5}$ concentrations show considerable variability from day to day, which is most likely caused for the most part by changing meteorology. Note that 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 $PM_{2.5}$ mass at all five sites is determined mostly by the same sources, namely regional sources upwind of this area.

A similar finding is seen for airborne $PM_{2.5}$ sulfate, shown in Figure 5. In fact, the points at the five sites show closer agreement for sulfate than for $PM_{2.5}$ 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_2. $PM_{2.5}$ mass, although containing a large fraction of sulfate, also contains other chemical species that may have local components in the city of Pittsburgh.

One example of a chemical species with a measurable local component is $PM_{2.5}$ nitrate, shown in Figure 6. On some days, the concentrations of nitrate at Florence and Greensburg are noticeably smaller than concentrations at the three urban sites. Florence, the most remote site, has the lowest concentration of the five sites on the majority of days during July. This is reasonable since a significant fraction of airborne nitrate is known to be emitted from motor vehicles. The three urban sites have the greatest vehicular traffic nearby, with less in Greensburg and much less in Florence.

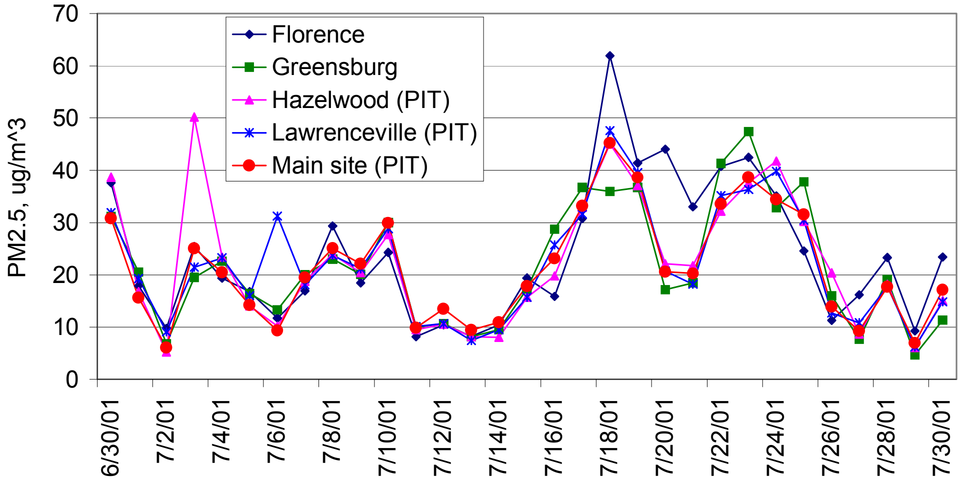


Figure 4. Time series of $PM_{2.5}$ mass measured at the central monitoring site and 4 satellite sites.

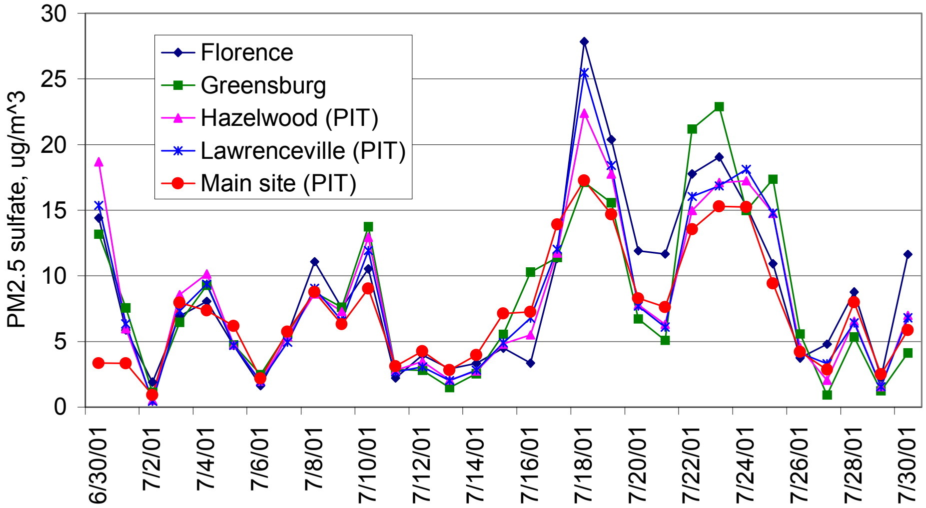


Figure 5. Time series of $PM_{2.5}$ sulfate measured at the central monitoring site and 4 satellite sites.

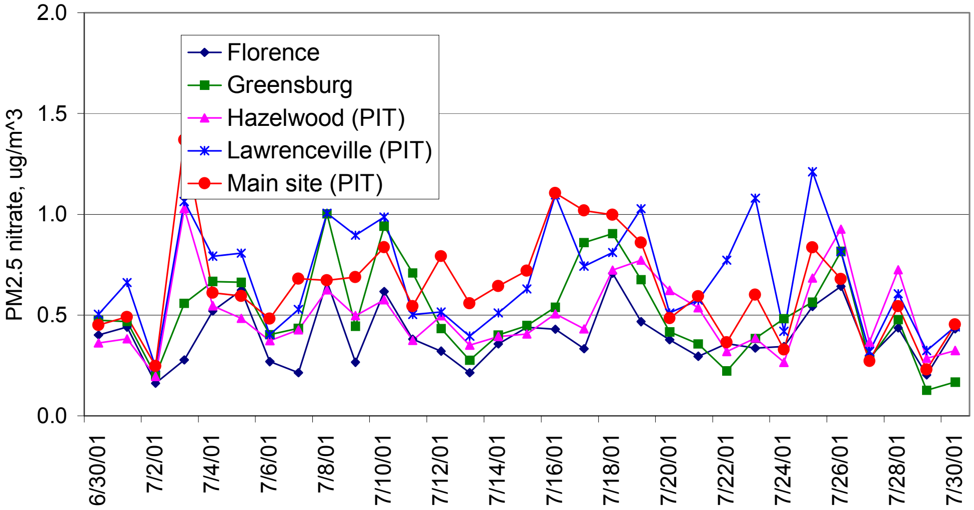


Figure 6. Time series of $PM_{2.5}$ nitrate measured at the central monitoring site and 4 satellite sites.

Instrument intercomparison

To evaluate the performance of advanced instrumentation we have begun to compare results measured by these instruments with those obtained with traditional filter based samplers. These advanced instruments often provide highly time resolved information with a fraction of the effort required for collecting integrated filter samples followed by manual analysis; however the results from these instruments must be validated against the traditional filter measurements.

Figure 7 compares daily measurements of $PM_{2.5}$ mass concentration made with the FRM to those made with a TEOM. The agreement between these approaches is excellent – note that we are using a 30°C TEOM in combination with a nafion dryer to minimize volatilization in the system. A linear regression of the data indicates a degree of high correlation with an R^2 of 0.93.

Figure 8 compares 24-hour average sulfate concentration measured with R&P 8400S with measurements made with the CMU inorganic sampler for the month of July. Reasonable agreement is observed. A linear regression of the data yields an R^2 value of 0.80. The slope of this regression is 0.8 suggesting some bias between the two techniques – the sulfate values reported by the R&P instrument were on average 80% of those measured with the manual inorganic sampler.

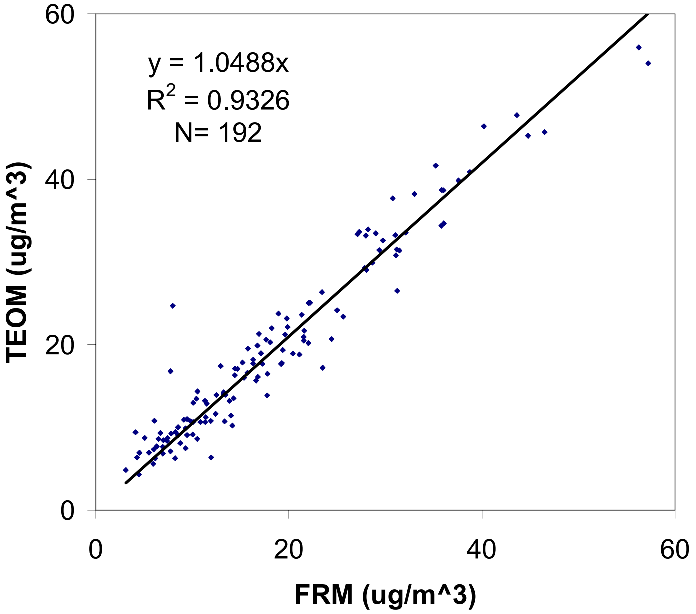


Figure 7. Plot of daily average $PM_{2.5}$ mass measured with a TEOM versus $PM_{2.5}$ mass measured with an FRM. A total of 192 points are shown from the period between July 1, 2001 and January 23, 2002. The line is a linear regression of the data.

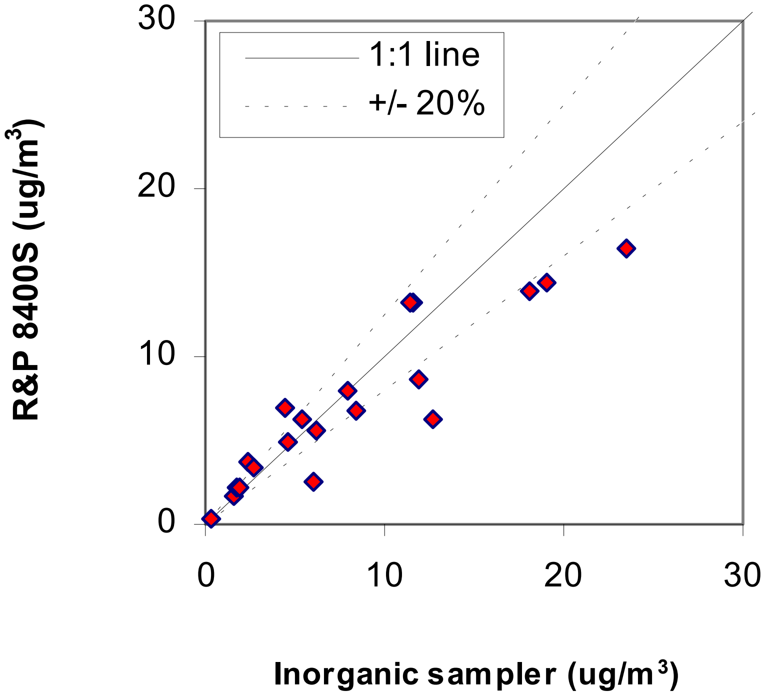


Figure 8. Plot of daily average $PM_{2.5}$ sulfate measured with R&P 8400S versus $PM_{2.5}$ sulfate measured with an integrated filter sampler for July of 2001.

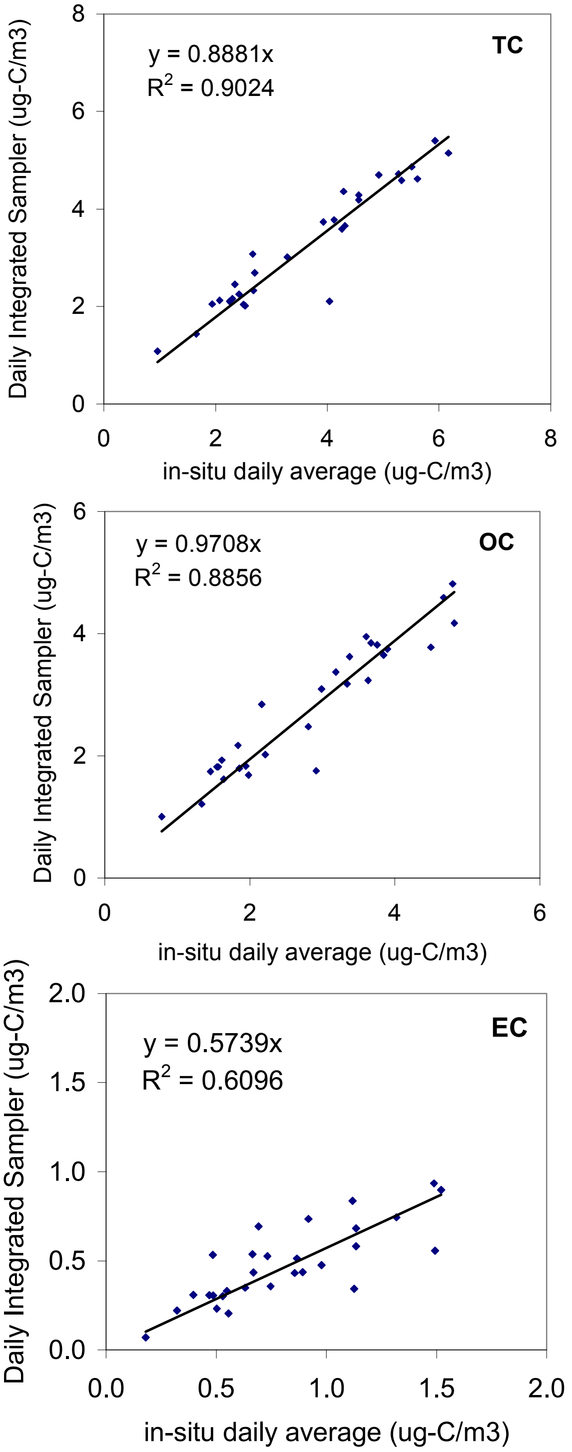


Figure 9. Comparison of daily average carbon $PM_{2.5}$ carbon levels measured with a Sunset Laboratories in situ carbon analyzer and an integrated filter pack sampler. The top pane compares total carbon, the middle pane compares organic carbon, and the bottom pane compares elemental carbon. The lines on each figure are a linear regression of the data.

Figure 9 compares 24-hour average carbon data measured with the Sunset Laboratory in situ carbon analyzer and filter-pack measurements made with the CMU denuder sampler for the month of July. There is excellent agreement between the in situ instrument and the manual measurement for total and organic carbon. There is more scatter and some bias in the elemental carbon data. Since both of these samples are analyzed using the thermal-optical transmission method the problems are not those commonly associated with measuring organic and elemental carbon with different techniques. We believe that the problem has to do with temperature drift of laser signal used to determine the split between OC/EC. This drift gets worse over time because of build up of Fe on the filter used to collect the sample in the *in situ* instrument. We are working on developing a methodology to correct the data, with the goal of developing an automated approach.

Nucleation and Ultrafine Particles

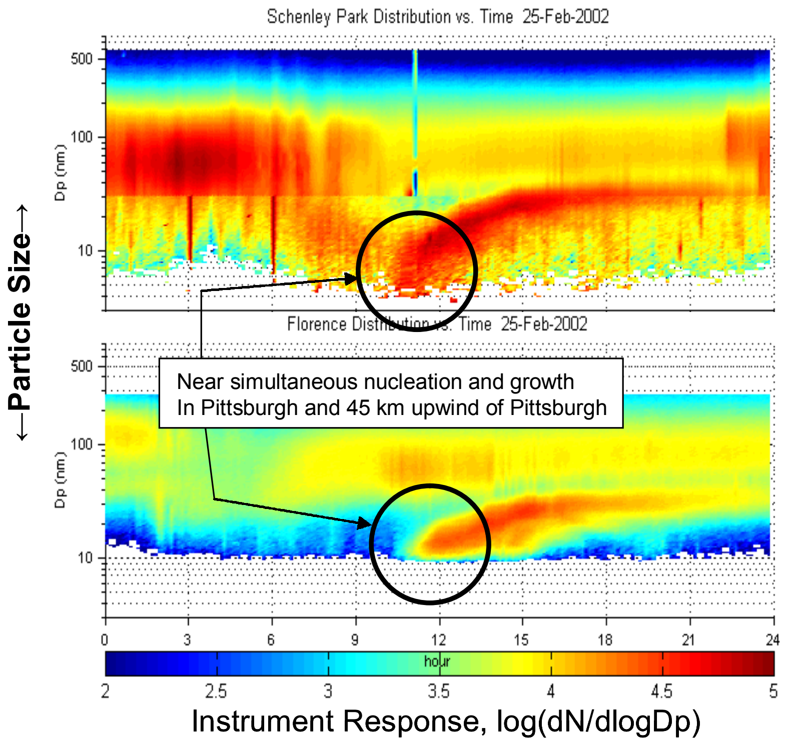
The total particle number concentration and ultrafine particles at the central monitoring site appear dominated by nucleation bursts. The nucleation bursts vary in intensity from weak increases in the ultrafine and nuclei mode particle counts to very intense events which increase the overall number concentration from typically less than 20,000 per cm^3 to over 100,000 per cm^3 in a few hours. Figure 10 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 11 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 (Figure 2). The preliminary results from the Florence site suggest that the nucleation events may be regional in nature, and therefore will influence particle counts and size distributions throughout Western Pennsylvania.

A major challenge of the PAQS is to determine the chemistry and meteorology that govern these nucleation bursts. Initial investigations shows that 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 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 model for sulfuric acid-water nucleation which showed that gas-phase sulfuric acid production rates are probably too low to account for the observed nucleation.

The problem 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.



Near simultaneous nucleation and growth
In Pittsburgh and 45 km upwind of Pittsburgh

Figure 10. 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 late February. This indicates a regional cause of the nucleation bursts.

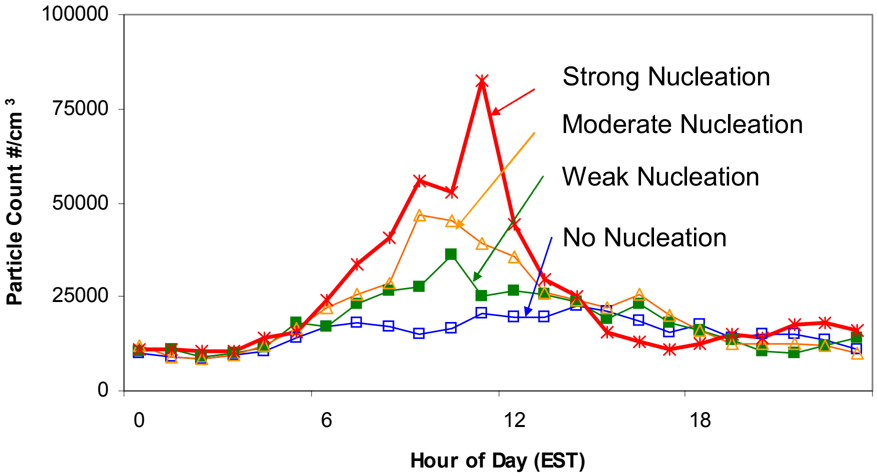


Figure 11. Total particle number concentration as a function of time of day for strong, moderate, weak, and no nucleation cases. Data is for the Schenley Park sampling station during July.

CONCLUSIONS

Several preliminary findings of the project have been discussed in this report:

1. The temporal variation of $PM_{2.5}$ levels in Pittsburgh is episodic in character, with the overall levels largely determined by meteorological patterns and regional transport.

2. The performance of the continuous instruments appears to have been very good with their results in strong agreement with the traditional filter measurements.

3. Total particle number and ultrafine particles at the site appear dominated by nucleation bursts.

4. The Federal Reference Method for $PM_{2.5}$ appears to over report $PM_{2.5}$ mass during the summer and fall months and under-report for winter periods.

FUTURE PLANS

The effort this next project period will continue to focus on ambient monitoring. The site will continue to be operated in baseline mode (see Table 1) through this entire project period. A major milestone this project period will occur on July 1, 2002, which is the one-year anniversary of the baseline sampling. One year is the minimum length of the daily dataset required for epidemiology time series analysis that is part of the health effects component of the project. Preliminary review of the data suggests that we have collected a reasonably complete data set of different atmospheric and air quality conditions; the major missing piece is a significant stagnation event that leads to sustained high pollution levels. These events typically occur during the summer months, and we hope to characterize one in the upcoming season. We will also continue to operate more instrumentation at the upwind satellite site to investigate the nucleation bursts and organic composition of the regional contribution.

Analysis of the ambient data will continue this project period. Preliminary findings from the work will be presented at the upcoming NETL fine particulate conference in April. We also have approximately 10 journal papers in preparation that we hope to submit to the first special journal issue describing results from the EPA supersite network. The deadline for submission to this special issue is June.

We will also continue to ramp up the source characterization effort. This will primarily be a planning and preparation effort. We will continue to work to get access to important sources. We also anticipate making some preliminary measurements in the tunnel and the fence line monitoring sites. The major fieldwork for the source characterization will begin in the fall of 2002.

REFERENCES

Peters, A.; Wichmann, E.; Tuch, T.; Heinrich, J.; Heyder, J. Respiratory Effects are Associated with the Number of Ultrafine Particles, *Am. J. Respir. Crit. Care Med*. **1997**, *155*, 1276-1383.

Donaldson; Stone; Gilmour; Brown; MacNee. Ultrafine particles: mechanisms of lung injury. *Philosophical Transactions: Mathematical, Physical & Engineering Sciences*. **2000**, *358*, 2741-2749.

Woo, K.S.; Chen, D.R.; Pui, D.Y.H.; McMurry, P.H. Measurement of Atlanta Aerosol Size Distributions: Observation of Ultrafine Particle Events. *Aerosol Sci. and Technol.* **2001**, *34*, 75-87.

Shi, J.P.; Evans, D.E.; Khan, A.A.; Harrison, R.M. Sources and concentration of nanoparticles (<10 nm diameter) in the urban environment. *Atmos. Environ.* **2001**, *35*, 1193-1202.

Weber, R.J.; McMurry, P.H.; Mauldin, L.; Tanner, D.J.; Eisele, F.L.; Brechtel, F.J.; Kreidenweis, S.M.; Kok, G.L.; Schillawski, R.D.; Baumgardner, D. A Study of New Particle Formation and Growth Involving Biogenic and Trace Gas Species Measured During ACE1. *J. Geophys. Res.* **1998**, *103*, 16385 – 16396.

Ruuskanen, J.; Tuch, T.; Brink, H.T.; Peters, A.; Khlystov, A.; Mirme, A.; Kos, G.P.A.; Brunekreef, B.; Wichmann, H.E.; Buzorius, G.; Vallius, M.; Kreylilng, W.G.; Pekkanen, J. Concentrations of Ultrafine, Fine, and PM2.5 Particles in Three European Cities. *Atmos. Environ.* **2001**, *35*, 3729-2738.

Pirjola, L.; Kulmala, M; Wilck, M.; Bischoff, A.; Stratmann, F.; Otto, E. Formation of Sulfuric Acid Aerosols and Cloud Condensation Nuclei: An Expression for Significant Nucleation and Model Comparison. *J. Aerosol Sci*. **1999**, *30*, 1079-1094.

Turpin, B. J. and H. J. Lim (2001). “Species contributions to PM2.5 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

This section lists the presentations and publications for this project period.

Presentations

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” Presented 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”, Presented 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” Presented 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” Presented at the 20th Annual Conference of the American Association for Aerosol Research, October 15-19, 2001, Portland OR.

Lake, D.A.; Johnston, M.V.; Young, D.; Eiceman, G.A. “A Portable Instrument for Real Time Aerosol Particle Characterization” Presented at the 20th Annual 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” Presented at the 20th Annual Conference of the American Association for Aerosol Research, October 15-19, 2001, Portland OR.

A. Khlystov, C. O. Stanier, and S. N. Pandis), “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.

S.N. Pandis “PM2.5 Modeling: Insights from the Pittsburgh Air Quality Study", MARAMA Regional Air Quality and Data Analysis Meeting, Baltimore, January 23-24 2002.

Publications

Cabada, J.C.; Pandis S.N.; Robinson, A.L. “Sources of Atmospheric Carbonaceous Particulate Matter in Pittsburgh, Pennsylvania”, accepted for publication, Journal of the Air & Waste Management Association.

Table 1. Measurements in the Pittsburgh Supersite Program for the Period of 8/1/01 – 1/31/02.

Measurement	Instrumentation	Institution	Frequency Baseline	Frequency Intensives
Filter-Based Composition				
Wet and dry aerosol number distribution (3 nm – 10 µm)	Ultrafine SMPS: Scanning Mobility Particle Spectrometer (TSI model 3936N25) for 0.003-0.150 µm SMPS: Scanning Mobility Particle Spectrometer (TSI model 3934L) for 0.01-1.0 µm APS: Aerodynamic Particle Sizer Spectrometer (TSI model 3320) for 0.5-1.0 µm	Carnegie Mellon University	10 min	10 min
Aerosol surface area distribution	Epiphaniometer	Paul Scherrer Institute	10 min	10 min
Mass measurements				
PM$_{2.5}$ mass	R&P FRM	Carnegie Mellon University	1 day	1 day
PM$_{2.5}$ mass	Andersen DICHOT	Carnegie Mellon University	1 day	1 day
PM$_{2.5}$ mass	R&P TEOM (30°C + dryer)	Carnegie Mellon University	10 min	10 min
PM$_{10}$ mass	Andersen DICHOT	Carnegie Mellon University	1 day	1 day
PM$_{x}$ mass	MOUDI	Carnegie Mellon University	1 day	1 day
Filter-Based Composition				
PM$_{2.5}$ ions, PM$_{2.5}$-$_{10}$ ions, HNO$_3$ vapor, NH$_3$ vapor	CMU Sampler + IC	Carnegie Mellon University	1 day	1 day
Size-resolved ions and metals	MOUDI + IC and ICP-MS	Carnegie Mellon University	-	1 day
PM $_{2.5}$ OC and EC	CMU TQQQ sampler	Carnegie Mellon University	1 day	1 day
PM $_{2.5}$ OC and EC	CMU denuder sampler	Carnegie Mellon University	1 in 6 days	1 day
PM $_{2.5}$ OC and EC, ions, and metals	PC-BOSS system	Brigham Young University	-	1 day
PM $_{2.5}$ OC and EC	Sunset Labs in situ carbon analyzer	Rutgers University	2 hr	2 hr
PM$_{x}$ OC and EC	MOUDI	Carnegie Mellon University	-	1 day
PM$_{2.5}$ Organic speciation	Filter & PUF + GC-MS Schenley Park Site	Florida International University & Carnegie Mellon University	1 in 6 days	1 day

Table 1 (cont.)

Measurement	Instrumentation	Institution	Frequency Baseline	Frequency Intensives
Filter-Based Composition (cont.)				
$PM_{2.5}$ Organic speciation	Filter & PUF + GC-MS Florence Satellite Site	Florida International University & Carnegie Mellon University	-	1 day
$PM_{2.5}$ metals	Hi-Vol + ICP-MS	Carnegie Mellon University	1 day	1 day
PM_{10} metals	Hi-Vol + ICP-MS	Carnegie Mellon University	1 day	1 day
Organic size-resolved characterization	Hering Low pressure impactor + FTIR	Rutgers University	-	1 day
$PM_{2.5}$ Bio-aerosols	Epi-fluorescent microscopy, Molecular biology assays	University of Colorado at Boulder	1 day	1 day
Single Particle Composition				
Composition and size	Single Particle Mass Spectrometry: RSMS-III	University of California at Davis, University of Delaware	Continuous	Continuous
Elements and morphology	Filter + SEM	RJ Lee Group	-	1 day
Metals	Laser Induced Breakdown Spectroscopy (LIBS)	University of Maryland at College Park	-	-
Semi-continuous composition				
Semi-continuous metals	SEAS/GFAA	University of Maryland at College Park	-	-
$PM_{2.5}$ ions, HNO_3 vapor, NH_3 vapor	Steam Sampler + IC + FIA detector	Carnegie Mellon University	2 hr	2 hr
$PM_{2.5}$ nitrate	R&P 8400 Nitrate	Aerosol Dynamics & Carnegie Mellon University	10 min	10 min
$PM_{2.5}$ sulfate	R&P 8400 Sulfate	Aerosol Dynamics & Carnegie Mellon University	10 min	10 min
$PM_{2.5}$ carbon	Aerosol Dynamics Carbon Analyzer	Aerosol Dynamics	30 min	30 min
Gases				
VOCs	Cans & GC-FID, GC-MS	Carnegie Mellon University	1 in 3 days	1 day
in situ VOCs	GC-FID, GC-MS	University of California at Berkeley	-	1 hr
Total Peroxides	CSU Monitor	Colorado State University	30 min	10 min
Hydrogen Peroxide	CSU Monitor	Colorado State University	-	10 min

Table 1 (cont.)

Measurement	Instrumentation	Institution	Frequency Baseline	Frequency Intensives
Gases (cont.)				
Organic Peroxides	CSU Monitor	Colorado State University	-	10 min
Gases: O_3, NO and NOx, SO_2, CO	Gas Monitors	Carnegie Mellon University	10 min	10 min
Other				
Visibility	Nephelometer	Carnegie Mellon University	10 min	10 min
RH, T, P, Wind, UV and Solar Radiation	Met Station	Carnegie Mellon University	10 min	10 min
Fog and cloud composition	CSU sampler	Colorado State University	Variable	Variable

APPENDIX A. PROGRESS REPORT FROM UNIVERSITY OF DELAWARE

Preface

The role of the Johnston group is to develop, test and apply methods for real-time chemical characterization of aerosol particles that provide enhanced information over conventional single particle mass spectrometry (RSMS-3). The expectation is that these methods will provide improved source characterization and apportionment of the Pittsburgh aerosol.

In the original proposal, Johnston's group was to develop an on-line particle coating apparatus to improve the ability of RSMS-3 to characterize organic components in aerosols. This method was developed and field tested in 2001. While the method did not prove to be useful for organic component characterization, it did provide new information on the distribution of sulfate in the Pittsburgh aerosol.

Previous work in Johnston's group has shown that pure ammonium sulfate particles on the order of a few hundred nanometers or smaller in diameter cannot be detected by conventional single particle mass spectrometry.[1] However, the coating apparatus described above, when combined with a single particle mass spectrometer, allows these particles to be detected and analyzed. In the fall of 2001, this method was used to determine whether or not pure ammonium sulfate particles dominate the Pittsburgh aerosol.

Distribution of Sulfate in the Pittsburgh Aerosol

Introduction

The goal of this project was to determine the distribution of sulfate in the aerosol sampled at the Pittsburgh Supersite at Carnegie Mellon University. To detect the presence of pure (or nearly pure) sulfate particles, ambient particles were coated with 1-napthyl acetate in a flow cloud chamber prior to being sampled into a laser ablation single particle mass spectrometer (RSMS-3). Laboratory experiments have demonstrated that this method can enhance the detection of ammonium sulfate by more than an order of magnitude.[2] The detection efficiency of sulfate particles coated in this manner is similar to the detection efficiencies of other chemical components typically found in urban aerosols.

Experimental Details

The design and operation of the aerosol mass spectrometer and flow cloud chamber have been previously described.[2] In that work, an aerodynamic lens system was used as the aerosol inlet. This inlet draws a constant flow of aerosol and transmits a broad particle size range to the mass spectrometer ion source. In contrast, the aerosol mass spectrometer in Pittsburgh (RSMS-3) utilizes a size-selective aerodynamic focusing inlet.[3] With this inlet, size selection is accomplished by varying the pressure in the first region of the inlet (higher pressures select larger diameter particles). When the inlet pressure is varied, the flow rate of the aerosol into the inlet also changes. In order to keep the coating conditions constant, the coating apparatus had to be modified by adjusting the flow rates from the sampling and excess ports for each size range to keep the total flow through the FCC constant. (See Figure A1.)

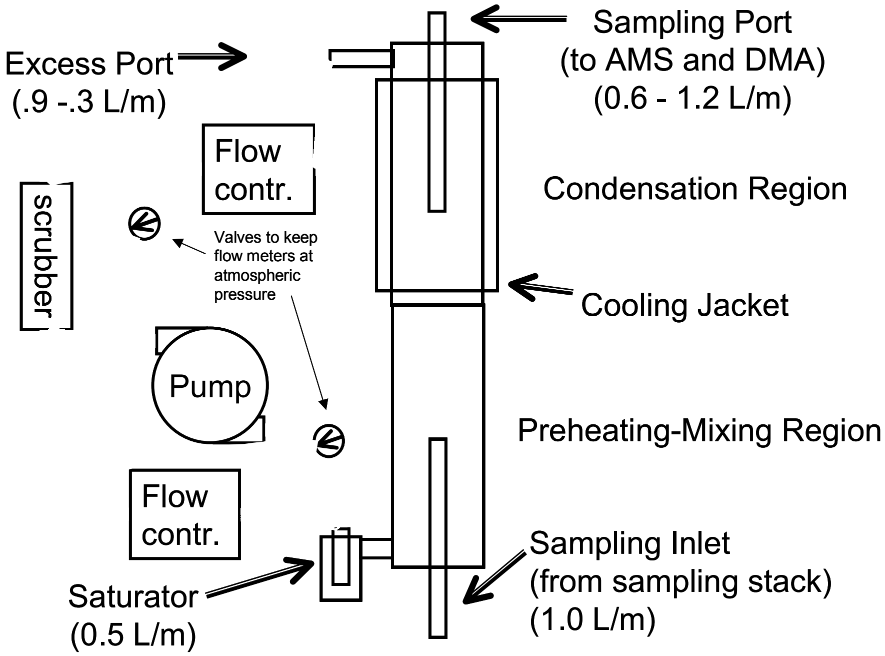


Figure A1. Schematic Diagram of the Flow Cloud Chamber.

The coating material used for these experiments was 1-naphthyl acetate. The flow cloud chamber was operated with the saturator at 40 °C and a dry air flow of 0.5 L/min, the entrance to the condensation region was at 45 °C, the wall of the condensation region was at 10 °C, and the total flow was 1.5 L/min. The presence of pure sulfate particles in the sampled aerosol was determined by comparing the fraction of particles exhibiting sulfate marker ions in the mass spectra with and without the coating. If pure sulfate particles are present in sufficient amounts, then the fraction of particles exhibiting sulfate marker ions will increase when the coating apparatus is used. If pure sulfate particles are not present in sufficient amounts, then the fraction of particles exhibiting sulfate marker ions will be unchanged when the coating apparatus is used.

Results

Over the course of four days from November 13, 2001 to November 16, 2001 eight experiments were performed to ascertain the presence/absence of pure sulfate particles. Table 1 shows a summary of the experimental conditions and details.

The particle mass spectra collected during these experiments were analyzed by comparing the fraction of the single particle mass spectra that contain sulfate in each particle size range in the ambient sample to the fraction that contain sulfate in the coated sample. The presence of sulfate in the particle mass spectra is determined by the presence of the HSO_4^- ion (m/z = 97) in the particle mass spectrum. Due to the limited resolution of the mass spectrometer and the possibility that other ions (e.g. SO_4^-, $H_2SO_4^-$, etc.) are produced, any ion signal that exceeded the detection threshold in the negative ion mass bins from m/z 96 – 101 was assumed to be sulfate.

Table A1. Summary of the coating experiments performed in Pittsburgh in November 2001.

Date	Start Time (Ambient)	Start Time (Coated)	Orifices[e]	D_{avg} (nm)[a]	Coating Thickness[b]	Notes
11-13-01	12:00	13:22	5,6,7,8,9	56	0	c
11-14-01	15:20	16:25	5,6,7,8,9	55	7	
11-15-01	8:21	9:54	6,7,8,9	56	14	
11-15-01	10:47	11:41	6,7,8,9	57	11	d
11-15-01	16:47	17:33	6,7,8,9	57	27	
11-16-01	12:48	12:01	6,7,8,9	42	20	
11-16-01	14:32	13:46	6,7,8,9	33	8	
11-16-01	16:25	15:40	6,7,8,9	39	3	

[a] mean diameter of (ambient) aerosol distribution entering the cloud chamber

[b] determined from mean diameter of aerosol distribution leaving the cloud chamber

[c] the mass spectra indicate that these particles are coated, although the thickness is too small to be measured

[d] detection threshold was set too low, which may invalidate the data

[e] orifice numbers correspond to selected particle sizes between 40 and 100 nm in diameter

Figure A2 shows a summary of the sulfate analysis. Here the difference between the fraction of particles that contain sulfate with and without the coating is plotted as a function of inlet pressure. Note that *smaller* orifice numbers correspond to *larger* inlet pressures and hence *larger* particle diameters. The particle diameter range spanned by these orifices is 40-100 nm. In this figure, a positive value means that a larger fraction of sulfate particles were observed from the coated particles than from the ambient particles.

Since the mass spectrometer scan mode allowed only up to about 30 particles to be detected for any orifice setting at any given time, the uncertainty in determining the increase in the fraction of sulfate particles is large, on the order of +/- 40%. As can be seen in Figure A2, all of the data fall within this range.

Conclusion

In this experiment, a relatively small sample set was analyzed (less than 600 particles total). Accordingly, the uncertainty associated with changes in the fraction of particles containing sulfate was large. Nonetheless, the results show that the Pittsburgh aerosol was not dominated by pure sulfate particles during the time period of the experiment. For example, if one half of the ambient particles during this time period corresponded to pure sulfate, then we would have been able to measure a statistically significant increase with the coating apparatus. While we cannot rule out the presence of much smaller numbers of pure sulfate particles, it is clear that the Pittsburgh aerosol was not dominated by these types of particles during the time period of the experiment. Depending upon the needs of the supersite project, this experiment can be repeated in the future with a larger data set to provide a quantitative measure of pure sulfate particles in the Pittsburgh aerosol.

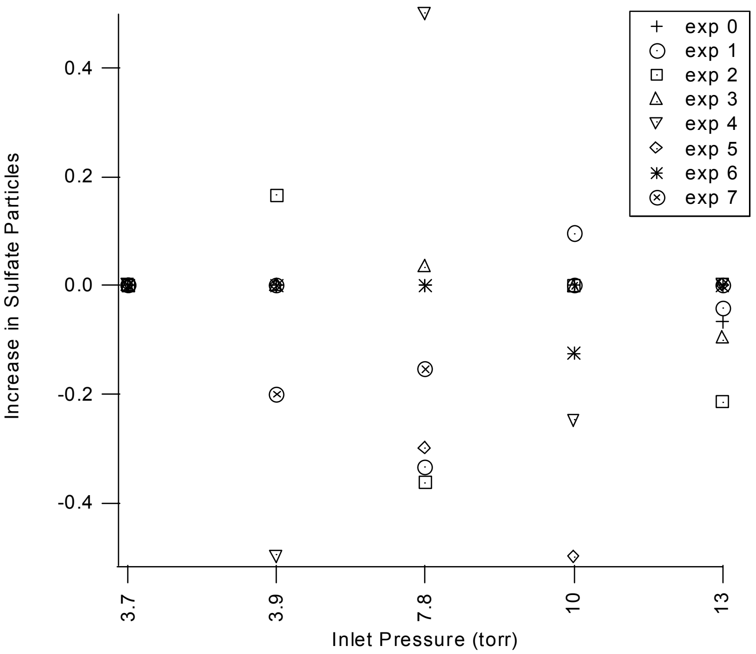


Figure A2. Increase/decrease in the fraction of particles that contain sulfate when ambient particles are coated to enhance sulfate detection.

References

1. D.B. Kane and M.V. Johnston, “Size and Composition Biases on the Detection of Individual Ultrafine Particles by Aerosol Mass Spectrometry”, Environmental Science and Technology (2000) 34, 4887-4893.

2. D.B. Kane and M.V. Johnston, “Enhancing the Detection of Sulfate Particles for Laser Ablation Aerosol Mass Spectrometry”, Analytical Chemistry (2001) 73, 5365-5369.

3. R.V. Mallina, A.S. Wexler, K.P. Rhoads, and M.V. Johnston, "High Speed Particle Beam Generation: A Dynamic Focusing Mechanism for Selecting Ultrafine Particles", Aerosol Science and Technology (2000) 33, 87-104.

Publications and Presentations

1. D. Kane, K. Frost, J.J. Wang, M.V. Johnston, “Detection of Negative Ions from Individual Ultrafine Particles”, Analytical Chemistry (2002) in press. [This manuscript discusses laboratory studies of negative ion detection; however, it does show an example of an ambient particle spectrum from the Pittsburgh supersite].

2. D. Kane, M.V. Johnston, “Detection of Negative Ions from Particles less than 200 nm in Diameter”, American Association for Aerosol Research Annual Meeting, Portland, OR, 10/01. [This talk discussed negative ion detection and the problem of detecting pure sulfate].

APPENDIX B. PROGRESS REPORT FROM UNIVERSITY OF MARYLAND

Introduction

The Buckley group at the University of Maryland deployed a laser induced breakdown spectroscopy (LIBS) system during the July 01 intensive period. The goals of this activity are to provide real-time elemental concentrations, source signatures for source apportionment, and, if possible, real-time particle size and composition analysis. The LIBS system has never been used for ambient particulate monitoring and therefore is primarily experimental in nature.

The deployed measurement system is based on an optical emission technique referred to as laser-induced breakdown spectroscopy (LIBS). The developed LIBS system uses a high peak power pulsed laser beam to form a small spark (i.e. breakdown) directly in the ambient air. The gas sample within this laser-induced spark (which is less than 1 mm in diameter) is converted to a plasma state, with temperatures approaching 25,000 K (45,000^{0}F). All molecules and small particles are dissociated into single atoms within the energetic plasma, and the electrons within these atoms subsequently gain energy, moving from their ground electronic state into excited electronic states. As the plasma cools, the electrons relax to their original condition (i.e. ground state), emitting light at characteristic wavelengths in a process known as atomic emission.

Each element in the sample is characterized by unique atomic emission bands, which like fingerprints enable the identification of constituent elements within the plasma. Furthermore, the intensity of the atomic emission lines can be used to quantify elemental concentrations. One unique feature of the deployed measurement system is that the collected light is dispersed from 200 to 900 nm, allowing the measurement and quantification of nearly all elements simultaneously. This information may be used for source apportionment, to determine relationships between various elements in particulate matter, or (with the assumption of a particular density) to approximate particle sizes.

Methods

The LIBS system deployed in Pittsburgh operates by firing the laser beam directly into a sample cell to create the laser-induced plasma. The emitted light from the plasma is collected and processed in real-time using a spectrometer and detector system controlled by a single PC.

The University of Maryland LIBS system has undergone significant changes since its first deployment at Pittsburgh in June 2001. This first deployment was plagued by difficulties with the spectrometer (which we later learned had been damaged in shipment from the vendor), as well as difficulties with the sampling system. Since that time, several components of the system have been changed to make substantial improvements. Both the original system and improvements will be briefly described in general terms here.

The LIBS system operates by firing the laser beam directly into a sample cell. The excitation source for the LIBS system is a Q-switched Nd:YAG laser operating at a wavelength of 1064 nm, with a nominal pulse width of 7 ns, maximum pulse energy of 300 mJ, and with a 20 Hz fixed pulse repetition rate. The laser beam is expanded to roughly 12 mm diameter using a 1.5x telescope. The beam expansion aids in the formation of a sharp focal spot for reliable plasma formation. The expanded laser beam is focused into the sample cell using a 75-mm UV grade lens to create the plasma (f/6.25). Plasma emission is collected at right angles and directed through a fiber optic into the entrance of a commercial echelle spectrometer (Mechelle 7500, Multichannel Instruments, SA). Due to differing rates of decay between the plasma continuum emission (Bremsstrahlung and recombination) and the atomic emission of targeted analytes, temporal gating is necessary for optimal detection. Temporal signal processing is achieved by gating the CCD intensifier, typically using delays from 5 to 50 μs with respect to the plasma-initiating laser pulse, and gate (shutter open) times of between 10 and 100 μs. The echelle grating disperses the light into several orders onto a DiCAM PCO 12-bit UV-optimized intensified CCD camera. Multichannel Instruments software deconvolves the several grating orders into a single continuous spectrum from 200 – 900 nm.

The original system fielded in Pittsburgh in June 2001 operated using in-house (University of Maryland) software that analyzes each laser shot to determine whether any elements were detected in that shot. If elements are detected in a particular shot, the software places that shot in the "hit" category. As metals in particular are primarily found in the atmosphere in condensed phases, these hits generally correspond to individual or several particle hits. This software has been plagued by problems inherent in the software drivers that were supplied to the University of Maryland by Multichannel Instruments. In addition, the fiber optic coupling was broken and the camera became misaligned in shipping from the vendor in Sweden to the U.S.

In addition to fixing problems related to the hardware and software, improvements in the collection optics, sample cell, and in the data collection methods have improved signal collection considerably. Improvements in the latter will be discussed below.

Results and Discussion

Figure B1 shows a spectrum from June 2001, during the time that the LIBS system was first running in Pittsburgh. Strong lines observed in the 700 – 900 nm region are primarily from O and N atom emission. Figure B1 can be contrasted with Figure B2, which is a similar spectrum from March 2002. In Figure B2, particular lines corresponding to a distinctive N_2 triplet in the 742 – 747 nm range and an O_2 peak at 777 nm are labeled. In comparison with Figure B1, it is observed that the wavelengths of the peaks in Figure B2 are shifted, and that the peaks are approximately 7 times stronger. The peak locations in Figure B2 are correct, while in the earlier spectra loose components inside the spectrometer and incorrect wavelength calibrations resulted in erroneous wavelength assignments that shifted from measurement to measurement. This issue was resolved at the factory. In addition, a broken fiber optic coupler was fixed, greatly increasing the optical throughput of the system, resulting in stronger signals.

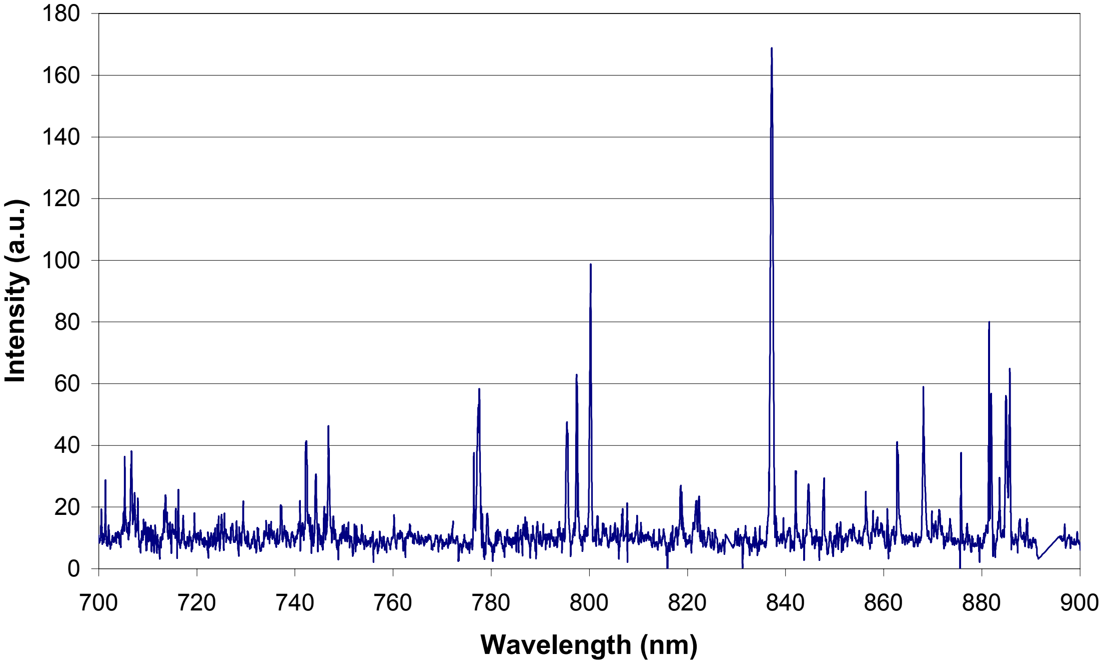


Figure B1: Spectrum illustrating performance of the Mechelle Spectrometer in June 2001.

Despite the improvements in the signal between June 2001 and present, the signal to noise in a typical single-shot measurement still limits the measurement capability of this spectrometer to large particles. Detection limits for individual elements vary greatly, according to the transition strength of the elemental line and the delay and gate selected for the measurement.[*] Substantial variation in signal strength is observed for each element depending upon the delay and gate. For most measurements here we choose a delay of 5 µs and a gate of 60 µs. This provides moderately good detection limits for nearly all species of interest. In the best cases (e.g. Na), a 200 fg mass detection limit appears possible, but this has not yet be achieved in the laboratory. As an example, 200 fg would correspond to the sodium mass in a pure 300 nm particle of Na_2O.

---

[*] B.T. Fisher, H.A. Johnsen, S.G. Buckley, D.W. Hahn, **"Temporal Gating for the Optimization of Laser-Induced Breakdown Spectroscopy Detection and Analysis of Toxic Metals,"** *Applied Spectroscopy*, 55 (10) pp 1312-1319 (2001).

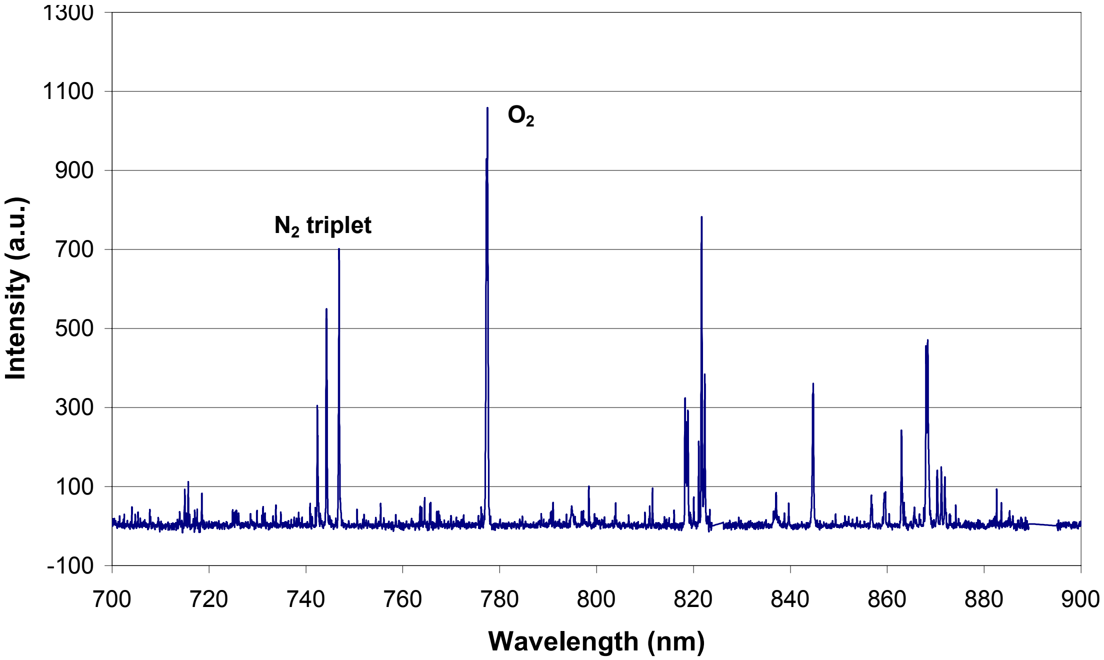


Figure B2: Spectrum illustrating performance of the Spectrometer in March 2002.

Finally, the laboratory has recently been deploying a new spectrometer system expected to have greater throughput than the Multichannel Instruments Mechelle. This system, a PI-MAX ICCD coupled to an Acton 0.25-meter spectrometer (Roper Instruments), has already been demonstrated in the laboratory. The system has a much faster response (> 20 Hz compared with 0.5 Hz) than the Multichannel Mechelle, in binning mode, and greater sensitivity. A measurement of the Mg (II) lines was made using the same laser, laser pulse energy, delay / gate, optical collection system, and concentration, by simply switching the fiber optic output from the collection optics from the Mechelle to the Roper system. The resulting Mg spectrum is shown in Figure B3. Obviously there is still substantial signal, in a situation where the Mechelle is at the signal-to-noise limit. The only disadvantage of the Roper system is that the maximum wavelength range for LIBS measurements is approximately 40 nm, so only particular multi-element combinations can be accommodated.

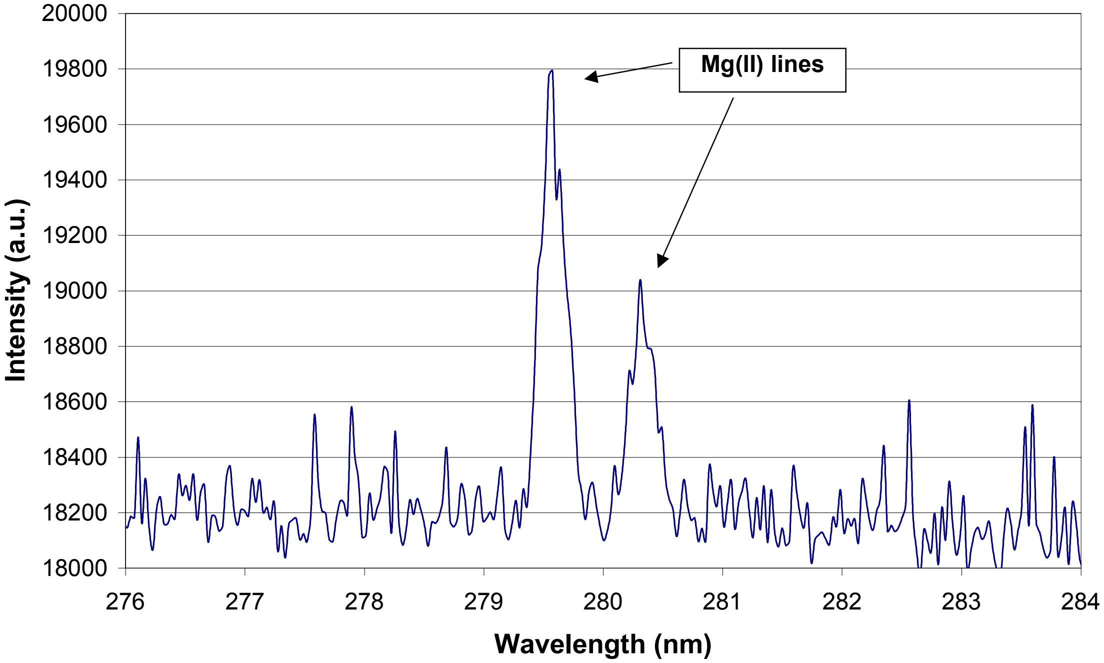


Figure B3: Mg (II) lines measured with Roper spectrometer.

An additional improvement since June 2001 has been in the area of signal processing. Previous measurements have been entirely on a single-shot basis, in which each spectrum was downloaded from the camera and processed on the computer. However, recently measurements have been made in which many spectra (i.e. 100) are averaged on the ICCD chip. In this mode, the charge is accumulated on the chip in advance of the amplification in the microchannel plate, which is the primary source of noise in the measurement. For this reason, the noise in single-shot measurements and in measurements accumulated on the CCD chip is comparable, *but the signal from repeated hits of a particular element is added*. This results in improved signal-to-noise that may be useful for relatively continuous signals.

Conclusions

Substantial progress has been realized in preparing an experimental LIBS system for real-time measurements of metals found in particulate matter. The next deployment of this system in Pittsburgh, to occur this spring, will focus on continuous metals measurements to compare with John Ondov's group. These measurements will be made in averaging-on-the-chip mode. Given the best detection limits observed for single-spectra (single-particle) measurements, the current Multichannel Instruments echelle spectrometer may not be suitable for single-particle measurements of multicomponent aerosols. Currently the lab is reassessing the elemental detection limits for the Mechelle system. It is anticipated that in the next deployment, single-particle measurements will be attempted with the Roper system.