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ABSTRACT

This report describes the technical progress made on the Pittsburgh Air Quality Study (PAQS) during the period of September 2003 through February 2004. Significant progress was made this project period on the analysis of ambient data, source apportionment, and deterministic modeling activities. Results highlighted in this report include chemical fractionation of the organic fraction to quantify the ratio of organic mass to organic carbon (OM/OC). The average OM/OC ratio for the 31 samples analyzed so far is 1.89, ranging between 1.62 and 2.53, which is consistent with expectations for an atmospherically processed regional aerosol. Analysis of the single particle data reveals that a on a particles in Pittsburgh consist of complex mixture of primary and secondary components. Approximately 79% of all particles measured with the instrument containing some form of carbon, with Carbonaceous Ammonium Nitrate (54.43%) being the dominant particle class. PMCAMx predictions were compared with data from more than 50 sites of the STN network located throughout the Eastern United States for the July 2001 period. OC and sulfate concentrations predicted by PMCAMx are within $\pm 30\%$ of the observed concentration at most of these sites. Spherical Aluminum Silicate particle concentrations (SAS) were used to estimate the contribution of primary coal emissions to fine particle levels at the central monitoring site. Primary emissions from coal combustion contribute on average $0.44 \pm 0.3 \mu\text{g}/\text{m}^3$ to $\text{PM}_{2.5}$ at the site or $1.4 \pm 1.3\%$ of the total $\text{PM}_{2.5}$ mass. Chemical mass balance analysis was performed to apportion the primary organic aerosol. About 70% of the primary OC emissions are from vehicular sources, with the gasoline contribution being on average three times greater than the diesel emissions in the summer.

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EXECUTIVE SUMMARY

With support from the US Department of Energy and the US Environmental Protection Agency, Carnegie Mellon University is conducting 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.

This document is the sixth semi-annual progress report for this project. This project period significant progress was made on analysis of ambient data, source apportionment, and deterministic modeling activities. Major results reported in this progress report include:

- Chemical fractionation of the organic fraction has been performed to quantify the ratio of organic mass to organic carbon (OM/OC). The average OM/OC ratio is 1.89, ranging between 1.62 and 2.53; values that are consistent with expectations for an atmospherically processed regional aerosol.
- Analysis of the single particle data reveals that a on a particles in Pittsburgh consist of complex mixture of primary and secondary components. Approximately 79% of all particles measured with the instrument containing some form of carbon, with Carbonaceous Ammonium Nitrate (54.43%) being the dominant particle class.
- A rich array of multi-component metal particles were identified in the single particle data; the most commonly observed ions were K^+ , Na^+ , Fe^+ , Pb^+ , and to a lesser extent, Ga^+ and Zn^+ . These particles were typically smaller in size, ranging from about 75 – 300 nm, and tended to be associated with specific wind directions. The

analysis of the wind roses for individual classes has facilitated the isolation of specific local industries to which the observed metal based classes may be attributed.

- PMCAMx predictions were compared with data from more than 50 sites of the STN network located throughout the Eastern United States for the July 2001 period. OC and sulfate concentrations predicted by PMCAMx are within $\pm 30\%$ of the observed concentration at most of these sites.
- Spherical Aluminum Silicate (SAS) particle concentrations were used to estimate the contribution of primary coal emissions to fine particle levels at the central monitoring site. Primary emissions from coal combustion contribute on average $0.44 \pm 0.3 \mu\text{g}/\text{m}^3$ to $\text{PM}_{2.5}$ at the site or $1.4 \pm 1.3\%$ of the total $\text{PM}_{2.5}$ mass. This is consistent with expectations that primary coal emissions are a small contributor to ambient fine particulate matter mass.
- Chemical mass balance analysis was performed to apportion the primary organic aerosol. About 70% of the primary OC emissions are from vehicular sources, with the gasoline contribution being on average three times greater than the diesel emissions in the summer. However, the gasoline/diesel split depends on the PAHs; coke production dominates the ambient PAH concentrations in Pittsburgh, even though coke emissions only contribute a small fraction of the OC. Woodsmoke is a smaller component, with significant contributions in the fall and winter seasons.

EXPERIMENTAL

This section provides an overview of the effort on various project activities. This project period the majority of the effort went into Activity 3 Source Characterization, Activity 4 Source Apportionment, and Activity 5 Three-Dimensional Modeling.

Activity 1. Project Management

During this project period a data analysis meeting was held in Anaheim California in October 2003 in conjunction with the American Association of Aerosol Research Annual Meeting. The workshop consisted of one full day sessions during which PAQS project team members described the status of the research and future plans. The QA/QC report for the ambient sampling has been submitted to EPA. A copy of this report is attached as an Appendix.

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. The ambient sampling phase of the Pittsburgh Air Quality Study was successfully completed at the end of September 2002. Approximately sixteen months of data were collected, including

three intensive sampling periods (July 2001, January 2002, and July 2002) and several special experiments (instrument intercomparison, nucleation, etc). The structure in Scheneley Park has been removed and the site restored to its original conditions per our agreement with the City of Pittsburgh. Work has continued on the analysis of the ambient data set. Selected results from this analysis are shown in the Results and Discussion section of this report.

Activity 3. Source Characterization

The purpose of this activity is to develop updated emission profiles for important source categories around Pittsburgh. Updated source profiles are being developed through a combination of source testing, fence line measurements, and analysis of highly time resolved data collected at the central site. We are completing the chemical and data analysis of samples that have been collected as part of this project. The only remaining data collection component of this task is the characterization of full-scale coal boiler.

The major activity this period was a second scoping study adjacent to a large steel production facility near Pittsburgh. Although there was some evidence of plume impactions from the fence line site, the signal was judged to be too small to develop a source profile and subsequent studies were not pursued.

We continue to analyze archived samples source samples collect during previous project periods from the coke production facility, tunnel, road dust, and vegetative detritus. A notable component of this work has been to look for new organic molecular markers in the coke samples, several hetero-S-PAH compounds have been identified that may be useful tracers for coke production.

We continued to work this project period to identify a full-sized coal fired power plant for characterization. DOE organized an informal meeting at the Air Quality 4 conference with EPRI, Southern Company, TVA, and UNDEERC. Carnegie Mellon is now working with UNDEERC to identify a plant leveraging their ongoing mercury control research. The identification of full-scale coal fired power plant is currently the only unaccounted component of the project.

Activity 4. Source Apportionment

The purpose of this activity is to quantify the contribution of different sources to the fine PM_{2.5} levels in Pittsburgh. Significant effort was expended on the source apportionment analysis including apportionment of primary organic aerosol by CMU, apportionment of primary emissions from coal fired power plants by the RJ Lee Group, the apportionment of particle number by Clarkson University, the use of data collected at different time scales for source apportionment by Clarkson University, and apportionment using single particle information. Results from this work are described in more detail in the Results and Discussion Section of this progress report.

Activity 5. Three-Dimensional Deterministic Modeling

The purpose of this activity is to evaluate the performance of the three-dimensional chemical transport model (PMCAMx) with air quality data collected by this and other projects. PMCAMx is a publicly available computer modeling system for the integrated assessment of photochemical and PM pollution. This CTM has been recently upgraded by the CMU team and ENVIRON to include state-of-the-art description of aerosol dynamics and thermodynamics, cloud chemistry, and wet removal processes. PMCAMx+ is the research version of the code and it includes the latest developments in Carnegie Mellon organic and inorganic aerosol and aqueous-phase chemistry modules. The aerosol module has flexible size resolution and includes three different descriptions of aerosol dynamics (equilibrium, hybrid, and dynamics). A different sub-module can be used for each computational cell for each timestep based on the timescale for equilibrium in this cell, the acidity differences among particles of different sizes, or the location of the cell. For example, the simplest and fastest approach is used for the cells far from the area of interest. A similar flexible approach is used by the Variable Size Resolution Model (VSRM) for cloud chemistry. These tools are as accurate as the descriptions used by other CTMs but are faster by one to two orders of magnitude.

During this project period Carnegie Mellon worked with LADCO on emission inventories and meteorology data. An extensive literature review was performed to update the emission profiles for coal-fired power plants, diesel engines, wood combustion, open burning, and natural gas combustion. The Mobile6 model was used to simulate vehicle emissions for specific days of the week (week day, Saturday, and Sunday). Finalized inventories have been developed for each month of the year. Meteorology data have been developed for the January 2002 intensive. Finally more extensive compares have been performed with data collected at other sites during the July 2001 intensive. These comparisons are presented in the Results and discussion section.

RESULTS AND DISCUSSION

Characterization of the Organic Fraction

The Rutgers University team focused on the analysis of the factor used to convert organic carbon measurements (OC) into organic mass. This factor is an estimate of the average organic molecular weight per organic carbon weight (OM/OC), stems from limited studies conducted during the nineteen seventies. A recent investigation based on literature analysis conducted by *Turpin and Lim* (2001) suggests that 1.4 is the lowest reasonable estimation for the OM/OC value for an urban aerosol and that 1.4 does not accurately represent the OM/OC ratio for non-urban aerosols. A ratio of 2.1 is proposed for non-urban aerosols; these aerosols tend to be influenced by atmospheric processing and therefore more oxygenated. Woodsmoke emissions also tend to increase the OM/OC ratio above 1.4.

Rutgers has developed an analytical methodology to estimate the average OM/OC ratio for the Pittsburgh area and to characterize the organic component of the atmospheric aerosol collected during the Pittsburgh Air Quality Study (PAQS). For this purpose, twenty-four hours PM_{2.5} samples were collected from July 2001 through July 2002 on 8 × 10 inch baked quartz fiber filters (QFF) at 40 cfm in an High Volume Sampler equipped with a PM_{2.5} inlet. To date, thirty-one samples and field and laboratory blanks have been extracted, fractionated by polarity, and analyzed for mass and organic carbon using the following procedure. Each was sonicated for 15 minutes in a mixture of hexane, dichloromethane and acetone (1:1:1), and then Soxhlet-extracted for 24 hours in the same mixture of solvents. Extraction recoveries were determined by analyzing the OC concentrations on the QFFs before and after the extraction processes. OC was analyzed by thermal-optical transmittance in a Sunset Laboratory Carbon Analyzer using the standard PAQS analysis protocol. The average OC recovery was found to be 80%. The extract volume was then reduced to a few milliliters in a rotary evaporator and filtered through a 0.2 μm pore Teflon filter. An aliquot of the extract (20 - 70 μL) was then spiked on a 1 cm² piece of pre-weighed aluminum foil, and the solvents were allowed to evaporate under the hood. It was equilibrated at 30-40% RH and 20-23 °C and weighed. It was then analyzed for OC by thermal-optical transmittance. The remaining extract was applied to the top of a 30 × 7 cm glass column containing 1.5 g of silica gel (activated at 150 °C for three hours). Increasingly polar compounds were eluted from the extract with a series of solvents (15-20 ml of hexane, dichloromethane, ethyl acetate, acetone and methanol, sequentially) using nitrogen pressure on the top of the column to obtain a flow of around 1.4 ml/min at the bottom of the column. Mass recoveries during fractionation varied between 76 and 97%. A small aliquot of each fraction was spiked a 1 cm² piece of pre-weighed aluminum foil and the mass and OC loading of each fraction was determined as described above. Aliquots of extract were also analyzed by ion-chromatography for ammonium nitrate and ammonium sulfate. It was our expectation that some ammonium nitrate would be partially soluble in the more polar solvents used. One filter blank for every ten filters samples was analyzed in an identical manner. Every mass measurement was corrected for the correspondent blank mass. Ammonium nitrate and ammonium sulfate were also subtracted from the mass measurements so that the measured mass represented OM. OC mass measurements were corrected for the corresponding OC_{blank} mass. The OM/OC ratio for each extract and for each fraction was then determined by dividing the resulting OM by the corresponding OC.

On average, the OM_{blank} mass was 3.5% of the extract mass, while the OM_{blank} masses in the different fractions were 4.3, 4, 7, 2.8 and 16.9% for the hexane, dichloromethane, ethyl acetate, acetone and methanol fraction masses, respectively. On average, the OC_{blank} mass was 6% of the extract OC mass, while the average OC_{blank} masses in the different fractions were 5.6, 3.3, 8, 2.9 and 11% for the hexane, dichloromethane, ethyl acetate, acetone and methanol fraction OC masses, respectively. The combined masses of ammonium nitrate and ammonium sulfate represented an average of 10.7% of the extract masses, and were found only in the acetone and methanol fractions. Replicate analyses were run for each step of this analytical procedure for 10% of the samples (both extracts and fractions) and the analytical precision for the estimation of the OM/OC ratio measurements was better than 4%.

Figure 1 shows the average percentage of the extract mass (blue; OM) eluted in hexane (1), dichloromethane (2), ethyl acetate (3), acetone (4) and methanol (5) and the average percentage of the extract mass that is carbon (green; OC/OM) for the 31 samples analyzed to date. For example, an average of 22.6% of the extract mass was eluted in hexane, and 15.6% of the extract mass was OC. Therefore the average OM/OC for the hexane fraction was $22.6/15.6 = 1.45$. The sum of the two medium polarity fractions (dichloromethane and ethyl acetate fractions) comprised, on average, 41.9% of the extract mass, while the sum of the most polar fractions (acetone and methanol fractions) comprised 35.5% of the extract mass.

The average OM/OC ratio for the 31 samples analyzed so far is 1.89, ranging between 1.62 and 2.53. These values are consistent with the expectations of *Turpin and Lim* (2001), who stated that a OM/OC ratio of 1.6 ± 0.2 is reasonable for an area impacted by recently-emitted primary (non-wood combustion) OC, and 2.1 ± 0.2 is reasonable for an area impacted by aged aerosols. The value can be even higher for woodsmoke-impacted samples. Figure 2 shows a plot of the average OM/OC ratio for each fraction (calculated from fractionated mass and carbon values and averaged over the 31 samples analyzed so far) versus the polarity index of the solvents used to solubilize each fraction (0, 3.1, 4.4, 5.1, and 5.1 for hexane, dichloromethane, ethyl acetate, acetone, and methanol, respectively). The average OM/OC values increase from 1.45 for the least polar fraction to 2.35 for the most polar fraction ($R^2 = 85\%$). The OM/OC ratio was calculated for each sample using both 1) OM and OC from the extract and 2) OM and OC for each fraction. These two independent estimates of the OM/OC ratio for each sample always agree within 9%, which adds confidence to the results.

We are currently analyzing another 31 samples to provide OM/OC ratios and OC fractionated by polarity for every 6th day over a one-year period. These will be examined for seasonal trends and evidence of the impact of woodsmoke and secondary OC on the polarity of particulate OC.

In addition, each fraction will be analyzed by Fourier Transform Infra Red (FTIR) spectroscopy to gain qualitative information about the functional group composition. An aliquot of each fraction will be sandwiched between two IR-transparent plates and analyzed in a Matteson Research Series 100 FTIR Spectrometer. Mass spectral analysis of fractions is also being considered.

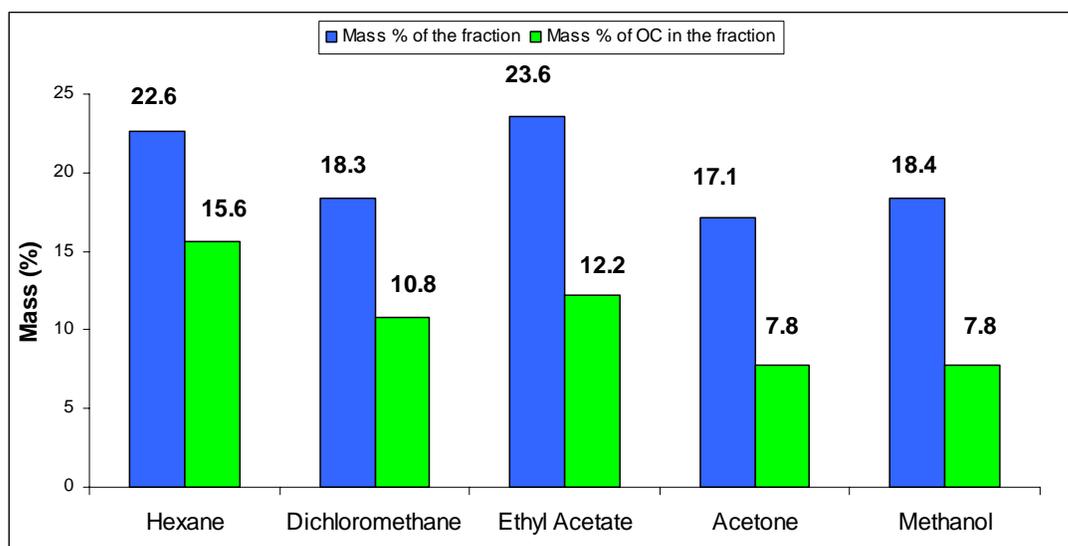


Figure 1. Average percent of organic matter in fraction (blue) and percent of organic carbon in fraction (green) for 31 paqs samples.

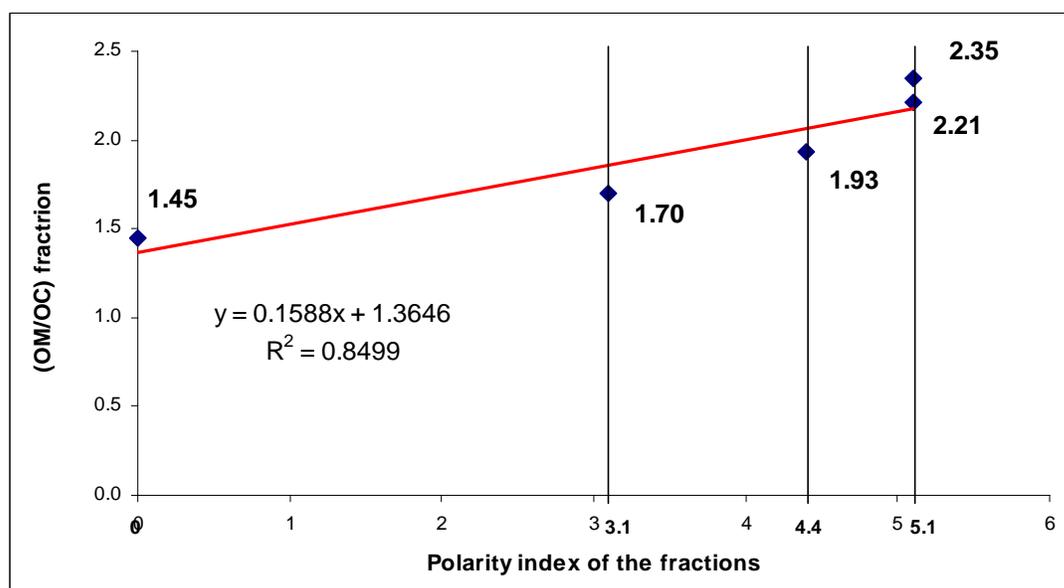


Figure 2. Average OM/OC ratio for each fraction and the polarity index of the solvents used to solubilize each fraction (0, 3.1, 4.4, 5.1, and 5.1 for hexane, dichloromethane, ethyl acetate, acetone, and methanol, respectively). OM/OC increases with polarity index, as expected.

Fine particle elemental concentrations

The University of Maryland used laser-induced breakdown spectroscopy (LIBS) to measure fine particle elemental concentrations. Elemental concentrations are determined

from LIBS spectra by measuring the peak-to-base (P/B) ratio and comparing it to a calibration. The P/B ratio is defined as the integral of the atomic emission peak normalized by the continuum emission of the plasma in the spectral region adjacent to the atomic peak. Calibrations are performed by sampling particle-laden streams of known metal concentration, and measuring the P/B ratio. Streams of known concentration are generated by nebulizing reference standard metal solutions using a constant output atomizer. The metal concentration in the output stream of the atomizer is determined by sampling with a Scanning Mobility Particle Sizer (SMPS). The composition of the particles is assumed, based on the nebulized solution, to deduce density and mass fraction of the metal species. The total particulate volume reported from the SMPS is then multiplied by the density of the particle and the mass fraction of the element of interest to yield the mass of the element per volume of gas. Ensemble averages of 1000 laser shots were used to determine the P/B ratio for a given concentration. Data points were fit with a linear regression, and regression coefficient (R^2) values ranged from 0.97 to 0.99 for the seven calibrations.

Data Acquisition and Analysis

The concentrations of seven metals (Al, Ca, Cr, Cu, Mg, Mn, Na) were measured during a one week period from August 26 to September 2, 2002. The system was run continuously for most of the period, with occasional breaks taken to perform minor maintenance and data backup. A spectral region of approximately 40 nm can be monitored at any given time, so elements can be measured simultaneously only if they have emission lines close to each other. To monitor a larger number of elements, spectral regions must be scanned, resulting in a loss of temporal resolution. The system continuously cycled through four spectral windows, acquiring 2000 shots in just under two minutes per window. The spectrometer position and the timing of the camera were controlled by computer, allowing the system to be fully automated.

Along with elemental concentrations, the LIBS technique can provide information about particle mass distributions. The LIBS signal is proportional to the concentration of analyte within the plasma volume. If the concentration is multiplied by the plasma volume, the mass of analyte can be calculated. When a single particle is hit the mass of analyte within the plasma is equal to the mass of analyte in the sampled particle. In this manner, the particle mass distribution of a given element can be determined.

Aerosol Sampling

Air was sampled using a particle concentrator from Eatough's group at Brigham Young. The particle concentrator consists of a $PM_{2.5}$ cyclone inlet and a virtual impactor. The virtual impactor removes excess air, producing a flow stream with an increased concentration of fine particles. The design and characterization of the system have been previously described by Ding et al. (2002) (note: the diffusion denuder and filter packs were removed for this study). In these experiments, the concentrator runs at a minor to total flow ratio of 20% and a total flow of $2.5 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}$ (150 l min^{-1}). This results in approximately a five-fold concentration of particles and a low cutoff of approximately

0.1 μm . The detection limit of the LIBS system is above 100 μm , therefore the concentrator losses should not significantly affect the LIBS performance.

After passing through the particle concentrator, the sample air is carried approximately three meters to the sampling cell of the LIBS system in 1.2 cm diameter Teflon™ lines. The sampling cell is a sealed 6 cm diameter cylindrical Teflon chamber with planar windows allowing optical access. The choice of Teflon™ may have adversely influenced our small particle hit rate due to electrostatic deposition of particles in the line; this should be avoided in future efforts of this kind. Because the repetition rate of the laser is fixed at 20 Hz and the flow rate from the concentrator was set at $5 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$ (30 l min^{-1}) in these experiments, a section of 5/8 cm stainless steel tube was used to accelerate the flow and introduce it to the plasma. The tube was positioned so that the plasma was approximately 1 cm from the opening of the tube. This ensured that the velocity was sufficiently high that fresh gas was sampled with each laser shot.

Ambient Metal Concentrations

The combination of the measured hits for each element allows the construction of an ensemble-averaged spectrum. The average concentration of each element is calculated for the entire week (Table 1). The concentrations ranged from tens of nanograms per cubic meter for four minor elements to hundreds of nanograms per cubic meter for Na, Mg, and Ca. Hourly concentrations of the three major elements are plotted in Figs. 1a-1c.

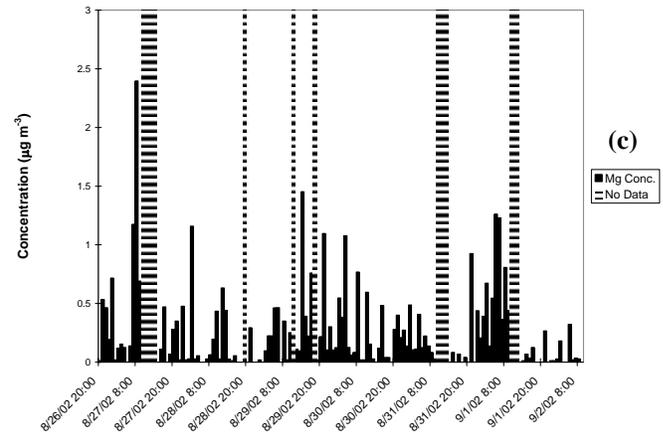
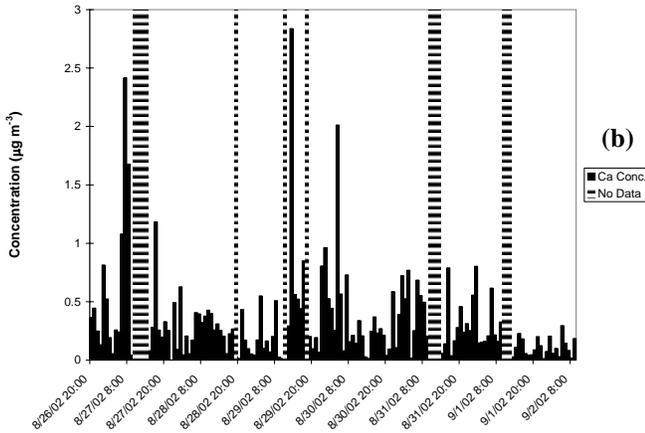
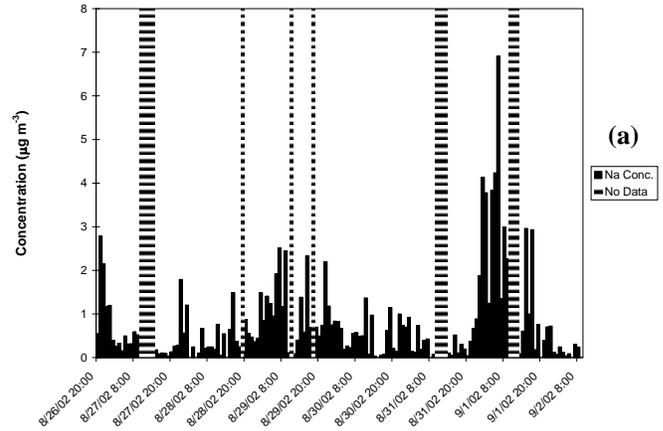
	Ca	Na	Mg	Cu	Al	Mn	Cr
Weekly Avg.	304	716	225	32	30	29	37
Mass L.O.D.	50	143	53	15	184	176	166

Table 1: Weekly average concentrations for measured elements (ng m^{-3}) and threshold mass detection limits (fg).

Relationships among element concentrations were measured by determining the Pearson correlation coefficients between sets of time averaged elemental concentrations. The correlation coefficients between Na, Mg and Ca are given for 1-, 4- and 12-hour averages in Table 2. Interestingly, magnesium shows a moderate correlation with both sodium and calcium, but sodium and calcium show essentially zero correlation. It is also interesting that both the Mg-Na and Mg-Ca correlations get stronger for longer averaging intervals. Further study is needed to determine whether this is due to actual short time-scale fluctuations of element concentrations, or if the hit frequencies are too low to obtain representative samples at the short time scale.

	Na:Mg	Na:Ca	Mg:Ca
1	0.336111		0.010386
4	0.468767	-0.04872	0.609318
12	0.512869	-0.10412	0.696781

Table 2: Correlation of Ca, Mg, and Na measurements at 1-, 4-, and 12- hour time scales, measured using the Pearson correlation coefficient.



Figures 3a-c: Measured hourly concentrations of (a) Sodium; (b) Calcium; and (c) Magnesium.

Particle Mass Distributions

Mass distributions were determined for the elements based on particle hits. Single shot element concentrations were multiplied by a plasma volume of 0.25 mm^3 . The distributions of Na, Mg and Ca all show that the distributions are dominated by particles near the detection limit. The distributions are truncated at the mass corresponding to the conservatively-determined detection threshold of the LIBS system. The mass detection limit for each element is shown in Table 1. The location of the mode of the full distribution, and how far below the detection limit it would be, cannot be determined. It is likely that the LIBS system is missing a significant number of the smallest particles and thus under predicts the mass concentrations of elements. This fact is ameliorated somewhat by the fact that the elemental mass concentrations are a weighted average of the mass number distribution, and hence the larger particles contribute the most to the mass determination.

While ambient particles are typically comprised of multiple compounds, as discussed below, it may be useful to determine an equivalent size based on a pure particle of assumed composition. For example, the mass detection limits in Table 1 for Ca and Mg would correspond to 342 nm CaO and 360 nm MgO particles. The ultimate mass concentration detection limit, which would be expressed in $\mu\text{g m}^{-3}$, is difficult to define for a LIBS monitor, due to the fact that discrete particle hits may be followed by an arbitrary number of non-hits. Each “miss” acts to lower the effective mass concentration detection limit by increasing the volume sampled. Hence the mass concentration detection limit depends both upon the particle size distribution and the mass detection limit.

Multiple-Element Spectra

Several individual spectra contained signal from more than one element. These multi-element spectra illustrate the potential for LIBS to determine complete particle composition and associations between elements. Fig. 3 shows a single particle containing Ca, Mn and Cr. Several other particle types were observed, including predominantly Mg particles with several additional species such as Si, Ca / Al particles, and Fe / Cu / Cr particles. Echelle spectrometers providing spectral coverage from UV to NIR are recently available. Successful implementation of such a device in a LIBS system could greatly improve the usefulness of LIBS for measurement of atmospheric particulate matter. In fact, an initial attempt was made by the authors to measure ambient particulate matter with an echelle spectrometer at the Supersite. Unfortunately the optical efficiency of this particular spectrometer was very poor, and single particles could not be detected. As the sensitivity of the LIBS technique improves, and with the use of large bandwidth echelle spectrometers, useful estimates of total composition and size (requiring assumptions about density and molecular composition) of single particles could potentially emerge, and source apportionment using the methods of Hopke and co-workers, e.g. (Ferguson et al. 2001) could be implemented.

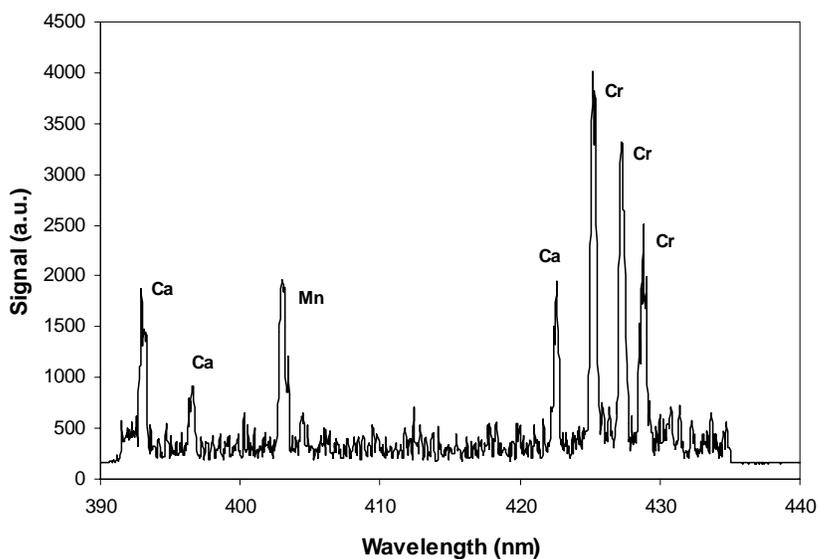


Figure 4: A multiple-element spectrum containing Ca, Mn and Cr.

Discussion

To our knowledge, the only previous measurement of ambient particles using LIBS was performed by Hahn and co-workers (Carranza et al. 2001). Their experiments demonstrated that LIBS could detect increased levels of Mg and Al introduced by fireworks displays during the July 4th holiday. They measured the daily concentrations of Mg, Na, Al, and Ca for several weeks around the fourth of July, sampling roughly 4 hours per day. This current study seeks to demonstrate the capability of LIBS to characterize ambient particulate matter in greater detail, by measuring an extended list of elements at greater continuous temporal resolution. The data from the current study will also provide benchmark accuracy data for verification once the corresponding MOUDI data becomes available.

It is important to note that Carranza et al. (2001) reported particle hit rates one to two orders of magnitude greater than were found in this study. This could be due to several factors, including either sampling issues or issues surrounding the detection limits of the system. One obvious sampling issue is that smaller particles may be trapped in the TeflonTM lines used in our experiments. In addition, environmental differences between Hahn's Florida location and our Pittsburgh location may result in substantial differences in elemental concentrations. Finally, the spark volume is expected to be roughly proportional to the laser pulse energy, and as a consequence Hahn's analytical volume should be significantly larger, as their energy is ~ 9 times greater than ours.

Considering factors influencing detection limits, the higher pulse energy used in Hahn's work results in a more repeatable plasma. Increased variability in the background signal necessitates more conservative detection thresholds. Hahn et al. also could have used a slightly more efficient optical setup for collecting light from the plasma or more optimal detection timing. In addition, they did use a different data processing technique, triggering on one emission line and quantifying using a second line. This method minimizes the influence of false hits, allowing lower thresholds, but can only be applied when more than one line is visible.

Overall, increases in sensitivity yield a greater ability to determine a complete picture of the particle mass distribution, and comparisons indicate that there is room for improvement in our current system. With better detection limits, and correspondingly higher hit rates, improved measurements of the particle mass distribution are certainly possible. However, given the fact that the mass is predominantly in the larger particles, the mass concentrations determined here, based on particles of roughly 300 – 400 μm in diameter and larger, are likely to be close to the actual values.

Single Particle Measurements

The University of California Davis deployed the RSMS 3 at the central Supersite. This instrument is a third generation dual polarity single particle mass spectrometer. The

measurement technique involves size-selective particle sampling, particle beam generation, laser desorption/ionization of individual particles and mass spectrometry. During this experiment, ambient air was drawn from outside the trailer at a height of 6.4 meters above ground through a 10 cm diameter stainless steel duct. Aerosol was sampled from the center of the duct through ¼ in. o.d. copper tubing and dried with a Nafion dryer prior to entering the inlet. Using a computer controlled 10-position rotary valve, the particle flow is then directed through one of nine differently sized flow-limiting orifices contained in an orifice bank. The size of the orifice determines the pressure just upstream of the critical focusing orifice. This inlet pressure, in conjunction with the geometry of the critical orifice, determines the particle size focused and transmitted into the instrument. The particle beam then travels through several differentially pumped skimming stages in which the carrier gas is removed using both mechanical pumps and split turbo pumps. Particles then enter the source region where they are vaporized and ionized by a co-linear, counter propagating and free-fired 193 nm excimer laser. Ions are initially accelerated by a dual gradient in the source region and then travel at constant velocity down their respective time of flight tubes until they impinge upon the micro-channel plate detectors. Current from each detector is recorded and digitized by two separate 500 MHz digitizer channels. Triggered by each laser pulse (50 Hz), the digitizer collects 5000 sample points with a sampling rate of 2 ns covering a mass-to-charge ratio range of ~1 – 300 Da for each detector.

RSMS-3 was fully automated for the entirety of the Pittsburgh Supersite experiment, controlled solely by the data acquisition software, except during times of maintenance or special studies. The measurement protocol was based on sampling intervals starting every three hours for the first four months (September to December, 2001) and every two hours for the remainder of the study (January to September, 2002). Each sampling interval consisted of cycling through the nine flow-limiting orifices, corresponding to nine different particle sizes transmitted into the instrument ranging from about 30 nm to 1.1 micrometers. The instrument was operated at each orifice until either 10 minutes expired or 30 particles were sampled, whichever came first. On average, ~ 1 hour was required to step through the entire orifice bank. Over the course of a day, the average number of single particle mass spectra acquired was ~1100. Of these 1100, ~ 15% had detectable signal from both positive and negative ions while the remainder had signal from positive ions only.

Data Processing and Analysis

Each single particle mass spectrum collected has been processed from its original state as follows: 1) It has been time to mass calibrated according to the relation $m/z = (at + b)^{1/2}$ where m/z is mass to charge ratio, a and b are experimentally determined constants and t is the time interval during which the ion current was detected. 2) A binned ion current for each m/z value was obtained by integrating +/- 0.5 Da about each integer m/z value. 3) The spectrum has been normalized according to a Euclidian norm. Calibration is the single most important step in this procedure. It is vital to the interpretation of the spectral peaks. Since the calibration constants are moderately dependent on the degree to which the particle and laser beams are coincident, they have a tendency to vary slightly from spectrum to spectrum. As a result, each spectrum has been

inspected and calibrated individually to ensure the quality of the data processing and the integrity of the analysis.

Using a data clustering algorithm, all spectra obtained during this experiment have been classified into unique particle classes (clusters) based upon the distribution of their mass peaks. In addition to data clustering, numerous other analysis techniques have been applied which sort, organize, correlate and count spectra. These have been used on the entire data set to determine the fraction of total particle hits by month, size and particle class. They were also applied independently to each particle class to establish the distribution of particle hits within the class by month, time of day, size and wind direction. Correlating single particle spectra with wind data is possible due to the time signature associated with each spectrum. It allows for the identification of the direction(s) from which each particle class is most frequently observed. This, in conjunction with knowledge of local industry, can be used to associate specific classes with nearby sources and has proven to be a very powerful technique for studying source attribution.

RSMS-3 began taking measurements on 20 September 2001 and was successfully sampling for 306 of the possible 372 operation days. During this period, 236,286 single particle mass spectra were acquired, 185,244 (78.4%) of which had positive ion signal only and 51,042 (21.6%) that had both positive and negative ion signal. There were very few instances of spectra with only negative ion signal. It is important to note that the existence of a complimentary negative ion spectrum is most commonly an indicator of atmospheric aging. This is simply due to the fact that the major negative ions detected are those of secondary particle components, specifically nitrates and sulfates. As a result, negative ion signal is seen predominantly in the spectra of particles from the larger size bins because there is simply more analyte in larger particles, making detection more likely. Note that small particles may have also undergone significant atmospheric transformations but this cannot be detected in the negative ion spectrum due to insufficient analyte. The fraction of total particle hits by month of the year indicates that the largest fraction of particles sampled, as well as the largest fraction containing negative ion spectra, was observed in the winter during the month of January. However, there are elevated levels in the summer months of June and July, falling outside the expected trend. Plotting frequency of occurrence versus wind direction for all wind observations greater than two meters per second shows that the wind comes predominantly from the west to northwest in the Pittsburgh area and is almost never observed originating from anywhere inside the first quadrant. This is an important issue to consider when interpreting wind signatures associated with specific particle classes. Particles are observed in the first quadrant, but little statistical significance is given to these observations in the context of identifying source-receptor relationships.

Data classification was performed in a series of steps designed to optimize the resolution of the classification. First, the entire data set was split into three groups based upon periods of similar operating conditions and instrument performance. The clustering algorithm was then applied independently to each of the three groups using positive ion spectra only. In total, over 500 clusters were isolated. These were individually inspected

and manually organized into approximately 100 sub-classes. Sub-classes were then categorized into 20 distinct particle classes, yielding a single average positive ion spectrum for each class. Identified particle classes and the percent of the total number of spectra belonging to that class are as follows: Carbonaceous Ammonium Nitrate (54.43%), Biomass Burning (10.87%), Elemental Carbon/Organic Carbon (6.59%), Sodium/Potassium (5.76%), Unidentified Organics (3.34%), Elemental Carbon (3.24%), Silicon/Potassium/Iron/Gallium (3.12%), Sodium/Potassium/Zinc/Lead (2.86%), Lithium/Sodium/Potassium (2.28%), Fe (1.16%), Sodium/Potassium/Tin/Lead (0.8%), Amines (0.68%), Aluminum/Silicon/Calcium (0.55%), Mixed Metals (0.5%), Nickel (0.45%), Calcium/Calcium Oxide (0.37%), Cerium/Iron (0.29%), Unidentified (0.26%), Chromium/Molybdenum/Tungsten (0.13%) and Sulfate (peaks in positive ion spectra only, 0.02%).

Negative ion spectra were classified independently within each positive ion class during the final step of classification. As stated above, sulfate and nitrate, secondary components, dominate the entire distribution. Every single negative ion class has some form of sulfate in it. Overall, seven negative ion classes were isolated. These include: Nitrate/Sulfate (70.3% of all negative ion spectra), Sulfate only (13.3%), Chlorine/Nitrate/Sulfate (11.1%), Elemental Carbon/Organic Carbon/Sulfate (4.1%), Fluorine/Chlorine/Sulfate (0.9%), Sodium Sulfate (0.2%) and HMSA/Chlorine (0.1%).

Apportionment of Particle Number

Clarkson University completed the source apportionment analysis of the particulate size distribution data acquired in Pittsburgh from July 2001 to June 2002. They analyzed the data using as a bilinear receptor model solved by Positive Matrix Factorization (PMF). The data were obtained from two Scanning Mobility Particle Spectrometers (SMPS) and an Aerodynamic Particle Sampler (APS) with a temporal resolution of 15 minutes. Each sample contained 165 size bins from 0.003 to 2.5 μm . Particle growth periods in nucleation events were identified and the data in these intervals were excluded from this study so that the size distribution profiles associated with the factors could be regarded as sufficiently constant to satisfy the assumptions of the receptor model. Analyses were made on monthly data sets to ensure that the changes in the size distributions from the source to the receptor site could be regarded as constant. The factors from PMF could be assigned to particle sources by examination of the number size distributions associated with the factors, the time frequency properties of the contribution of each source (Fourier analysis of source contribution values), and the correlations of the contribution values with simultaneous gas phase measurements (O_3 , NO, NO_2 , SO_2 , CO) and particle composition data (sulfate, nitrate, OC/EC). Seasonal trends and weekday/weekend effects were investigated. Conditional probability function (CPF) analyses were performed for each source to ascertain the likely directions in which the sources were located. The size distribution data were separated into five factors separated. Two factors, local traffic and nucleation are clear sources but each of the other factors appears to be a mixture of several sources that cannot be further separated.

Figure 5 shows the five factors for each month of the year. Table 3 summarizes the characteristics for each factor. Factor 1 has a number mode between 0.15 and 0.25 μm and a submode at 0.02 μm . Factor 1 includes secondary, aged primary aerosol particles and also fresh primary particles from local combustion sources. The number mode of Factor 2 is at 0.08~0.1 μm in July, August and September of 2001. In 2002, the number mode is at 0.06~0.07 μm . A daily pattern, caused by the reduction of mixing height at night, is clearly observed in this factor. Factor 2 is assigned as stationary combustion, including emissions from local combustion sources. It may also probably include wood burning in winter. The number mode of Factor 3 is at 0.04 μm in summer and 0.03 μm in the fall and winter. This factor has been associated with a collection of point sources and remote Pittsburgh traffic. These are particles produced in the city but not close to the measurement station, several kms away. Factor 4 has its number mode at 15 nm and is strongly correlated with local traffic flow. Factor 4 is associated with traffic within a few kilometers of the measurement station. Finally, factor 5 represents particles smaller 10 nm from nucleation.

Figure 6 illustrates the variation of the monthly mean number contribution from each factor. The fluctuations are within a factor of two. Factors 1 and 2 have similar seasonal trends, high in the fall and low in the winter. They all reach their highest concentrations in November 2001 and the SO_2 concentration is also the highest in that month. These high concentrations in November 2001 may be attributed to the dominant wind direction from the south where more coal power plants are located. Figure 7 indicates the monthly volume contribution variations. The volume contribution is calculated from the number contribution and size distribution of each factor. For Factor 1, the volume contribution only includes particles smaller than 0.5 μm for all months since the lack of APS data in some months prevents us from investigating the volume contribution over this size. The monthly variation of Factor 1 is similar to $\text{PM}_{2.5}$ mass concentration. In the summer of 2001, particles from all sources seem to be larger than in other seasons.

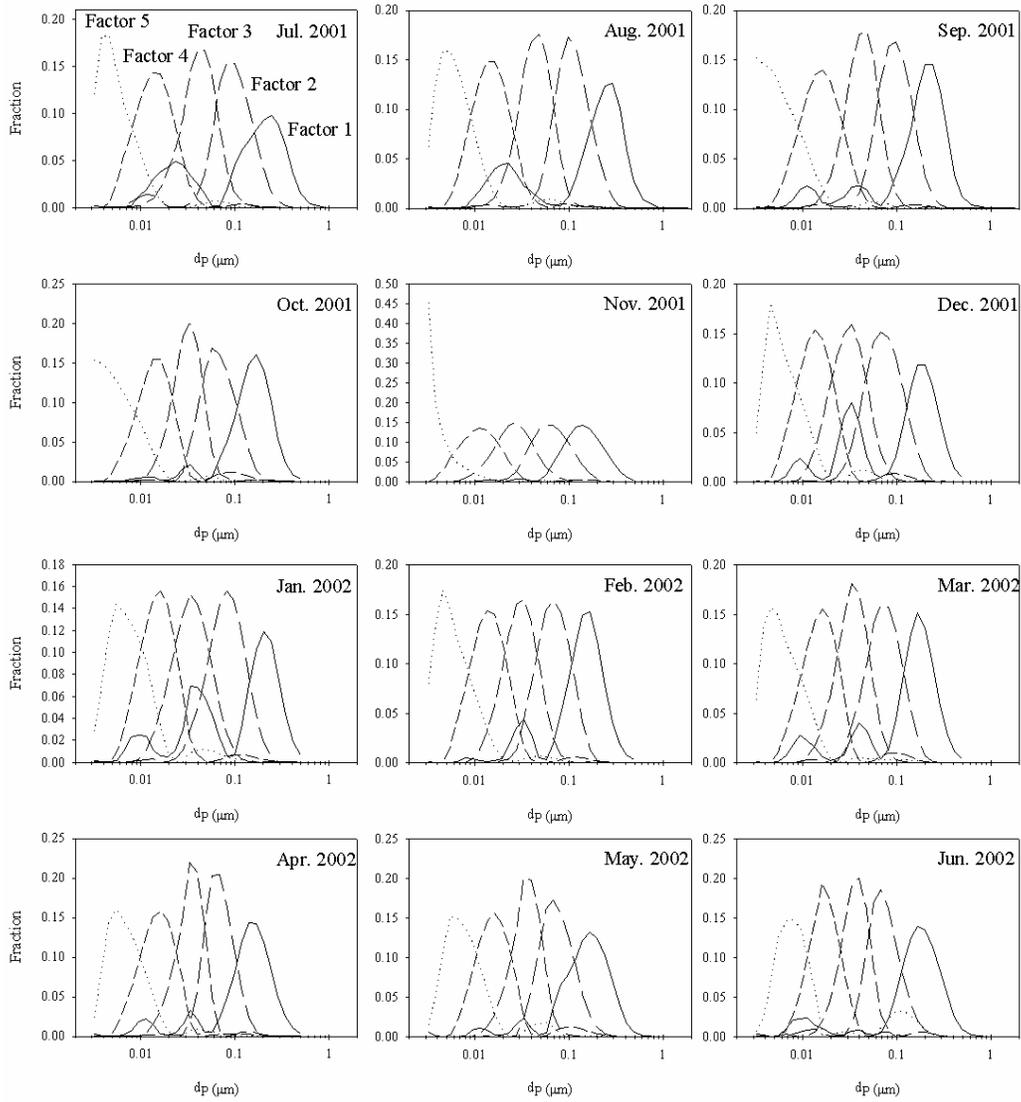


Figure 5. Size distribution profiles for each month.

Table 3. Summary of the characteristics of all factors

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Sources assigned	secondary and aged primary aerosol, fresh primary aerosol from local combustion sources	stationary combustion sources	remote Pittsburgh traffic, local point sources	local traffic	local nucleation
Size range	0.15~0.25 μm	0.08~0.1 μm in July, August and September 2001; 0.06~0.07 μm in other months	0.03~0.04 μm	15 nm	<10 nm
Diurnal pattern	very weak	weak	no	strong	Strong
Weekday/ weekend difference	Small	no	moderate	significant	No
Correlations with gas and particle composition data	no correlation with ozone; strong correlation with sulfate; correlations with other species	negative correlation with ozone; strong correlations with other gases; correlations with sulfate, nitrate and OC/EC	weak correlations with NO, NO _x and SO ₂ ; No correlations with other species	no obvious correlations with any species	a weak correlation with ozone; no correlations with other species
Dominant direction by CPF	South	south and southeast	southeast and northwest	no clear dominant directions	no clear dominant directions

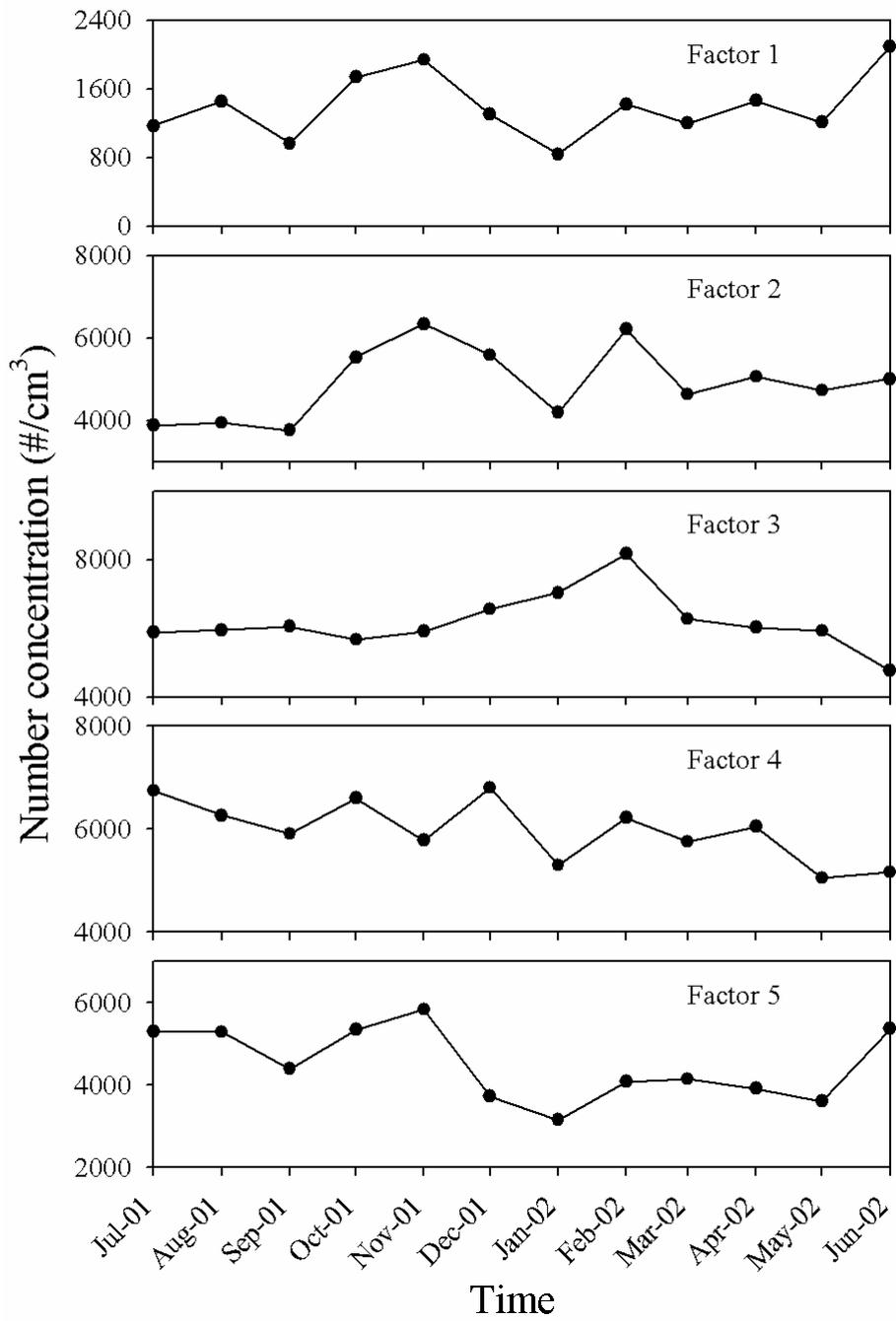


Figure 6. Monthly variations of average number contribution from each factor.

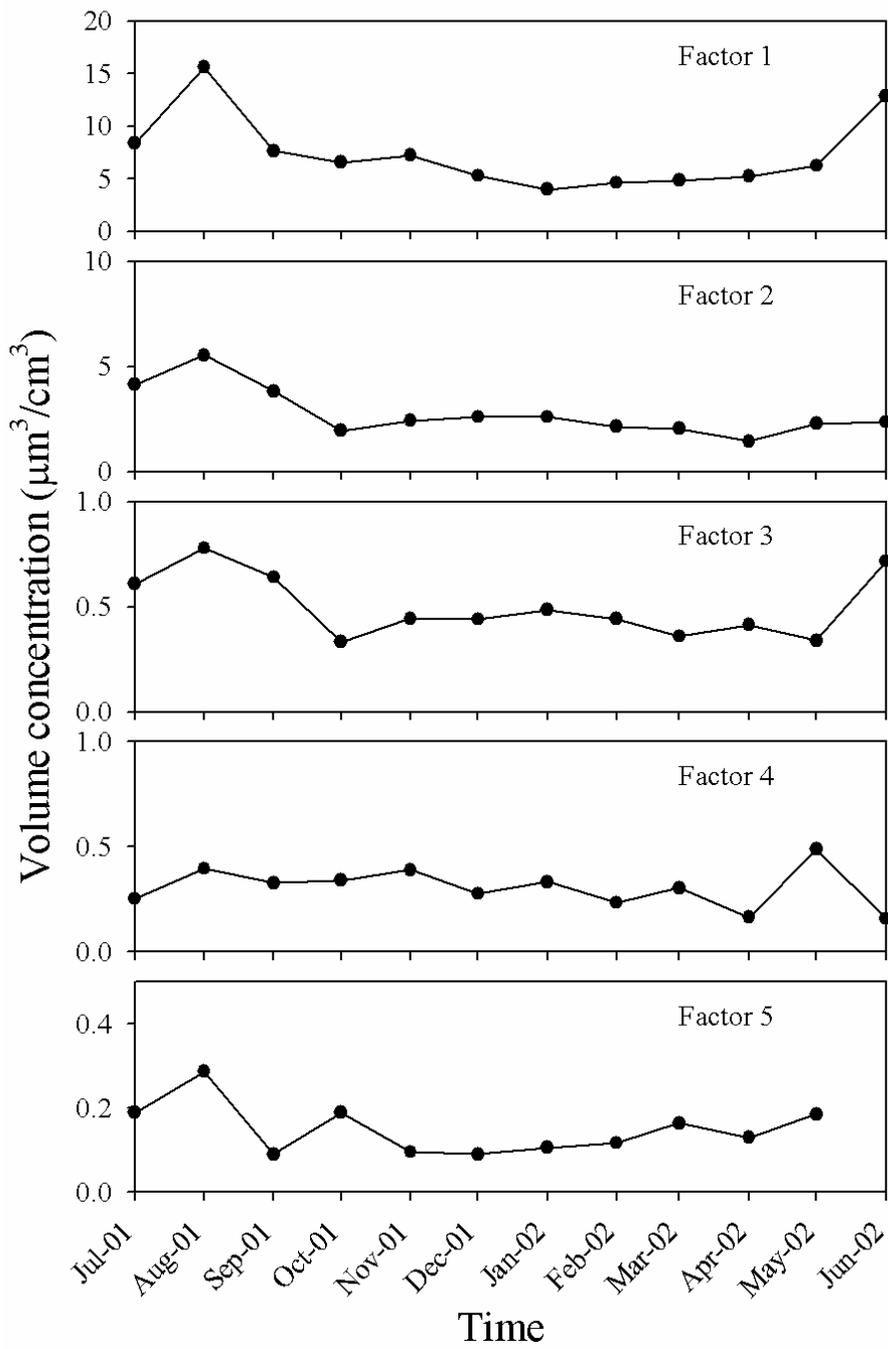


Figure 7. Monthly variations of average volume contribution from each factor

Apportionment of Primary Emissions from Coal-Fired Power Plants

RJ Lee Group used computer-controlled scanning electron microscopy (CCSEM) analysis of samples collected on polycarbonate filters to determine ambient spherical aluminum silicate (SAS) particle number concentrations on both source and ambient filters. SAS particles are thought to be a unique tracer for coal-fire power plant formed from the high temperature processing of fly ash (Fisher et al. 1978; Webber et al. 1985; Eatough et al. 1996).

CCSEM methods were used to measure the size and obtain the elemental composition for 2500 individual particles from each ambient and source sample. The maximum and minimum diameter measured during the analysis was used to calculate the volume of each particle and each particle was assigned a density based on a common oxide in proportion to the elements present, determined by the EDS analysis. Images and spectra collected during the analysis were then reviewed for each individual particle to distinguish SAS from non-spherical material. Table 4 summarizes PM_{2.5} mass and ambient SAS number concentrations for several days in Summer of 2001 and the winter of 2002.

Table 4. Ambient SAS number concentrations at the main site.

Date	PM _{2.5} (µg/m ³)	SAS Number (m ⁻³)
07/15/01	15.2	2.84E+04
08/01/01	56.3	1.40E+05
08/02/01	57.2	1.09E+05
08/03/01	46.5	1.41E+05
1/3/2002	20.8	8.93E+04
01/06/02	16.84	5.32E+04
01/10/02	15.25	1.37E+05

The SAS data shown in Table 4 can be used to derive an upper bound on the contribution of primary emissions from coal-fired power plants to ambient PM_{2.5} levels in Pittsburgh. The estimate is an upper bound because the analysis that there are no other sources of SAS particles. To estimate the contribution of primary coal emissions to ambient PM_{2.5} we need a SAS emission factor for coal combustion -- number of SAS particles/µg primary PM_{2.5} emissions. The contribution of primary coal-fired power plant emissions to the ambient PM_{2.5} was determined by dividing the total number of SAS per sample collection volume by the total number of SAS per µg of coal emissions.

SAS emission factors measured while firing three different types of coal and a coal-wood blend are shown in Table 5. These coals are common utility and industrial fuels representing a range of fuel properties: Prater Creek Coal is an eastern bituminous coal with low sulfur and ash content; Black Thunder Coal is a low-sulfur, high-calcium sub-bituminous coal from the Powder River Basin; and Bailey Mine Coal is a high-sulfur, Pittsburgh seam bituminous coal.

The SAS emission factors were determined based on CCSEM analysis on archived source test filters. The source tests were performed by Carnegie Mellon University using on dilution sampler on the Combustion and Environmental Research Facility (CERF) at the Department of Energy National Energy Technology Laboratory. The CERF is a pilot-scale pulverized-coal combustor designed to simulate the time-temperature history of a commercial coal boiler. At full load it consumes 20 kg of pulverized coal per hour, roughly 150 kW when burning a typical US bituminous coal. Coal is injected through a swirl-stabilized burner at the top of a 3-m tall and 45-cm diameter refractory lined combustion zone. Combustion products then flow into a horizontal convective section, through two flue gas coolers, heat-traced piping, and into a bag house. The filter samples considered here were collected after the bag house

Table 5. SAS emission factors (number of SAS particles/ μg primary $\text{PM}_{2.5}$ emissions) for different fuels.

Fuel	SAS/ μg
Prater Creek Coal (Test 1)	2.16E+05
Prater Creek Coal (Test 2)	2.14E+05
Bailly Mine Coal	1.25E+05
Powder River Basin	5.81E+05
Prater Creek Coal-Wood Blend	3.16E+05

Combining the emission factors shown in Table 5 with the ambient data in Table 4, we estimate that primary emissions from coal combustion contributes on average $0.44 \pm 0.3 \mu\text{g}/\text{m}^3$ to $\text{PM}_{2.5}$ at the site or $1.4 \pm 1.3\%$ of the total $\text{PM}_{2.5}$ mass. This is consistent with expectations that primary coal emissions are a small contributor to ambient fine particulate matter mass.

Source Apportionment of the Organic Fraction

Organic compounds emitted from both anthropogenic and biogenic activities form a significant component of ambient $\text{PM}_{2.5}$ in the Pittsburgh region. The organic mass varies slightly through the year, contributing approximately 20% of total mass in the summer, 30% in the fall, and 20% in the winter, for a study average contribution of 23% of the FRM-measured $\text{PM}_{2.5}$ mass. The vast majority of the primary $\text{PM}_{2.5}$ is organic aerosol.

To apportion the primary organic aerosol we are using receptor model in combination with measurements of molecular marker concentrations. Molecular markers are individual organic compounds that quantify the contribution of different sources to the ambient organic mass. For example, levoglucosan is used as a marker for wood smoke (Simoneit et al. 1999; Schauer et al. 2001); hopanes are used as a marker for vehicle emissions (Rogge et al. 1993; Schauer et al. 1999; Schauer et al. 2002); and cholesterol is used as a marker for meat cooking (Rogge et al. 1991; Schauer et al. 1999). Using these and other molecular markers and the Chemical Mass Balance (CMB) model, researchers have identified the relative contribution of sources such as automobiles,

diesel trucks, meat cooking, and wood smoke to urban organic aerosol (Schauer et al. 1996; Schauer and Cass 2000; Schauer et al. 2002).

Application of CMB model requires source profiles. As part of this project, speciated source profiles are being developed for road-dust, vegetative detritus, emissions from coke production, and an average vehicular fleet composition. To evaluate the applicability of literature profiles to the Pittsburgh region, extensive comparisons were performed between published profiles and ambient data and between published profiles. An example of such a comparison is shown in Figure 8 which is an edge plot of different hopanes. Hopanes are used as tracers for vehicular emissions. The ambient data falls between the emission profiles for gasoline and diesel vehicles indicating the mixture of emissions from these two source classes can explain the ambient levels. Similar comparisons have been performed for other important molecular markers.

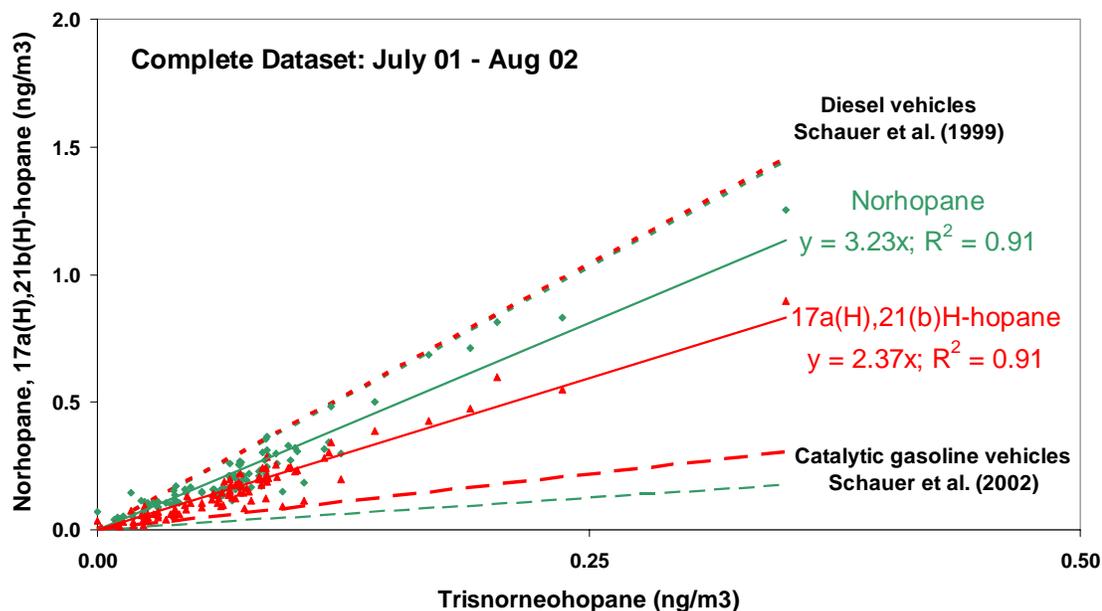


Figure 8. Comparison of ambient data and published emission profiles for three hopanes.

Results from the CMB analysis for the July 2001 period are shown in Figure 11. About 70% of the primary OC emissions are from vehicular sources, with the gasoline contribution being on average three times greater than the diesel emissions in the summer. However, the gasoline/diesel split depends on the PAHs; coke production dominates the ambient PAH concentrations in Pittsburgh, even though coke emissions only contribute a small fraction of the OC. Woodsmoke is a smaller component, with significant contributions in the fall and winter seasons.

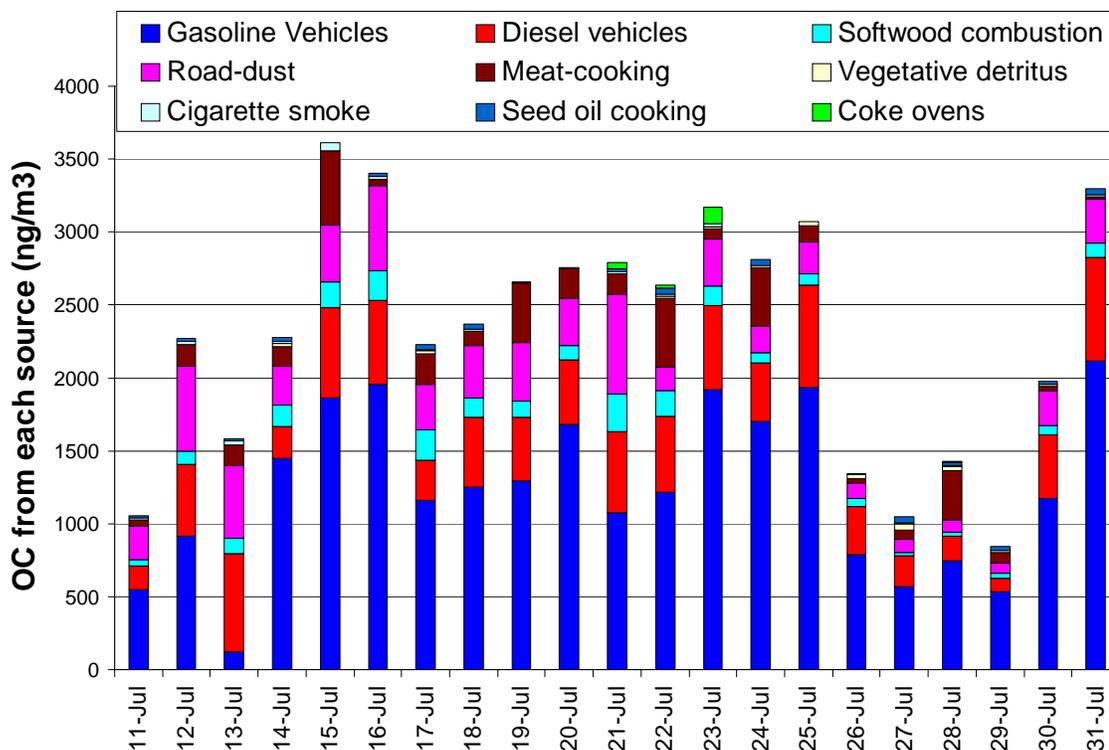


Figure 9. CMB source apportionment of primary organic aerosol during July 2001.

Evaluation of PMCAMx

During this project period we continued to evaluate the performance of PMCAMx for the second half of the July 2001 Eastern Supersites Intensive (July 12-July 28, 2001). Good model-measurement comparison has been observed with the measurements taken as part of this project. Results from these comparisons were shown as part of the last progress report. As previously discussed, much effort was expended to update emission inventories for the modeling and to build meteorology input files for the January 2002 period. We also compared predictions with fine particle composition data collected by the US EPA speciation trends network (STN).

Comparisons of PMCAMx predictions versus measured 24-hr SO₄ and OC concentrations at more than 50 STN sites in the Eastern US are shown in Figures 10 and 11. The solid and dashed lines in the figure indicate the 1:1 line and $\pm 30\%$, respectively. For the majority of the sites, good agreement is observed between the model measurement predictions providing confidence in the ability of PMCAMx to predict the spatial variation in fine particle concentrations. We are in the process of closely examining outliers to improve model performance. We are still working on some wet deposition and transport issues with the sulfate aerosol. We also have not run the model with the update OC inventory. We anticipate completing the model verification activities for both the July 2001 and January 2002 periods during the summer of 2004 at which point the model will be used to evaluate different control scenarios.

After the evaluation of the modeling tool, we will use it to investigate the source-receptor relationships in the Eastern US and to synthesize the measurements of the Pittsburgh Supersite. Examples include investigations of the response of the system to SO₂ emission controls and the potential for increase in nitrate, the role of ammonia in the formation of ammonia nitrate, the responses of the PM to changes in NO_x and VOC emissions, the relative role of primary and secondary organic aerosol, the identification of the major precursors of secondary organic aerosol, etc.

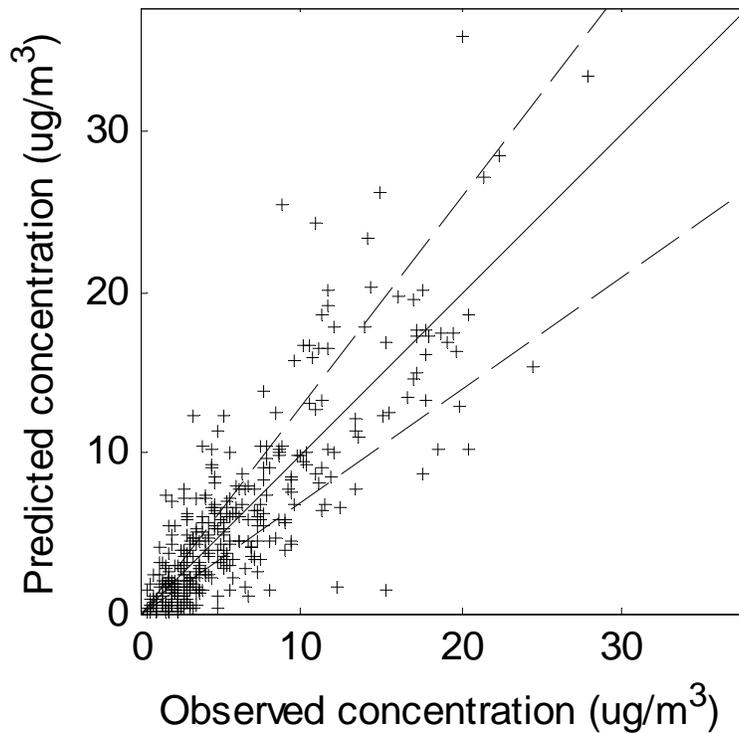


Figure 10. Model-measurement comparison of 24-hr sulfate concentrations at more than 55 STN sites during July 2001.

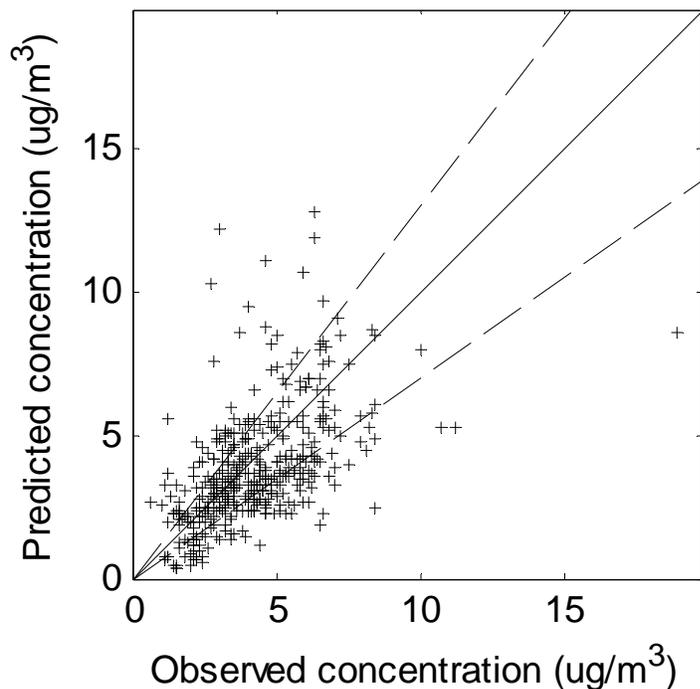


Figure 11. Model-measurement comparison of 24-hr OC concentrations at more than 55 STN sites during July 2001.

CONCLUSIONS

Significant progress was made this project period on the analysis of ambient data, source apportionment, and deterministic modeling activities. The analysis of the single particle data from the RSMS-3 by the Davis group indicates that particulate pollution in Pittsburgh was predominantly carbonaceous in nature with ~ 79% of all particles sampled containing some form of carbon. These particles were observed in all size bins and from almost every direction for the duration of this study. The majority of these particles are thought to be emitted from vehicular traffic and biomass burning. In addition, there was a significant amount of ammonium nitrate observed in these particles.

Besides carbon and secondary components, metals were recognized as the next largest constituent of Pittsburgh aerosol. Although a rich array of multi-component metal particles was identified, the most commonly observed ions were K^+ , Na^+ , Fe^+ , Pb^+ , and to a lesser extent, Ga^+ and Zn^+ . These particles were typically smaller in size, ranging from about 75 – 300 nm, and tended to be associated with specific wind directions. The analysis of the wind roses for individual classes has facilitated the isolation of specific local industries to which the observed metal based classes may be attributed. Results

indicate that high temperature furnaces are the single largest source of ultrafine metal particles in the Pittsburgh area.

The University of Maryland group has illustrated the usefulness of LIBS for long-term measurements of multiple elements in ambient air. These methods are equally applicable to thermal process streams or other situations where dilute particle suspensions mass and composition are of interest. Weekly and hourly mass concentrations illustrate the efficacy of the LIBS technique for temporal measurements, and the potential for LIBS to reveal elemental associations that may be important for understanding chemistry or for source apportionment. Particle mass distributions were limited in this work by the threshold detection limit, illustrating the importance of optimizing laser pulse energy, detection timing, and optical design to lower the detection threshold. However, mass concentrations determined here are likely to be largely correct, due to the preponderance of the mass in the larger size particles. Multi-element spectra suggest the potential of LIBS as a means for understanding particle formation chemistry through observed elemental affinities, and for source apportionment.

PMCAMx predictions were compared with data from more than 50 sites of the STN network located throughout the Eastern United States. PMCAMx predictions are within $\pm 30\%$ at most of these sites. We are continuing to revise PMCAMx and the associated emission inventories.

Spherical Aluminum Silicate particle concentrations (SAS) were used to estimate the contribution of primary coal emissions to fine particle levels at the central monitoring site. Primary emissions from coal combustion contribute on average $0.44 \pm 0.3 \mu\text{g}/\text{m}^3$ to $\text{PM}_{2.5}$ at the site or $1.4 \pm 1.3\%$ of the total $\text{PM}_{2.5}$ mass. This is consistent with expectations that primary coal emissions are a small contributor to ambient fine particulate matter mass.

About 70% of the primary OC emissions are from vehicular sources, with the gasoline contribution being on average three times greater than the diesel emissions in the summer. However, the gasoline/diesel split depends on the PAHs; coke production dominates the ambient PAH concentrations in Pittsburgh, even though coke emissions only contribute a small fraction of the OC. Woodsmoke is a smaller component, with significant contributions in the fall and winter seasons.

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Appendix Quality Assurance Final Report for the Pittsburgh Air Quality Study Pittsburgh Supersite

QUALITY ASSURANCE FINAL REPORT

FOR THE

**PITTSBURGH AIR QUALITY STUDY
PITTSBURGH SUPERSITE**

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Quality Assurance Final Report

This report summarizes the quality of the measurement data sets and provides a context for interpretation of measurements collected during the Pittsburgh Air Quality Study (PAQS) Supersite. Data quality is evaluated using particular data quality indicators (DQIs), selected by the PAQS Quality Assurance Manager and Principal Investigators, and the findings of the technical system and performance audits conducted during the field campaign. Additional information about PAQS can be found in the Quality Assurance Program Plan (Khlystov et al., 2001), a publication which provides an overview of the PAQS measurements and preliminary scientific findings (Wittig et al., 2003a), and various publications focusing on measurements collected at the PAQS Supersite (Cabada et al., 2003a; 2003b; 2003c; Khlystov et al., 2001; 2003; Rees et al., 2003; Stanier et al., 2003a; 2003b; Subramanian et al., 2003; Takahama et al., 2003; Wittig et al., 2003b).

1. Technical System and Performance Audits

Data quality was assured by performing two types of audits of all instruments and systems used during PAQS. A single technical system audit of all sample custody forms, logs and standard operating procedures was performed at the beginning of the study. The intent of this audit was to refine the forms and procedures to be used for the duration of the study. Two performance audits were also performed during the field campaign to evaluate the performance of the field instruments by external personnel (who were not normally responsible for the instruments) using external standards (which were not normally used to evaluate the instrument performance). Audit findings were immediately communicated to and discussed with the investigators. In few cases, the performance audits helped to diagnose instrument issues before the measurements were compromised. In even fewer cases, measurements were invalidated as a result of performance audit findings. In a majority of cases, the audits confirmed the stable performance of the instruments. Appendix 1 of this report presents the technical system and performance audit findings and the responses of the investigators to issues raised during the audits.

2. Data Quality Indicators

The Data Quality Indicators (DQI) used to evaluate the PAQS data set include precision, accuracy, minimum detection limits (MDLs) and completeness. When appropriate, measurement comparability was also evaluated. Measurement representativeness was evaluated for the site as a whole.

A list of all the measurements collected during the PAQS field campaign and the actual DQI values for a majority of the indicators are presented first in Table 1. Data quality objectives (DQOs), determined when possible for each instrument and system prior to use during PAQS, are also listed in Table 1. A brief description of each indicator and the method of calculating the indicator at PAQS is presented next. The actual methodology for determining each indicator is stated in the individual SOPs and RPs. In a few instances typically associated with newly developed instruments, the DQI was greater than the DQO. In these cases, the possible explanation for the discrepancy between the DQIs and DQOs is presented as well.

Table 1. Observable Resolution, Frequency, Period of Operation, Data Quality Objectives (DQO) and Indicators (DQI) at the PAQS Supersite.

Observable	Method ¹	Group ²	Resolution	Frequency	Period of Operation ³	MDL ⁴ DQI and (DQO)	Precision ⁴ DQI and (DQO)	Accuracy ⁴ DQI and (DQO)	Completeness ⁴ DQI and (DQO)
<i>Aerosol mass</i>									
PM ₁₀ mass	Dichot sampler/Gravimetry	CMU	24 hr	Daily	7/1/01-7/1/02	1.2 µg/m ³ (2 µg/m ³)	1.43% (10%)	0.6% (10%)	86.6% (70%)
PM _{2.5} mass	FRM sampler/Gravimetry	CMU	24 hr	Daily	7/1/01-7/1/02	0.9 µg/m ³ (2 µg/m ³)	1.43% (10%)	0.6% (10%)	92.5% (70%)
PM _{2.5} mass	Dichot sampler/Gravimetry	CMU	24 hr	Daily	7/1/01-7/1/02	1.2 µg/m ³ (2 µg/m ³)	1.43% (10%)	0.6% (10%)	86.6% (70%)
PM _{2.5} mass	R&P 1400a TEOM with SES	CMU	10 min	Continuous	7/1/01-7/1/02	0.65 µg/m ³ (1 µg/m ³)	2.2% (10%)	1.2% (10%)	94% (70%)
PM _x mass	MOUDI sampler/Gravimetry	CMU	24 hr	Daily	7/1/01-7/1/02 *	1.7 µg/m ³ (2 µg/m ³ PS)	1.43% (10% PS)	0.6% (10% PS)	84% (70%)
PM _x mass	MOUDI sampler/Gravimetry	CMU	8 hr	3 per day	7/22-25/01, 7/31-8/3/01	1.5 µg/m ³ (2 µg/m ³ PS)	1.43% (10% PS)	0.6% (10% PS)	100% (70%)
<i>Aerosol size distribution</i>									
Number, surface area, and volume distribution	TSI SMPS	CMU	10 min	Continuous	7/1/01-7/1/02	N/A	30% (30%)	20% size 30% count (N/A)	70% (70%)
Number, surface area, and volume distribution	TSI APS	CMU	10 min	Continuous	7/1/01-7/1/02	N/A	30% (30%)	10% size 30% count	28% (70%)
Surface area distribution	Epiphaniometer	PSI	30 min	Semi-continuous	6/11/01-9/18/01	N/A	- (30%)	N/A	- (70%)
<i>Aerosol Characteristics</i>									
Light scattering	Optec NGN-3 nephelometer	CMU	10 min	Continuous	7/16/01-6/30/02	N/A	-	-	-
Hygroscopicity	CMU DAASS	CMU	1 hr	Semi-continuous	7/1-8/31/01, 1/1-7/1/02	N/A	30%	20% size 30% count	70%
Cloud condensation behavior	DH Associates M1 CCN	CMU	4 hr	Semi-continuous	9/01	N/A	-	-	-

Observable	Method ¹	Group ²	Resolution	Frequency	Period of Operation ³	MDL ⁴ DQI and (DQO)	Precision ⁴ DQI and (DQO)	Accuracy ⁴ DQI and (DQO)	Completeness ⁴ DQI and (DQO)
<i>Aerosol chemical composition</i>									
PM ₁₀ inorganic ions	CMU Speciation sampler/ IC	CMU	24 hr	Daily	7/1/01-7/21/02	- (0.1 µg/m ³)	- (20%)	- (15%)	- (70%)
PM _{2.5} inorganic ions	CMU Speciation sampler/ IC	CMU	24 hr	Daily	7/1/01-12/31/01	0.01-0.5 µg/m ³ (0.1 µg/m ³)	6.2-59.4% (20%)	-5.6 to +.1% (15%)	53-77% (70%)
PM _{2.5} inorganic ions	CMU Speciation sampler/ IC	CMU	24 hr	Daily	1/1/02-7/21/02	0.02-0.37 µg/m ³ (0.1 µg/m ³)	6.3-42.1% (20%)	-1.9 to-5.7% (15%)	65-79% (70%)
PM _{2.5} inorganic ions	CMU Speciation sampler/ IC	CMU	4-6 hr	5 per day	ESP01 Intensive	0.03-0.62 µg/m ³ (0.1 µg/m ³)	6.2-59.4% (20%)	-5.6 to +.1% (15%)	53-77% (70%)
PM _{2.5} inorganic ions	BYU PC-BOSS	BYU	4-6 hr	5 per day	ESP01 Intensive	0.05 µg/m ³ (SO ₄)	8%	8%	77%
PM _x inorganic ions	MOUDI sampler/IC	ADI	24 hr	Daily	7/1/01-7/1/02 *	- 0.01-0.67 µg/m ³ (0.1 µg/m ³ PS)	- 5% (20% PS)	- - (20% PS)	- 78% (70%)
PM _{2.5} nitrate	R&P 8400N (ICVC)	ADI	10 min	Semi-continuous	7/1/01-8/1/02	0.16 µg/m ³ (1.0 µg/m ³)	19.5% (10%)	3.1% (25%)	89% (85%)
PM _{2.5} sulfate	R&P 8400S (ICVC)	CMU	10 min	Semi-continuous	7/1/01-9/1/02	0.96 µg/m ³ (1.0 µg/m ³)	20.9% (10%)	-8.1% (25%)	83% (85%)
PM _{2.5} water soluble anions	CMU Steam sampler/IC	CMU	1-2 hrs	Semi-continuous	7/1/01-9/21/02	0.02-0.18 µg/m ³ (0.2 µg/m ³)	15% (10%)	-8% (20%)	87% (70%)
PM _{2.5} water soluble cations	CMU Steam sampler/IC	CMU	1-2 hrs	Semi-continuous	7/1/01-9/21/02	0.17-0.19 µg/m ³ (0.2 µg/m ³)	15% (10%)	-17% (20%)	86% (70%)
PM _{2.5} water soluble NH ₄ ⁺	CMU Steam sampler/OAD	CMU	10 min	Continuous	7/1/01-9/21/02	- -	- -	- -	- -
PM ₁₀ elements	Hi-Vol sampler/ICPMS	CMU	24 hr	Daily	7/12/01-8/02/02	- (0.1 µg/m ³)	- (20%)	- (20%)	- (70%)
PM _{2.5} elements	Hi-Vol sampler/ICPMS	CMU	24 hr	Daily	7/11/01-9/30/02	- (0.1 µg/m ³)	- (20%)	- (20%)	- (70%)
PM _{1.3} elements	UMD SEAS/GFAA	UMD	30 min	Semi-continuous	7/8-8/10/01, 3/29-4/17/02	0.12-7.2 ppb	5-10%	10-15%	100%
PM _x elements	MOUDI sampler/ICPMS	CMU	24 hr	Daily	ESP01, 02 Intensives *	- (0.1 µg/m ³ PS)	- (20% PS)	- (20% PS)	- (70%)

Observable	Method ¹	Group ²	Resolution	Frequency	Period of Operation ³	MDL ⁴ DQI and (DQO)	Precision ⁴ DQI and (DQO)	Accuracy ⁴ DQI and (DQO)	Completeness ⁴ DQI and (DQO)
<i>Aerosol chemical composition</i>									
PM _{2.5} organic/elemental carbon	CMU TQQQ sampler/TOT	CMU	24 hr	Daily	7/1/01-7/31/02 *	0.17-0.53µgC/m ³ (0.5 µgC/m ³)	8% (30%)	2.3-5.7% (30%)	99% (70%)
PM _{2.5} organic/elemental carbon	CMU TQQQ sampler/TOT	CMU	4-6 hr	5 per day	ESP01 Intensive	0.17-0.53µgC/m ³ (0.5 µgC/m ³)	8% (30%)	2.3-5.7% (30%)	99% (70%)
PM _{2.5} organic/elemental carbon	CMU Denuder sampler/TOT	CMU	24 hr	6 th day	7/1/01-6/1/02 *	0.3 µgC/m ³ (0.5 µgC/m ³)	2% (30%)	10% (30%)	75% (70%)
PM _{2.5} organic/elemental carbon	CMU Denuder sampler/TOT	CMU	24 hr	Daily	ESP01, 02 Intensives	0.3 µgC/m ³ (0.5 µgC/m ³)	2% (30%)	10% (30%)	95% (70%)
PM _{2.5} organic/elemental carbon	BYU PC-BOSS	BYU	4-6 hr	5 per day	7/9/01-7/29/01	0.05 µgC/m ³ (0.1 µgC/m ³)	8% (5%)	8% (5%)	77% (70%)
PM _{2.5} organic/elemental carbon	SLCarbon (TOT) analyzer	RU	2-4 hr	Semi-continuous	7/1/01-9/1/02	- (0.3 µgC/m ³)	- (10%)	- (10%)	- (70%)
PM _x organic/elemental carbon	MOUDI/TOT	CMU	24 hr	Daily	ESP01, 02 Intensives *	.12-.21 µgC/m ³ (0.5 µgC/m ³ PS)	8% (30% PS)	2.3-5.7% (30% PS)	66% (70%)
PM _x organic/elemental carbon	MOUDI/TOT	CMU	8 hr	3 per day	7/22-25/01, 7/31-8/3/01	- (0.5 µgC/m ³ PS)	- (30% PS)	- (30% PS)	- (70%)
PM _{2.5} speciated organics	Organic sampler/GC-MS	FIU	24 hr	6 th day	7/1/01-7/1/02 *	- (N/A)	- (N/A)	- (N/A)	- (N/A)
PM _{2.5} speciated organics	Organic sampler/GC-MS	FIU	24 hr	Daily	ESP01, 02 Intensives	- (N/A)	- (N/A)	- (N/A)	- (N/A)
PM _x speciated organics	LPI/FTIR	RU	24 hr	Daily	ESP01, 02 Intensives	- (N/A)	- (N/A)	- (N/A)	- (N/A)
PM _{2.5} biological material	Epi-fluorescent microscopy with assays	UColo	24 hr	Daily	7/7/01-7/1/02	- (N/A)	- (N/A)	- (N/A)	- (N/A)
PM _{2.5} fog composition	Collector/IC/TOC/pH	CSU	Per event	8 events	7/1/01-9/1/02	1.3-27.9µM (N/A)	0.5-6.7% (N/A)	1-19.6% (N/A)	100% (N/A)
PM _{1.0} size resolved composition	Aerodyne Mass Spectrometer (AMS)	UCB, Aerodyne	5 min	Semi-continuous	9/6/02-9/21/02	- (N/A)	- (N/A)	- (N/A)	- (N/A)
<i>Single Particle Chemical Composition</i>									
Polar organics	RSMS-III	UCD,UD	10 min	Semi-continuous	9/20/01-10/1/02	- (N/A)	- (N/A)	- (N/A)	- (N/A)
Ion composition	RSMS-III	UCD,UD	10 min	Semi-continuous	9/20/01-10/1/02	- (N/A)	- (N/A)	- (N/A)	- (N/A)
Particle morphology	Nuclepore filter/SEM	RJL	24 hr	Daily	ESP01, 02 Intensives	- (N/A)	- (N/A)	- (N/A)	- (N/A)

Observable	Method ¹	Group ²	Resolution	Frequency	Period of Operation ³	MDL ⁴ DQI and (DQO)	Precision ⁴ DQI and (DQO)	Accuracy ⁴ DQI and (DQO)	Completeness ⁴ DQI and (DQO)
<i>Gaseous Species</i>									
Light (C ₂ -C ₁₂) hydrocarbons	Canister/GC-FID	CMU	24 hr	3 rd day	9/1/01-7/31/02 *	0.0-0.25 µg/m ³	33%	20%	65%
Light (C ₂ -C ₁₂) hydrocarbons	Canister/GC-FID	CMU	24 hr	Daily	ESP02 Intensive	-	-	-	-
Total peroxides	CSU Monitor	CSU	1 hr	Continuous	7/1/01-9/1/02	-	-	-	-
O ₃	API 400A	CMU	10 min	Continuous	7/1/01-9/1/02	0.09 ppbv (0.2 ppbv)	2.8% (20%)	-2.2% (20%)	94% (70%)
NO and NO _x	API 200A	CMU	10 min	Continuous	7/1/01-9/1/02	0.14 ppbv (0.6 ppbv)	1.7% (10%)	1.1% (10%)	95% (80%)
SO ₂	API 100A	CMU	10 min	Continuous	7/1/01-9/1/02	0.39 ppbv (0.4 ppbv)	2.3% (10%)	1.2% (10%)	90% (80%)
CO	API 300	CMU	10 min	Continuous	7/1/01-9/1/02	0.34 ppbv (0.4 ppbv)	6.9% (10%)	-0.8% (10%)	94% (80%)
						0.1 ppmv (0.4 ppmv)	1.1% (10%)	1.1% (10%)	94% (80%)
Inorganic gases	CMU Speciation sampler/ IC	CMU	24 hr	Daily	7/1/01-7/1/02 *	-	-	-	-
Inorganic gases	CMU Speciation sampler/ IC	CMU	4-6 hr	5 per day	ESP01 Intensive	(0.5 µg/m ³)	(30%)	(30%)	(70%)
						-	-	-	-
Water soluble inorganic gases	CMU Steam sampler/ IC	CMU	1-2 hr	Semi-continuous	7/1/01-9/21/02	(0.5 µg/m ³)	(30%)	(30%)	(70%)
						0.02-0.19 µg/m ³	15%	86%	-
						(0.2 µg/m ³)	(10%)	(20%)	(70%)

Observable	Method ¹	Group ²	Resolution	Frequency	Period of Operation ³	MDL ⁴ DQI and (DQO)	Precision ⁴ DQI and (DQO)	Accuracy ⁴ DQI and (DQO)	Completeness ⁴ DQI and (DQO)
Hydrocarbons	UC Online GC-FID/MS	UCB	1 hr	Semi-continuous	1/9-2/12, 7/10-8/10/02				
1-butene						1.0 ppt	2%	7%	96.5%
1-methylcyclopentene						0.7 ppt	2%	7%	99.2%
1-pentene						0.8 ppt	2%	7%	96.5%
2-methyl-1-butene						0.8 ppt	2%	7%	96.5%
2-methylpropene						1.0 ppt	2%	7%	96.5%
3-methyl-1-butene						0.8 ppt	2%	7%	96.5%
3-methylfuran						2.2 ppt	6%	8%	99.2%
acetone						47.3 ppt	4%	7%	96.1%
alpha pinene						1.1 ppt	13%	14%	96.0%
benzene						25.6 ppt	7%	9%	96.3%
butanol						27.6 ppt	6%	8%	99.1%
butane						1.0 ppt	2%	7%	96.5%
c-2-butene						1.0 ppt	2%	7%	96.5%
perchloroethylene						0.6 ppt	6%	9%	96.3%
c-2-pentene						0.8 ppt	2%	7%	99.2%
dichloromethane						33.9 ppt	12%	14%	99.2%
acetaldehyde						82.2 ppt	9%	11%	94.0%
acetonitrile						38.1 ppt	13%	14%	96.7%
chloroform						1.0 ppt	4%	7%	96.2%
cyclopentane						0.8 ppt	2%	7%	96.5%
cyclopentene						0.8 ppt	2%	7%	99.2%
dimethylsulfide						3.2 ppt	6%	8%	99.2%
ethylbenzene						1.6 ppt	6%	9%	96.3%
ethanol						15.7 ppt	15%	17%	90.8%
hexane						0.7 ppt	2%	7%	96.5%
isopropanol						22.8 ppt	13%	15%	91.1%
isobutane						1.0 ppt	2%	7%	96.5%
isopentane						0.8 ppt	2%	7%	96.5%
isoprene						0.8 ppt	2%	7%	99.2%
methacrolein						11.3 ppt	6%	8%	99.2%

Observable	Method ¹	Group ²	Resolution	Frequency	Period of Operation ³	MDL ⁴ DQI and (DQO)	Precision ⁴ DQI and (DQO)	Accuracy ⁴ DQI and (DQO)	Completeness ⁴ DQI and (DQO)
Hydrocarbons methyl ethyl ketone methanol methylpentanes methyl-t-butyl ether methyl vinyl ketone m-xylene o-xylene pentanal pentane propane propene propyne p-xylene t-2-butene t-2-pentene toluene	UC Online GC-FID/MS	UCB	1 hr	Semi-continuous	1/9-2/12, 7/10-8/10/02	10.2 ppt 372.9 ppt 0.7 ppt 1.7 ppt 6.8 ppt 5.3 ppt 2.4 ppt 19.3 ppt 0.8 ppt 1.4 ppt 1.3 ppt 1.3 ppt 3.4 ppt 1.0 ppt 0.8 ppt 22.3 ppt	9% 15% 2% 4% 5% 6% 18% 9% 2% 2% 2% 2% 6% 2% 2% 4%	11% 17% 7% 7% 8% 9% 20% 11% 7% 7% 7% 7% 9% 7% 7%	96.3% 88.0% 96.5% 96.3% 99.2% 96.3% 96.1% 99.1% 96.5% 96.5% 96.5% 96.5% 96.3% 96.5% 96.5%

Observable	Method ¹	Group ²	Resolution	Frequency	Period of Operation ³	MDL ⁴ DQI and (DQO)	Precision ⁴ DQI and (DQO)	Accuracy ⁴ DQI and (DQO)	Completeness ⁴ DQI and (DQO)
<i>Meteorology</i>									
Wind speed	MetOne 014A	CMU	10 min	Continuous	7/1/01-9/1/02	0.5 m/s (N/A)	- (10%)	- (10%)	99% (80%)
Wind direction	MetOne 014A	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Temperature	Campbell HMP45C	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Relative Humidity	Campbell HMP45C	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Pressure	Campbell CS105	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Precipitation	MetOne 370	CMU	10 min	Continuous	7/1/01-9/1/02	0.254 mm (N/A)	- (10%)	- (10%)	99% (80%)
UV Radiation	Kipp&Zonen CUV3	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Solar Radiation	Kipp&Zonen CM3	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)

- 1 Methods – ADI: Aerosol Dynamics Inc.; APS: Aerodynamic Particle Sizer; BYU: Brigham Young University; CMU: Carnegie Mellon University; CSU: Colorado State University; FRM: Federal Reference Method; FTIR: Fourier Transform Infrared Spectrometry; Grav: Gravimetry; IC: Ion Chromatography; ICPMS: Inductively Coupled Plasma Mass Spectrometry; ICVC: Integrated Collection and Vaporization Cell; LPI: Low Pressure Impactor; GC-FID: Gas Chromatography with Flame Ionization Spectroscopy; GC-MS: Gas Chromatography with Mass Spectroscopy; GFAA: Graphite Furnace with Atomic Absorption; OAD: Online Ammonium Detector; R&P: Rupperecht and Patashnick, Co.; RSMS: Rapid Single particle Mass Spectrometer; SEAS: Semi-continuous Environmental Aerosol Sampler; SEM: Scanning Electron Microscopy; SL: Sunset Labs; SMPS: Scanning Mobility Particle Sizer; TEOM with SES: Tapered Element Oscillating Microbalance with a Sample Equilibration System; TOC: Total Organic Carbon; TOT: Total Optical Transmittance; UCB: University of California at Berkeley; UCD: University of California at Davis.
- 2 Groups – ADI: Aerosol Dynamics, Inc.; BYU: Brigham Young University; CMU: Carnegie Mellon University; CSU: Colorado State University; FIU: Florida International University; PSI: Paul Scherrer Institute; RJI: R. J. Lee Instruments, RU: Rutgers University; UC: University of California at Berkeley; UCB: University of Colorado at Boulder; UCD: University of California at Davis; UD: University of Delaware; UMD: University of Maryland.
- 3 Period of operation – ESP01 Intensive: July 1, 2001 – August 3, 2001; ESP02 Intensive: January 1, 2002 – January 15, 2002; *: Except during periods when samples were collected at a higher time resolution as noted in the entry below.
- 4 Data quality indicators and (Data quality objectives); N/A: Not applicable; Values for MOUDIs and LPIs are per substrate (stage or filter).

2.1 Minimum detection limit (MDL)

Analytical procedures and sampling equipment impose specific constraints on the determination of detection limits. MDL is defined as a statistically determined value above which the reported concentration can be differentiated from a zero concentration, and was calculated for a majority of measurements using Equation 1.

$$\text{Equation 1} \quad \text{MDL} = t_{(n-1, 0.99)} \bullet s$$

where s is the standard deviation of the replicate zero analyses, and t is the student's t -test value for a standard deviation estimate with $n-1$ degrees of freedom at a 99% confidence level. Measurement results below MDLs of the instrument were reported as measured and to the level of precision of the instrument, but flagged accordingly.

For continuous gas monitors, the MDL accounts for all sampling and analytical procedures and therefore represents a detection limit that can be applied to ambient concentrations. For gas monitors, MDLs were based on the response of the instruments to purified air. MDLs for filter-based or canister-based instruments were determined from field and laboratory blank tests. At PAQS, approximately 10% of all substrates (filters or canisters) handled were field or laboratory blanks. The field blank was a substrate that underwent all the preparation, transportation, storage, and analysis activities as and with the sample substrate. A laboratory blank was a substrate that underwent the preparation and analysis activities as and with the sample substrate. However, because the analytical standards used to evaluate field blank and laboratory blank substrates for filter-based or canister-based measurements are prepared and used in the laboratory, the MDL is not an ambient MDL but instead an instrument MDL.

2.2 Precision

Precision is a measure of the repeatability of results or of the agreement among individual measurements of the same parameter under the same prescribed conditions. The number of replicate analyses needed to properly assess the precision of each instrument was independently determined by each PAQS investigator.

Precision of analytical instruments was evaluated by repeated analysis of independent traceable standards that were separate from the standards used for instrument calibration. Precision of continuous gas monitors was evaluated using purified air. Precision of semi-continuous aerosol instruments was evaluated, when possible, by using artificially generated analytes. When possible, precision of filter-based methods was assessed by running collocated samplers. For each series of replicate analyses, the precision was calculated using Equation 2, where s is the standard deviation between the replicate analyses and $\{x\}$ is the mean of the replicate analyses.

$$\text{Equation 2} \quad \text{Precision (\%)} = 100 [2 s] / \{x\}$$

2.3 Accuracy

Accuracy (bias) is the closeness of a measurement to a reference value, and reflects the systematic distortion of a measurement process. To the extent possible, accuracy was determined from replicate analyses of authentic, traceable standards that were not used in the calibration of the instrument. For each instrument tested, multiple challenge data points were collected. The accuracy of the instrument was determined by:

$$\text{Equation 3} \quad \text{Accuracy (\%)} = (100 * [S - \{x\}]) / S$$

where S is the standard value of the authentic traceable standard and {x} is the mean of the instrument responses to the replicate analysis.

2.4 Completeness

Completeness of a measurement data set indicates the percentage of the scheduled sample collections or measurements that resulted in ambient observations that were valid and met the data quality objectives established in the QAPP. Completeness was calculated using Equation 4, where N represents the number of measurements.

Equation. 1 Completeness (%) = (N valid measurements/total N measurements) • 100

2.5 Comparability

Comparability refers to how confidently one data set can be compared with another. Ideally, two instruments that measure the same observable should be statistically comparable. The existence of several overlapping techniques will allow the intercomparison of existing measurement approaches and also the evaluation of new and emerging approaches. Table 2 presents a list of observables for which multiple measurement methods were used.

Table 2. Comparison of methods

Observable	Methods that will be compared ^a	Methods that will not be compared ^a
PM ₁₀ Mass	Dichot/Gravimetry v. MOUDI/Gravimetry	-
PM _{2.5} Mass	FRM/Gravimetry v. Dichot/Gravimetry, MOUDI/Gravimetry, and TEOM with SES	-
PM _{2.5} plus gas Ammonium	Speciation sampler/IC v. Steam sampler/IC	RSMS-III ^{1,2}
PM _{2.5} Nitrate	Speciation sampler/IC v. ICVC ¹ , and PC BOSS ²	RSMS-III ^{1,2}
PM _{2.5} Sulfate	Speciation sampler/IC v. ICVC ¹ , PC BOSS ² , and Steam sampler/IC	RSMS-III ^{1,2}
PM _{2.5} Carbon	TQQQ sampler/TOT v. Denuder sampler/TOT and TOT carbon analyzer ¹	ICVC ^{1,4} , RSMS-III ^{1,2}
PM _{2.5} Elements	-	Speciation Sampler/ICPMS ⁶ v. LIBS ^{1,2,4} , RSMS-III ^{1,2} , SEAS/GFAA ^{1,2}
PM _{2.5} Polar Organics	-	Detailed Speciation/GC-FID v. LPI/FTIR ² , RSMS-III ^{1,2}
Particle sizing	MOUDI/Gravimetry v. APS ³ and SMPS ³	RSMS-III ^{1,2} , Epiphaniometer ⁴
VOCs	Canister/GC-FID v. On-line GC-FID/MS	-
^a 1: State-of-the-art measurement method 2: Measurement method that is not quantitative 3: Measurements only collected during intensive study periods (July 2001 and possibly January 2002) 4: Limited availability of measurements due to excessive instrument malfunction 5: At overlapping region only 6: Measurement analysis not completed at the time the QAFR was written.		

In this report, comparisons between measurement methods were performed only for data that met the precision, accuracy and completeness data quality objectives. These select comparisons are presented in the figures that follow, as are the major axis regression statistics (assuming a linear relationship) used to gage comparability. Comparability was not determined for state-of-the-art measurement methods that were not quantitative; when only one method was used to measure a particular observable; and if there was limited overlap of the particular observable due to excessive malfunction of an instrument. More detailed comparisons and instrument evaluations have already been performed by several PAQS investigators (Cabada et al., 2003a; 2003c; Rees et al., 2003; Stanier et al., 2003a; Subramanian et al., 2003; Wittig et al., 2003b).

Figure 1. Comparison of aerosol mass measurements (Cabada et al., 2003c): a) 24-hour Dichot PM₁₀ mass v. 24-hour MOUDI PM₁₀ mass, b) 24-hour FRM PM_{2.5} mass v. 24-hour average of 5-min TEOM PM_{2.5} mass, c) 24-hour FRM PM_{2.5} mass v. 24-hour Dichot PM_{2.5} mass, and d) 24-hour FRM PM_{2.5} mass v. 24-hour MOUDI PM_{2.5} mass. Also shown are the 1:1 lines (dashed lines).

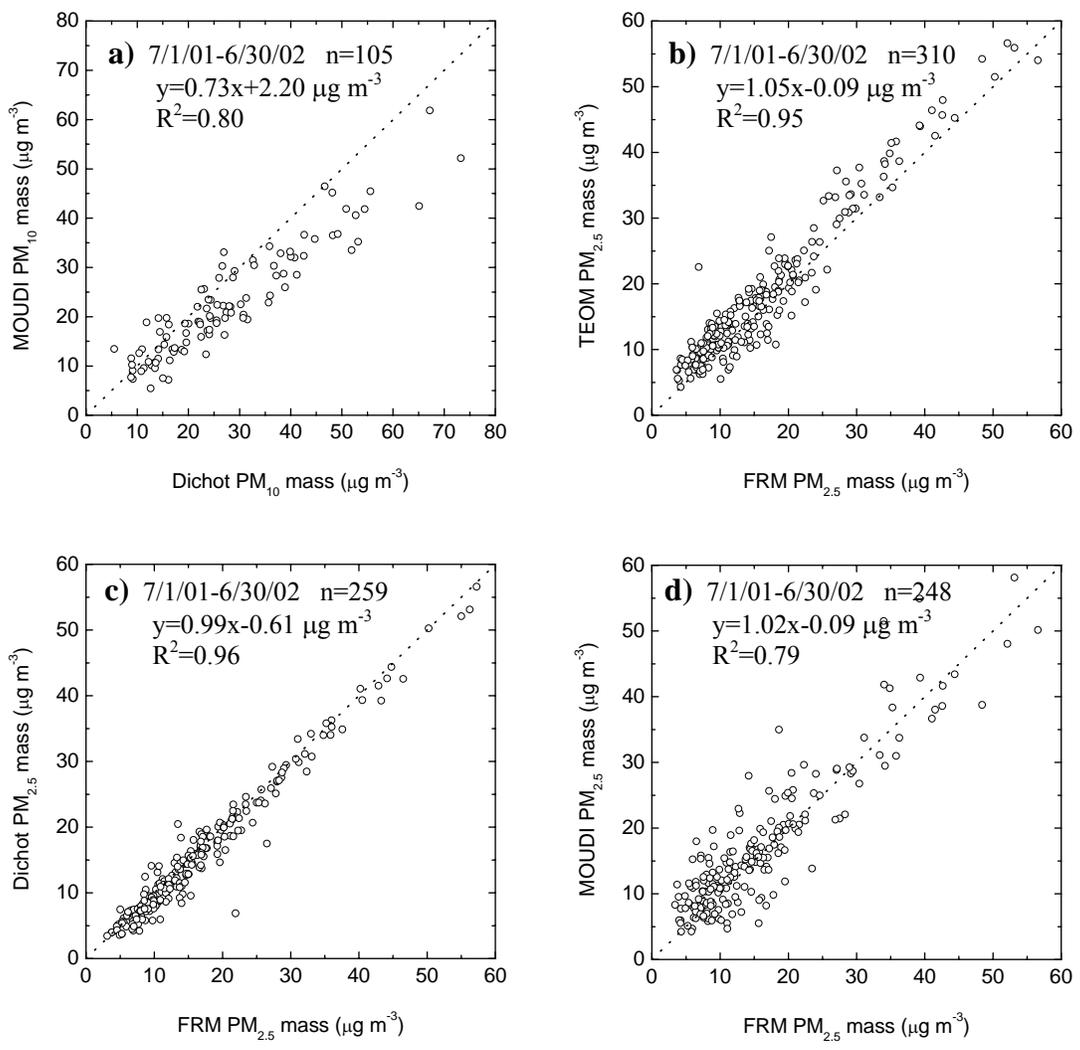


Figure 2. Comparison of PM_{2.5} plus gas ammonium measurements: a) 24-hour average of July 2001 4-hour and 6-hour speciation sampler and 24-hour speciation sampler for remaining months v. 24-hour average of 1-hour or 2-hour steam sampler. Also shown is the 1:1 line (dashed line).

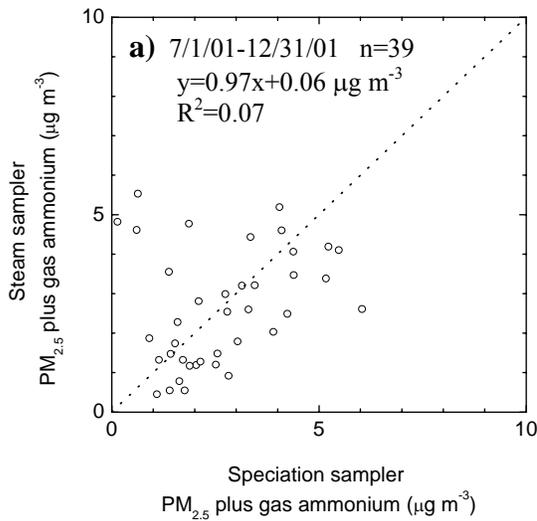


Figure 3. Comparison of PM_{2.5} nitrate measurements (Wittig et al., 2003a): a) 24-hour average of July 2001 4-hour and 6-hour speciation sampler and 24-hour speciation sampler for remaining months v. 24-hour average of 1-hour R&P 8400N and b) 24-hour average of July 2001 4-hour and 6-hour speciation sampler v. 24-hour PCBOSS. Also shown are the 1:1 lines (dashed lines).

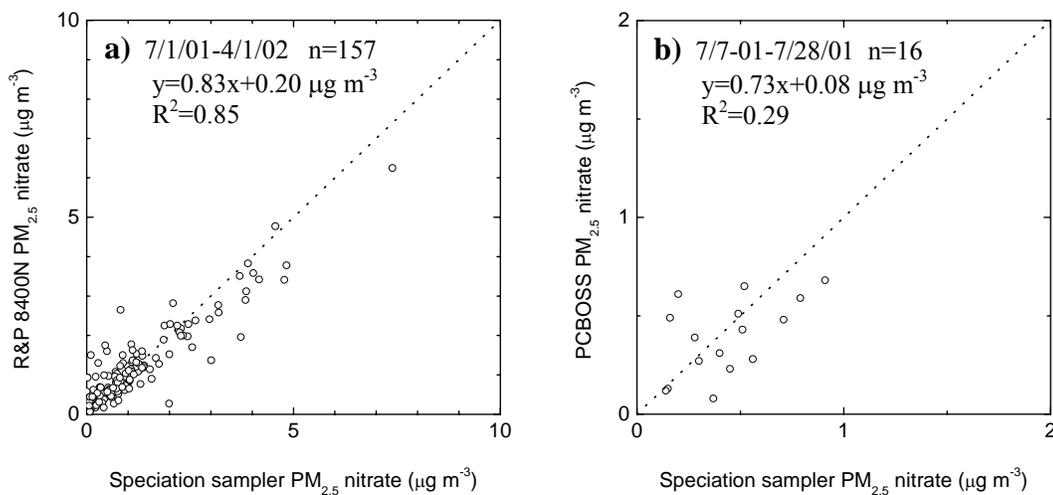


Figure 4. Comparison of PM_{2.5} sulfate measurements (Wittig et al., 2003a): a) 24-hour average of July 2001 4-hour and 6-hour speciation sampler and 24-hour speciation sampler for remaining months v. 24-hour average of 1-hour or 2-hour steam sampler/IC, b) 24-hour average of July 2001 4-hour and 6-hour speciation sampler and 24-hour speciation sampler for remaining months v. 24-hour average of 1-hour R&P 8400N, and c) 24-hour average of July 2001 4-hour and 6-hour speciation sampler v. 24-hour PCBOSS. Also shown are the 1:1 lines (dashed lines).

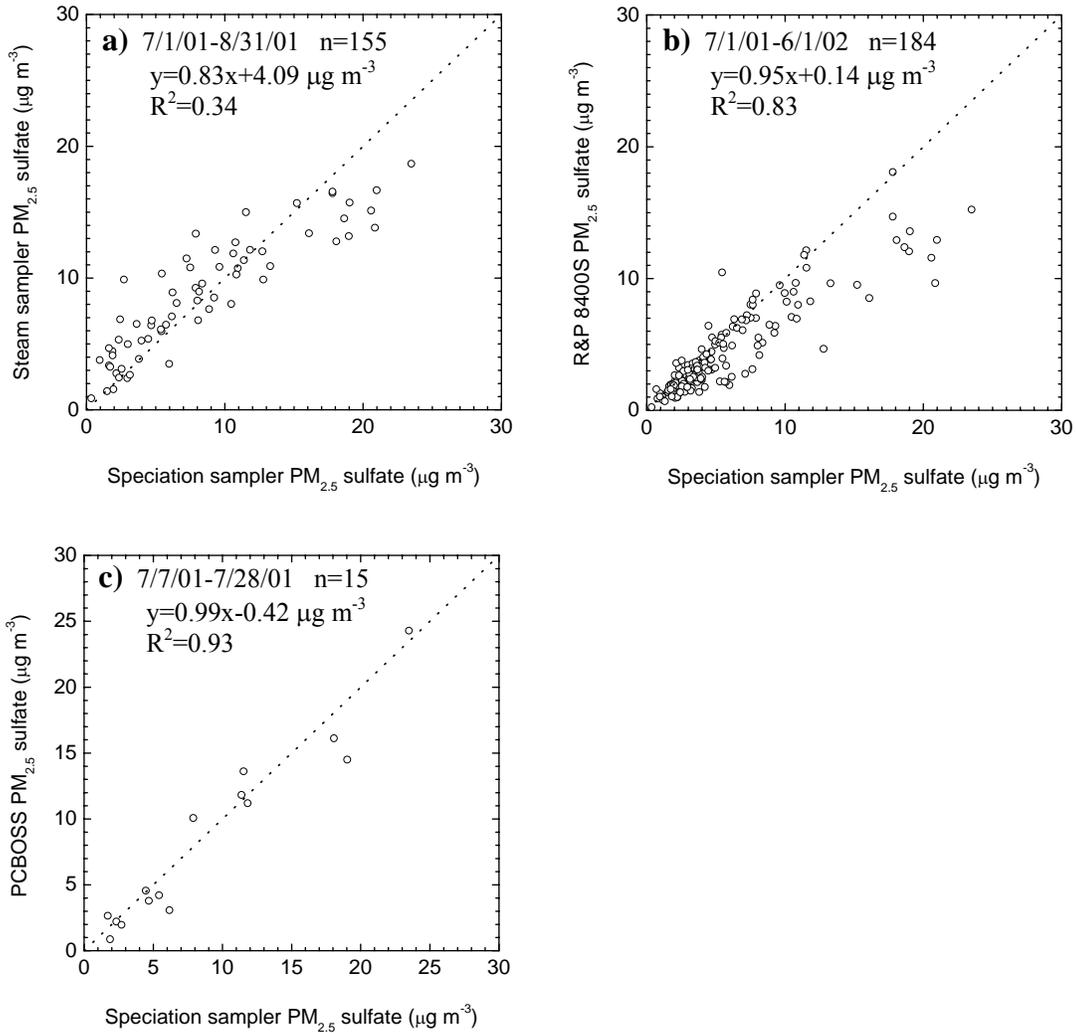


Figure 5. Comparison of PM_{2.5} organic carbon measurements: a) 24-hour TQQQ sampler v. 1-in-6 day 24-hour Denuder sampler, b) 24-hour TQQQ sampler v. 24-hour average of 2-hour to 4-hour TOT carbon analyzer. Also shown are the 1:1 lines (dashed lines).

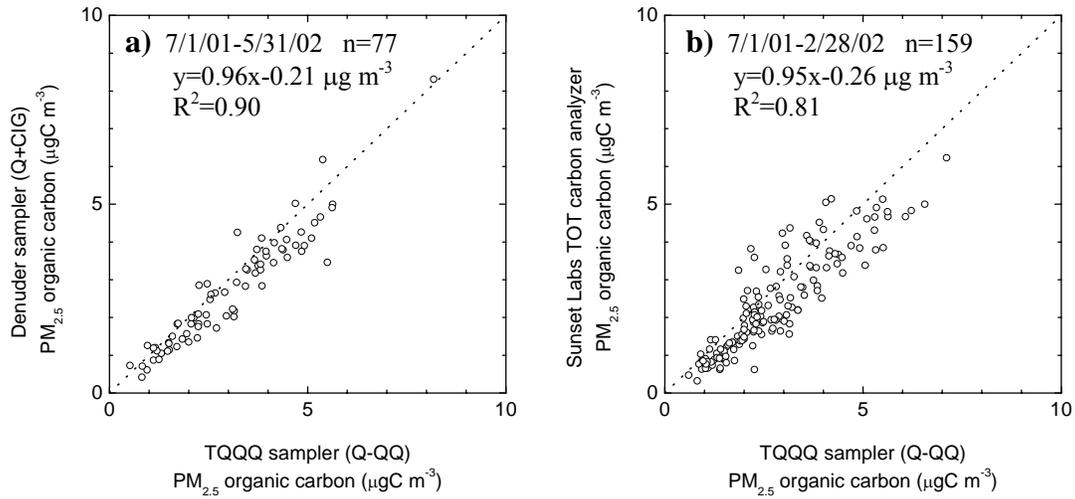


Figure 6. Comparison of PM_{2.5} elemental carbon measurements: a) 24-hour TQQQ sampler v. 24-hour Denuder sampler, b) 24-hour TQQQ sampler v. 24-hour average of 2-hour to 4-hour TOT carbon analyzer. Also shown are the 1:1 lines (dashed lines).

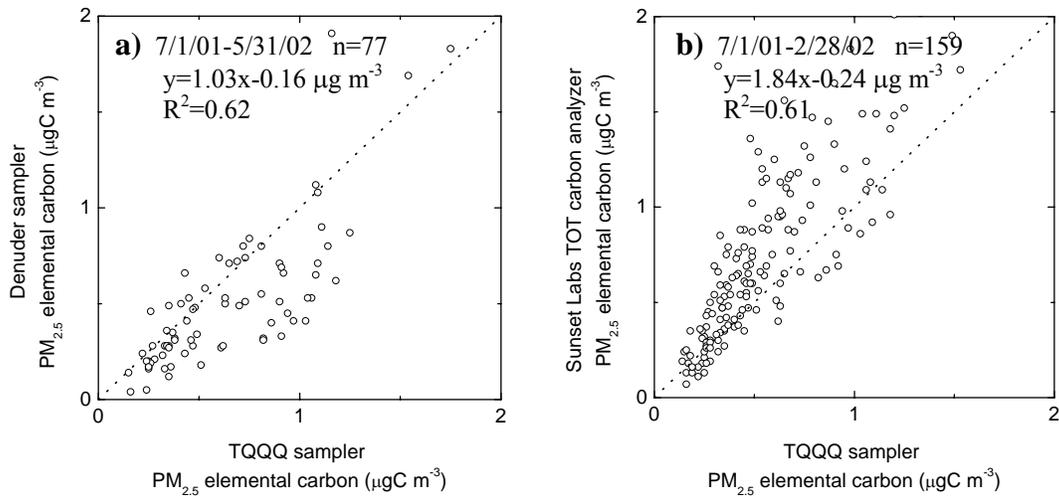


Figure 7. Comparison of the geometric mean of the aerosol diameter: 24-hour MOUDI sampler v. 24-hour average of 5-minute SMPS measurements. Also shown is the 1:1 line (dashed line).

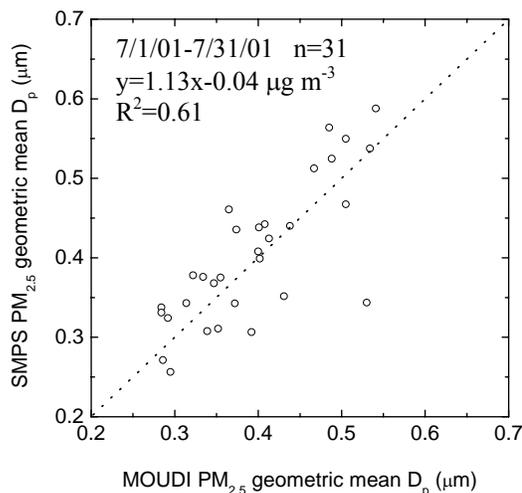
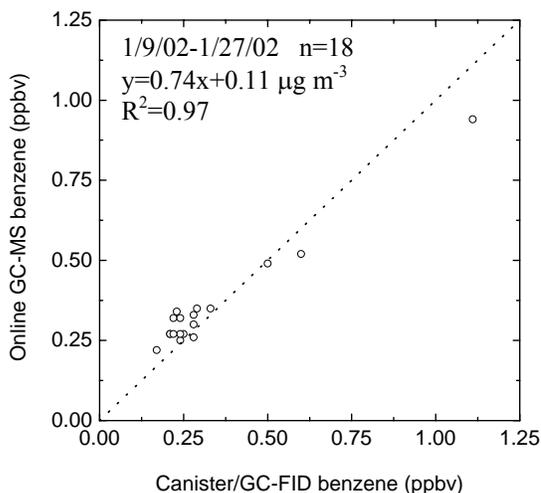


Figure 8. Comparison of gas-phase benzene measurements: 24-hour Canister sample with GC-FID analysis v. 24-hour average of 1-hour Online GC-MS measurements. Also shown is the 1:1 line (dashed line).



Overall, the select methods compare reasonably. In a few instances, best estimate data sets were produced to address the QA concerns of these methods (PM_{2.5} sulfate, nitrate, and ammonium).

2.6 Representativeness

Representativeness expresses how closely a sample reflects the characteristics of the surrounding environment and can be quantified in terms of a spatial scale for monitoring. The main monitoring site is located in Schenley Park in the Oakland district of Pittsburgh. The site is on top of a grassy hill adjacent to the CMU campus, several hundred meters from the nearest heavily traveled street (Forbes Avenue), and fifty meters past the end of a dead end street on campus. There are no major sources within several hundred meters of the site. Schenley Park extends more than a kilometer

to the south and west, the predominant upwind directions. The exposure of the surrounding environs represents both an ‘urban’ and ‘neighborhood’ scale for particle monitoring.

2.7 Data Quality Objectives Not Met During PAQs

In a few instances, the data quality objectives were not met at PAQS. Typically, these instances were associated with newly developed instrumentation that did not perform as well as expected, and are summarized in Table 3. When possible, best estimate data sets were produced to address the QA concerns of these measurements (PM_{2.5} sulfate, nitrate, and ammonium). In addition, several sets of data were not completely analyzed by the time this report was completed. These are marked with a dash in Table 1.

Table 3. Observables for which the DQI did not meet the DQO at PAQS.

Observable	Method	Issue
Number, surface area, and volume distribution	TSI APS	Data completeness - The instrument broke during fall of 2001 and was not repaired and returned by the manufacturer until March of 2002.
PM ₁₀ , PM _{2.5} , and PM _x mass	FRM, Dichot, and MOUDI samplers/ Gravimetry	MDL – Table 1 shows the MDL DQO as 2 µg/m ³ for FRM, Dichot and MOUDI samplers. The DQOs for these instruments were erroneously reported as 0.2 µg/m ³ in the QAPP.
PM _{2.5} nitrate and sulfate	R&P 8400N/S (ICVC)	Precision - The DQOs were overly optimistic, given the fact that these instruments were newly commercialized. In actuality, the instruments were less precise than expected. However, a rigorous quality control plan allowed these issues to be tracked over the course of the study (Wittig et al., 2003b).
PM _{2.5} sulfate	R&P 8400S (ICVC)	Data completeness - The instrument experienced more frequent malfunctions than expected (typically strip breakage) as well as a fatal error a month before the end of the study.
PM ₁₀ and PM _{2.5} elements	Hi-Vol sampler/ICPMS	MDL, precision, accuracy, data completeness - measurements were not finalized by the time this report was compiled.
PM _{2.5} water soluble NH ₄ ⁺	CMU Steam sampler/OAD	MDL, precision, accuracy, data completeness - measurements were not finalized by the time this report was compiled.
PM ₁₀ and PM _{2.5} inorganic ions	CMU Speciation sampler/IC	MDL, precision, accuracy, data completeness - PM ₁₀ measurements were not finalized by the time this report was compiled. Precision - NH ₃ gas was present in extremely low concentrations so the DQO was not achieved. Completeness – PM _{2.5} sampler malfunction as well as loss or destruction of samples prior to analysis were responsible for recovery levels below DQOs for all species, except SO ₄ which met the DQO.

Observable	Method	Issue
Size segregated chemistry: inorganic ions, EC/OC	MOUDI/IC,TOT	MDL – Calcium had a high MDL due to instrument problems; all other inorganic ions achieved the DQO. Accuracy – No accuracy was determined for the inorganic analyses due to lack of an absolute standard. Completeness – Instrument problems for the EC/OC analyses resulted in 66% completeness, below the 70% target DQO.
PM2.5 total carbon	ADI Carbon analyzer (ICVC)	MDL, precision, accuracy, data completeness – Data will not be submitted due to instrument difficulties.
Light hydrocarbons (C1-C12)	Canister/GC-FID	MDL, precision, accuracy, data completeness – Measurements for ESP02 Intensive (sampling once daily) not yet finalized by the time this report was compiled.
Meteorology	All methods	MDL, precision, accuracy - The standard operating procedures (and manufacturer recommended procedures) did not allow these DQIs to be calculated.

3. Conclusions

- A majority of the data quality indicators showed the PAQS central site instruments performed as expected or better.
- In a few instances, PAQS central site instruments could not be evaluated because the data were not finalized by the time this report was produced (PM_{2.5} water soluble NH₄⁺ using the CMU Steam sampler/IC and PM₁₀ and PM_{2.5} elements using the Hi-Vol sampler/ICPMS).
- Most data quality objectives that were not met were associated with newly developed instrumentation that did not perform as well as expected. When possible, best estimate data sets were produced to address the QA concerns of these measurements (PM_{2.5} sulfate, nitrate, and ammonium).

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