Overview of the 1999 Atlanta Supersites Project

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Abstract

This paper presents an overview of the 1999 Atlanta Supersites Project coordinated through the Southern Oxidants Study and the Georgia Institute of Technology and funded by the US EPA along with other sponsors who provided in-kind support primarily through existing studies. The Atlanta Supersites Project was located at the existing SEARCH/ARIES site on Jefferson St. in NW Atlanta, GA. The primary objective of the Atlanta Supersites Project was to evaluate and compare advanced measurement methods for particulate matter mass and its components. Methods included filter/denuder based time-integrated or discrete samplers, a variety of semi-continuous methods measuring mass, its major components (sulfate, nitrate, ammonium, organic carbon, elemental carbon, trace elements) and gas phase precursors, and for the first time ever, a comparison among particle mass spectrometers, four in total. These data were complemented by meteorological data as well as gas phase criteria pollutant measurements and other supplemental data, such as particle physical properties, VOC, oxygenated VOC, and NOy. The primary and supplemental data also were used to better understand the formation and accumulation of PM in Atlanta and to better understand source-receptor relationships. This paper overviews the study, summarizing objectives, the site and measurements, the relative reference data used for comparisons, overviews the meteorological and chemical characteristics of pollution in Atlanta during the study, puts the study in context of Atlanta and the Southeast US, and finally summarizes the key findings from the over 30 publications published, submitted, or in preparation. This paper also provides as complete a list as is currently available of those publications. Others certainly will be emerging over time. The comprehensive database is available through the Atlanta Supersites Project web site sponsored by GIT (http://www-wlc.eas.gatech.edu/supersite/).

1. **Introduction**

The Clean Air Act requires EPA to revise or update National Ambient Air Quality Standards (NAAQS) based on a review of the latest scientific information on known and potential human health and welfare effects associated with ambient levels of particulate matter (PM) found in air. In 1997, EPA promulgated new rules for PM, based on the 1996 PM Air Quality Criteria Document (EPA 1996), that included, in addition to slight revisions for PM10, new standards for PM2.5 (Federal Register 1997a). (PM10 is used here to denote particulate matter with aerodynamic diameters of 10 µm or less and PM2.5 particulate matter with aerodynamic diameters of 2.5 µm or less.) EPA also was required to implement a PM2.5 monitoring program to support compliance monitoring and develop data for implementation strategies to reduce PM levels in areas exceeding the PM2.5 standards. Where possible these data also will support health and exposure studies. The current program consists of three integrated monitoring networks. The first or base network is the Federal Reference Methods network designed to monitor PM2.5 mass at a large number of locations (> 1100) throughout the US. The purpose of this network is for compliance with the NAAQS for PM.

The second network is the National PM2.5 Chemical Speciation Trends Network (STN) (EPA 1999b) designed to measure PM2.5 mass and the major chemical components of PM (sulfate, nitrate, ammonium, organic material, elemental carbon, and crustal related material) at about 250 sites nationwide. Of these, 54 are part of EPA's long-term NAMS (National Air Monitoring Stations) network for measuring trends in atmospheric pollutants (e.g., ozone, CO, SO_2, PM2.5, PM10), while the remaining are part of the SLAMS (State and Local Air Monitoring Stations) network. The STN supports development of State Implementation Plans (SIPs) for reducing PM concentrations in air.

The third network is EPA's PM Supersites Program (EPA 1998). This program has three major objectives:

1. SIPs....support development of SIP's through improved understanding of source-receptor relationships leading to improved design, implementation, and tracking of control strategy effectiveness in the overall PM program;

2. health effects and exposure.....development of monitoring data and samples to <u>support</u> health and exposure studies to reduce uncertainty in NAAQS setting and to enable improved health risk assessments; and

3. methods testing....comparison and evaluation of emerging sampling methods with routine techniques to enable a smooth transition to advanced methods.

The PM Supersites Program (http://www.epa.gov/ttn/amtic/supersites.html) consists of eight projects nationwide, covering distinctively different geographic areas with different emissions and meteorological influences. To meet the above objectives the PM Supersites Program is designed to be

1. hypothesis driven;
2. regional in nature, consisting of a single central site or regional studies composed of several sites augmented by other private and public Networks;
3. an ambient monitoring program, providing measurements and data in support of health related studies, but not actually funding health related studies;
4. a successful leverage of resources with other ambient programs, with health related studies, and with other National Networks (FRM, STN, etc); and
5. a cooperative agreement between EPA and universities.

The Atlanta Supersites Projects is the first of EPA's PM Supersites Projects to be established (http://www-wlc.eas.gatech.edu/supersite/). This was done under Phase 1 of the program along with the Fresno Supersites Project (http://www.epa.gov/ttn/amtic/fresno.html). The goals of the Atlanta Supersites Project are twofold: first, to provide a platform for testing and contrasting a variety of advanced and more routine PM and gas phase measurement methods, and second, to provide data to advance our scientific understanding of atmospheric processes regarding the formation and accumulation of PM in Atlanta.

Specific objectives are:

1. to characterize the performance of emerging and/or state-of-the-science "PM Measurements Methods"[1];
2. to compare and contrast similar and dissimilar PM Measurements Methods;
3. to evaluate the precision, accuracy, and completeness of information that can be gained from the planned EPA "PM mass and chemical composition" networks;
4. to evaluate the scientific information gained by combining various independent and complementary PM measurements, particularly measurements at high time resolution with 24-hr integrated sampling; and
5. to address various scientific issues and their ozone- and PM-related policy implications.

The Atlanta Supersites Project was conducted during August 1999 in Atlanta, GA. This 4-week intensive study (August 3 to September 1, 1999) brought together over 150 scientists and technicians making a variety of measurements using advanced state-of-the-science systems, such as the particle mass spectrometers, semi-continuous species specific PM methods, and discrete chemical speciation samplers for mass and the major chemical components of mass. The study was coordinated by the Southern Oxidants Study (SOS) in collaboration with numerous universities and agencies that comprise SOS as well as several on-going air quality research programs occurring in Atlanta at the time of this study. The collaborating studies included the Southeastern Aerosol Research Characterization study (SEARCH; Edgerton et al. 2000a) and the Aerosol Research Inhalation Epidemiology Study (ARIES; Van Loy et al. 2000), both sponsored by EPRI and Southeastern

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[1] "*PM Measurements Methods*" includes methods to determine the physical and chemical characteristics of PM, identify their chemical precursors and meteorological driving forces, and ultimately understand the public-health impacts and visibilityltering properties of airborne PM.

utilities; the Southern Center for the Integrated Study of Secondary Aerosols (SCISSAP) (http://www-wlc.eas.gatech.edu/scissap), an EPA grant awarded to the Georgia Institute of Technology (GIT); and the Assessment of Spatial Aerosol Composition in Atlanta, 1999 (ASACA) funded by Georgia Power and operated by GIT (Butler et al. 2003).

The comprehensive database developed as a result of this study is available publicly through the GIT via the web at the following address (http://www-wlc.eas.gatech.edu/supersite/). Files are zipped, *.dbf files, and are organized by pollutant type: particle phase, gas phase, meteorology and radiation, and data codes. Data descriptions also are given. Other relevant information given at this web site includes the study protocol, methods descriptions for most methods, pictures of the site, and more. The Atlanta Supersites Project database also is available publicly via the NARSTO web site. This long-term archive is located at the NARSTO Permanent Data Archive (PDA) operated by the NASA Langley Research Center Distributed Active Archive Center (DAAC). The Langley DAAC provides no-cost ordering and FTP retrieval of NARSTO project data at URL: http://eosweb.larc.nasa.gov/project/narsto/table_narsto .html . Atlanta Supersites project data files are stored in the NARSTO Data Exchange Standard (DES) format. The DES is a self-documenting format and saved as ASCII comma-separated value (.csv) files. A DES file contains header information about the contents of the file and the data originator, metadata entries that identify sites, flags, units, and sampling and analysis methods, and a main data table of measurement results. The DES file can be directly imported into an Excel spreadsheet or other software. Project documentation about the data collection is associated with the data set in the PDA. The particle mass spectrometer data were saved in custom formats.

This overview paper serves at least two primary purposes. First it provides a summary of the 1999 Atlanta Supersites Project, its objectives, the site, measurements, and a summary of key findings. Secondly, it provides a complete listing of papers published or submitted for publication as of the date of submission of this paper. Undoubtedly this rich database will continue to be mined for several years, as participants and others look deeper into the data.

Experimental

2.1. Site Description

The Atlanta Supersites Project was located at the Georgia Power Company facility on Jefferson St., approximately 4 km NW of downtown Atlanta (Figure 1). The ongoing SEARCH and ARIES programs have used this site since July 1998. The site was located in a mixed commercial-residential neighborhood within approximately 200 m of a bus maintenance yard and several warehouse facilities, and approximately 200 meters and 40 meters, respectively of Jefferson and Ashby Streets (Figures 1 and 2). The Supersites Program Quality Assurance Manager assessed site exposure or representativeness of the Jefferson St. site (Mikel 2001). Based on that review, site representativeness (Federal Register 1997b) was identified as urban scale (4-50 km) for ozone and neighborhood scale (0.5 – 4 km) for particulate matter. Local sources, such as the bus maintenance yard to the south, the road to the west, or the container storage area to the north would have little influence on the intercomparison. In terms of understanding source-receptor relationships, the local sources proved to be an asset, since the semi-continuous methods were able to show the local vs regional influence of PM pollution at the site (see for example, Weber et al. 2002). Integrated methods likely would have had problems deciphering local and regional impacts, especially based on pollution that varied on short time scales.

The general site layout is given in Figure 2 with trailer (multi-group) and platform specifics given in Figures 3a and 3b. Located at the north end of the site were two approximately 20 m long platforms (Figures 2), on which most of the integrated samplers were located as well as two continuous mass samplers. The SEARCH/ARIES trailer (D in Figure 2) has been located at the site since July 1998. Trailers operated by Georgia Institute of Technology, University of Miami, University of Maryland, and University of Delaware (see F - I in Figure 2) were located at the south end of the site, while the Radar Profiler (University of Alabama; A in Figure 2) and an aerosol and ozone LIDAR (NOAA; C in Figure 2) were operated at the north end of the site. To evaluate spatial continuity across the platforms two FRM samplers were located diametrically from each other on the two platforms (Figure 3b, spaces A and R). To evaluate vertical representativeness of the samplers on the platforms with the continuous sampler inlets protruding from the roof of the trailers, a third FRM was located on the roof between the two main trailers as shown in Figure 3a. These results are reported in Solomon et al. (2003) and indicate no practical or statistical difference between the monitors on a 24-hr average basis.

2.2 Sampling Schedule

The intensive measurement program began on August 3, 1999 at 0600 EST (local time: EDT = EST + 1) and operated continuously until 0600 EST (local time – 0700 EDT) on September 1, 1999. This schedule allowed sampling to begin before the breakup of the early morning inversion and before rush hour emissions impacted the site. It also allowed operators to change filters during daylight hours rather then at mid-night.

Five sampling schedules were employed during the study to allow investigators to meet group and individual objectives. These are referred to as Schedules A, B, C, M, and S and are defined as follows:

> Schedule A – Alternate Day Schedule: On this schedule, samples were collected for 24-hrs sampling periods beginning at 0600 EST (local time – 0700 EDT) on alternate days, beginning with the first day of the study, August 3. This schedule also became known as the odd-day schedule. This schedule provided a total of 15 sampling periods and allowed for 24-hr sample collection with single event, manual samplers. All of the discrete, 24-hr filter-based mass and chemical speciation samplers operated on this schedule and their results have been compared in Solomon et al. (2003) and described for the GIT particle composition monitors (PCM) in Baumann et al. (2003). On even calendar days investigators were asked to sample for 12-hr periods or even divisor of 12-hrs so data could be easily combined to compare with the longer duration discrete data or so data from the semi-continuous samplers could be easily combined for comparison to the shorter term discrete data.

Schedule B – Base Schedule: This schedule consisted of continuous day and night sampling with the two sampling periods beginning at 0600 EST and 1800 EST. Sampling periods were slightly less than 12 hours to allow for sample changing, which took place at the end of each sampling period. This schedule was employed by two of the MOUDI samplers collecting samples for analysis of mass and major components and by one of the SEARCH/ARIES PCM. These samplers provided a consistent uninterrupted set of data through out the entire study along with data on day and night pollutant concentrations.

Schedule C – Continuous Schedule: This schedule was for the continuous and semi-continuous samplers with high time resolution - minutes to hours. Data collected by these samplers were averaged to one hour for comparison purposes, although the number of data points with in an hour varied from 1 to 6. Results from these samplers have been compared by Genfa et al. (2002) for nitrous and nitric acid, Lim et al. (2003) for OC and EC, and Weber et al. (2003) for sulfate and nitrate. Also included in this category are the particle mass spectrometers. These data were compared in unique ways since they are not quantitative and focus on single particles (Middlebrook et al. 2003).

Schedule M – Multiday Schedule: This schedule allowed for sample collection times greater than 24-hours for chemical analyses that required large sample amounts, such as for some trace metal analyses and organic speciation on the MOUDI size segregated samples.

Schedule S -- SEARCH/ARIES Schedule: While discrete samplers operated for the purpose of the comparison study began collection at 0700 each day, the SEARCH/ARIES program continued to operate on a mid-night to mid-night schedule to meet its long-term objectives. As mentioned above, a second SEARCH/ARIES PCM operated on continuous 12-hr sampling periods.

2.3 Measurements and Quality Assurance

A wide variety of particle and gas phase measurements were obtained during the Atlanta Supersites Project. To facilitate instrument intercomparisons, the PM methods used during the Atlanta Supersites Project have been divided into three categories: discrete filter-based methods, automated semi-continuous or continuous methods for high-time resolution particle chemistry, and single particle mass spectrometry methods. Table 1 provides a complete listing of these measurements as well as all supporting measurements. The latter includes measurements of physical properties of particles, gas phase criteria pollutants and reactive gases, meteorological measurements at the surface and aloft, and ozone and aerosol backscatter aloft. Details of the measurements published to date can be found in the references at the end of this paper.

Each participant was responsible for their own quality control as described in the Quality Assurance Program Plan for the study Mikel and Momberger (1999). EPA Region 4 conducted quality assurance performance and systems audits of most samplers. Performance tests were limited to flow rates or audits of temperature and pressure. Most audits occurred before the start of the study; although a few were completed during the first week. The results of the audits are given in the quality assurance final report (Mikel 2001).

2.4 Relative Reference Data

Evaluation of methods used to determine the chemical composition of atmospheric aerosols is challenging since reference standards for determining accuracy or true bias of the methods do not exist. Therefore, methods intercomparison studies are conducted that provide comparability or equivalency among the instruments tested (Fehsenfeld et al. 2001). However, some benchmark is still needed for comparison. To that end, the Atlanta Supersites Project's science team suggested the development of relative reference data sets for both the 24-hr integrated samplers and for the semi-continuous methods.

The discrete filter-based relative reference data (Table 2) were calculated for each species on a daily basis and for the study period using only data from the samplers that operated for 24-hr periods on the alternate day sampling schedule (Schedule A), in this case 15 sampling periods. This reference data included data from the EPA operated samplers (FRM, AND, MET, URG, RPS, and VAPS,), GIT, PCB(TVA), and PCB(BYU) (see Table 1 for definition of acronyms); although not all species were measured on filters collected by all samplers. For example, only the EPA samplers and GIT measured trace elements using XRF, so only data from those samplers were included in the average for those species. Missing data were excluded from all averages since data capture was high (> 93% overall) and random due typically to sampler problems during collection. Table 2 presents the daily and study period relative reference data set for the 24-hr discrete samplers used as a baseline for study comparisons. This data set also is available at the GIT Atlanta Supersites Project web site (http://www-wlc.eas.gatech.edu/supersite/). Solomon et al. (2003) describe the comparison of the discrete filter based methods, including the use of the FRM and VAPS samplers as alternative relative reference samplers for stable species and organic carbon, respectively

A relative reference data set for hourly particle species concentrations was developed based on the semi-continuous measurement methods. $PM_{2.5}$ mass, sulfate, nitrate, ammonium, organic carbon, and elemental carbon were each measured by three to five different semi-continuous methods, with sampling periods from a few minutes to two hours. “Best estimate” hourly concentrations were calculated as the weighted, geometric mean of the measured values as described in Appendix A. This approach compensated for bias among methods for periods when data were available from only some instruments. The objective is to provide data analysts with a complete data set that captures the hour-by-hour changes in a consistent fashion, and as such is suitable for model evaluation and interpretive analyses. Indeed, these values were used to compare the particle mass spectrometers (Middlebrook et al. 2003). This data set is available at the GIT Atlanta Supersites Project web site (http://www-wlc.eas.gatech.edu/supersite/).

Example “best estimate” values are shown in Figure 4 together with data from each of the semi-continuous measurements for the three-day period beginning August 20,1999. Even though reported concentrations differed, the hourly variations in the semi-continuous measurements are similar, and this is captured by the “best estimate” values. The daily profiles shown are typical of those seen throughout the study period. Sulfate was the major constituent, most often reaching a maximum concentration midday. Nitrate values were low, and consistently exhibited a small peak in the morning, around 0700 EST. Elemental carbon had a sharp peak in the morning, and a lower broad maximum in the evening, as expected for vehicular emissions. Organic carbon did not have as consistent a pattern.

2.5 General Chemical and Meteorological Characteristics

2.5.1 Meteorological Characteristics

Three meteorological regimes manifested during the study. The first was a prolonged period of stable, stagnant conditions from the beginning of the study through August 23. During this time period, a high pressure system established itself over the Southeast US yielding weak synoptic scale pressure gradients, high temperatures, moderate dew points, relatively few clouds, and no synoptic scale wind flows to disperse pollutants. Small-scale circulations did exist allowing for mixing of urban and point source plumes. The second regime resulted from the movement of a cold front across Georgia on August 24, which included rain on that day followed by moderate westerly winds and cooler temperatures for the next two days. This resulted in a flushing of pollutants from the region. The resulting clean period can be seen easily in the time series of gas and aerosol phase pollutants plotted in Figure 5. The third meteorological regime was established due to the movement of Hurricane Dennis northward along the Atlantic coast, which produced a period of northeasterly flow across the Atlanta area. This resulted in warmer temperatures after the cold front, and while it allowed pollution levels to increase once again, the synoptic scale wind flows produced some dispersion of pollutants and aerosol loadings and burdens of trace gases remained lower than during the first (stagnant) meteorological regime. As discussed below, the intensity and duration of the stable conditions during the first 23 days of August were very favorable for the accumulation of precursor species and production of secondary pollutants, resulting in unusually high pollution levels for Atlanta, making this an excellent period for this inter-comparison of advanced PM and gas phase ambient measurement methods.

The diurnal variation of wind speed, during the first meteorological regime, contributed to the morning buildups of EC and OC and likely the afternoon peaks for sulfate. Figure 6 shows the hourly averaged wind speeds for the period of August 3 to August 24. These are the averages of the measurements by the Baumann and Edgerton groups. Frequently during the predawn hours, and occasionally during the majority of the night, wind speeds dropped below 1 m s^{-1}. During these periods, accumulations of EC and OC drove the $PM_{2.5}$ mass to local maxima, which were usually less than afternoon PM2.5 mass maxima. As wind speeds increased in the morning OC and EC concentrations tended to decrease. The close correlation of these relative maxima to low wind speeds suggests accumulation from localized sources. During the afternoon, the higher average wind speeds, approaching 3 m s^{-1} on average, suggest that the sulfate dominated periods might be due to transport from more distance sources.

2.5.2 Chemical Characteristics

PM2.5 mass and composition data obtained on the alternate day schedule are given in Table 2, i.e., the relative reference data. The major components of PM mass on average for the study period were organic material (OC times 1.4) (~35%), sulfate (~34%), ammonium (~12%), elemental carbon (~3%), nitrate (~2%), and crustal material (~3%). The other, approximately 11%, consists of species that are not measured, such as, for example, other trace species or water associated with the mass measurement or due to the application of a low correction factor for estimating organic material from the OC measurement (Turpin and Lim 2001). Results in this paper used a factor of 1.4, recommended for urban aerosols by Turpin and Lim; however, the correct factor could be 1.6 or higher, which would account for at least an additional 5% of the other category.

Based on the alternate day, 24-hr sampling schedule, the average PM2.5 mass for the study period was 31.3 μg m^{-3}, with a peak value of 47.2 μg m^{-3}, occurring on August 5, 2001. This mass was directly measured on a Teflon filter by difference (Federal Reference Method protocol) and not corrected for sampling artifacts. These results indicated that the 24-hr PM2.5 standard was not exceeded during August 1999 in Atlanta. Three other lower peaks in PM2.5 mass concentrations were observed during the study occurring on August 11, 17, and 27. The lowest PM2.5 mass concentration (24-hr average, alternate day schedule) was observed on August 25, 2001, the day following the cold front that moved through Atlanta bringing rain for most of the 24th. Sulfate and ammonium followed a similar trend and were well correlated with PM2.5 mass ($R^2 = 0.85$). Organic carbon and elemental carbon were not as well correlated with mass (R^2 = 0.36 and 0.11, respectively) and they both showed less temporal variation (24-hr average; alternate day schedule) during the study, ranging from about 6 to 10 μg m^{-3} for OC and 0.7 to 1.4 μg m^{-3} for EC, except for August 25, 2001 when it rained during the day and all species were low.

Twenty-four hour averages were calculated from the 1-hr estimates of the semi-continuous data for mass and sulfate. The mass data are from the 50E C TEOM operated by Bergin, while the sulfate is the average of data reported by Weber, Hering, and Slanina. These values are plotted in Figure 5. The study period average of these data for mass and sulfate were 30.7 μg m^{-3} and 13.3 μg m^{-3} respectively. The alternate day schedule missed several peaks in PM2.5 mass that occurred on August 10 (41.0 μg m^{-3}), August 12 (37.9 μg m^{-3}), August 18 (34.8 μg m^{-3}), and on August 22 (36.3 μg m^{-3}), all local maximum for the 2-4 day episodes that occurred around those peak periods. Overall the TEOM mass and integrated filter mass agreed well with an average ratio (continuous/discrete) of 0.95 and a coefficient of variation (CV) of 6.6%. The average of the continuous samplers for sulfate on alternate days was 12.8 μg m^{-3}. This is about 23% higher than sulfate values reported by the alternate day discrete samplers (10.6 μg m^{-3}, Table 2.). Additional details of the comparison among discrete samplers and among semi-continuous samplers can be found in Solomon et al. 2003 (discrete filter-based), Weber et al. (2003) (continuous sulfate and nitrate), Lim et al. (2003) (continuous organic and elemental carbon), and Genfa et al. (2002) (HNO_2 and HNO_3).

A MOUDI impactor was used to obtain consecutive 12-hr size resolved samples (backup filter < 0.056 µm to < 6.2 µm in eight stages, listed here from stage 1 to 8: 3.1, 1.8, 1.0, 0.56, 0.32, 0.18. 0.10, and 0.056 m aerodynamic diameter) throughout the month that were subsequently analyzed for trace metals at the Georgia Institute of Technology (personal communication C. Bayer and A. Cook, GIT). Sixteen trace metals were determined in each size range. The metals with the highest total concentrations were Fe, Ti, Mn, Cr, Ni, Zn, Cu, and Pb while the remaining metals (Al, Mg, V, Co, Cd, Si, K, Ca, and Na) were present but at low levels and did not significantly impact the total daily metal concentrations. Higher 12-hr average concentrations of Pb, Ni, Ti, Cu, and Zn occurred prior to August 20, similar to the other pollutants at the site, than during the latter part of the study. In contrast, highest concentration values for Fe and Mg were observed during the latter part of the study. Metals low in concentration showed little trend during the month. Size distribution results using only data collected during the day (06:00 – 18:00) when PM was highest, indicated that most metals were distributed among the various particle sizes with maximum concentrations observed on only one or two stages. Highest concentrations of metals were observed on stages 1-3 (Ti-1, Co-2, K-2, Zn-3) and stages 5-8 (Cr-5, Cu-5, Al-6, Si-6, Na-6, V-6, Fe-7, Mg-7, Mn-7, Ca-7, Cd-8, Ni-8, Pb-8). The lowest metal concentrations were predominantly observed on stages 0-2, with a few exceptions (Al, Fe, Cr, K, Ti), which were observed on stages 4-6. As expected, on average larger particle sizes (> 0.5 µm) were dominated by crustal related elements (Fe, Ca, Mg, Al, Si), although Al showed peaks at lower sizes as well.

Figure 5 also provides a summary of peak values observed each day for O_3, SO_2, NOy ($NO+NO_2+HNO_3$+PAN+other odd nitrogen compounds; Solomon, 1994), and CO. These averages were calculated from 1-hr averages based on available data, for example, ozone and SO_2 were calculated using the average of data from Baumann and Edgerton, while NOy was primarily data from Edgerton. Hourly ozone concentrations at the site exceeded the 1-hr National Ambient Air

Quality Standard (NAAQS) for ozone on 7 days, for multiple hours each day, and all prior to August 20, 2001. The maximum 1-hr ozone concentration observed was 168 ppb on August 19, 2001 at 4 PM. This was based on data from the non-regulatory samplers used at Jefferson St. The Georgia Department of Natural Resources reported ozone concentrations exceeding the 1-hr NAAQS for ozone on 14 of the first 20 days in August, based on the regulatory monitors around the Atlanta metropolitan area. NOy and CO also tended to peak on days when ozone had its highest concentrations, but not necessarily at the same time of day. SO_2 had no correlation with ozone, as one might expect since SO_2 is a primary pollutant and ozone is a secondary pollutant.

Continuous data for mass and sulfate and for sulfate and SO_2 are plotted in Figures 7a and 7b, respectively. These figures also illustrate the advantage of the semi-continuous monitors relative to every other day sampling (Figure 7a) where 24-hr average values miss much of the short-term variability in these pollutants. The high frequency data in Figure 7b shows how sulfate and SO_2 were often decoupled, illustrating perhaps the impact of aged aerosol vs fresher plumes reaching the site. Note, periods when SO_2 was high and sulfate was low (labeled 'a' in Figure 7b) and the more frequent periods when sulfate was high and SO_2 was low (labeled 'b' in Figure 7b).

The short-term measurements allowed for a better understanding of the balance between ammonia and major acidic species in the Atlanta air (Weber et al. 2003, Weber et al. 2002, Baumann et al. 2003). Results from these analyses clearly showed that the collected PM was close to or neutral (ammonium is balanced by sulfate and nitrate) when the aerosol was collected on a 24-hr time scale on filters that were subsequently brought back to the laboratory for chemical analysis. Neutralization can occur during the extended collection periods, during transport, storage, or while filter were being prepared for chemical analysis. On the other hand, the short duration measurements clearly showed periods when the aerosol was acidic, ranging from neutral to over 450 neq m^{-3} in acidity (Weber et al. 2002).

Unique to the Atlanta Supersites project was the collocation of four particle mass spectrometers (PMS). Results from the PMS are briefly summarized here. Rhoads et al. (2003) was the only PMS able to examine ultrafine particles (< 100 nm) and found these to be dominated by particles containing carbonaceous material from all wind directions and time of day. While ultrafine particles were dominated by carbon, larger particles (> 300 nm and up to 1.5 μm) had substantial fractions of particles containing other elements and species (nitrate and minerals), although on average virtually all sizes contained carbon. Wenzel et al. (2003) employing the aerosol time of flight mass spectrometer (ATOFMS, Gard et al. 1997) observed similar results for particles greater than 0.2 μm. Rhoads et al. (2003) also examined composition and size with wind direction and found that the composition of the larger size particles tended to correlate with specific wind directions, have characteristic size particle distributions, and peaked during the day or night. A companion paper reporting results from Houston using the Delaware PMS, TX are given in Phares et al. (2003).

Lee et al. (2002) using the PALMS examined particles in the size range from 0.35 to 2.5 μm in aerodynamic diameter. They found the particle composition to be complex in nature and in general, internally mixed. They also showed that the predominant particle was internally mixed consisting of organic species and sulfate that often contained other components such as nitrate, ammonium, halogens, metals, soot/hydrocarbon, and aluminosilicates. Many of the soot/hydrocarbon particles in Atlanta had water-soluble species including sulfate, nitrate, and oxidized organic compounds in addition to metals, while mineral particles were detected as large aluminosilicates internally mixed with sulfate and nitrate. Lead was observed on nearly half the spectra. Many of the aerosol components were not strongly dependent on wind direction suggesting these aerosols were characteristic of the Atlanta metropolitan area.

Lee et al. (2003) examined in greater detail nitrate and organic acid results. Nitrate showed a maxima in the early morning when RH was high as well as a smaller peak in the afternoon that coincided with the formation of HNO_3. Organic acids were often internally mixed with hydroxymethanesulfonate (HMS) and both were observed in the larger particles with maximum similar to nitrate, larger early morning peak and smaller afternoon peak, although the afternoon peak occurred only on the organic-sulfate particles. Similarities between organic acids and nitrate for size dependence, temporal variation, and dependence with temperature and RH suggest they may have been formed though similar pathways.

Liu et al. (2003) and Wenzel et al. (2003) examined particles in the size range from 0.2 μm to 2.5 μm using the ATOFMS with simultaneous collection of both negative and positive ion mass spectra. In general, they found the aerosol also to be internally mixed and extremely complex. They classified the aerosol into primary particles, secondary particles, and particles containing both primary and secondary species. The major species detected included sodium, carbon (OC and EC), dust (Ca, Fe, Al), sulfate, nitrate, and ammonium. Complex mixtures of primary and secondary species dominated the aerosol, indicating the high reactivity of atmosphere during this intensive monitoring period. Similar composition results were observed with this PMS, including domination of the aerosol by sulfate and carbon, that the fine fraction (< 1 μm) is dominated by carbon but includes other secondary species as well, while larger particles are dominated by sulfate, dust related species, and other metals; although carbon was observed in the coarse particle mode as well. EC and OC were commonly detected as internal mixtures and during certain episodes other organic compounds were identified, including PAHs, other aeromatics, alkylamines, and possibly unsaturated esters.

Jimenez et al. (2003) operating the aerosol mass spectrometer (AMS) also indicated that the major components of the aerosol in Atlanta during August were sulfate and organic material with a minor fraction of nitrate. They found the particle size distributions and the time evolutions of the different aerosol chemical components to be significantly different. A marked diurnal cycle was observed for aerosol nitrate in Atlanta, but not for sulfate. A simple model fit was used to illustrate the integration of data from several chemical components measured by the AMS together with data from other particle instruments into a coherent representation of the ambient aerosol. Results from the Riverside group have not yet been prepared.

The temporal and spatial representativeness of the 1999 Atlanta Supersites project is given in Figures 8a through 8c. As illustrated in Figure 8a, the highest ozone and PM2.5 pollution observed in 1999 occurred during August. In fact, August 1999 appears to be high for PM2.5 and ozone during the 2-year period from August 1998 to August 2000 based on these results. Figure 8b illustrates the 24-hour integrated spatial representativeness of PM2.5 mass and the chemical components of mass observed at the Jefferson Street site with other sites that operated in Atlanta, GA during the study (Butler et al. 2003). On average for the study period (Aug. 3 - Sept. 1), the mass and the components of mass are fairly uniform through out Atlanta, with mass not differing on average by more than about 13%, ranging from 31.3 to 35.6 μg m^{-3} at the four sites. Sulfate is the most consistent among the sites varying by only about 1 %, while ammonium, EC, and nitrate vary by about 40%, 35%, and 74% respectively among the sites. Unidentified mass ranges from zero to about 13%, with the highest unidentified percent of mass being found at Jefferson St. The larger variability for nitrate might be due to its very low levels, and thus, the ability of the different monitors to measure it accurately. Since ammonium was associated predominately with sulfate, differences in ammonium and EC also may have been due to differences in the collection and analysis methods (Norris et al. 2002). This may be further substantiated by the fact that OC, EC, ammonium, and nitrate were all about 30-40% lower at the Jefferson St. site, while the mass was only 13% low relative to the peak site. In fact, better consistency was observed among the three sites operated by the same group (ASACA) with the largest differences occurring at Jefferson St. Thus, the spatial representativeness within Atlanta, based on 24-hour integrated measurements may be even greater than the data presented here indicates.

The spatial representativeness of the Jefferson St. site within the Southeast US for the month of August is illustrated in Figure 8c. Here, mass and the major chemical components are presented for 4 urban-rural pairs located in the Southeast, US. These data are courtesy of the SEARCH network. Birmingham, AL and Atlanta, GA, the two largest metropolitan areas, exhibited the highest PM levels during the study period on average. As well, the rural site paired with each of these urban locations had higher average PM concentrations than the sites in Florida and Mississippi, the latter two located near the Gulf of Mexico. Overall, the Jefferson Street site during the month of August was an excellent location and time for conducting the Atlanta Supersites Project methods intercomparison study. It afforded high concentrations of most pollutants over multiple days, as well as a few low days following the passage of a cold front, providing dynamic range in concentrations for the experiments.

3. Results and Discussion

The Science Team organized the methods into four categories: A) discrete samplers, B) semi-continuous methods, C) particle mass spectrometers, and D) supporting measurements. For the purpose of comparative analysis four general categories were developed:

1) self-evaluation papers (those describing the performance of a single instrument),
2) co-evaluation papers (those comparing the performance of instruments in one of the three categories (A-C) above,
3) cross-evaluation papers (those comparing the performance of instruments among the three categories (A-C) above, and
4) integration papers (those answering questions regarding cross cutting science or technical issues and requiring data from multiple methods in categories (A-D) above.

This section summarizes key findings in the four categories (1-4) described above, beyond the descriptive characteristics described in Section 2.5,.

3.1 Self-Evaluation Results

Ten papers fell into this category, one on a new method for measuring particle density (McMurry et al. 2001); three on gas phase measurements of formaldehyde (Li et al. 2001), of hydrogen peroxide and hydroxymethyl hydroperoxide (Li and Dasgupta 2000), and of oxygenated volatile organic compounds (OVOC) (Stabenau et al, 2001); and six on particulate matter mass and composition measurements (Modey et al. 2002; Modey et al. 2001; Baumann et al. 2003; Weber et al. 2001, Jimenez et al. 2003, Wenzel et al. 2003). Evaluations of some of the other methods operated in Atlanta were described in the co- and cross-evaluation papers.

McMurry et al. (2001) described their system for measuring the density of particles based on a mass-mobility relationship. This unique system first selected particles of known electrical mobility with a differential mobility analyzer and then measured the mass using Ehara's aerosol particle analyzer (APM). For spherical particles, electric mobility equivalent diameter equals the geometric diameter and density was then determined using the measured mass. The paper described laboratory experiments to verify the accuracy of the method and then the application of the method during the Atlanta Supersites Project. Laboratory results indicated an accuracy of 5% for spherical particles in the 0.1 to 0.3 μm size range. During the study, particle densities for the most abundant mass fell between 1.54 and 1.77 g cm^{-3} (RH in the range of 3-6%) and these densities agreed with calculated densities based on collocated size-resolved chemical composition data to within about 5%. Lower mass particles had "effective densities" of about 0.25 to 0.64 g cm^{-3}, while more massive particles had "effective densities" of 1.7 to 2.2 g cm^{-3}.

Li and Dasgupta (2000) and Li et al. (2001) described new automated methods for the continuous measurement of hydrogen peroxide and hydroxymethyl hydroperoxide, and for formaldehyde, respectively. The formaldehyde and peroxide methods used a diffusion scrubber to collect the species of interest from the gas phase into water followed by reaction with appropriate reagents to develop a fluorescing compound that was detected using a light-emitting diode-liquid-core waveguide based fluorometer. The papers described optimization in the laboratory of the methods with regards to wavelengths of detection, reagents employed to develop the fluorescing species, and minimization of interferences, and then application during the Atlanta Supersites project. Atmospheric limits of detection were achieved at about 30 pptv and 13.5 pptv for formaldehyde and the peroxides, respectively. Ambient measurements indicated all three species have similar diurnal patterns as ozone, peaking in the middle of the day, indicating photochemical production as a source of these species. Formaldehyde has a less striking diurnal pattern then hydrogen peroxide, and the authors suggested this was the result of a local source impacting the site. Mean concentrations for hydrogen peroxide and formaldehyde were given as 1.3 and 7.8 ppbv, respectively, where the formaldehyde concentration was above 4 ppbv most of the time, while hydrogen peroxide went almost to zero each night. Lowest concentrations of all three species were observed on August 24, 2001 with the passage of the cold front and associated precipitation.

Stabenau et al. (2001) described the evaluation of a method for collecting and analyzing OVOC in near real time. They identified 84 volatile compounds with an estimated precision of about 25% and detection limits raging from 2 to 28 ppt for 100 ml ambient air samples. Samples were collected in Atlanta and two other locations. In Atlanta, hourly data were reported for most of the study. Samples were collected for the first minute of the hour followed by analysis for about 40 minutes. Stabenau et al. (2001) used these data and examined the relationship of OVOC (hourly averages) and particulate organic carbon, PM2.5 total organic carbon, and particle number. Calculations indicated that gas to particle conversion (i.e., secondary organic aerosol) was a significant source of new fine particulate organic material during the summer in Atlanta. Correlation of VOC and PM2.5 total organic carbon suggested the possibility that selected gas phase organic compounds could be used to predict PM2.5 organic aerosol formation and, by extension, be an indicator of air quality in Atlanta.

Three discrete samplers employed technology to collect PM2.5 and account for loss of semi-volatile species and to examine sampling artifacts for organic carbon. Two papers described the use of the PC-BOSS for collecting PM2.5 mass and chemical composition (Modey et al. 2001, Modey et al. 2002) and another described the use of the Georgia Institute of Technology Particle Composition Monitor (GIT-PCM) (Baumann et al. 2003). All three papers evaluated the performance of their samplers, including sampler components, such as the particle concentrator in the PC-BOSS and the denuders (e.g., gas and particle phase collection efficiencies), sampling artifacts, and corrections to the data for loss of the semi-volatile species ammonium nitrate and semi-volatile organic carbon (SVOC). Results indicated that there were significant amounts of semi-volatile material that may not be accounted for using the standard FRM for PM2.5 mass. Modey et al. (2001) indicated losses relative to Teflon or quartz-filters of up to 50% for nitrate, and about 32% for organic material on average. Baumann et al. (2003) carefully examined assumptions in calculating a mass balance between the sum of the species and the measured dry PM2.5 mass collected on a Teflon filter. After accounting for artifacts, except the loss of SVOC, they accounted for 87 ± 10% of the collected mass. An improved mass balance was obtained when SVOC was added to the sum of the species.

Weber et al. (2001) described a newly developed semi-continuous method for the collection of ionic species in PM2.5. Particles were grown by super saturation in a particle growth chamber after gas phase species that can interfere with the measurement of the PM components (i.e., HNO_3 for nitrate) were removed by denuders. The grown particles were then collected by impaction onto a vertical glass plate that was continually washed with a constant flow of water at 0.1 ml min^{-1}. The flow was divided and then analyzed by a duel column ion chromatograph for anion and cation species. Samples were collected for 4.3 min followed by analysis yielding a sample concentration value for all species determined about every 7 min. An atmospheric detection limit of about 0.1 $\mu g\ m^{-3}$ was obtained for sulfate, nitrate, sodium, ammonium, calcium, and potassium. Results were described on the testing and optimization of the various components of the system. Diurnal patterns of the sulfate and nitrate were described along with identification of periods when pollution plumes may have impacted the site resulting in short-term periods of high sulfate and when the aerosol appeared to be considerably more acidic. This was not observed in the results from the discrete samplers, which were typically neutral.

Jimenez et al. (2003) described the AMS developed by Aerodyne, Research, Inc. and the use of the instrument at two sites, one being the 1999 Atlanta Supersites Project, the other in the Boston area the following month. The paper also describes the process for quantifying and identifying the chemical components of the measured aerosol. The AMS was designed to measure size-resolved mass distributions and total mass loadings of volatile and semi-volatile chemical species associated with sub-micrometer particles. The AMS was operated in two modes: 1) a continuous mass spectrum mode without size information; and 2) a size distribution measurement mode for selected m z^{-1} settings of the quadruple mass spectrometer. Trends in mass concentrations of sulfate and nitrate measured with the AMS in Atlanta compared well with those measured with ion chromatography-based instruments after AMS calibration factors were applied.

Wenzel et al. (2003) show how scaling factors can be developed, using other data obtained during the Atlanta Supersites project, to obtain concentration data from the ATOFMS. In this case, sized resolved unscaled particle counts from the ATOFMS were compared with those of the Laser Particle Counter (LPC) (Woo 2001). Comparison of periods when particles were detected but no mass spectra was obtained, "missed particle types" to the semi-continuous measurements indicated that the missed particles were predominantly composed of ammonium sulfate and most prevalent in less than 1 μm particle size range.

3.2 Co- and Cross-Evaluations

This section summarizes results of intercomparisons of similar types of instruments within a given category, i.e., discrete, semi-continuous, and PMS. Five papers associated with the study describe intercomparisons among 1) discrete chemical speciation samplers for PM2.5 mass and major components plus up to 10 elements (Solomon et al. 2003), 2) semi-continuous methods for nitrous and nitric acid (Genfa et al. 2002), 3) semi-continuous methods for sulfate and nitrate (Weber et al. 2003), 4) semi-continuous methods for organic and elemental or light adsorbing carbon (LAC) (Lim et al. 2003), and 5) a comparison of the four single particle mass spectrometry methods results (Middlebrook et al. 2003). Each of the semi-continuous papers and the PMS paper go beyond comparing just like samplers, having short sections where the instruments were compared to the discrete relative reference data (semi-continuous papers) or to the semi-continuous relative reference data (PMS). Thus, papers in this section cover both co- and cross-evaluations, as papers that focus in detail on comparing across the measurement categories have not yet been prepared.

Discrete or time integrated chemical speciation samplers operated on the alternate day schedule collecting samples for 24-hr periods (samplers and methods are described in Solomon et al. 2003).

These filter-based methods used in some, but not all cases, denuders and reactive filters to collect PM or its components with minimal bias. For example, nitrate was usually collected with a denuder and reactive filter pair, while most samplers did not use denuders for the collection of organic carbon. Those that did used either XAD-4 coated annular denuders or carbon impregnated denuders to remove gas phase organic material before collection of particles on a filter. Back up filters, if used, were not included in the analysis due to the lack of knowledge of their collection efficiencies or the efficiencies of the denuders. Results indicated significant and real differences among the methods for organic carbon, elemental carbon, and nitrate (Solomon et al. 2003). Sulfate agreed well among the methods. Comparability among most of the samplers for a given species were reported: mass (± 20%); sulfate (± 10%); nitrate (± 30-35%); ammonium (± 10-15%); organic carbon either with or without denuders (± 20%) or including both with and without denuders (± 35-45%); elemental carbon (± 20% to ± 200%) the latter if different analysis methods were used in the comparison; and minor and trace elements (± 20-30%). In a related paper, Dookwah et al. (2001) discuss sampling artifacts associated with the determination of organic carbon using quartz-fiber filters with and without XAD denuders, which supports the evidence suggested by Solomon et al (2003) for the differences observed in OC measurements obtained by the integrated samplers.

A net positive organic carbon-sampling artifact on quartz-fiber filters was estimated from the intercept of the FRM PM2.5 mass (x-axis) regressed against OC concentrations from each sampler (Solomon et al. 2003) and was in the range of 1-4 $\mu g\ m^{-3}$ (average OC for the study was 7.5 ± 1.7), comparable to that observed with these types of samplers during a comparison conducted in the winter (Solomon et al. 2000). This is a net estimate (positive plus negative) that assumes loss from both filter types (quartz and Teflon is similar).

Three different semi-continuous methods were used to measure nitric acid, whereas two methods were used to measure nitrous acid. One method (ARA) used a two-channel NO-O_3 chemiluminescence based analyzer to measure NOy in one channel and NOy minus HNO_3 in the other channel. A KCl denuder was used to remove HNO_3 in the second channel. One minute average HNO_3 concentrations were computed by the difference between the NOy reported in the two channels. The other two instruments used wet denuders, one rotating (ECN), the other a parallel plate denuder (TTU), to collect HONO and HNO_3 separate from particulate nitrite and nitrate. The effluent of the denuders was then injected into an ion chromatograph (IC) for the determination of nitrate and nitrite. Different solutions were used in the denuders of these two systems to remove the acidic gases and ammonia. The wet rotating denuder system reported gas phase acids and ammonia as well as anions and cation species in the collected PM once per hour for a 15 min sample, rotating through each set of species every 15 min. Results for HNO_3 from the ECN and TTU instruments agreed well when the instruments were operating properly. The ARA chemiluminescence method reported values typically a factor of two higher for HNO_3. Compared to data from the GIT-PCM, described above, the ARA compared well, while the other two methods reported results that were significantly lower. Either the PCM and ARA are collecting compounds other than nitric acid or ECN and TTU are underestimating HNO_3. TTU and ECN reported similar HNO_2 concentrations when the two instruments were believe to be operating properly (Genfa et al. 2002). HONO showed a strong diurnal trend with nighttime peaks up to about 5 ppbv, while HNO_3 peaked in the middle of the day with peak values ranging from 3-6 ppbv throughout the study period.

Weber et al. (2003) performed an intercomparison of five semi-continuous methods for PM2.5 sulfate and nitrate. The instruments measured these anions at rates ranging from every 5 min to once per hour. The techniques included a filter sampling system with automated extraction and on-line analysis by IC, two methods that collected particles into water followed by on-line IC analysis (GIT, ENC), and two systems that converted particulate nitrate (ADI, ARA) and sulfate (ADI) either catalytically or by flash vaporization to gases (NOx or SO_2, respectively) that were measured with gas analyzers. Most instruments were in rational agreement by the end of the study with correlation coefficients (R^2) between 0.7 and 0.94. Based on comparison with the mean of all the semi-continuous methods for sulfate and nitrate and comparison to the relative reference values for the discrete samplers most instruments were within 20-30% for nitrate (0.1-0.2 $\mu g\ m^{-3}$) (note, nitrate values were low with an average mean for the study of 0.5 $\mu g\ m^{-3}$) and 10-15% for sulfate (1-2 μg

m^{-3}). Results also suggested that the semi-continuous methods suffered less from sampling artifacts than the filter based methods, both due to the shorter sampling periods and the method of collection. Of considerable importance are the facts that 1) several of these methods are new prototype instruments that will undergo additional improvements over time, 2) the methods, having different approaches, seem to agree reasonably well, and 3) that the high time resolution data provides important temporal information on the behavior of these species that can not be obtained easily using integrated filter-based technology. This last statement of course is true for all semi-continuous methods relative to discrete methods.

Lim et al. (2003) compared results from five semi-continuous samplers that measured OC, EC, or TC (OC + EC) at sampling frequencies from 1 min to 2 hrs. The different samplers were described in Lim et al. Two methods measured OC and EC using thermal desorption with (RU) and without (R&P) optical correction for pyrolysis, the latter not expected to occur since the sample was always heated in air, two methods used optical absorption to obtain estimates of light adsorbing carbon (PSAP, Aethalometer-AET), and one method (ADI) used flash volatilization, similar to that described above for sulfate and nitrate but the evolved gas (CO_2) was quantified with a NDIR carbon dioxide analyzer. The ADI method provided an estimate of oxidizable carbon, which when multiplied by 2 provided an estimate for organic carbon. Semi-continuous carbon results were averaged to the longer integration time of the MOUDI samplers (12-hr) or the discrete samplers (24-hr) for comparison to the filter-based methods, the latter being the 24-hr relative reference values for OC and EC. For OC the two similar methods (R&P and RU) compared better with each other than with the flash volatilization method. Results for elemental carbon were mixed with some comparisons being highly correlated (0.97, PSAP vs AET) but having a slope that is near 50% or having a slope near 1 and a lower correlation coefficient ($R^2 = 0.74$, RU vs R&P). On the average, for samplers that measured OC, ADI < R&P < RU, for EC PSAP < RU < R&P/AET, and for TC, R&P was approximately equal to RU. The authors note that the semi-continuous methods have lower inter-sampler coefficients of variation (CV), ranging from 7%, 13%, and 26% for TC, OC, and EC, respectively, while the integrated filter based methods have CV in percent of 25, 28, 66, respectively. The high CV for EC is in part due to method-dependent differences in definition of OC and EC. Higher differences in integrated OC CV value may in part be due to differences in the observed sampling artifacts on quartz-fiber filters, where some of the integrated samplers used denuders to minimize positive and perhaps enhance negative artifacts, while other samplers did not use denuders and did not correct for adsorption on the sampling filter (Solomon et al. 2003).

The last co-evaluation paper compared, for the first time, results from four particle mass spectrometers (Middlebrook et al. 2003). This comparison met significant challenges since the methods produce a wealth of data and each have a different approach resulting in fairly unique data bases. Three of the instruments used laser desorption/ionization to volatilize and ionize the particles and components (PALMS, ATOFMS, RSMS-II), while the forth (AMS) volatilized the particles after impaction onto a heated surface in the ion source of a quadrupole mass spectrometer. Although the AMS has single particle sensitivity for selected species, complete mass spectra can only be obtained for particle ensembles. In contrast, the laser-based instruments generate complete mass spectra from individual particles. Design differences existed as well amongst the three laser desorption/ionization methods. For example, the RSMS-II measured particles as small as 15 nm, while the ATOFMS and PALMS have lower particle size cuts around 0.2 and 0.35 μm aerodynamic diameter, respectively. The three laser-based instruments also used different ionization laser wavelengths and energies. Despite these differences, the laser-based methods found similar classifications among the detected particles and their relative fractions among the different particle sizes were generally consistent. The AMS thermal method was better correlated with the semi-continuous methods for nitrate and sulfate then the PALMS.

3.3 Integrative Analyses – Science questions

Papers in this section incorporate additional analyses beyond comparisons and begin to address scientific questions about the atmosphere in Atlanta, the possible implications of results from Atlanta on the design and monitoring approaches for current long-term national monitoring networks and epidemiological health studies or model evaluation.

Carrico et al. (2003) examined PM2.5 optical and radiative properties directly measured or deduced from other measurements performed at the site. For example, they use MOUDI data to estimate the scattering and adsorption coefficients (σ_{sp} and σ_{ap}) as a function of particle diameter to determine the particle sizes responsible for atmospheric light extinction. They found the geometric mean light scattering and adsorbing diameters to be 0.54 ± 1.5 and 0.13 ± 3 μm, while the PM2.5 and EC geometric mean diameters were at 0.47 ± 2 and 0.27 ± 6.6 μm AD, indicating that light scatting and PM2.5 mass were described by a rather narrow mode of particles in the accumulation mode ($0.1 < Dp < 1$ μm), whereas EC mass and absorption had a broader peak, although shifted towards lower particle sizes. Other parameters estimated include single scattering albedo, visual range, aerosol mass and adsorption efficiencies, and direct aerosol radiative forcing. Average single particle albedo was estimated at equal to 0.87 ± 0.08 (50% RH), which indicates the importance of light adsorbing species in Atlanta. Average visual range (1.9 [total extinction]$^{-1}$) was estimated at 15 ± 8 km (50% RH), which might be a factor of 2 lower at ambient RH values (~80-90%), noting that Rayleigh scattering only (clean air, low RH) results in a visual range of about 150 km. Estimates of average direct aerosol radiative forcing in Atlanta indicated a cooling (-11 ± 6 Wm^{-2}), which was substantially larger than the global mean radiative forcing attributed to anthropogenic aerosol particles (~ -1 W m^{-2}) or that due to anthropogenic greenhouse gases (~ +2.5 W m^{-2}). Thus, aerosols in urban areas can have a substantial impact on radiative transfer with potential implications for climate, photochemistry, photosynthesis, and atmospheric stability. Diurnal trends in several of these parameters were described indicating the influence of morning rush hour with lower inversions and higher afternoon mixing heights on optical properties, with the largest impacts on scattering and adsorption in the morning.

McMurry and co-workers obtained particle size distribution measurements in the size range from 3 nm to 2 μm at the ARIES sampling site in Atlanta (Jefferson St. location) beginning in August of 1998, including the Atlanta Supersites Project sampling period, and beyond. These measurements required three different analyzers to cover the full spectrum of particle sizes: a nano-scanning mobility particle sizer (3 < 50 nm); a standard scanning mobility particle sizer (20 nm – 0.25 μm); and a laser particle counter (0.1 μm – 2 μm). The ultrafine particle measurements were obtained by a new method that allowed for the determination of particle size distributions down to 3 nm. McMurry et al. (2000) described results of those measurements for the size range from 3-10 nm during the first 13 months of the ARIES study. McMurry and Woo (2001) discussed results of these measurements for the 25-month period beginning August 1998 with a focus on the seasonal patterns of particles in the 3-100 nm size range. Woo et al. (2001) describe the size distribution measurements over the entire size range from 3 nm to 2 μm during the 24-month period beginning in August 1998. Results showed that ultrafine particle number concentrations can increase with decreasing particle size down to their lower limit of 3 nm during nucleation events and that the nucleation mode observations were consistent with theory (McMurry et al. 2000). The extended time period examined in McMurry and Woo (2001) allowed for a further evaluation of the seasonal patterns of ultrafine particles. This analysis indicated that ultrafine particles tended to have two modes (3 - 10 nm and 10 - 100 nm) with different temporal dependencies. The 3 - 10 nm size particles tended to be due to nucleation from the gas phase during the spring and summer with the highest particle concentrations occurring during mid-day. During cold weather, maximum concentrations tended to occur during rush hour, suggesting an association with motor vehicle sources. McMurry and Woo also observed an increase in concentrations of particles in the size range from 10 - 100 nm during rush hour that were higher on weekdays than weekends and during the summer and winter. Particle distributions tended to be log normal except when affected by processes other than direct primary particle emissions. Woo et al. (2001) also noted that ultrafine (< 10 nm) particles were elevated during rush hour, while larger diameter particles (10 - 100 nm and 100 - 2000 nm) had higher concentrations during the night than during the daytime reaching their highest concentration values during rush hour as well. Woo et al. (2001) also identified three types of ultrafine events for particles in the 3 - 10 nm range, 10 - 35 nm range, and 35 - 45 nm size range and these were described in the paper.

The hourly average data from the semi-continuous monitors allowed for the detailed analysis of the temporal distribution within given days, rather than 24-hr average analyses examining temporal distributions over months and years. The most striking feature of the hourly average data was the wide variations observed on an hourly or several hour basis (see for example, Figures 4 and 7 in this paper, and various figures in Weber et al. 2001, 2002, 2003). Figure 9 in this paper shows the deviation of the hourly average data for fine particle dry mass versus the 24-hr average dry mass. Considerable variation was observed with 15-20 μg m^{-3} or greater deviations from the 24-hr average values occurring frequently throughout the study period. Separate time series plots are shown in Figure 4 for each of the major components over a three-day period from August 20 to August 23. These data clearly showed sulfate peaking in the afternoon due to photochemical processing, whereas nitrate peaks occurred in the early morning, just before sunrise when temperatures were coolest and RH was highest. Weber et al (2002) provided a time series for the entire study for mass, sulfate, organic carbon, and elemental carbon and compared the short-term data to the 24-hr data. As with the mass, there was considerable variation in all species on an hourly or several hour basis.

Weber et al. (2002) also evaluated the sum of the species vs versus the measured hourly mass using mass data obtained by the 50 C TEOM. These results showed that the sum of the results from the individual component methods used to obtain the major components agreed well with the semi-continuous mass estimates, although once again, on an hourly basis there was considerable variation (± 15-20 μg m^{-3}) between the sum of the species and the measured mass on average.

Lim and Turpin (2002) presented data from the Rutgers University/OGI in-situ thermal-optical carbon analyzer. Mean 1-hr average concentrations (ranges in parentheses) of PM2.5 OC, EC, and total carbon in the summertime urban polluted area of Atlanta during the Atlanta study were 8.3 (3.6 - 15.8), 2.3 (0.3 - 9.6), and 10.6 (4.6 - 24.6) μg C m^{-3}, respectively. Carbonaceous matter (organic material 40%; EC 8%) comprised about 48% of PM2.5 mass in Atlanta. Results suggested that motor vehicles were the predominant source of elemental carbon and of primary organic carbon at the downtown Atlanta site. However, substantial evidence existed suggesting that secondary formation was responsible for approximately 46% of the organic aerosol on average (range between 24 and 88 %) during this summertime experiment, and that this material was both 1) formed through afternoon photochemical processes locally and 2) transported to the site from aloft with ozone during the night.

The high temporal data for the major components of PM provided insight into the nature and sources of transient PM2.5 events impacting the site and whether those sources were local (say within several miles or less) versus ones from outside the Atlanta metropolitan area. Results presented by Weber et al. (2002) focused on several peak PM events observed during the study. The hourly data indicted two types of events, morning peaks dominated by carbonaceous material and afternoon events dominated by sulfate. As mentioned above (Meteorological Characteristics), low wind speeds at night and during the early morning tended to drive the accumulation of local emissions, while higher wind speeds during the day were often associated with higher sulfate periods, possibly linking sulfate to more distance sources. In the cases studied, these two constituents account for approximately 75% of aerosol mass during peak carbon or sulfate events. Although only a minor component of the PM2.5 mass, nitrate was observed by several methods to be generally highest in the morning when daily relative humidity was highest and temperatures were at there lowest during the diurnal cycle (Weber et al., 2001; Jimenez et al., 2003; Lee et al., 2002).

Zhang et al. (2003) used the 1999 Atlanta Supersites Project's data to test the validity of the assumption of thermodynamic equilibrium between PM2.5 nitrate and ammonium and gas-phase nitric acid (HNO_3) and ammonia (NH_3). Equilibrium was tested by first calculating the equilibrium concentrations of HNO_3 and NH_3 implied by the PM2.5 inorganic composition (i.e., Na^+, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-}), temperature, and relative humidity observed at the site, and then compared these calculated equilibrium concentrations with the corresponding observed gas-phase concentrations. The observed PM2.5 composition and gas phase species are based on 5-minute averaged data (particle phase inorganic ions – Weber et al. 2001; HNO_3 and NH_3 – Edgerton et al. 2000b, and Slanina et al. 2001). The equilibrium gas-phase concentrations are calculated using the ISSORROPIA model of Nenes et al. (1998). Results indicated that relatively small downward adjustments in the measured PM2.5 SO_4^{2-} (or apparent acidity) brought the calculated and measured

NH_3 and HNO_3 into agreement. Moreover there was a close correspondence between the SO_4^{2-} correction needed for HNO_3 and that needed for NH_3 with average relative corrections in SO_4^{2-} (i.e., 14.1% for HNO_3 and 13.7% for NH_3, respectively) approximately the same as the estimated uncertainty in the SO_4^{2-} measurement. These results suggested that thermodynamic equilibrium did apply to the inorganic PM2.5 composition during the Atlanta Supersites Project and either: 1. The PM2.5 SO_4^{2-} concentration measured by the PILS had a systematic overestimate of ~15%, 2. The ISORROPIA model systematically underestimated the pH of the PM2.5 encountered during the experiment, and/or 3. The PM2.5 encountered during the Atlanta Supersites Project had an unknown alkaline component that was not identified by the PILS.

4. Summary and Conclusions

For the first time ever, multiple semi-continuous chemical speciation monitors were collocated in a manner that allowed for immediate intercomparison of the data among the various methods. Also for the first time, particle mass spectrometers were collocated, in this case four instruments were deployed. As well, a series of nearly a dozen filter and denuder based discrete samplers were compared and collocated with the semi-continuous and particle mass spectrometers. These data were supplemented with a full suite of additional chemical and physical particle property measurements and meteorological measurements, including unique measurements of particle size distributions from 3 nm to 2 μm, particle density, size resolved chemical composition and mass data using MOUDI samplers, and upper air data from Radar Profilers with Radio Acoustic Sounding System (RASS) and an ozone and aerosol LIDAR. This unprecedented intercomparison study has already resulted in over 30 publications either published, submitted, or in preparation.

Overall, the semi-continuous and single particle mass spectrometry methods agreed well amongst themselves. The semi-continuous methods appeared to have better precision amongst themselves than the discrete samplers amongst themselves, although differences among collection and analytical techniques as well as larger sampling artifacts were the likely cause for the poorer precision amongst the discrete samplers. Results from the semi-continuous data showed the great advantage of these instruments over the discrete samplers, with large variations in species concentrations observed within several hours. Observations made possible from the high resolution measurements included periods of high acidity, not observed in the 24-hr data, periods when the aerosol was dominated by carbonaceous material and most likely very local sources, and periods when the aerosol was dominated by sulfate resulting from photochemical production from sources outside of Atlanta. Implications suggest the need to continue to "promote" the collection of the high time resolution data to augment the regulatory networks to aid in source and control strategy development.

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6. Disclaimer

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Table 1. List of measurements.

Sch[1]		Investigator[2]	Organization	#	Instrument & Measured Parameters	Reference
Integrated Particle Samplers with alternate 24-hr and 12-hr Collection beginning @ 0700 EDT						
A		Baumann	Georgia Institute of Technology	1	PCM: Multi-channel denuder filter pack system for PM2.5 mass, ions,, OC, EC, gaseous ammonia, nitric and light organic acids, and sulfur dioxide	Baumann et al., 2003.
A		Gundel	Lawrence Berkeley Laboratory	2	IOGAPS: integrated gas and particle sampler for organic speciation	Gundel and Lane 1999; Gundel and Hering 1998; Lane 1999.
				1	Low volume IOGAPS: OC, EC, selected PAH analysis	
				1	High flow filter-PUFF for organic speciation method development	
A		Tanner	Tennessee Valley Authority		PC-BOSS sampler for PM2.5 mass, ions, trace elements, OC, and EC	Tanner and Parkhurst 2000.
A		Eatough	Brigham Young University		PC-BOSS sampler for PM2.5 mass, ions, trace elements, OC, and EC	Modey et al. 2001; 2002.
A		Solomon	Environmental Protection Agency, ORD	5	4 types of Speciation Samplers: Andersen, Met One, URG, and VAPS for PM2.5 mass, ions, trace elements, OC, and EC	Solomon et al. 2003.
				3	FRM PM2.5 samplers with Teflon filters for mass and trace elements	
				1	FRM PM2.5 sampler with quartz filter for OC, and EC	
				1	Auto Dichotomous sampler with electron microscopy and XRF analysis of fine and coarse PM	
Integrated Particle Samplers with daily 12-hr Collection beginning @ 0700 EDT						
B		Savioe	University of Miami	1	MOUDI for ions and trace elements Cutpoint of MOUDI stages – 0: >6.2 μm 1: 3.16-6.2 2: 1.78-3.16 3: 0.97-1.78 4: 0.56-0.97 5: 0.37-0.56 6: 0.18-0.37 7: 0.098-0.18 8: 0.056-0.098 Back-up: < 0.056	Solomon et al. 2003.
				1	MOUDI for OC, and EC.	
B		Edgerton	Atmospheric Research and Analysis, Inc.	1	PCM particle composition monitor for PM2.5 mass, trace elements, water-soluble metals, ions, OC, and EC	Van Loy et al. 2000.

Sch[1]		Investigator[2]	Organization	#	Instrument & Measured Parameters	Reference
On-Line Particle Mass Spectrometry						
C		Middlebrook	NOAA Aeronomy Laboratory	1	PALMS: Particle Analysis by Laser Mass Spectrometry	Lee et al. 2002.
C		Prather	University of California Riverside	1	ATOFMS: aerosol time of flight mass spectrometer	Gard et al. 1997.
C		Jimenez / Jayne / Worsnop	Aerodyne Research Inc.	1	AMS: aerosol mass spectrometer	Jimenez et al. 2003.
C		Wexler	University of Delaware	1	RSMS2: second generation rapid single particle mass spectrometer	Rhoads et al. 2003.
Continuous and Semi-Continuous Particle Chemistry						
C		Dasgupta	Texas Tech University	1	Automated IC with continuous parallel plate denuder collection and analysis system for acid gases	*Collection system similar to:* Samanta et al. 2001.
				1	Automated IC with non-water collection system for sulfate, nitrate, nitrite, chloride, and oxalate	*Analytical system similar to:* Simon and Dasgupta 1995.
C		Edgerton	Atmospheric Research and Analysis, Inc.	1	Automated catalytic reduction system for ammonium, nitrate, and sulfate. Commercial (R&P) for OC, and EC	Weber et al. 2003. Lim et al. 2003.
C		Hering	Aerosol Dynamics, Inc.	1	ICVC: Integrated collection and vaporization cell for automated nitrate, sulfate and particulate carbon	Stolzenburg and Hering 2000.
C		Slanina	Netherlands Energy Research Foundation	1	1. SJAC: Steam jet aerosol collector for chloride, nitrate, sulfate and ammonium ion and automated IC for on-line analysis. 2. Rotating wet denuder for collection of HCl, HONO, HNO_3, SO_2 and NH_3 and automated IC for on-line analysis.	Slanina et al. 2001.
C		Ondov	University of Maryland	1	Automated Steam Collection followed by GFAA for continuous metals	Kidwell and Ondov 2001.
C		Turpin	Rutgers University	1	In-situ carbon analyzer for organic and elemental carbon	Turpin et al. 1990.
C		Weber/Lee	GIT/Brookhaven National Lab	1	CPCIC: CNC-based collection for aerosol ion chromatography	Weber et al. 2001.

Sch[1]		Investigator[2]	Organization	#	Instrument & Measured Parameters	Reference
Continuous and Semi-Continuous Particle Mass						
C		Koutrakis	Harvard School of Public Health	1	CAMMS: pressure drop mass measurement	Babich et al. 2000.
C		Russell	Georgia Institute of Technology	1	TEOM[3]: tapered element-oscillating microbalance for particle mass, with RH control.	Butler et al. 2003.
C		Eatough	Brigham Young University	1	RAMS for continuous particle mass	Eatough et al. 2001.
Continuous and Semi-Continuous Particle Physical Characterization						
C		McMurry	University of Minnesota	1	TDMA measurements of water uptake DMA-APM measurements of particle density	McMurry et al. 2001.
				1	DMPS [3]: Particle size distributions 3 nm-3 μm	Woo et al. 2001.
C		Maring	University Miami	1	TSI nephelometer for particle light scattering at three wavelengths	Maring et al. 2000. Anderson et al. 1996.
Continuous and Semi-Continuous Supporting Measurements						
C		Edgerton	Atmospheric Research and Analysis, Inc.	1	Met[3]: meteorology station at 10 m for wind speed, wind direction, temperature, barometric pressure, solar radiation and relative humidity.	Edgerton (personal communication, ARA, Inc., Cary, NC).
				1	Criteria and reactive gases[3] (O_3, NO_X, NO, NO_2, SO_2, CO, NO_Y, HNO_3, NH_3)	
C		Baumann	Georgia Institute of Technology	1	Met and criteria gases (p, T, RH, WS, WD, global and UV radiation, NO, NO_Y, O_3, CO, SO_2.).	Baumann (personal communication, GIT, Atlanta, GA).
C		Bergin	Georgia Institute of Technology	1	Aerosol optical depth, spectral radiometer, sun photometers, RH-controlled TEOM.	Carrico et al. 2003.
C		Hardesty	NOAA	1	LIDAR: boundary layer O_3 and aerosol backscatter	
C		Dasgupta	Texas Tech University	1	Semi-continuous HCHO and H_2O_2 (gas)	Li et al. 2001; Li et al. 2000;
C		McNider	University of Alabama, Huntsville	1	Radar wind profiler and Radio Acoustic Sounding System (RASS) for winds and virtual temperature aloft	*Wind Profiler:* Carter et al. 1995 *RASS:* Angevine and Ecklund 1994
C		Zika	University of Miami	1	On-line GC for volatile organics and oxygenates	Stabenau et al., 2001.

Sch[1]		Investigator[2]	Organization	#	Instrument & Measured Parameters	Reference
Multiday Sample Collectors						
M		Savoie	University of Miami	1	MOUDI for organic speciation	Tremblay et al. 2000
				1	MOUDI for mass, heavy molecular weight organic compounds	Stabenau et al. 2001
M		Ondov	Univ. of Maryland	1	Mega volume for trace metals	Heller-Zeisler et al. 1999.
M		Koutrakis	Harvard School of Public Health	1	High volume sampler for sample archiving	Kavouras et al. 2000.
Particle and Vapor Collection through SEARCH/ARIES (24-hr beginning at 0100 EDT)						
S		Rasmussen	Oregon Graduate Institute	1	Canisters for VOC analysis via TO-14, TO-15, and for oxygenates	EPA 1999a. Rasmussen (personal communication, OGI, Beaverton, OR);
S		Burge	Harvard School of Public Health	1	Burkard Sampler for Pollen and Molds [3]	Macher and Burge 2001.
S		Edgerton	Atmospheric Research and Analysis, Inc.	1	PM2.5 FRM mass [3]	Van Loy et al. 2000.
				1	PM10 FRM mass (dichotomous sampler) [3]	
				1	PCM particle composition monitor for PM2.5 mass, trace elements, water soluble metals, ions, OC, and EC[3]	
S		Koutrakis	Harvard School of Public Health	1	HEADS for gaseous ammonia, particle acidity and sulfate [3]	Koutrakis et al. 1988.
S		Zielinska	Desert Research Institute	1	Particle Organics Collector [3]	Watson et al. 1998.
Supporting Laboratory Analyses						
		Jahren	Georgia Institute of Technology		Isotope analysis of PM2.5 (C13 and N15)	Jahren (personal communication, GIT, Atlanta, GA).
		Bayer	Georgia Institute of Technology		Trace metal analysis of MOUDI samples. Metals: ICP-MS following acid digestion	Bayer (personal communication, GIT, Atlanta, GA).

1. Sch: Schedule code,
   A – Alternate day schedule, 24-hr samples beginning at 0700 EST on Aug. 3 (odd sampling days) and 12-hr sampling beginning at 0700 EST on Aug. 4. (Even sampling days).
   B – Base schedule, 12-hr samples beginning at 0700 EST and 1900 EST every day from Aug. 3.
   C – Continuous or semi-continuous beginning at 0700 EST Aug. 3.
   S – SEARCH schedule for existing SEARCH sampling program, 24-hr samples beginning at midnight EST.
   M – Multi-day sampling:
2. See Hering 1999 for a full list of investigators organizations and addresses.
3. SEARCH/ARIES instrumentation operating under different protocol and Quality Assurance.

Table 2. Relative reference value for 24-hr integrated samplers.

Date	Mass	SO4	NO3	NH4	OC	EC	S	Si	K	Ca	Mn	Fe	Cu	Zn	Pb	As
	µg m^{-3}						ng m^{-3}									
8/3/99	34.3	10.64	0.41	3.73	8.30	1.41	4230	219	65.7	62.4	3.54	152	3.40	23.5	19.0	1.6
8/5/99	47.2	18.54	0.48	6.10	8.68	1.08	7120	359	65.7	103.2	3.76	198	1.68	11.4	3.4	1.6
8/7/99	40.3	13.70	0.52	4.42	10.11	0.92	5430	224	64.1	111.6	3.02	201	3.02	12.8	6.6	1.3
8/9/99	28.3	9.91	0.51	3.27	6.34	0.98	3900	189	52.9	82.4	1.98	114	2.27	11.5	3.2	1.5
8/11/99	37.2	11.05	0.57	3.93	9.41	1.21	4910	274	88.0	70.4	3.51	161	15.26	24.2	4.6	1.9
8/13/99	27.4	6.89	0.52	2.27	8.68	1.42	3070	395	110.6	234.3	3.40	192	5.09	14.2	4.4	1.9
8/15/99	24.5	6.54	0.41	2.52	8.00	0.71	2910	150	77.6	53.0	1.87	92	1.26	13.9	5.7	1.2
8/17/99	34.0	10.85	0.52	3.67	10.25	1.37	4520	259	77.8	88.5	3.31	165	2.74	13.8	3.6	1.7
8/19/99	32.9	9.56	0.46	3.42	10.01	0.97	4280	320	78.1	101.6	3.36	173	7.30	20.7	5.2	1.1
8/21/99	30.1	12.56	0.56	4.27	6.94	0.90	4780	134	57.6	76.0	2.56	125	2.69	15.5	3.3	1.3
8/23/99	27.9	10.12	0.56	3.16	6.43	0.87	4040	148	56.6	48.5	3.20	103	7.62	11.1	5.4	1.0
8/25/99	16.2	5.27	0.51	1.74	3.81	0.77	2010	69	33.9	18.7	1.00	45	1.61	6.6	2.1	1.3
8/27/99	36.6	14.73	0.70	4.96	6.99	1.33	5510	180	61.0	111.0	3.46	177	3.54	19.9	4.1	1.9
8/29/99	36.6	15.29	0.36	5.27	6.46	0.76	5790	147	40.1	35.4	1.85	145	1.58	10.3	5.5	2.4
8/31/99	16.0	2.72	0.49	1.07	6.77	0.92	1110	129	52.6	51.6	4.09	137	6.20	46.2	10.2	1.1
Avg	31.3	10.56	0.51	3.59	7.81	1.04	4241	213	65.5	83.2	2.93	145.22	4.35	17.05	5.75	1.52
StdDev	8.4	4.12	0.08	1.34	1.79	0.25	1526	93	19.1	50.3	0.87	43.64	3.66	9.50	4.13	0.39
Max	47.2	18.54	0.70	6.10	10.25	1.42	7120	395	110.6	234.3	4.09	201.07	15.26	46.17	19.00	2.42
Min	16.0	2.72	0.36	1.07	3.81	0.71	1110	69	33.9	18.7	1.00	44.76	1.26	6.64	2.11	1.00

Figure Captions

Figure 1. Location of the Atlanta Supersites Project on Jefferson St. in NW Atlanta, GA. The red star represents the location of the site.

Figure 2. Aerial views of the Atlanta Supersites Project site: I. Looking south towards downtown Atlanta, note bus maintenance yard (c) to the west, the warehouse (a) to the east, and the Georgia Power facilities (b); Jefferson St. is between the Georgia Power facilities and the bus maintenance yard. II. Looking southwest at the site showing light industry to the south and north of the site. III. Close-up of the site looking north showing close-up of the storage warehouse (a) to the North and Ashby St. to the west. Location of trailers and sampling platforms are depicted in III and labeled in the margin.

Figure 3. A. Schematic showing the layout of the trailers that housed the majority of the semi-continuous speciation samplers and the particle mass spectrometers. Note, the location of FRM on the roof of the trailer for evaluating vertical representativeness on a 24-hr average. Investigators locations are described in the margin. B. Description of sampler locations on the sampling platforms. Note location A and R are FRM samplers sited with the one on the roof of the trailers to evaluate spatial representativeness across the site on a 24-hr average.

Figure 4. Temporal distributions of hourly average data for PM2.5 mass and the major components of mass (sulfate, ammonium, nitrate, organic carbon, elemental carbon, and PM2.5 mass) based on data collected using semi-continuous monitors for the three day period August 20-23, 2001. Also plotted (heavy weight line) is the "best estimate" or relative reference value for each variable shown. See Appendix A for description of the best estimate calculation method.

Figure 5. Temporal distribution of major gas phase pollutants (O_3, SO_2, CO, and NOy) and PM2.5 mass,-sulfate, and carbonaceous material (OC*1.4 + EC) during the study period. PM2.5 mass,

sulfate, and carbonaceous material are 24-hr averages (7 AM to 7 AM local time) of the 1-hr data; ozone, SO_2, CO, and NOy are peak 1-hr values observed between 7 AM and 7 PM local time. PM2.5 mass is from the TEOM operated by Bergin, sulfate is an average of data from Weber, Slanina, and Hering, and carbonaceous material is an average of data from Turpin and Edgerton. Gases are either from Edgerton or Baumann or their average values. Note, the 1-hr standard for ozone of 120 ppb was exceeded on 7 occasions during the first half of the study, but the 24-hr average PM2.5 standard of 65 μg m^{-3} was not exceeded, however, PM2.5 concentrations remained well above the annual average PM2.5 standard of 15 μg m^{-3}. Note also the decrease in concentrations of all species on August 24, during passage of a cold front and precipitation.

Figure 6. Hourly averaged wind speeds from the period August 3 – 24, 1999, at the Jefferson Street site. Morning minima wind speeds, often less than 1 m s^{-1}, were correlated with the accumulation of EC and OC.

Figure 7. Temporal distribution of dry PM2.5 mass, PM2.5 sulfate, and SO_2. Top plot shows relationship of PM2.5 mass to sulfate relative to the 24-hr average values of each. Note, large deviations of the 1-hr data from the 24-hr average values and the good correlation between sulfate and PM2.5 mass. Lower plot shows the relationship between sulfate and SO_2. Note the two are correlated at times, perhaps from the same distance source or sources and not at other times, suggesting different sources. Weber (mass and sulfate) and Edgerton (SO_2) collected these data.

Figure 8. Temporal and spatial representativeness of the Atlanta Supersites Project. A. Temporal representativeness of the Atlanta Supersites Project during the two-year period from August 1998 - August 2000. Note, August was the highest month for ozone and PM during the 2-yr period. Figure courtesy of SEARCH. B. Spatial representativeness of PM2.5 mass and components observed at the Jefferson St. site compared with other sites within the Atlanta metropolitan area. Figures courtesy of ASACA. C. Spatial representativeness of the Jefferson St. site compared with other sites within the Southeast United States. Figures courtesy of the SEARCH project.

Figure 9. Daily 24-hour average of the dry fine aerosol mass compared to the deviation from the average based on a 1-h mean measurement. The new EPA annual and 24-hour standards also are identified.

Appendix A. Calculation of "Best Estimate" Hourly Concentrations

For the Atlanta Supersites Project, "best estimate" one-hour concentration profiles were derived for $PM_{2.5}$ sulfate, nitrate, ammonium ion, organic carbon, refractory or "elemental" carbon, and mass. Each of these parameters was measured by three to five different automated, semi-continuous methods, with time resolutions from a few minutes to two hours. But not all instruments were operational throughout the study period, and systematic differences among methods were noted. Thus it was desired to develop a consistent average for each hour that was not influenced by changes in the cohort of operational instruments.

Several steps were taken to arrive at an averaging method that would yield the most consistent results across the study period. First, data completeness was examined for each hour, using hourly averages calculated for all of the semi-continuous data. Second, differences among methods were tested for statistical significance. Systematic differences were quantified by comparison to integrated data sets or to the method mean. Finally, the 'best estimate' data set was then constructed as a weighted, geometric mean based on the results of the regression analysis.

Hourly Averages and Data Completeness

Hourly concentrations were calculated for data sets from the individual semi-continuous instruments. Values were retained whenever values were reported for at least 20% of the hour. The reason for this low threshold was to allow those instruments with a low duty cycle to be included in the analysis. For the RU-OGI carbon measurements, which reported concentrations every other hour, data were interpolated to fill in the intervening periods (using the average of values from the preceding and following hour).

For individual instruments the data recovery was generally above 75%, but the number of periods with data from all instruments was small. Hours with complete data from all instruments for sulfate, nitrate and ammonium ion were 35%, 32% to 44%, respectively and for organic and elemental carbon it was 50% to 69%. The lower values for the inorganic ions reflect the fact that one of the systems did not become operational until the midpoint of the study. Statistically, the number of periods of simultaneous data is proportional to the product of individual data recoveries. Only 22% of the hourly periods had data from all 22 speciation and mass instruments. Thus the cohort of operational instruments within the data set varied considerably throughout the study period. Because of systematic differences among methods, noted below, the variable cohorts needed to be taken into account in the calculation of the "best estimate" hourly means.

Assessment of Differences among Methods

A Friedman analysis of variance by rank was used to test whether observed differences among the semi-continuous methods were statistically significant. For each constituent, data for periods with measurements by each method were chosen for analysis. Within each period the methods were ranked from highest to lowest, and the variance in ranking was examined to test whether the ranking among methods was systematic or random. This analysis tested whether one or more of the instruments differed significantly, but it did not indicate which instrument, or how many instruments, may have accounted for the difference. For sulfates, nitrates, ammonium ion, organic and elemental carbon, these tests showed statistically significant differences at or above the 99% confidence level.

The magnitude of the systematic differences among the individual semi-continuous measurements C_i was determined by comparison to the corresponding integrated measurements. This was done using a single parameter fit to a reference data set of the form $C_i = mC_{ref}$. For sulfate, ammonium ion, organic and elemental carbon, the reference data set C_{ref} was the average of the MOUDI and ARA filter measurements. The MOUDI and ARA filter data were nearly continuous throughout the study, with two 12-hour samples each day. This "12-hour Average" data set provided 58 points for comparison. For the MOUDI carbon, the after-filter data was included to be consistent with potential artifacts that may be present in the filter data with which it was being averaged. For mass, the comparison was examined using the alternate 24-hr data. For nitrate, neither the 12-hr nor 24-hr data could provide a reasonable basis of comparison. There were known experimental limitations in the 12-hr data, and the 24-hr data were so scattered that the correlation coefficients for a normal linear regression were generally below 0.2 Yet the Friedman statistics indicated that systematic differences were significant. Thus the individual semi-continuous samplers were compared against their internal average for those 12-hr periods with data from all 5 systems.

Results of these comparisons are shown in Table A1. Given are the regression slope *m*, the 95% confidence interval for that slope, and the number of data points in the fit. For the sample sizes listed, the 95% confidence interval is between 2.0 and 2.1 standard deviations of the mean.

Best estimate Calculation

The "best estimates" of the one-hour concentration values for each constituent, $C_{b.e.}$, were

$$C_{b,e} = m_{geom}\left[\prod_{i=1}^{n} \frac{c_i}{m_i}\right]^{1/n}$$

calculated according to the relationship:

where n is the number of instruments operational during the hour, C_i is the constituent concentration value from instrument i for that hour, m_i is the slope from the single parameter fit for instrument i, and m_{geom} is the geometric mean of the slopes. The multiplication by the geometric mean yielded a "best estimate" value equal to the geometric mean when all of the semi-continuous instruments were operational. When data were missing, the weighted average was equivalent to estimating the missing value(s) based on the measured values and the parameterization of systematic differences, and then including this estimate in the geometric average. Essentially, the integrated data were used to provide a point of reference to determine the appropriate weighting for averaging the automated data to account for systematic bias among the methods.

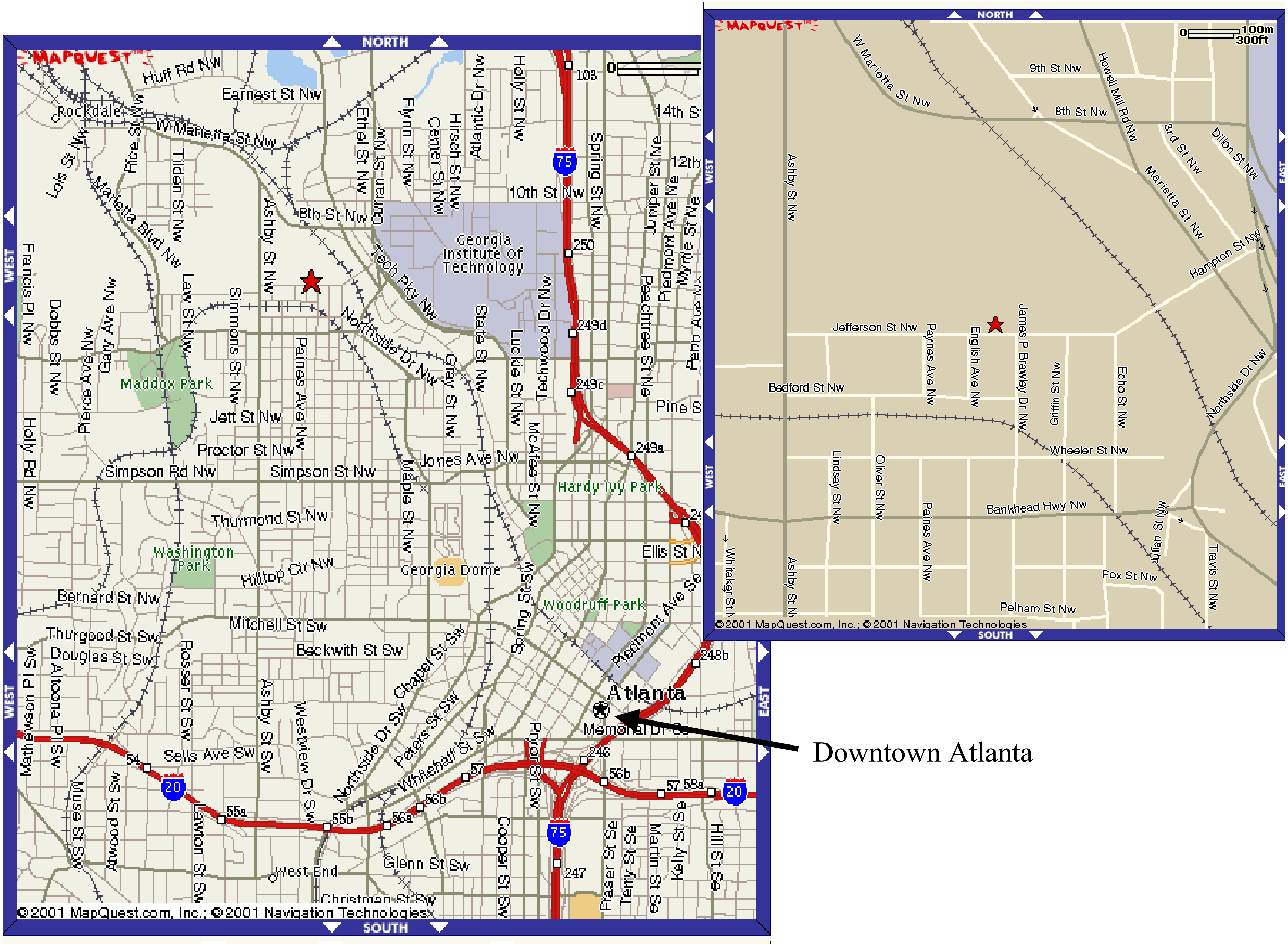
In summary, differences among semi-continuous methods were found to be significant using a Friedman analysis of variance. These systematic differences were quantified by single parameter fits to a reference data set. In most cases this reference was the average of the 12-hr filter and MOUDI data collected every day. For each chemical constituent, weighting factors for individual instruments were determined as the ratio of the geometric mean of the regression slopes from all instruments, divided by the regression slope for that instrument. This approach yielded an average that equaled the geometric mean of all values for those periods when all instruments were operational. When data were missing, the weighted average compensated for bias among methods. The resulting "best estimate" data set captured the time variability in concentration profiles seen in the individual data sets, and provides a consistent measure of hourly concentrations throughout the study period. The "best estimate" hourly concentration data is posted at http://www-wlc.eas.gatech.edu/supersite/.

Table A1. Single Parameter Fits

Constituent	Comparison Data[1,]	Method[1]	N	Slope, m_i	95% Confidence Interval
Sulfate	Daily 12-hr average of MOUDI[2] and ARA Filter Sampler	ECN	52	1.317	0.062
		GIT-BLN	25	1.386	0.059
		TT	47	1.007	0.068
		ADI	56	1.399	0.063
		Geometric Mean, m_{geom}		1.266	
Nitrate	12-hr periods with data from all semi-continuous nitrate instruments	ARA	23	1.092	0.126
		ECN	23	0.961	0.090
		GIT-BLN	23	0.857	0.097
		TT	23	1.160	0.078
		ADI	23	0.929	0.077
		Geometric Mean, m_{geom}		0.994	
Ammonium Ion	Daily 12-hr average	ARA	45	0.976	0.079
		ECN	41	1.037	0.049
		GIT-BNL	27	1.060	0.061
		Geometric Mean, m_{geom}		1.024	
Organic Carbon	Daily 12-hr average	RU-OGI	49	1.300	0.057
		ARA: R&P5400[2]	55	1.131	0.043
		ADI	41	1.078	0.070
		Geometric Mean, m_{geom}		1.166	
Elemental or Black Carbon	Daily 12-hr average	RU-OGI	49	1.252	0.094
		ARA: R&P5400	54	1.431	0.105
		HSPH: Aethalometer	43	1.417	0.082
		ARA-RR PSAP[2]	55	0.665	0.060
		Geometric Mean, m_{geom}		1.140	
Mass	Alternate day, 24-hr filter reference	ARA-GIT	15	0.980	0.034
		GIT	15	0.959	0.027
		Geometric Mean, m_{geom}		0.970	

[1] ARA = Atmospheric Research and Analysis, Inc.; ADI = Aerosol Dynamics Inc., BNL = Brookhaven National Laboratories; ECN = Netherlands Energy Research foundation; GIT = Georgia Institute of Technology, HSPH = Harvard School of Public Health, RU = Rutgers University; TT = Texas Tech University.

[2] MOUDI = micro-orifice uniform deposit impactor; R&P5400 = Rupprecht and Patashnick carbon analyzer, RR PSAP = Radiance Research particle absorption

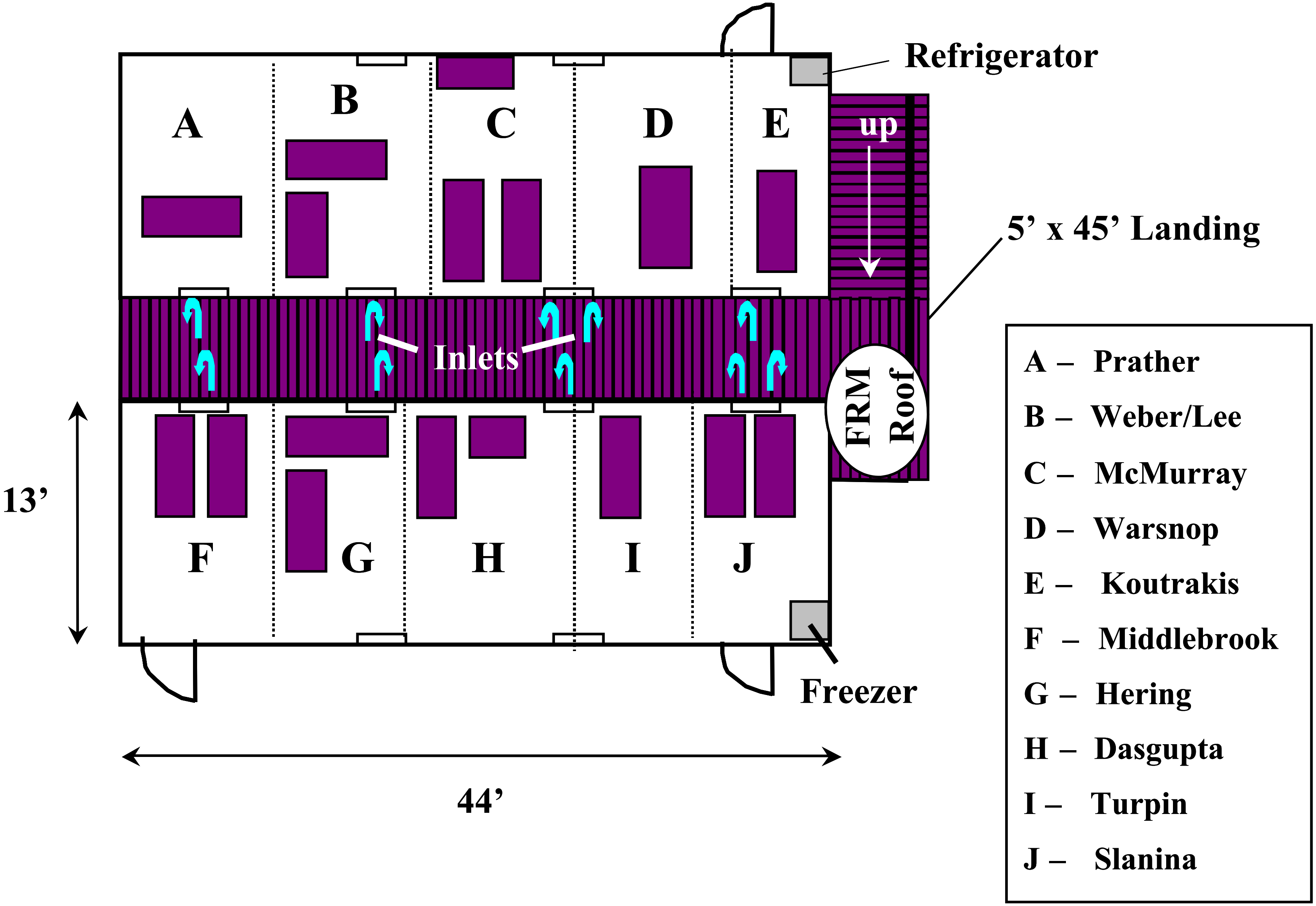


Downtown Atlanta

Figure 1

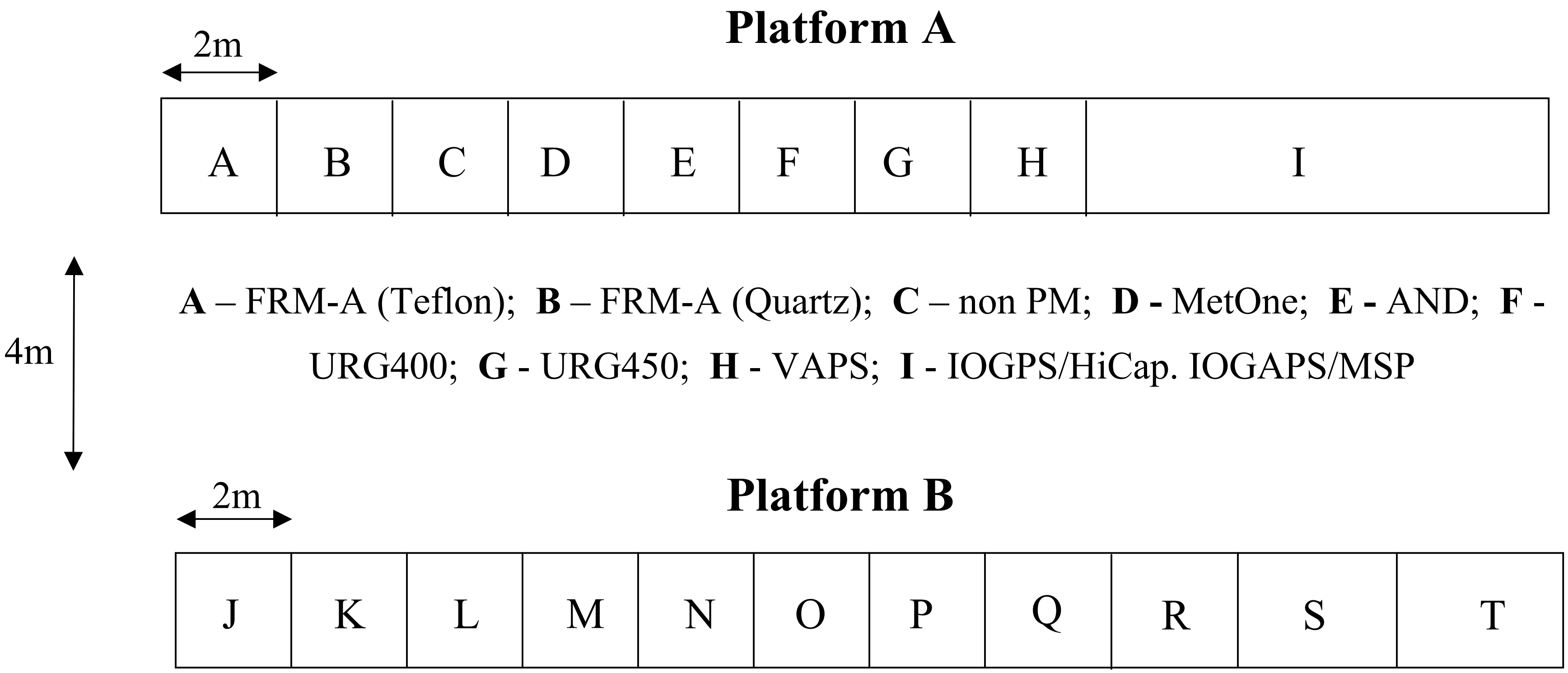
A – Radar Profiler with RASS
B – Integrated Samplers Platform
C – LIDAR
D – SEARCH/ARIES Trailer
E – Single Particle & Continuous Samplers
F – GIT
H – Univ. Miami
G – Univ. Maryland
I – Univ. Delaware

Figure 2



A – Prather
B – Weber/Lee
C – McMurray
D – Warsnop
E – Koutrakis
F – Middlebrook
G – Hering
H – Dasgupta
I – Turpin
J – Slanina

Figure 3a



A – FRM-A (Teflon); **B** – FRM-A (Quartz); **C** – non PM; **D -** MetOne; **E -** AND; **F -** URG400; **G** - URG450; **H** - VAPS; **I** - IOGPS/HiCap. IOGAPS/MSP

J - Empty; **K** – R&P Dichotomous Partisol; **L** - ARIES/SEARCH PCM(12-hr); **M -** R&P Chemical Speciation Monitor; **N** - PC-BOSS (TVA); **O** - PC-BOSS 24-hr (BYU); **P** - PC-BOSS 12-hr (BYU); **Q** - CAMM; **R** – FRM-B; **S** - HVOPS; **T** - RAMS; FRM - roof; KB-PCM operated on the roof of the GIT trailer; MOUDI – UMiami Trailer

Figure 3b

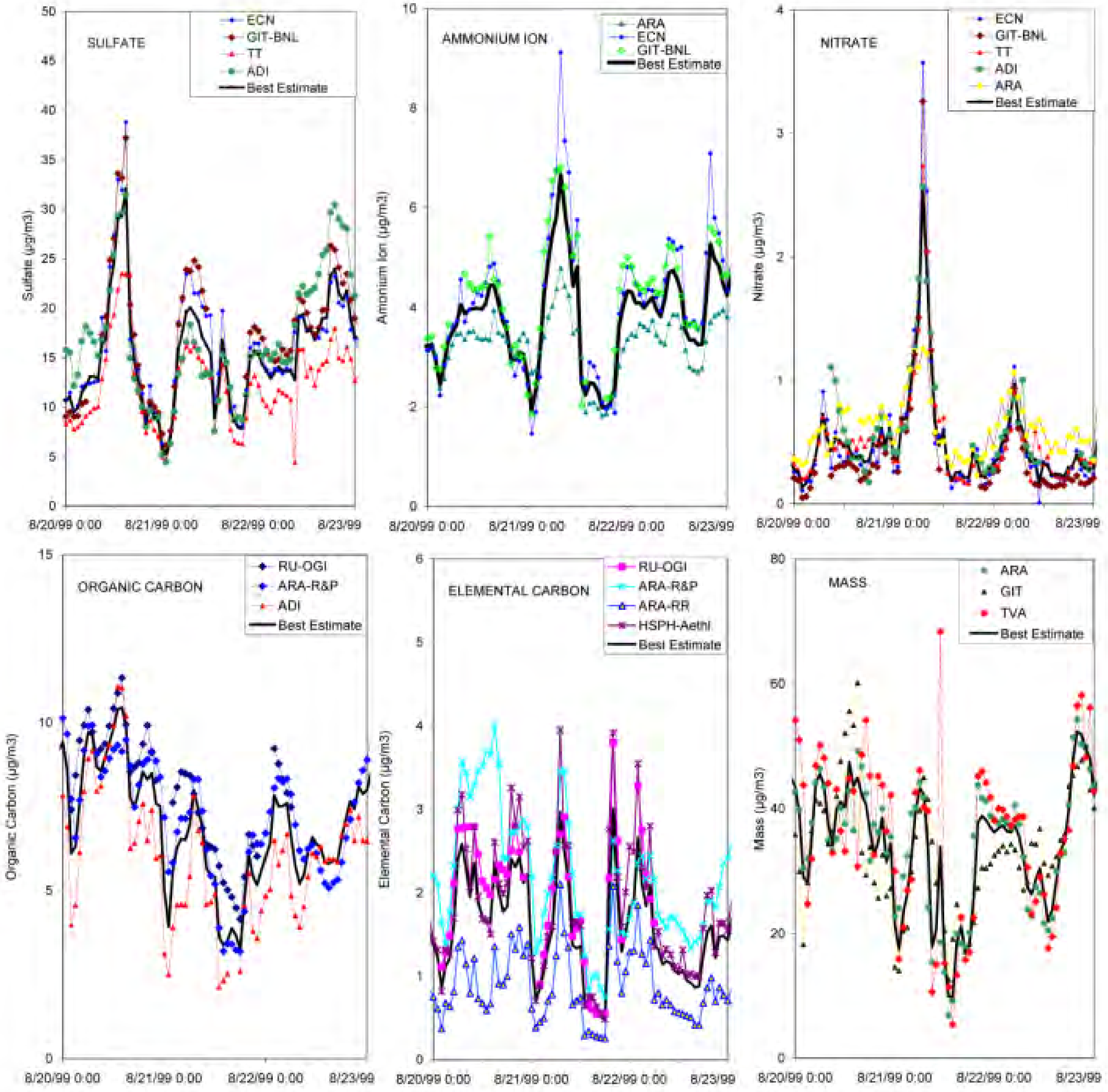

SULFATE
ECN
GIT-BNL
TT
ADI
Best Estimate
Sulfate (µg/m3)
0
5
10
15
20
25
30
35
40
45
50
8/20/99 0:00
8/21/99 0:00
8/22/99 0:00
8/23/99
AMMONIUM ION
ARA
ECN
GIT-BNL
Best Estimate
Ammonium Ion (µg/m3)
0
2
4
6
8
10
NITRATE
ECN
GIT-BNL
TT
ADI
ARA
Best Estimate
Nitrate (µg/m3)
0
1
2
3
4
ORGANIC CARBON
RU-OGI
ARA-R&P
ADI
Best Estimate
Organic Carbon (µg/m3)
0
5
10
15
ELEMENTAL CARBON
RU-OGI
ARA-R&P
ARA-RR
HSPH-Aethl
Best Estimate
Elemental Carbon (µg/m3)
0
1
2
3
4
5
6
MASS
ARA
GIT
TVA
Best Estimate
Mass (µg/m3)
0
20
40
60
80

Figure 4

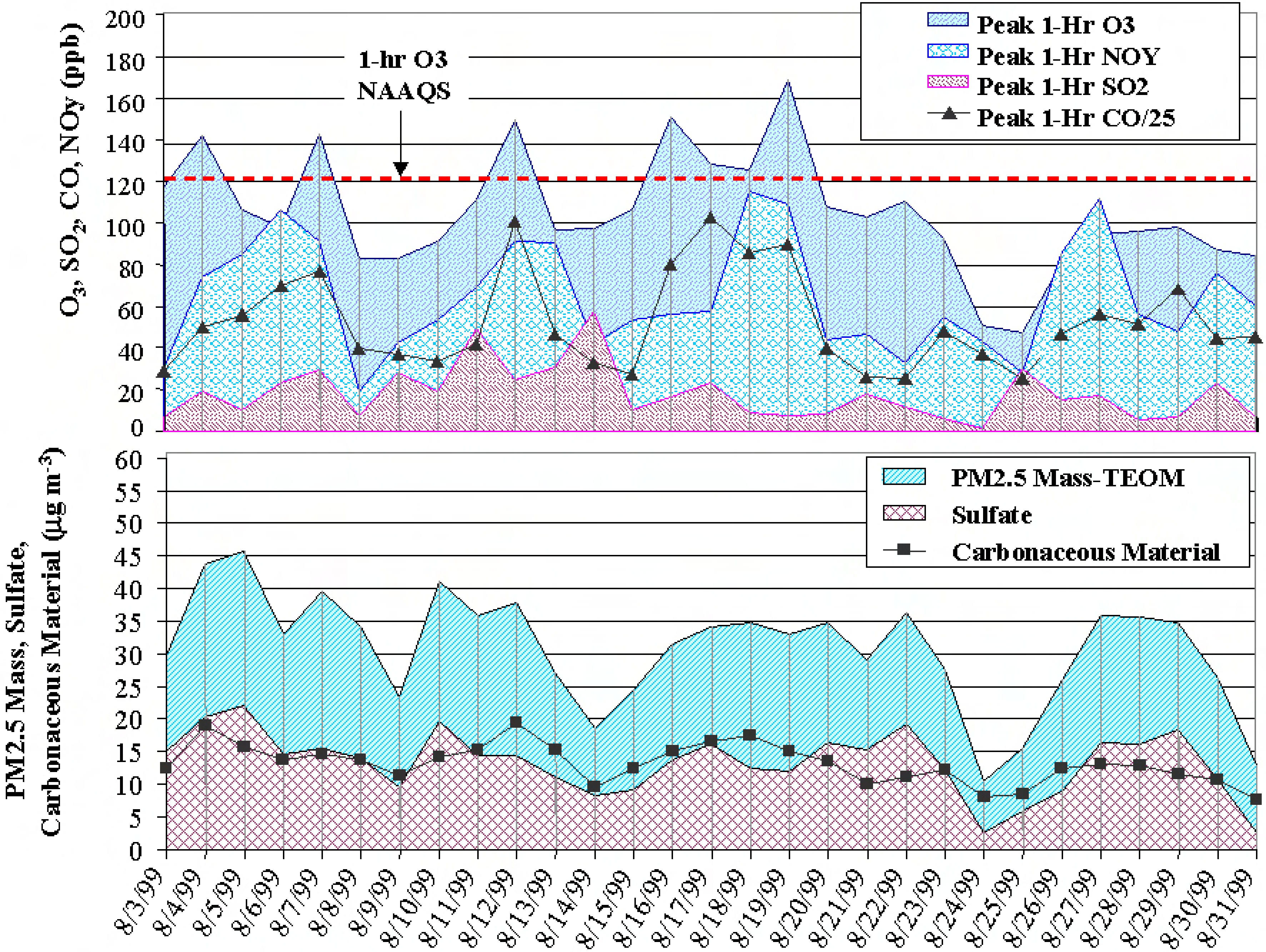

O₃, SO₂, CO, NOy (ppb)
200
180
160
140
120
100
80
60
40
20
0
1-hr O3
NAAQS
Peak 1-Hr O3
Peak 1-Hr NOY
Peak 1-Hr SO2
Peak 1-Hr CO/25
PM2.5 Mass, Sulfate, Carbonaceous Material (µg m⁻³)
60
55
50
45
40
35
30
25
20
15
10
5
0
PM2.5 Mass-TEOM
Sulfate
Carbonaceous Material
8/3/99
8/4/99
8/5/99
8/6/99
8/7/99
8/8/99
8/9/99
8/10/99
8/11/99
8/12/99
8/13/99
8/14/99
8/15/99
8/16/99
8/17/99
8/18/99
8/19/99
8/20/99
8/21/99
8/22/99
8/23/99
8/24/99
8/25/99
8/26/99
8/27/99
8/28/99
8/29/99
8/30/99
8/31/99

Figure 5

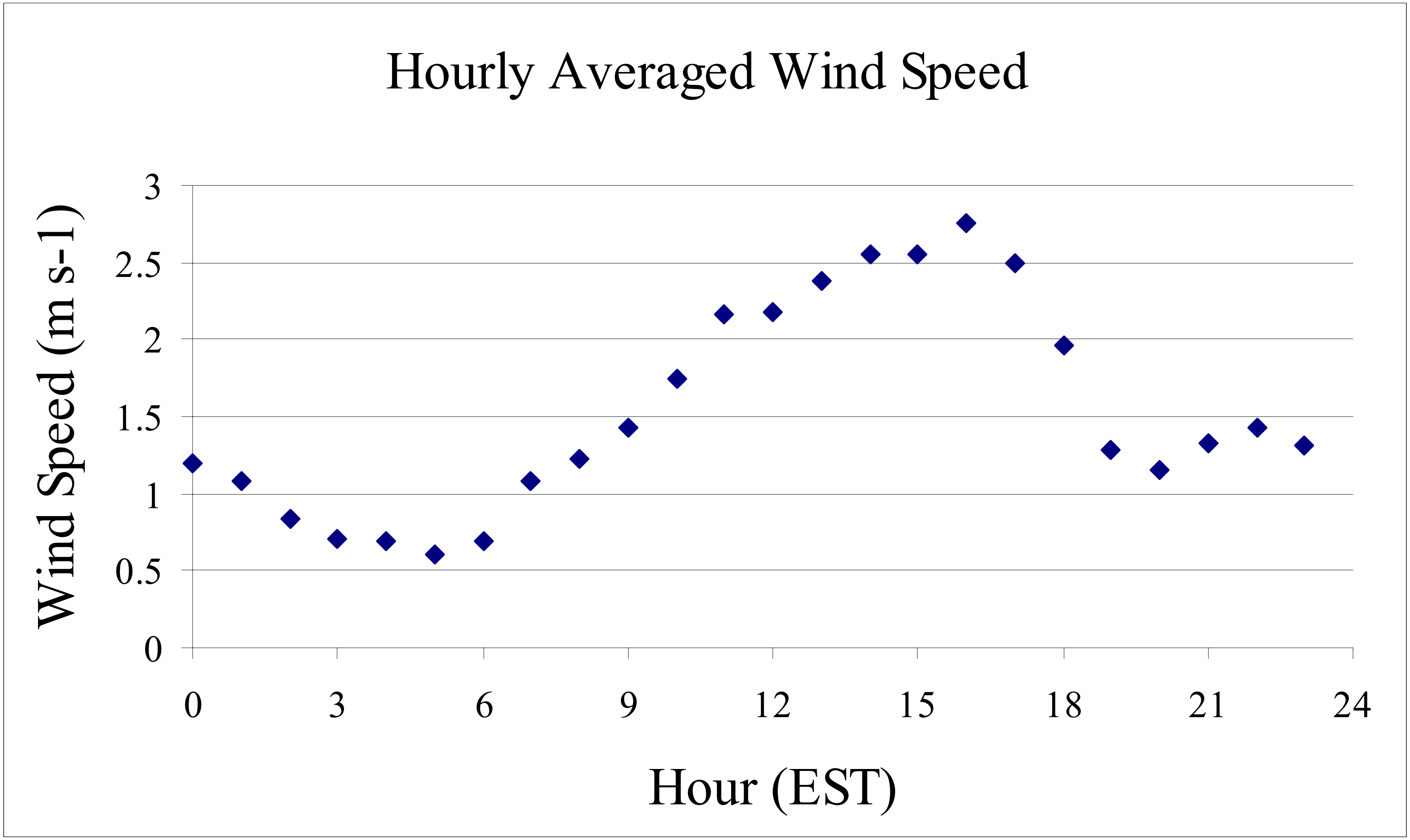

Hourly Averaged Wind Speed
Wind Speed (m s-1)
3
2.5
2
1.5
1
0.5
0
0
3
6
9
12
15
18
21
24
Hour (EST)

Figure 6

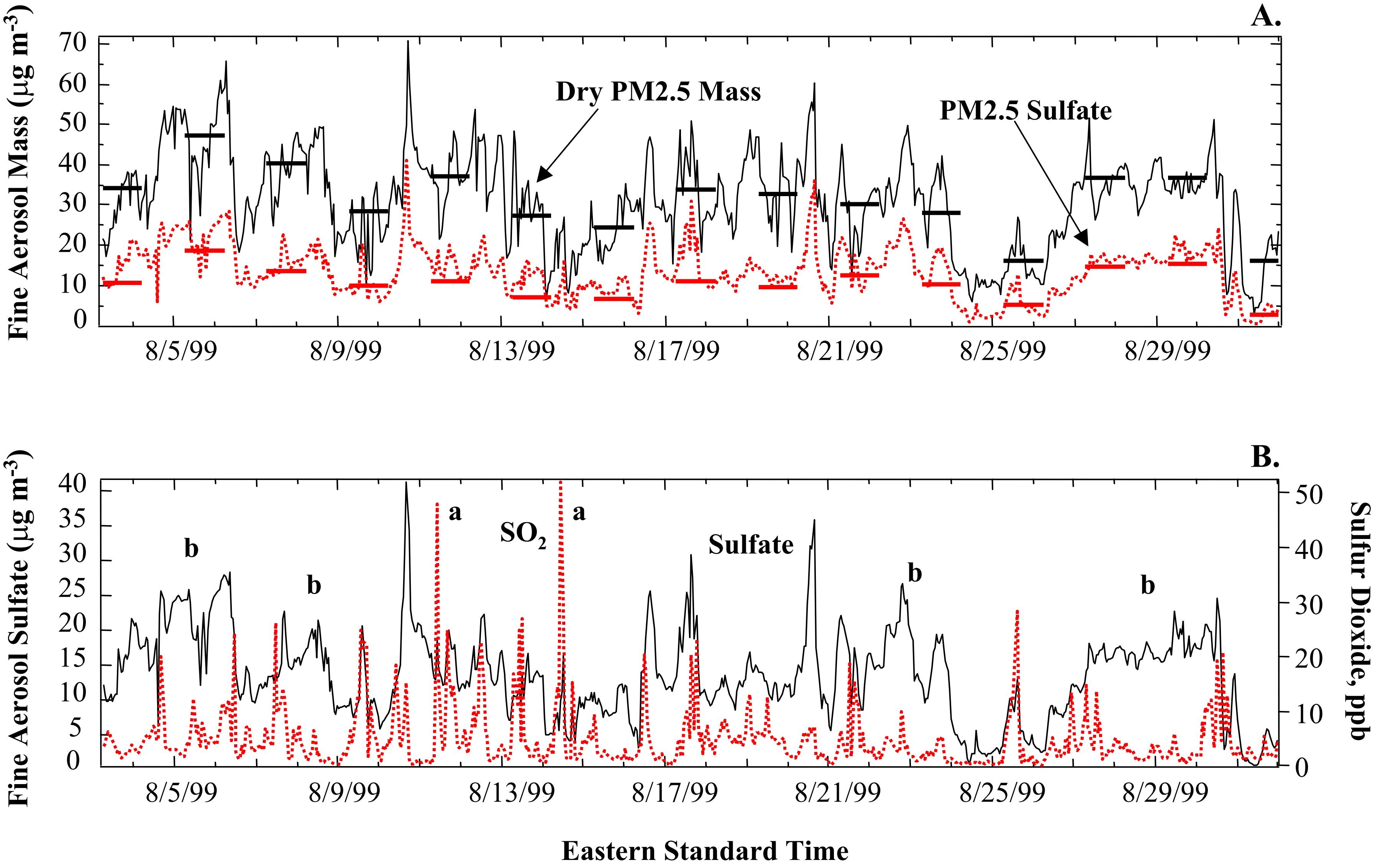
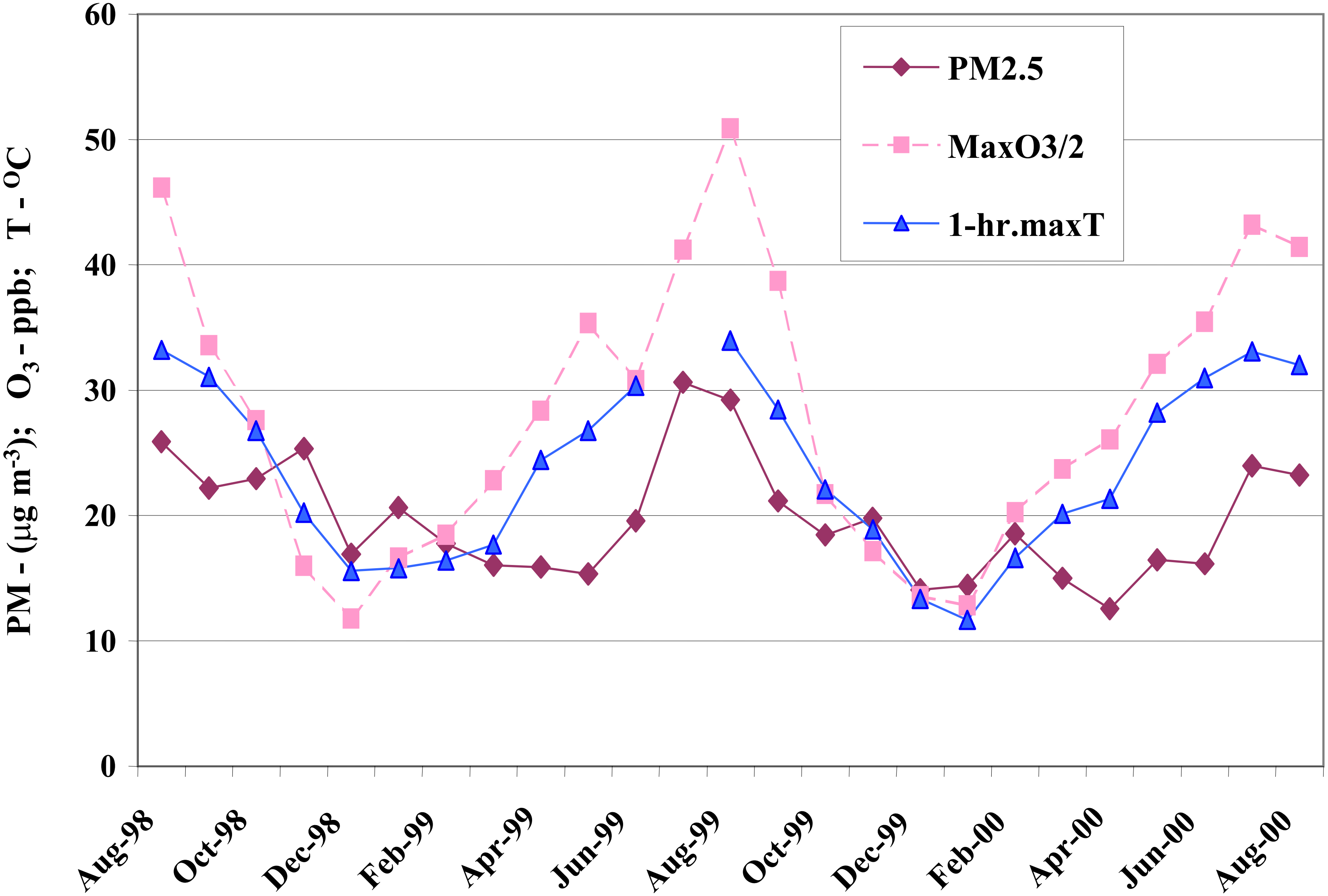

A.
Fine Aerosol Mass (μg m⁻³)
70
60
50
40
30
20
10
0
Dry PM2.5 Mass
PM2.5 Sulfate
8/5/99
8/9/99
8/13/99
8/17/99
8/21/99
8/25/99
8/29/99
B.
Fine Aerosol Sulfate (μg m⁻³)
40
35
30
25
20
15
10
5
0
b
b
a
SO₂
a
Sulfate
b
b
Sulfur Dioxide, ppb
50
40
30
20
10
0
8/5/99
8/9/99
8/13/99
8/17/99
8/21/99
8/25/99
8/29/99
Eastern Standard Time

Figure 7



PM - (µg m-3); O3 - ppb; T - oC
60
50
40
30
20
10
0
PM2.5
MaxO3/2
1-hr.maxT
Aug-98
Oct-98
Dec-98
Feb-99
Apr-99
Jun-99
Aug-99
Oct-99
Dec-99
Feb-00
Apr-00
Jun-00
Aug-00

Figure 8a

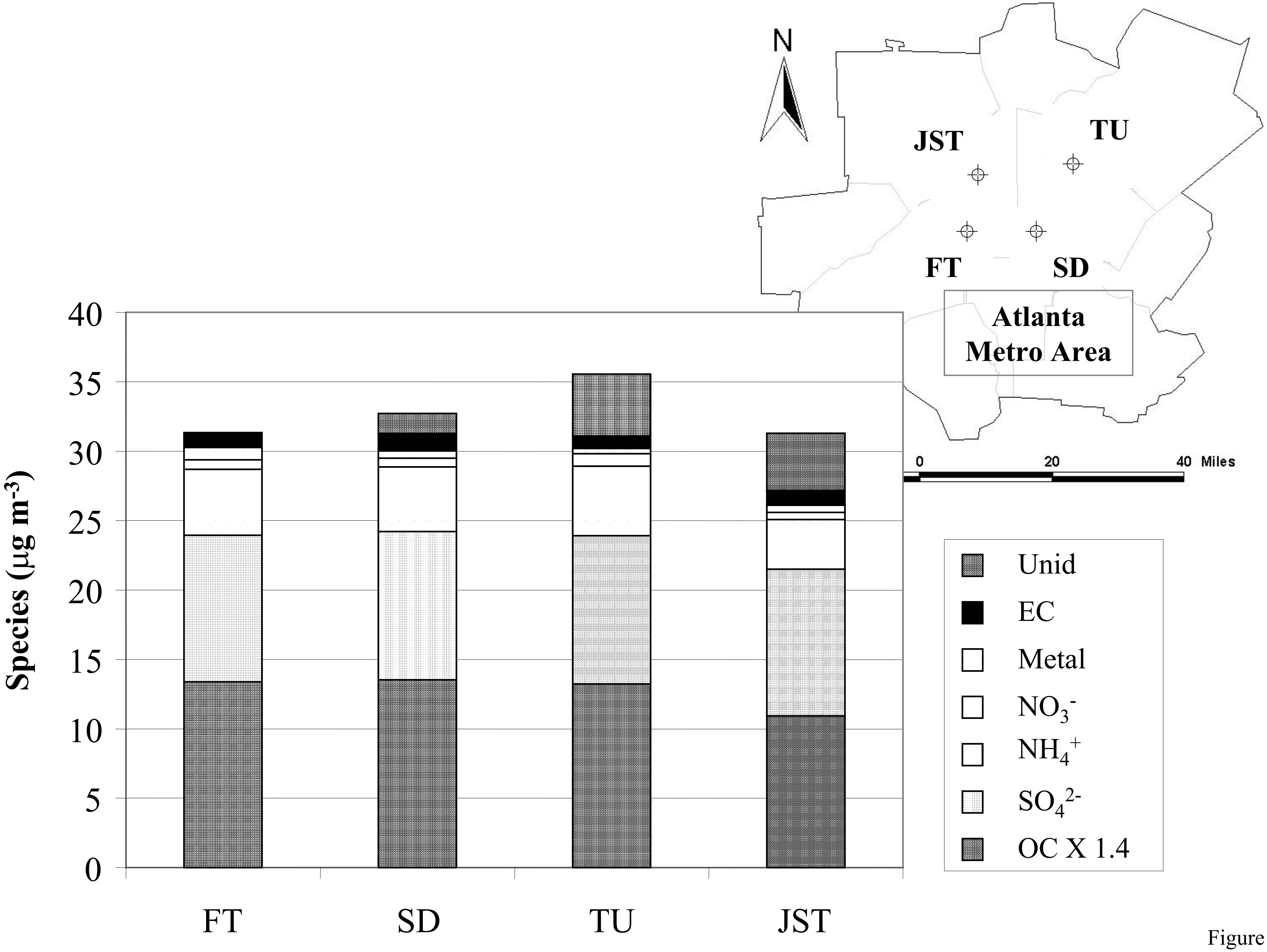

N
JST
TU
FT
SD
Atlanta Metro Area
0
20
40 Miles
Species (μg m-3)
40
35
30
25
20
15
10
5
0
FT
SD
TU
JST
Unid
EC
Metal
NO3-
NH4+
SO42-
OC X 1.4

Figure 8b

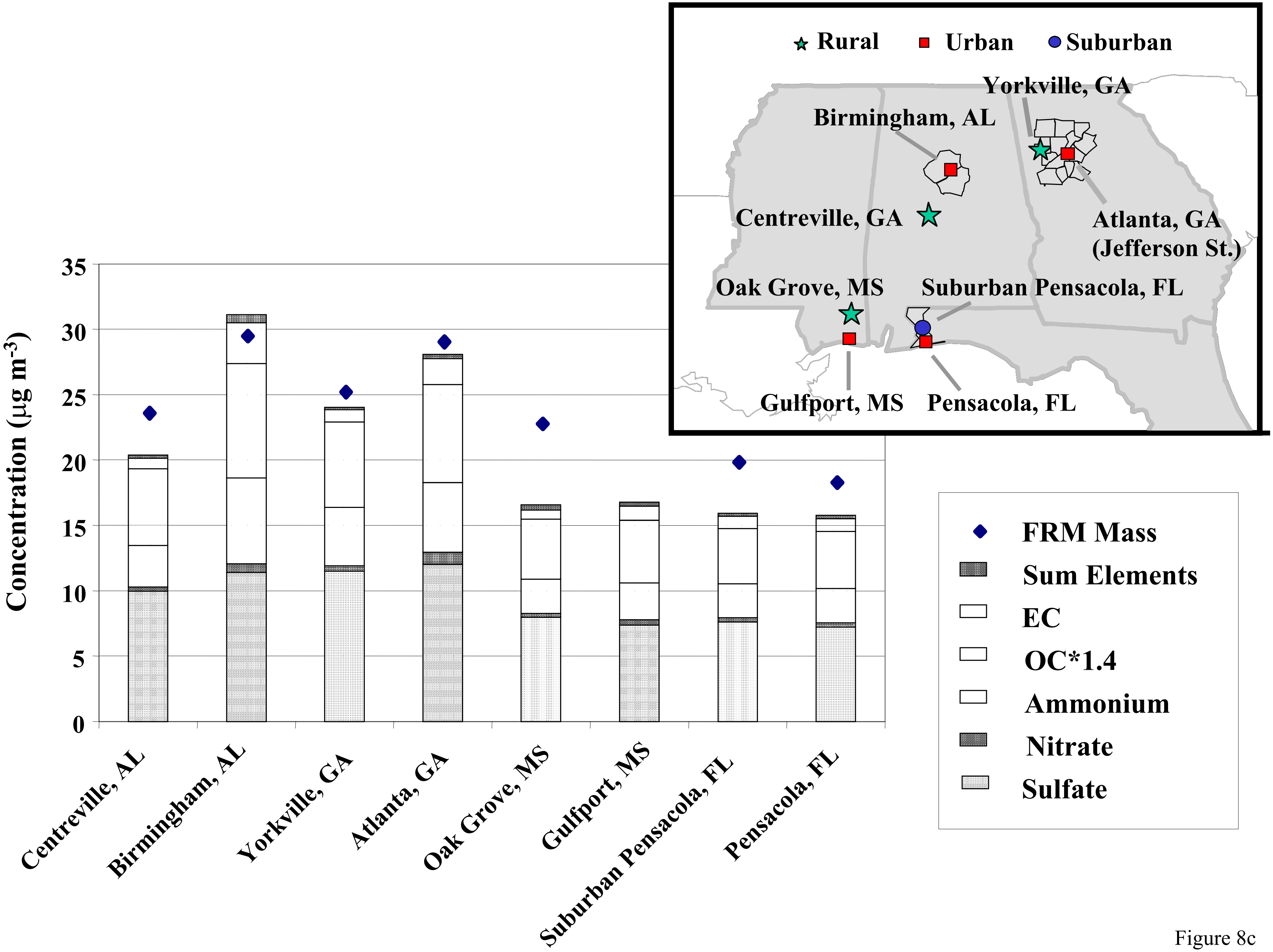

★ Rural
■ Urban
● Suburban
Yorkville, GA
Birmingham, AL
Centreville, GA
Atlanta, GA (Jefferson St.)
Oak Grove, MS
Suburban Pensacola, FL
Gulfport, MS
Pensacola, FL
Concentration (μg m^{-3})
35
30
25
20
15
10
5
0
Centreville, AL
Birmingham, AL
Yorkville, GA
Atlanta, GA
Oak Grove, MS
Gulfport, MS
Suburban Pensacola, FL
Pensacola, FL
◆ FRM Mass
▩ Sum Elements
☐ EC
☐ OC*1.4
☐ Ammonium
▩ Nitrate
░ Sulfate

Figure 8c

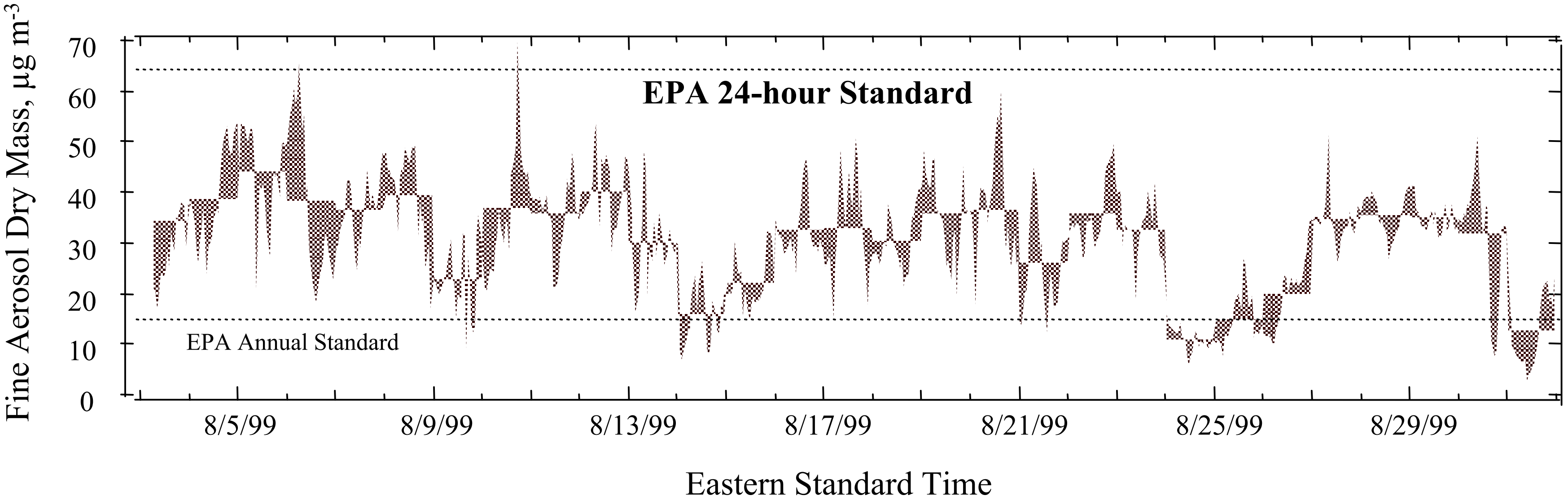

Fine Aerosol Dry Mass, μg m-3
70
60
50
40
30
20
10
0
EPA 24-hour Standard
EPA Annual Standard
8/5/99
8/9/99
8/13/99
8/17/99
8/21/99
8/25/99
8/29/99
Eastern Standard Time

Figure 9