

C. ABSTRACT

Research Category: Particulate Matter "Supersites" Program (99-NCERQA-X1)

Title: The Pittsburgh PM Supersite Program: A Multi-Disciplinary Consortium for Atmospheric Aerosol Research

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Project Period: January, 2000 – December, 2004

Project Cost: \$3,400,000

Project Summary: Airborne particulate matter (PM) continues to pose serious health risks for susceptible members of the U.S. population and for sensitive ecosystems. Design of cost-effective PM control strategies is limited by the lack of understanding of the PM-health effects links which is exacerbated by a paucity of physiological data, the difficulty of establishing the PM source-receptor relationships, and finally the limitations of existing instrumentation for PM measurements. A comprehensive multidisciplinary study is proposed for the Pittsburgh region, which will address all of the above issues.

The proposed hypothesis-driven program will have six components:

- Ambient monitoring in a central supersite and a set of satellite sites in the region (leveraged against Department of Energy Federal Energy Technology Center (DOE/FETC) funds).
- An epidemiological study (to be leveraged against funds from NIH and others).
- An indoor monitoring study (extension of work currently funded by DOE and EPA).
- An instrument development and evaluation study (leveraged against current NSF and other EPA funds).
- A comprehensive modeling component (currently funded by the EPA STAR program).
- A data analysis and synthesis component (hypothesis testing).

In addition to the above resources the program leverages funds and resources from local industry (Bayer), local government (Allegheny County Health Department), state government (Pennsylvania Department of Environmental Protection), and cost sharing by Carnegie Mellon University.

The objectives of the EPA-funded part of the Pittsburgh Supersite Program are: to characterize PM (size, surface, and volume distribution, chemical composition as a function of size and on a single particle basis, morphology, and temporal and spatial variability) in the Pittsburgh region; to quantify the impact of the various sources (transportation, power plants, biogenic, etc.) to the PM concentrations in the area; and to develop and evaluate the next generation of atmospheric aerosol monitoring techniques (single particle measurements, continuous composition measurements, ultrafine aerosol measurements, improved organic component characterization, etc.). Combining the ambient monitoring study supported by the EPA Supersites program with the proposed indoor, health, and modeling studies (funded by other sources) will allow the proposed program to: elucidate the links between PM characteristics and their health impacts; quantify the relationship between indoor and outdoor concentrations; and quantify the responses of PM characteristics to changes in emissions to support SIP development. These objectives address all the goals of the EPA Supersites Program and will be achieved through the investigation of approximately twenty hypotheses addressing issues in ambient aerosol characterization, measurement methods, atmospheric processes, aerosol properties, source-receptor relationships, health effects, and indoor exposure.

The measurement program will feature a central supersite located in Pittsburgh near the CMU campus and a set of satellite sites. Baseline monitoring is planned for an 18-month period that will include detailed characterization of PM size, surface, and volume distributions, chemical composition as a function of size, continuous single-particle size and composition measurements, organic aerosol speciation, measurement of the distribution and composition of ultrafine aerosols, semi-continuous measurements of metals, nitrate, sulfate, and aerosol carbon, measurements of bioaerosols, aerosol precursors, cloud and fog composition in the area, aerosol optical and hygroscopic properties, and meteorological variables. Three intensive sampling periods are planned to examine temporal variations and to collect detailed data for model testing and validation. The data from this project will be made available through an easily accessible electronic database. The Supersite team with the help of the CMU Computer Science School will post the available raw data (real-time and continuous measurements) and the remaining data as soon as they become available to a web site accessible by the EPA researchers. This rapid exchange of information will facilitate the collaboration with our EPA colleagues. Throughout the program, we will look for opportunities to minimize adverse environmental effects of the sampling effort without compromising the quality of the data.

The following benefits are expected from the Pittsburgh Supersite program:

- Comprehensive characterization of the PM in the Pittsburgh area. This will include, size distribution, composition as a function of size and for individual particles, temporal and spatial variation, optical and hygroscopic properties, and morphology.
- Development and evaluation of state-of-the-art instrumentation and measurement approaches (single particle instruments, continuous measurement approaches, etc.)
- Apportionment of the measured PM (both primary and secondary) to sources as a function of time. These results should be valuable for SIP development.
- Establishment of links between the PM characteristics and health effects in the study area.
- Quantification of the relationship between indoor and outdoor PM levels in the region.
- Development of a dataset (in coordination with the other Supersites) for the evaluation of the approaches used for the description of PM processes in atmospheric chemistry models.

D. PROJECT DESCRIPTION

1. INTRODUCTION

In July of 1997, the U.S. Environmental Protection Agency (EPA) revised the National Ambient Air Quality Standards (NAAQS) to address ambient air concentrations of particulate matter (PM) with an aerodynamic diameter of 2.5 micrometers or less (PM_{2.5}). Concern for the elevated concentrations of PM derives mainly from persistent evidence of human health effects associated with atmospheric particles. The epidemiological literature has more than 100 published papers, which, for the most part, support association of PM with increases in morbidity and/or mortality. However, no epidemiological study has identified particular PM chemical constituents as potential causative agents. The PM_{2.5} standard promulgated by the EPA defines PM_{2.5} mass measured according the Federal Reference Method (FRM PM_{2.5}) as the indicator for health effects. In 1997, the EPA also proposed regional haze regulations for pristine areas; fine particulate is the single greatest contributor to visibility impairment in these areas. Based on the limited existing data of ambient PM_{2.5} concentrations, it appears likely that many areas of the country may exceed these new standards.

Large gaps exist in our understanding of the nature of, effects of, and control of ambient PM. These gaps are due to the fact that PM is a complex mixture of multicomponent particles whose size distribution, composition, and morphology can vary significantly in space and time. Atmospheric aerosol size ranges from a few nanometers to tens of micrometers. Major components include sulfate, nitrate, ammonium, and hydrogen ions; trace elements (including toxic and transition metals); organic material; elemental carbon (or soot); and crustal components. PM is emitted directly from sources such as diesel engines and is also formed in the atmosphere from gaseous precursors. The development of effective control strategies requires a better understanding of the link between PM_{2.5} and the observed health effects. A number of aerosol characteristics (Table 1) have been proposed as the potential causes of the observed health effects.

Table 1. Possible PM Characteristics Resulting in Health Effects

PM Characteristics	Symbol (Units)
Total Number Concentration	N (cm ⁻³)
Number Concentration of particles larger than x nm	PN _x (cm ⁻³)
Total Surface Area	S (μm ² cm ⁻³)
Surface Area of particles between diameters x and y	S _{xy} (μm ² cm ⁻³)
Particle mass less than x, 2.5, or 10 μm	PM _x , PM _{2.5} , PM ₁₀ (μg m ⁻³)
Metal PM _{2.5} or PM ₁₀ Concentration (Fe, Mn, etc.)	M _{1.2.5} M _{1.10} (ng m ⁻³)
Sulfate PM _{2.5} and PM ₁₀	Sulf _{2.5} , Sulf ₁₀ (μg m ⁻³)
Nitrate PM _{2.5} and PM ₁₀	Nit _{2.5} , Nit ₁₀ (μg m ⁻³)
OC PM _{2.5} and PM ₁₀	OC _{2.5} , OC ₁₀ (μg C m ⁻³)
EC PM _{2.5} and PM ₁₀	EC _{2.5} , EC ₁₀ (μg C m ⁻³)
Acidity	H ⁺ (ng m ⁻³)
Bioaerosol number concentration	B (cm ⁻³)
Polar, Non-polar organics	POC, NPOC (μg m ⁻³)
Hydrogen peroxide, Organic peroxides	H ₂ O ₂ , RO ₂ (ppb)
Total soluble PM _{2.5} and PM ₁₀	SPM _{2.5} , SPM ₁₀ (μg m ⁻³)
Specific Sources (diesel or gasoline combustion, power plants, etc.)	Source _i (μg m ⁻³)
Gas-phase co-pollutants	CO, O ₃ , NO, NO _x , SO ₂ (ppb)

The link between ambient PM and health effects is further complicated because of the large uncertainty in the relationship between ambient PM concentrations and actual human exposure (NRC, 1998). Indoor measurements are critical for assessing exposures because individuals spend, on average, about 90% of the time indoors (70% in homes). Significant uncertainties exist in the penetration of outdoor aerosol to the indoor environment. If exposures are not adequately characterized, then causal relationships between ambient PM and health effects may be erroneously attributed. Understanding the relationship between the outdoor and indoor PM concentrations in a typical house in the area will be one of the objectives of the Pittsburgh Supersite Program.

Identifying the PM characteristics and/or sources that cause negative health effects requires a comprehensive data set of PM measurements and epidemiological data. Such a data set does not exist. Standard PM measurement techniques such as the Federal Reference Method for PM_{2.5} mass (FRM PM_{2.5}) do not measure most of the aforementioned characteristics. Indicative of the difficulty of the PM measurements is the often-observed lack of agreement between the measured PM concentration and the sum of the concentrations of the individual PM components in the Eastern US. The unexplained mass can be as much as 30% of the total and has been speculated to be the result of errors in estimating the organic aerosol mass from the measured organic carbon, residual water, errors in estimating the dust contribution, or the unlikely existence of some unidentified major component (Andrews et al., 1999).

The difficulty and cost of PM measurements have impaired our ability to characterize their temporal and spatial variability, understand the processes that control their formation and removal, and quantify the exposure of populations to them. Overcoming these difficulties requires the evaluation of existing PM measurement methodologies and development of new technologies which will allow the cost-effective, accurate measurement of PM characteristics. The proposed Pittsburgh Supersite program has been designed to foster this measurement evolution process. Examples of emerging technologies that will be evaluated include semi-continuous metal measurements by GFAA and LIBS, single particle composition and size measurements by time of flight mass spectrometry, continuous nitrate, sulfate and carbon measurements by integrated collection and vaporization cell, continuous polar organic aerosol measurements by single particle mass spectrometry, semi-continuous OC and EC measurements, enhanced organic aerosol speciation by GC/MS, ultrafine aerosol size distribution measurements, semivolatile organic aerosol partitioning measurements, bioaerosols, continuous direct surface area measurements, etc.

The state-of-knowledge of organic PM illustrates the need for advanced instrumentation. Carbonaceous compounds comprise 20-70% of the dry fine particle mass in both urban and rural areas. Although more than 100 individual organic compounds have identified (Rogge et al. 1991, 1993a-e, 1994, 1997a,b, 1998, 1999a-d; Simoneit et al., 1993, 1998, 1999; Fraser et al., 1998; Schauer et al., 1999a,b), only about 20% of the organic fine particle mass has been identified on a molecular level. In addition, few measurements exist of the ambient concentrations of organic precursors that lead to secondary organic aerosol. Improved understanding of the organic PM phase requires further development of *in-situ* measurement techniques such as single particle mass spectrometry and improved analytical methods for examining filter samples. The proposed study using a number of new techniques will also address some of the most important questions regarding organic PM in the study area. What is the primary versus secondary organic PM fraction? What is the contribution of biogenic PM

sources (primary aerosol or oxidation of terpenes and sesquiterpenes) to organic PM? How do the semivolatile organic PM components partition between the gas and aerosol phases?

Design of effective State Implementation Plans (SIPs) and other regulatory policies requires knowledge of source-receptor relationships that link ambient PM_{2.5} levels with emissions. The design of these strategies is complicated by the importance of secondary aerosol to PM_{2.5}. Of particular concern are non-linearities between emissions and ambient PM levels. For example, reductions in SO₂ and sulfate can free the associated ammonia in aerosol ammonium sulfate. This additional ammonia can react with available nitric acid vapor forming aerosol ammonium nitrate (Seinfeld and Pandis, 1998). In extreme cases in specific areas in the NE US controls in SO₂ could result in a small increase in PM concentrations during the winter (West et al., 1999). Similar non-linearities are expected in the response of the PM concentrations to NO_x and ammonia emission changes. Recent developments in our understanding of the partitioning of semi-volatile organic aerosol components between the gas and aerosol phases suggest that the organic aerosol system is often non-linear (Odum et al., 1996). The proposed study will provide quantitative information about the possible non-linearity of the source-receptor relationships in the study area, especially for secondary particulate matter and also determine if there are any reactants controlling the secondary PM formation (e.g., ammonia).

Deterministic modeling with appropriate input data allows detailed examination of the contribution of different sources to secondary aerosol formation. Several of these models (including two models by the Carnegie Mellon and University of Delaware teams) are at various stages of development (see Seigneur et al., 1998 for a review). However, the evaluation and application of these models in the Eastern US is limited by the lack of suitable measurements. The Supersites together with the proposed EPA Speciation site network could provide the much needed information for the evaluation of these models.

Additional understanding of atmospheric aerosol chemistry and physics is needed to develop the next generation of deterministic air pollution models and establish the source-receptor relationships for secondary PM. For example, little is known about the relative importance of fine PM production and removal in fogs and low clouds in polluted urban areas of the eastern US such as Pittsburgh. The importance of nucleation as a source of ultrafine particles is unknown. Our lack of understanding of the interactions of ambient PM with water limits our ability to estimate their atmospheric lifetimes and transport distances. These gaps in understanding make the estimation of the local versus regional contributions to the PM levels in an urban area like Pittsburgh very uncertain. The proposed study includes a number of innovative approaches (e.g., single particle mass spectrometry coupled with Tandem Differential Mobility Analysis, continuous measurements) which will shed light on the above issues.

1.1 Overview of the Pittsburgh Supersite Program

We propose a comprehensive, multi-disciplinary PM investigation to characterize the ambient PM in the Pittsburgh region, to improve our understanding of the links between ambient PM and public health, and to develop new instrumentation for PM measurements. The centerpiece of this effort will be an ambient PM monitoring study that is the focus of this proposal. In addition to the EPA Supersite funds, the ambient monitoring study will receive substantial in-kind assistance (equipment, operation of satellite sites, and access to facilities) and cost-sharing (in excess of \$2M) support from DOE/FETC. The resources of DOE/FETC will be

combined with the EPA resources to support a unique combination of experts and state-of-the-art measurements in an important airshed. A letter describing the DOE/FETC support is attached.

The ambient monitoring study has been designed to test a set of hypotheses, which are described in a subsequent section of the proposal. It will feature a central supersite located near the Carnegie Mellon University campus near downtown Pittsburgh and a set of satellite sites. Baseline monitoring is planned for an 18-month period that will include among others detailed characterization of PM size, surface, and volume distribution, PM chemical composition as a function of size and on a single particle basis. Three fourteen day long intensive sampling periods are planned to examine temporal variation and to collect detailed data for model testing and validation. The data from the project will be made available as an easily accessible database.

A collaborative team of 20 research groups from 13 universities, 2 companies, a national laboratory and a federal agency will participate in the project. The curriculum vitae from these collaborators are attached. Local and state air pollution agencies are supporting the effort. Letters of support from these agencies are also attached to the end of the proposal. The Pittsburgh Supersite will build upon the DOE/FETC Upper Ohio River Valley Project (UORVP) that has provided initial characterization of the fine particulates in the Pittsburgh area (DOE/FETC, 1999). The UORVP has been operating 5 monitoring sites around Pittsburgh since April 1999. At two of these sites, the UORVP is measuring PM₁₀ and PM_{2.5} mass (both with FRMs and continuously with TEOMs) and standard gas species (O₃, CO, SO₂, NO_x); they are also performing basic speciation (OC/EC, metals, major ions) on a 1 in 6 day schedule. A more limited suite of measurements is being performed at the final 3 sites. To date the UORVP has focused on comparing the performance of different samplers. The objective of the UORVP is to characterize the contribution of fossil-fuel-based power systems to ambient PM_{2.5}. This scope is clearly insufficient to address the much broader objectives of the EPA Supersite Program.

Four of the UORVP sites will be used as satellite sites for the Pittsburgh Supersite; the equipment at the final UORVP site will be moved to the Pittsburgh Supersite to provide a basic suite of sampling equipment. The proposed Supersite will substantially expand the characterization effort of the UORVP by adding a wide range of state-of-the-art measurements and increasing the frequency to at least daily.

An epidemiology study, a comprehensive modeling study, and an indoor exposure study are also planned in parallel to leverage the results from the ambient PM monitoring. These additional studies provide the opportunity to test critical hypotheses relating to health effects, exposure, and control strategies. This additional work will not be supported by EPA Supersite funds. However, these studies are an important part of the overall research plan and therefore are briefly described in this proposal. Support letters are included.

1.2 Site Selection: Why Pittsburgh?

There are many compelling reasons to conduct an intensive PM monitoring campaign in Pittsburgh. These include:

- There are roughly two million people living in the Pittsburgh Metropolitan Statistical Area. Elderly people represent a significant fraction of the population.
- The area is located between the power plants of the Midwest and the large urban centers of the East. Study of the pollution in Pittsburgh and the surrounding area can provide valuable insights about the transport of PM and its precursors from the Midwest to the Eastern US.

- Pittsburgh is an area influenced by reasonably well-defined local, remote, and biogenic sources (see Figure A.1 in Appendix 2). This will make source-receptor relationships much easier to quantify compared to areas closer to the eastern seaboard where the urban centers interact with each other strongly.
- The ongoing DOE/FETC program provides a unique opportunity for leveraging EPA resources.
- There is a considerable database of PM measurements in Pittsburgh and in the proposed Supersite area. The CMU team is the main contributor to this database.
- Despite the available database a number of important issues regarding PM composition, properties, regional and local sources, etc., have yet to be elucidated.
- Pittsburgh is likely to exceed the proposed PM_{2.5} standards (Falke, 1999).

2. OBJECTIVES

The main objectives of the EPA funded ambient monitoring components of the Pittsburgh Supersite Program are:

- Characterization of the PM in the Pittsburgh region. These characteristics include the PM size, surface, and volume distribution; chemical composition as a function of size and on a single particle basis; temporal and spatial variability.
- Development and evaluation of current and next generation atmospheric aerosol monitoring techniques (single particle measurements, continuous measurements, ultrafine aerosol measurements, improved organic component characterization, and others).
- Quantification of the impact of the various sources (transportation, power plants, natural, etc.) to the PM concentrations in the area.

Combining the ambient monitoring study with the proposed indoor, health, and modeling studies (funded from other sources) will allow:

- Elucidation of the links between PM characteristics and their health impacts in this area.
- Quantification of the relationship between indoor and outdoor concentrations in the area.
- Quantification of the responses of the PM characteristics to changes in these emissions in support of the emission control decision making in the area (SIP development, etc.)

3. HYPOTHESES TO BE TESTED

The Pittsburgh Supersite Program has been designed to test a wide range of complementary hypotheses. The first group of hypotheses fall solely under the purview of the EPA Supersite program and can be tested with atmospheric measurements related to meteorology and air quality, specifically gas-phase pollutant concentrations and the size and composition of PM. A wide range of data will be collected under funding primarily from DOE that will supplement the ambient measurements and support other aspects of the measurement program such as indoor air quality assessment. Finally, health effects data will be collected under funding from other agencies, and combined with the ambient and indoor measurements will provide a rich data set for the planned epidemiological study. The hypotheses to be tested and the corresponding approach are discussed in Section 5. A brief summary of the corresponding topics is presented below:

1. Ambient aerosol characterization: The Supersite measurements will attempt to resolve the lack of mass balance often observed in the PM samples in the Eastern US and will quantify the total number and surface area concentrations continuously.

2. Measurement methods: A number of new PM measurement technologies (single particle measurements, semi-continuous measurements of elements, nitrate, sulfate, and carbon) will be developed further and will be evaluated against the traditional filter techniques. Artifacts introduced during the nitrate and semivolatile organics sampling in the area will be investigated.

3. Atmospheric processes: The sources of particle number (emissions versus nucleation), the contributions of biogenic sources (primary and secondary), the role of fogs and clouds in the sulfate production, the response of the PM to sulfate changes and the role of ammonia, the relative contributions of primary and secondary organic PM sources, and the impact of local versus regional sources will all be investigated based on a set of six hypotheses.

4. Source-Receptor Relationships: One of the main hypotheses of the proposed program is that the combination of state-of-the-art-techniques like the single particle measurements, organic PM tracers, continuous elemental concentration measurements, etc., together with meteorological information (e.g., air trajectories) and source-receptor models will allow an unprecedented resolution of source contributions to local air quality by receptor modeling techniques.

5. Aerosol Properties: The interactions of particles with water (growth, deliquescence, crystallization, existence of metastable phases, and cloud droplet formation) and their optical properties will be quantified as a function of their chemical composition.

6. Health Effects: The combination of the Supersite data set with the epidemiological study will allow the testing of practically all of the hypotheses that have been proposed to explain the PM effects on mortality and morbidity.

7. Indoor Exposure: The combination of the Supersite measurements with the indoor monitoring study will examine the relationships between ambient and indoor PM levels as a function of particle size, chemical composition, season, housing stock characteristics.

4. APPROACH

4.1 Overview

The proposed study consists of the following six components:

- (1) Ambient monitoring at a central supersite and a set of satellite sites in the Pittsburgh region
- (2) An instrument development and evaluation study
- (3) A comprehensive modeling component (currently funded by the STAR program of EPA),
- (4) An epidemiological study (additional funding will be requested by other agencies)
- (5) An indoor monitoring study (extension of currently funded DOE and EPA studies), and
- (6) A data analysis and synthesis component.

The EPA Supersite Program funds will only be used to support activities of components (1), (2) and (6). DOE funds will also be leveraged to support the same components. The proposed approaches for each of these components are summarized below.

4.2 Ambient Monitoring

The central sampling site will be located next to the Carnegie Mellon University campus near downtown Pittsburgh. The site location is described in Section 8. The basic suite of sampling equipment at this site (FRMs, TEOMs, gas analyzers, etc.) will be provided by DOE/FETC by relocating the equipment at the Lawrenceville site of their UORVP. Satellite sites are planned for Holbrook, Pennsylvania (a rural area); Athens, Ohio; Morgantown, West Virginia; and South Park, Pennsylvania (a suburb of Pittsburgh). These four sites are currently being operated and will continue to be operated by FETC as part of their UORVP. Existing PM sampling sites of the regulatory network in the area will be used as additional satellite sites. Discussions are currently underway with the Air Quality Program of the Allegheny County Health Department to determine which regulatory network sites will be chosen for sampling. A letter from Roger Westman, Manager of the Air Quality program, is included in Appendix 1. The Health Department has agreed to increase the frequency of sampling to accommodate the proposed Supersite program, as explained in the letter. A letter from Jim Salvaggio, Director of the Bureau of Air Quality of the Pennsylvania Department of Environmental Protection, is also attached explaining their support of the proposed Supersite program. Figure 1 shows the location of the central site, the four satellite sites of UORVP, and some additional potential satellite sites.

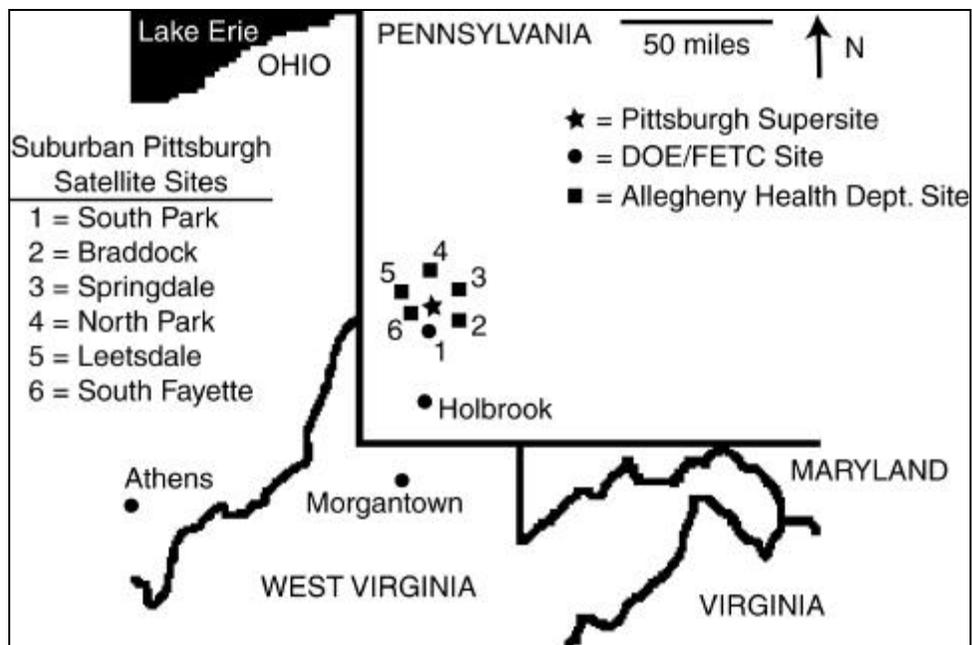


Figure 1. Map of Pittsburgh region showing the approximate location of the Supersite, the four DOE/FETC UORVP sites that will be used as satellite sites, and five candidate satellite sites that are currently Allegheny County Health Department sampling sites.

The measurement campaign will last for 18 months (May 2001-October 2002) to include two summers and will consist of regular measurement periods and three 14-day intensive periods. The measurements can be categorized as follows:

- PM size distributions
- PM mass characterization
- PM chemical composition
- Single particle characterization
- Continuous PM composition
- Bioaerosols
- Aerosol acidity
- Aerosol light scattering
- PM Hygroscopicity
- Meteorology
- Gases
- Fogs and clouds

Each of these measurement categories is listed in Table 2 with instrumentation, frequency of sampling, and name of investigator. A brief discussion of each measurement category follows. Additional details can be found in Appendix 2.

4.2.1 PM Size Distributions

This category includes number and surface area size distributions. The Pandis group using a variety of real-time instruments will measure at the central site and at the Holbrook rural site number distributions. These instruments will provide data in the full range 3 nm to 10 μm (see Table 1). The separate overlapping distributions from these instruments will be inverted and combined using the MICRON code (Wolfenbarger and Seinfeld, 1989; Pandis et al., 1990; Weber et al., 1998). The Baltensperger group using Epiphaniometers will measure at the central site and at the Holbrook rural site surface area concentrations. This instrument provides a signal proportional to the Fuchs surface (Gäggeler et al., 1989; Baltensperger et al., 1997), namely, the surface of aerosols actually “seen” by a diffusing atom or molecule (Pandis et al., 1991; Rogak et al., 1991). The instrument operates continuously and averaging times of 10-30 min have been used in the past (Lugauer et al., 1998; Pandis et al., 1991). This will provide a unique opportunity to investigate potential health effects of aerosol surface area without assuming that the atmospheric particles are spherical.

4.2.2 PM Mass Characterization

The PM mass concentration will be measured by the Davidson group using the gravimetric approach and a variety of samplers. The $\text{PM}_{2.5}$ and PM_{10} mass concentrations will be measured using Federal Reference Method (FRM) samplers, Tapered Element Oscillating Microbalance (TEOM) samplers, and denuder/filter systems. Dichotomous samplers with a 2.5 μm cut-off will be used for independent measurements of the coarse fraction ($2.5 < d_p < 10 \mu\text{m}$). This will enable us to determine the extent to which the difference between PM_{10} and $\text{PM}_{2.5}$ mass concentrations reflects the concentration in this size range.

An electrical low pressure impactor (ELPI) and a Micro-Orifice Uniform Deposit Impactor (MOUDI) will be used to sample PM_x , i.e., mass concentrations associated with particle diameters less than x micrometers (where x will be determined by the cut-offs of the various impactor stages). These measurements will be performed daily during the regular sampling periods and five times per day during the intensive runs. Gravimetric analysis will be conducted in the class 100 Clean Lab at CMU used in several other studies (e.g., Davidson et al., 1993, 1996, Bergin et al., 1995). A humidity-controlled chamber will be used for equilibrating the filters according to standard protocol.

4.2.3 PM Chemical Composition

Inorganic Components. The inorganic speciation samplers (PM_{2.5} and PM₁₀) for the Supersite will consist of a combination of denuders and filters. The sampler arrangement for PM_{2.5} is shown in Figure 2; a modified arrangement will be used for PM₁₀. The figure lists several ionic species as well as organics (discussed below) and trace elements; the last category will include more than 20 species analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The sampling frequency will be once per day during the regular period and five times per day

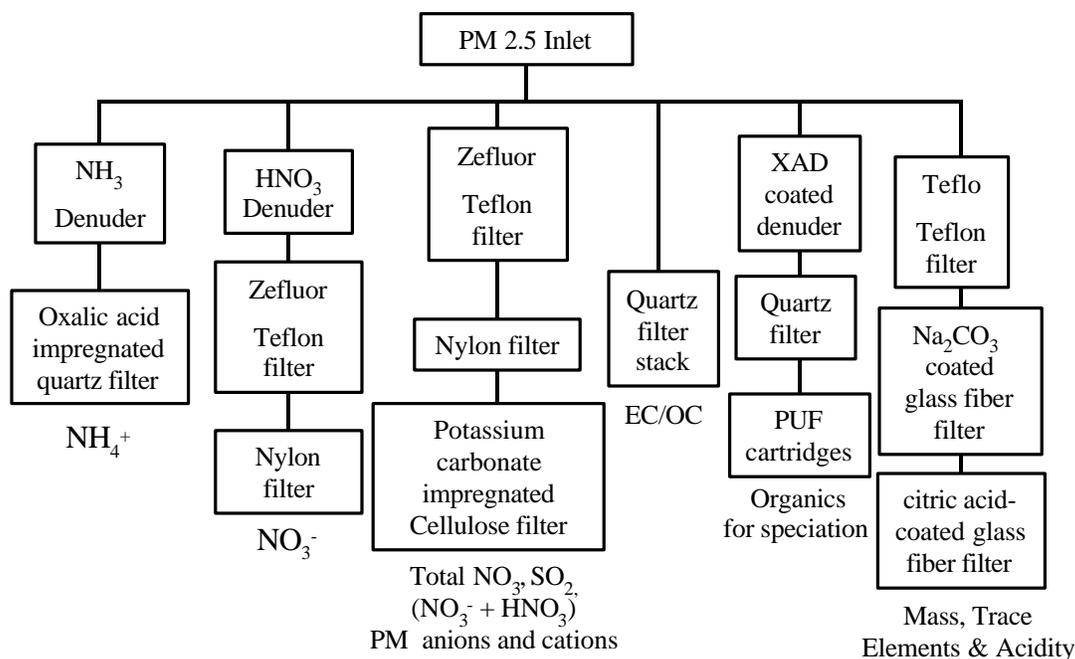


Figure 2. CMU PM_{2.5} sampler for chemical analysis. A similar system will be used for PM₁₀ but without the potassium carbonate cellulose filter and without the quartz filter analyzed for organics. Dichotomous samplers will also be used to investigate the hypothesis that coarse particle concentrations can be determined from PM_{2.5} and PM₁₀. Methods of analysis are listed in Table 1.

during the intensives, with 4-hour samples during the day and 6 hour samples at night. There will also be chemical analyses from the dichotomous sampler; the species will be chosen after quantifying uncertainties for different chemical species in the filter samples. A detailed characterization of the losses of semivolatile particulate matter in the denuders will be conducted during the first year of the project. These experiments will involve monodisperse model (ammonium nitrate, ammonium sulfate, and organics) and ambient particle size and composition measurements before and after the denuder. The results of these characterization experiments will allow better design of the denuder operation to minimize losses as well as provide information about the magnitude of the losses that can be used for correction of the measurements. Potential losses of HNO₃ on the sampling system inlets and walls will be directly measured during the sampler development phase and the sampling system will be designed to minimize them.

MOUDI impactor samplers will also be analyzed for inorganic chemical composition during the intensive periods.

Besides these samples, OC and EC will be measured during intensive runs and during regular sampling periods by the Turpin group using their improved *in situ* carbon analyzer. The *in situ* carbon analyzer collects PM_{2.5} samples on a quartz fiber filter mounted inside a thermal-optical carbon analyzer. Thus, the analytical method is very similar to that used for the speciation sampler. Sample collection and analysis are performed continuously and automatically through computer control. The prototype instrument compares favorably with the *in situ* photoacoustic spectrometer developed at Ford Motor Company (Turpin et al., 1990), and has been used to investigate secondary organic aerosol formation (Turpin and Huntzicker 1991; 1995).

Two types of size-resolved organics sampling will be conducted; both restricted to periods of intensive runs. First, samples from an electrical low-pressure impactor (ELPI) will be analyzed for OC and EC by the Robinson group. Second, samples from a Hering Low Pressure Impactor (LPI) will be analyzed by the Turpin group by Fourier Transform Infrared Spectroscopy (FTIR) to provide information on the functional groups of the organics. Such information is valuable for understanding aerosol processes (Blando et al., 1998; Carlton et al., 1999).

Artifacts during sampling will be investigated by the Eatough group using the PC-BOSS diffusion denuder sampler (Eatough, 1999) during the intensive sampling periods. This sampler includes a PM_{2.5} inlet with a fine particle concentrator, denuder, and several filters (Quartz, Teflon, Nylon, and Charcoal-impregnated), as illustrated and discussed in Appendix 2. The sampler will provide data for OC and EC as well as semivolatile organics lost from particles during sampling. In addition, analyses will be conducted for sulfate, nitrate, and ammonium.

Special Organics Study: Polycyclic Aromatic Hydrocarbons (PAHs). A sampling system assembled by the Miguel group will be used during intensive runs to collect size-resolved samples for analysis for PAH compounds. Sampled air will first pass through an AIHL-design cyclone separator (John and Reischl, 1980) at 30 lpm allowing particles with diameter less than 1.8 μm to pass through it together with the gas-phase. A XAD-4 coated annular denuder placed downstream of the cyclone will trap semi-volatile organics while allowing transmission of particles smaller than 1.8 μm , which then flow into a MOUDI impactor. Blow off from the impactor's backup filter will be trapped with two polyurethane foam plugs (PUF) placed in series behind it. Samples will be extracted and analyzed using recently developed methods (Miguel et al., 1998; Marr et al., 1999; Schauer et al., 1996; Schauer et al., 1998; Schauer, 1998). All data will be corrected for chemical reactivity (Friedlander et al., 1996, Miguel et al., 1986). The ambient PAH concentrations at each site will be used by the Miguel group to separately apportion black carbon and associated toxic components to gasoline- and diesel-fueled vehicles using the EPA Chemical Mass Balance receptor model. PAH source signature data are available in the literature (Miguel et al., 1998, Marr et al., 1999, Venkataraman and Friedlander, 1994).

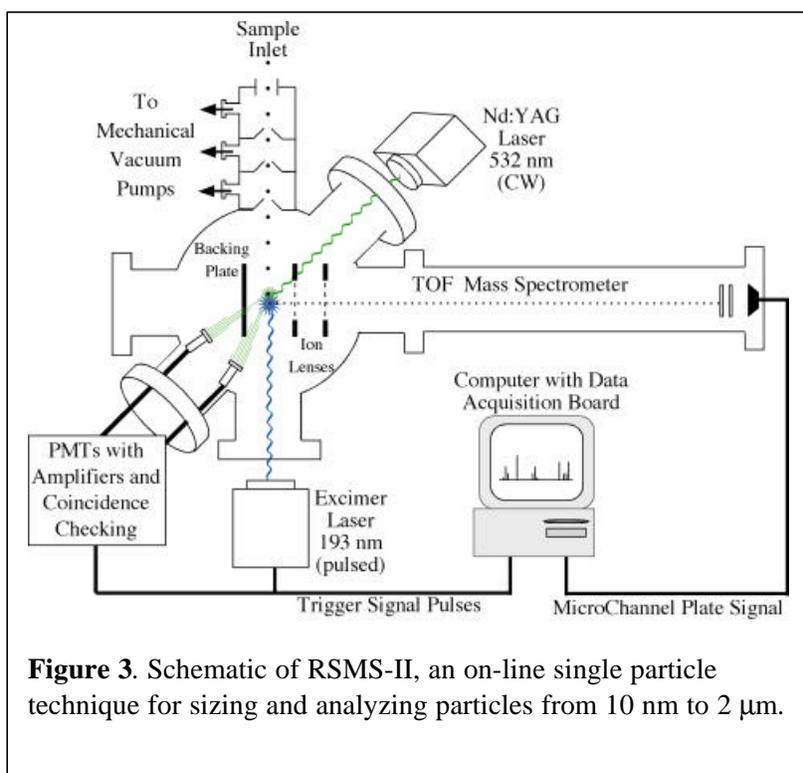
4.2.4 Single Particle Characterization

Single Particle Mass Spectroscopy. The groups of Wexler and Johnston will use an on-line single particle analysis technique (RSMS-II) to measure the particle-by-particle size and composition over the size range from 10 nm to 2 microns. As shown in Figure 3, particles of a narrow size range are focused aerodynamically to the source region of a mass spectrometer. The

size that is focused can be selected from 10 nm to 2 microns by adjusting the upstream pressure. An excimer laser beam collinear with the particle beam is periodically fired. If a particle is in the beam, it is desorbed and ionized. The ions are analyzed in a time-of-flight mass spectrometer. Spectra from each particle are recorded and stored on a PC. The instrument is described in more detail in Carson et al. (1997) and Ge et al. (1998).

RSMS-II can analyze for a wide range of compounds and compound classes including a) speciation of inorganics such as metals and metal oxides, refractory crustal materials such as silicon dioxide, and electrolytic compounds such as sulfates and nitrates, b) speciation of aromatic organic compounds, and c) distinguishing elemental from organic carbon. A new RSMS-II instrument will be built for the Supersite that will require relatively little operator intervention and will have improved analytical capabilities. This instrument will be deployed for entire sampling period. Further information about RSMS-II and its operation is given in Appendix 2.

The Wexler/Johnston group plan to expand the capabilities of the RSMS-II to examine the polar organic compounds in single particles using an aerosol matrix-assisted laser desorption ionization (MALDI) technique (see, e.g., Mansoori et al., 1996).



technique to obtain mass spectra of highly polar compounds. The proposed on-line, single particle experiment mixes ambient aerosol with a small flow of hot vapor matrix material that strongly absorbs the laser radiation. The matrix vapor will condense on aerosol particles creating a matrix/analyte mixture similar to that created in a conventional MALDI experiment. The matrix-aerosol mixture will then be irradiated with a pulsed laser beam to eject intact analyte ions without fragmentation, which are then characterized with the mass spectrometer.

Laser-Induced Breakdown Spectroscopy (LIBS).

The Buckley group will use Laser-Induced Breakdown Spectroscopy (LIBS) to measure the elemental composition of single particles in the atmosphere. In LIBS, a tightly focused, pulsed laser is used to create a microplasma. The high temperature of the plasma breaks all of molecular bonds, and thermally excites the electronic states of the atoms. Using atomic emission, the mass concentration of a number of elements (Be, Cd, Cr, Na, K, V, Ni, Si and Pb) within the spark volume can be quantitatively measured (Buckley et al., 1999). To concurrently measure particle size, a single-shot spectrum containing emission from a single particle is analyzed, and

the total mass of each atomic constituent is determined (Hahn, 1998). The LIBS system will be deployed during two of the intensive sampling periods and during 1 month of the baseline-sampling period. Additional information about the system can be found in Appendix 2.

SEM analysis. During the intensive periods, samples will also be collected for analysis by scanning electron microscopy (SEM). Analyses will be conducted at the laboratories of R.J. Lee, Inc. Under the conditions required for SEM analysis, wet aerosol particles lose their water rapidly. During this rapid evaporation their morphology changes significantly and the SEM images are not representative of the actual particle shape. However, during periods of low relative humidity the SEM morphology information is expected to be relatively accurate. This will yield complementary information about the elemental composition and morphology (during periods of low RH) of individual larger particles that will not be provided by the single particle spectrometer.

4.2.5 Continuous and Semi-Continuous PM Composition

In addition to the previously mentioned continuous (or semi-continuous) measurements of the aerosol size distribution, OC and EC, and single particle size and composition a number of additional state-of-the-art techniques will be further developed and used in the proposed Supersite program.

Semi-continuous elements. The Ondov group will measure the concentration of 18 metals species (As, Cu, Mn, Ni, Cr, Cd, Se, Ag, Pb, Al, Fe, Zn, Ca, Bi, V, Ti, Be, and Ba) during the intensive periods at both the central Supersite and the rural satellite site in Holbrook. The semi-continuous system consists of a high-frequency aerosol sampler (HFAS) (dynamic aerosol concentrator) and a true simultaneous multi-element Graphite Furnace Atomic Absorption (GFAA) spectrometer. After as little as 10 minutes of sampling (depending on ambient concentrations), enough slurry is collected to permit 4 suites of 4 or 5 elements to be determined, each in triplicate. In addition to high temporal resolution, tests with NIST Standard Reference Material 1648 (“Urban Particulate Material”) confirm that analytical concentration measurements are accurate. The initial target collection rate will be 6 samples per hour, pending ambient concentrations.

Nitrates, sulfates, and aerosol carbon. Aerosol Dynamics Inc. (ADI) will provide automated, near-continuous measurements of aerosol nitrate, sulfate, and carbon in airborne particles below 2.5 μm diameter over the 18-month sampling period following the method of Stolzenburg and Hering (1999). With this method, the aerosol stream is first denuded to remove interfering vapors such as vapor organics. The sample stream is then humidified to prevent bounce-off (Winkler, 1974; Stein et al., 1994) and the particles are collected by impaction on a metal substrate inside an integrated collection and vaporization cell (ICVC). At the end of collection the cell is filled with a carrier gas, the substrate is heated resistively, and the particles thermally decompose to vapors that are measured using a commercial gas phase analyzer. A unique flow system eliminates the need for valves on the sampling line.

Sulfate analysis will be achieved using air as the carrier gas, with quantification of the evolved vapors for SO_2 , as described by Roberts and Friedlander (1974). Nitrate analysis will be achieved by low-temperature heating in nitrogen carrier gas, with analysis of the evolved nitrogen oxides as described by Yamamoto and Kosaka (1994). Carbon will be detected through quantification of the evolved CO_2 . Because the sample is concentrated, the analyses can be done

using proven, robust gas analyzers. Results using this method compare favorably with more conventional methods as illustrated in Appendix 2.

4.2.6 Bioaerosols

The Hernandez group will investigate the combined utility of high volume sampling, direct epi-fluorescent microscopy, and newer molecular biology methods to characterize outdoor bioaerosols in the size range between 0.2–20 μm . Initial laboratory experiments will be performed to determine the effects of sample capture on the structure, survival and activity of indigenous atmospheric microbioaerosols. Once the response to high volume sample capture is determined, field studies will be initiated. Multi-season surveys will be performed with samples collected at the Pittsburgh Supersite. These surveys will: (i) determine the effects of common sampling devices on outdoor microbiological aerosols during extended sampling periods, (ii) obtain accurate measurements of microbiological particulate inventories in outdoor air including, biomass, volume, and size distributions (between 0.2- 20 μm), and (iii) determine the abundance and identity of microbioaerosols (bacteria, fungi, and their spores) using direct microscopy combined with novel molecular biological assays. Details are presented in Appendix 2.

4.2.7 Aerosol Acidity

The aerosol acidity will be estimated using the method proposed by Saxena et al. (1993) combining the measured aerosol composition with the state-of-the-art aerosol thermodynamic models GFEMN, AIM2, and SCAPE2 (Ansari and Pandis, 1999). This method provides a better characterization of the actual ambient aerosol acidity compared to the extractable acidity by the pH method (e.g., using the method of Koutrakis et al., 1988). These estimates will be available for all aerosol-sampling periods, with the intensive periods providing the most useful information. The extractable acidity will be measured for selected samples by the Eatough group using the PC-BOSS and the pH method of Koutrakis et al. (1988).

4.2.8 Aerosol Light Scattering

The aerosol scattering coefficient and backscatter will be measured using a three wavelength (450, 550, and 700 nm) integrating nephelometer (TSI Model 3653) (Bodhaine et al., 1991). Periodically, an automated ball-valve built into the inlet will be activated to divert the air sample through a high-efficiency filter, allowing the measurement of the particle-free air signal. The sample temperature and relative humidity will be measured inside the nephelometer and will be kept practically equal to the ambient conditions (for $\text{RH} < 95\%$). The visual range will also be measured during the measurement periods and additional observations will be collected from the airports in the area and archived. Pictures (in electronic form) of the area surrounding the Supersite will be taken every hour during the intensive sampling period and every six hours during the rest of the study period for the calculation of the visual range and documentation of the prevailing conditions.

4.2.9 PM Hygroscopicity

The ability of ambient fine particles to absorb water and grow will be quantified using the Tandem Differential Mobility Analyzer (TDMA) technique (Zhang et al., 1993) by the Pandis

group. These measurements during the intensive periods will provide the growth factors as a function of particle size and particle group. The measurement of aerosol size as function of RH (from around 10 to 95 percent) will allow the quantification of the aerosol liquid water content at the RH of PM mass measurement and will provide input for the visibility calculations. The Cloud Condensation Nuclei concentration will be measured using the CCN counter of DH Associates. The CCN concentration is directly related to the ability of the particles to become cloud droplets and thus provides valuable information about their atmospheric lifetimes.

The TDMA system will be combined with the single particle instrument during specific periods to establish the links between the hygroscopic particle properties and their chemical composition. Two experiments are planned. In the first monodisperse particles will be selected by the first DMA and then they will be humidified to a RH of around 90%. The second DMA will be used for the quantification of the size change of the particles (how many particles grew how much) and the RSMS-II will be used for the measurement of their chemical composition. In the second experiment the particles will be pre-humidified (RH around 80-90%) and then a monodisperse part will be selected by the first DMA. The particles will then be exposed to a low relative humidity environment (around 10%). The second DMA will quantify once more their size change (how many particles lost how much water) while the RSMS-II will measure the chemical composition of the various particle groups. These experiments will provide the link between chemical composition and hygroscopic properties of individual ambient particles.

4.2.10 Meteorology

Several meteorological parameters will be measured during the sampling period, including temperature, relative humidity, precipitation, wind speed and direction, UV intensity, and solar intensity. In addition, the Kahl group will compute backward 10-day air mass trajectories twice daily over the 18-month sampling period (Harris and Kahl, 1994). This will provide (i) an assessment of the day-to-day variability in transport pathways and source regions for air sampled at the Supersite, (ii) an assessment of the dependence of aerosol chemical composition on the possible source regions, and (iii) an atmospheric transport climatology for the Pittsburgh region. Additional information on the trajectories is provided in Appendix 2.

4.2.11 Gases

Several gases will be measured continuously during the 18-month period and reported as 1-hour average concentrations. These include O₃, NO, NO_x, CO, and SO₂. In addition, air will be collected in canisters and analyzed for VOCs by GC-FID and GC-MS techniques. Methods of Lewis et al. (1999) will be applied here; these techniques enabled quantification of roughly 130 compounds in Atlanta air. Samples will be collected over six-day periods for analysis, except during intensive runs where there will be five samples collected and analyzed per day. In addition, the Collett group will measure hydrogen peroxide and soluble organic peroxides using a monitor based on the method of Lazrus et al. (1986). Details of the VOC analyses and the peroxide measurements are given in Appendix 2.

4.2.12 Fogs and Clouds

The Collett group will measure the cloud and fog composition during the winter period using the compact version of the Caltech Active Strand Cloudwater Collector known as the CASCC2

(Demoz et al., 1996). Fog will be sampled at the central site while cloudwater will be sampled on the roof of the 160 m high Cathedral of Learning at the nearby University of Pittsburgh. The building is often immersed in clouds, which will give us a unique opportunity to characterize the cloud composition in the area.

Collected fog/cloud samples will be analyzed on-site for pH and sample aliquots will be prepared for later analysis of major anion and cation concentrations at CSU. A subset of samples will also be aliquotted and stabilized for later analysis of total organic carbon (TOC), formaldehyde, and trace metal catalysts (Fe and Mn).

4.2.13 Green Design Considerations

The proposed sampling program will have adverse environmental effects, including use of resources and energy as well as production of pollutants. We will take the first steps in an effort to minimize these effects to the extent possible without compromising the quality of the data. For example, we will identify those materials where production is the most resource and energy intensive, and will investigate whether substitution of alternate materials is feasible. We will also consider the energy consumption of the project and determine whether alternative strategies can save energy. This includes energy used by the sampling equipment, air conditioning, clean laboratories, analytical instruments, and transportation of people and equipment. The effort will be assisted by faculty and students in the Green Design Initiative at Carnegie Mellon where there have been several projects on minimizing environmental effects of products and processes (e.g., Hendrickson and McMichael, 1994; Lankey and Davidson, 1997).

Table 1. Measurements in the Pittsburgh Supersite Program

Measurements	Instrumentation	Frequency Regular	Frequency Intensives	Investigator
Aerosol number distribution	Ultrafine SMPS ¹ , SMPS ² , APS ³ , ELPI ⁴ , Ultrafine CPC ⁵	10 min	5 min	Pandis
Aerosol surface distribution	Ultrafine SMPS, SMPS, APS, ELPI, Ultrafine CPC, Epiphaniometer	10 min	5 min	Pandis
Aerosol volume Distribution	Ultrafine SMPS, SMPS, APS, ELPI, Ultrafine CPC	10 min	5 min	Pandis
PM _{2.5} mass	FRM ⁶ , TEOM ⁷ , CMU Sampler ⁸ , LPI ⁹ , MOUDI ¹⁰	1 day	4-6 hr	Davidson
PM ₁₀ mass	FRM, TEOM, CMU Sampler, LPI, MOUDI	1 day	4-6 hr	Davidson
PM _k mass	LPI, MOUDI	1 day	4-6 hr	Davidson
PM _{2.5} ions and elements	CMU Sampler/ IC ¹¹ & ICPMS ¹²	1 day	4-6 hr	Davidson
PM _{2.5-10} ions, elements	CMU Sampler/ IC & ICPMS	1 day	4-6 hr	Davidson
HNO ₃ vapor	CMU Sampler/ IC & ICPMS	1 day	4-6 hr	Davidson
NH ₃ vapor	CMU Sampler/ IC & ICPMS	1 day	4-6 hr	Davidson
Size-resolved ions and metals	MOUDI/IC and ICPMS	-	4-6 hr	Davidson
PM _{2.5} OC and EC ¹³	Organic sampler/thermal	1 day	4-6 hr	Robinson

	PC-BOSS system ¹⁴ In-situ carbon analyzer	- -	4-6 hr 1-2 hr	Eatough Turpin
PM ₁₀ OC and EC	Organic sampler/thermal R&P sampler ¹⁵	1 day 1 hr	4-6 hr 1 hr	Robinson Robinson
PM _x OC and EC	ELPI/thermal	-	4-6 hr	Robinson
Organic speciation	Organic sampler/GC-MS ¹⁶	2 weeks	4-12 hr	Rogge
Organic size-resolved characterization	LPI/FTIR ¹⁷	-	24 hr	Turpin
Polycyclic Aromatic Hydrocarbons	MOUDI-PUF system ¹⁸ /GC-MS, HPLC ¹⁹ -fluorescence	-	12 hr	Miguel
Polar Organics	RSMS-II ²⁰	Continuous	Continuous	Wexler
Single Particle Chemical Composition	RSMS-II Filter/SEM ²¹ LIBS	Continuous - -	Continuous 4-6 hr Continuous	Wexler RJ Lee Buckley
Semi-continuous metals	HFAS/GFAA ²²	-	10-60 minutes	Ondov
Continuous nitrate	ICVC	Continuous	Continuous	Hering
Continuous sulfate	ICVC	Continuous	Continuous	Hering
Continuous carbon	ICVC	Continuous	Continuous	Hering
Bioaerosols	Epi-fluorescent microscopy, Molecular biology assays	1 day	Variable	Hernandez
Acidity	Filter-Thermodynamics	1 day	4-6 hr	Pandis
Visibility	Nephelometer Photos/Visual Range	Continuous 6 hr	Continuous 1 hr	Pandis
Growth with RH CCN concentration	TDMA ²³ /RSMS-II CCN Counter ²⁴	Variable Variable	Variable Variable	Pandis Pandis
RH, T, Wind UV and Solar Trajectories		Continuous Continuous 1 day	Continuous Continuous 4 hr	Davidson Pandis Kahl
VOCs	GC-FID ²⁵ , GC-MS	6 days	4-6 hr	Pandis
Hydrogen Peroxide	CSU Monitor	12 hr	1 hr	Collett
Organic Peroxides	CSU Monitor	12 hr	1hr	Collett
O ₃	Ozone Monitor	1 hr	1 hr	Pandis
NO and NO _x	NOx Monitor	1 hr	1 hr	Pandis
SO ₂	SO ₂ Monitor, Filter	1 hr	1 hr	Pandis
CO	CO Monitor	1 hr	1 hr	Pandis
Fog and cloud composition	CSU Collector ²⁶	Variable	1 hr	Collett

See Appendix 2 for a list of instrumentation acronyms

4.3 Instrument Development and Evaluation

The proposed Pittsburgh Supersite program will allow the further development of a number of PM measurement methods, provide comparisons among methods to be used in the next few years, and will serve as a platform for field comparisons of emerging methods that have the potential of addressing current PM measurement needs.

4.3.1 Further development of methods

Single Particle Measurements (RSMS-II). A number of improvements will be made to the current single particle instrument of the University of Delaware to make it more suitable for long-term Supersite use. A new RSMS-II instrument will be built for the Supersite that is relatively free of operator intervention and has improved analytical capabilities. A power monitor will be added to the rear of the laser to record pulse energies. The on-site computer will record the pulse power with each spectrum and if the power becomes too low automatically refill the laser gas. The instrument will record inlet flow and pressure and store them with each spectrum. The relationship between flow and pressure will be checked by the computer. Off calibration will indicate that the flow/pressure control orifices are clogged and need to be cleaned. Extra orifices of the smallest sizes will be included with each instrument since these clog more easily. Operator intervention to change orifices is straightforward.

Epiphaniometer. A calibration method for the conversion of the epiphaniometer signal to aerosol surface area will be developed by the Baltensperger and Pandis teams based on the laboratory work of Pandis et al. (1991) and Baltensperger et al. (1997). This will allow the use of the epiphaniometer as a continuous surface area monitor in urban areas.

Organic Aerosol Speciation. The Rogge team will add one more derivatization step, silylation using BSTFA [bis(trimethylsilyl)trifluoroacetamide], to their state-of-the-art organic extraction procedure. A suitable derivatization procedure will be developed that can be used in sequence with the current derivatization technique that uses diazomethane. Furthermore, a library of organic compounds, which are susceptible to BSTFA derivatization, will be generated that contains ion fragmentation patterns for those target derivatized compounds. This approach will among others detect levoglucosan, a tracer for cellulose formed from biomass burning (Simoneit et al., 1999).

Aside applying whole sample derivatization, a method will be developed based on the work of Simoneit et al. (1999) that fractionates sample extracts according to polarity into up to eight fractions that then will be derivatized and analyzed separately. By fractionating a sample extract according to polarity, more single compound resolution is obtained that will allow us to increase the pool of identifiable compounds.

Polar Organics. The University of Delaware team will develop a technique (described in 4.2.4) for the continuous measurement of the polar organic aerosol concentration on single particle basis.

Continuous-measurements. The proposed program will allow the continued development of a number of continuous PM measurement techniques to make them suitable for long-term monitoring. These methods include the continuous elemental (Ondov, Buckley), sulfate, nitrate, and carbon (Hering), ultrafine PM (Pandis), OC and EC (Turpin) measurements.

Bio-aerosols. The Hernandez group will develop rapid, quantitative aerosol assays to characterize the identity, distribution, and activity of microbiological components present in ambient aerosols.

4.3.2 Comparisons and evaluation of methods

The existence of several overlapping techniques will allow the intercomparison of existing measurement approaches and also the evaluation of new and emerging approaches. These intercomparisons are summarized in Table 3.

Table 3. Comparison of methods

Observable	Methods
Number distribution	SMPS – ELPI – APS – RSMS-II
Surface area	Epiphaniometer – SMPS/APS – ELPI
PM _{2.5} and PM ₁₀ mass	FRM – TEOM – Speciation Sampler – LPI – ELPI – MOUDI
PM Elements	Speciation Sampler/ICPMS – HFAS/GFAS – RSMSII – LIBS
PM Sulfate, Nitrate	Speciation Sampler/ICPMS – ICVC –RSMSII
PM Carbon	Speciation Sampler – Rutgers Sampler – ICVC – PC BOSS – RMSII – R&P Sampler
Polar Organics	Detailed Speciation – FTIR – RSMSII/MALDI

4.4 Indoor Exposure Research

Researchers in the Indoor Environment Department (IED) at Lawrence Berkeley National Laboratory (LBNL) will conduct an indoor PM_{2.5} study in Pittsburgh in conjunction with the Supersite program (not supported by the EPA Supersite funds). A letter of intent from LBNL is attached. The objective of this work is to better understand the relationship between ambient PM_{2.5} and actual exposures. The proposed work in Pittsburgh will build upon previous and current indoor aerosol studies conducted by LBNL. In particular, it will build upon a just-initiated LBNL project to develop and test a semi-empirical model for predicting indoor PM concentrations based on outdoor PM measurements. This LBNL project will be conducted in collaboration with the on-going San Joaquin Valley study (see, for example, Chow et al., 1993) and the new Supersite study in Fresno, CA (located in the San Joaquin Valley). The LBNL research group has also just initiated a complementary study with EPA sponsorship to investigate factors influencing indoor exposures to particles of outdoor origin.

The proposed indoor study in Pittsburgh is an important extension to the current LBNL research because of differences between Pittsburgh and the San Joaquin Valley. Significant differences include: differences in housing stock (e.g. older, with different construction), differences in climate (e.g. colder wintertime temperatures and higher summertime relative humidities), and differences in PM composition (e.g. sulfate instead of nitrate). As is the case in the LBNL San Joaquin Valley project, the proposed Pittsburgh study would take advantage of the extensive and detailed outdoor data collected by the intensive Supersite study. Knowledge about the composition and temporal variability of the outdoor 'source term' is critical to understanding the exposures indoors.

The indoor study will employ both experiments in an unoccupied research house and monitoring in one or more occupied homes. The research house will permit detailed examination of some of the factors influencing aerosol transport into and behavior within the house under controlled conditions. Examples of these factors include aerosol characteristics, housing characteristics, and weather conditions. Detailed measurements will include indoor aerosol size and concentration profiles and chemical speciation, as well as building and indoor environment characteristics. The research house will be located close to the central Supersite. For the duration

of the Supersite monitoring period, a more limited set of instruments will be used in one or more occupied homes or other residential buildings to examine the effect of human activity on relationship between indoor and outdoor PM.

An important result of this work will be the ability to test the semi-empirical indoor-PM_{2.5} model derived from the LBNL San Joaquin Valley study with data from Pittsburgh. Such a model would enable estimation of indoor exposures from the Supersite data. Detailed planning for the indoor study will be based on results from the LBNL study in the San Joaquin Valley (sampling is expected to begin 11/99) and on the detailed and intensive outdoor measurements to be performed at the Pittsburgh Supersite.

4.5 Epidemiological Study

The proposed monitoring study with its wide range of epidemiology-relevant measurements (see Tables 1 and 2), its daily sampling schedule, and 18 month duration in a populated urban area will result in a dataset of high quality and quantity. Availability of not only PM_{2.5}, PM₁₀ mass concentration and composition, but also PM_x, number distributions including the ultrafine size range, surface area (measured directly with the epiphaniometer), surface area distribution, organic speciation and polar organics, concentrations of aerosols from specific sources, etc., will provide a comprehensive data set for epidemiological studies. Samet and his group (in a study not funded by the Supersites program) will address the effects of particulate air pollution on readily available health indicators, including daily mortality counts and morbidity measures, such as hospitalization rates in general or among the elderly, rates of emergency room utilization, and rates of outpatient utilization. A number of publicly available data resources will be used for such analyses, supplemented by data from health care organizations or other provider networks. The basic study design will draw on time-series methods, already widely applied in air pollution research. The Pittsburgh Supersite program will provide a unique opportunity to discover the size, composition, and source of the particulate matter that most likely causes observed increases in mortality and morbidity. This first level analysis using traditional timeseries analysis techniques will be funded with available resources of the Johns Hopkins group. Additional resources for a panel epidemiological study in the Pittsburgh region will be requested by other funding agencies as soon as the EPA funds are committed. Groups of potentially susceptible individuals (persons with asthma, both children and adults, chronic obstructive pulmonary disease (COPD), ischemic heart disease, etc.) from the Pittsburgh community will be identified and their health status prospectively monitored and evaluated in relation to air pollution concentrations. The basic design will involve the identification of a feasible number of patients, generally ranging from 20 to 100, who are enrolled into a protocol involving daily assessment of health status, typically using both questionnaires and physiological measurements, and estimated exposure. A letter by Samet is included in the proposal.

The EPA Supersites program would be most informative if parallel data collection efforts were initiated at all sites. Coordinating as much as possible the various Supersites to use a wide range of common instrumentation, will allow the use of all Supersites data in conjunction to produce a much richer data set for epidemiological study. If gradients of heterogeneity in exposures within the selected communities could be defined, then analyses could be further stratified by location.

4.6 Three-Dimensional Modeling Study

The Pandis and Davidson groups are members of the EPA-STAR funded research consortium (Research Consortium on Ozone and Fine Particle Formation in California and in the Northeastern United States) investigating the interactions between the ozone and the PM problems in the Eastern United States. The objective of this research is to advance the understanding of emissions/air quality relationships for ozone and fine particles in the two most populous areas of the United States: California and the Northeastern states. The models developed are currently applied in both to study the effects of emissions controls on both ozone and fine particle air quality.

In collaboration with Ted Russell in Georgia Tech., these groups have created a comprehensive three-dimensional model for the study of PM_x in the region (see Appendix 2 for a description). The model includes a state-of-the-art description of PM processes and describes the complete aerosol size/composition distribution using user-selected chemical and size resolution. The model is also coupled to a sensitivity analysis module so it can calculate directly the sensitivities of PM concentrations to small changes in source strength.

The Pittsburgh Supersite Program will use the results of this parallel activity. For the EPA-STAR program the region around Pittsburgh will be described with high spatial resolution (5x5 km) and selected simulations will be run for the intensive periods focusing on:

- the lifetime and transport distances of PM reaching Pittsburgh
- the relationships between total nitric acid and sulfate in Pittsburgh and the NO_x and SO₂ emissions in the modeling domain, and
- the sensitivity of the PM in the area to these NO_x, SO₂, and VOC emissions
- the contribution of primary organic aerosol sources to the OC in Pittsburgh
- the contribution of primary and secondary biogenic aerosol to the organic PM in Supersite area.

5. HYPOTHESES AND THEIR TESTING

5.1 Ambient Aerosol Characterization

Hypothesis 1.1 *The measured aerosol mass can be fully explained if one accounts for the water retained by organics and inorganics, the full organic aerosol contribution, and the full crustal contribution.*

The available measurements will allow us to quantify all the known contributions to the aerosol mass. The TDMA measurements by the Pandis group will provide the residual water for the RH (30-40%) corresponding to the measurement of the aerosol mass. The FTIR measurements by the Turpin group together with the organic chemical speciation by the Rogge team will allow the estimation of the organic aerosol H, O, C, and N content and the accurate quantification of the total organic aerosol mass. The crustal component contribution will be quantified using the approach described by Andrews et al. (1999). The sum of these individual contributions will then be compared with the PM concentration.

Hypothesis 1.2 *The ambient aerosol surface area can be calculated with an error less than 20% using aerodynamic size measurements and assuming that all particles are spherical.*

The Epiphaniometer measurements will be used for the direct calculation of the surface area concentration of the particles as a function of time. These results will be compared with the surface area concentration estimated from the number distribution measurements of the two Differential Mobility Analyzers and the Aerodynamic Particle Sizer assuming spherical particles. The results of the two approaches will be compared to quantify the magnitude of the error introduced by assuming spherical particles. The samples will be analyzed by SEM during periods where the two measurements are in agreement or when large discrepancies appear to independently check the particle shape.

5.2 Measurement Methods

Hypothesis 2.1 *Single Particle Mass Spectrometers can be used to obtain the full number and mass composition distributions of ambient aerosols.*

The Wexler team is currently developing methods for the quantitative interpretation of the single particle measurements. The millions of available measurements (a typical rate is one particle per second) will be combined to produce a multi-dimensional aerosol size/composition distribution. These distributions will be compared with the ones measured by the traditional instruments (impactors, filter-based measurements, differential mobility analyzers, aerosol particle sizers, and others) and the method will be further developed if necessary. The results of the single particle instrument will also be compared against the suite of continuous measurements in the site (continuous sulfate, nitrate, metals, and size distributions). Our hypothesis is that by the end of the proposed program, an approach will be available both for the operation and the analysis of the single particle mass spectrometer data that will allow it to produce quantitative results in agreement with the traditional instruments.

Hypothesis 2.2 *Semi-continuous nitrate, sulfate, carbon and elements measurement technique can quantify their concentrations under conditions prevalent at the site.*

The semi-continuous measurements of nitrate, sulfate, and carbon by ADI, and the elemental measurements by Ondov and Buckley will be compared with the more traditional filter and impactor based measurements to evaluate their performance.

Hypothesis 2.3 *There is a negative artifact from sampling nitrate over several hours and it can be avoided by employing semi-continuous techniques.*

Size-resolved measurements of the PM in the Eastern US have indicated that the available nitrate often exists in particles larger than 1 micrometer or so, while the smaller aerosol particles are often acidic. Interaction among the two groups of particles can result in volatilization of the available nitrate, even for sampling systems using denuders and after-filters. This hypothesis will be tested by the comparison of the daily and 4-6 hr measurements with the continuous measurements of the Hering team. The sodium carbonate backup filters will also be analyzed to quantify this effect.

5.3 Atmospheric Processes

Hypothesis 3.1 *Aerosol nucleation (biogenic precursors or SO₂) can be a major source of aerosol number in both urban and rural areas in the study region.*

The measurements of the ultrafine aerosol number concentration both in the central site and in the rural Holbrook site will allow the Pandis group to quantify the contribution of nucleation as a source of particle number. The primary contributions to ultrafine particle concentration (e.g.,

from transportation) will be quantified. These contributions are usually plumes that influence the site for a few minutes at random periods. Nucleation events in urban areas like Atlanta (McMurry personal communication) and Leipzig, Germany (Weidensholer et al., 1998) last for an hour or more and sometimes are associated with significant photochemical activity but sometimes they occur early in the day. Comparing the measurements in both sites will allow us to investigate if these nucleation events are a regional phenomenon or a local phenomenon. The contribution of these events to particle number concentrations will be quantified. Correlations of these events with the measurements of SO₂, RH, Temperature and biogenic concentrations will provide insights about the species involved in the nucleation events. The single particle measurements of the University of Delaware team will be used to quantify for the first time the composition of these nuclei. Understanding the source of these particles will be a major advancement for the atmospheric chemistry research area.

Hypothesis 3.2 *Biogenic primary and secondary aerosols are a major component of the organic aerosol in the Pittsburgh region.*

Recent laboratory, source, and field studies (Table 3) have identified a number of tracer compounds for primary and secondary biogenic aerosols. The Rogge group will measure their concentrations and the contributions of the corresponding sources or precursors will be estimated using them as tracers (Rogge et al., 1993a).

The contribution of these biogenic sources to PM will also be estimated theoretically during the EPA-STAR project by the Carnegie Mellon team. As a third way of quantification of the biogenic contribution selected samples will be composited and sent for ¹⁴C analysis to provide the non-fossil component.

Table 3. Some Tracer compounds for Biogenic Organic Aerosols

Organic Aerosol Component	Tracer Compounds	Reference
Primary Biogenic	C ₂₇ , C ₂₉ , C ₃₁ , C ₃₃ n-alkanes	Mazurek and Simoneit (1984) Simoneit (1984) Rogge et al. (1993c)
Secondary – a-pinene	Pinonaldehyde Pinonic acid Pinic acid	Kamens et al. (1998) Kavouras et al. (1999)
Secondary – b-pinene	Nopinone	Paulson et al. (1989)

Hypothesis 3.3 *Fogs and low clouds are responsible for extreme acid sulfate conditions in the Pittsburgh region since (a) there is substantial SO₂ imported from the west, and (b) aqueous phase oxidizers, such as hydrogen peroxide, are present in significant concentrations.*

Published rate laws will be used by the Collett group along with measured cloud/fog composition and gaseous H₂O₂, O₃, and SO₂ concentrations to determine rates of aqueous phase sulfate production in sampled clouds/fogs. Rates will be compared for several possible S(IV) oxidation pathways, including oxidation by H₂O₂, oxidation by O₃, and trace metal catalyzed auto-oxidation, in order to test our hypothesis that aqueous sulfate production is limited by the availability of H₂O₂. Concentrations of major ions in the cloud/fog samples (µg/l) will be multiplied by fog/cloud liquid water content (I_{H₂O}/m³_{air}) to determine the total concentrations of major ionic species contained in fog/cloud drops per unit volume of air (µg/m³). These values will be compared to measurements of total airborne concentrations of these species made at the

site in order to determine the fraction of each species undergoing cloud/fog processing. In several cases, cloud/fog concentrations must be compared with the sum of aerosol and gas concentrations (e.g., aqueous nitrate is derived from scavenging of both aerosol nitrate and gaseous nitric acid). The contribution of the fogs in the area will be estimated combining these measurements with the frequency of these events in the study area. The possibility of these events leading to high concentrations of sulfate the day after the fog episode will be investigated.

Hypothesis 3.4 *The response of $PM_{2.5}$ to changes in sulfate is highly non-linear during the winter and linear during the summer and is controlled by the ammonia availability.*

Ansari and Pandis (1999) suggested that the response of the fine PM to sulfate concentration changes can be estimated by describing the atmospheric condition space by three parameters, the total (gas and particulate) nitric acid, the temperature, and a parameter:

$$GR = (\text{total ammonia moles} - 2 * \text{sulfate moles}) / (\text{total nitrate moles})$$

West et al. (1998; 1999) showed that daily aerosol samples are sufficient for the calculation of the system response to sulfate. All of the above quantities will be measured by the Davidson group, allowing the parametric investigation of the changes of the observed sulfate concentrations with respect to these three parameters. The linearity of the relationship will be investigated based only on the measurements during the 18 months of sampling (more than 1000 samples should be available). The response of the PM to total ammonia availability for constant temperature and GR values will be quantified. This analysis will provide the sensitivity of the PM concentrations to ammonia availability. The sensitivity of the PM concentrations to sulfate and nitric acid will be quantified by a similar analysis. The sensitivities of the system to these components will be quantified based on the measurements and will be compared with each other.

These results will be compared with the graphical approach of Ansari and Pandis (1999). The modeling work of the CMU group (funded by the EPA-STAR program) will be used to further investigate this relationship and also to elucidate the links between NO_x , and SO_2 emissions and nitric acid and sulfate concentrations in Pittsburgh.

Hypothesis 3.5 *The secondary aerosol contribution to OC exceeds 50% during the peak PM days, but is around 20% on a yearly average basis (based on similar contributions estimated for the Western US).*

The calculation of the primary and secondary organic aerosol contributions to the organic aerosol concentrations in the area will be one of the major tasks of the Supersite Project. Three different approaches (Strader et al., 1999) will be used:

(a) The OC/EC ratio method will be used by the Turpin group especially for the intensive sampling periods where 1-2 hr measurements will be available. Time-resolved elemental carbon concentrations will be used as a tracer for primary combustion-derived aerosol. The relationship between elemental carbon and organic carbon on days when secondary formation is unlikely and the approach of Strader et al. (1999) will be used to develop an expression that describes the primary organic carbon as a function of the elemental carbon concentration. Secondary organic carbon will be considered to be the difference between total and primary organic carbon. Thus, one-hour average organic and elemental carbon will be reported, as well as primary and secondary organic carbon.

(b) The organic tracer method will be used by the Rogge group to quantify the contributions of the various primary sources and to estimate the secondary organic aerosol fraction.

(c) The direct modeling method for the quantification of the secondary contribution will be used by the parallel modeling effort of the CMU/Georgia Tech. groups.

Hypothesis 3.6 The regional contributions to the PM_{2.5} levels in the Pittsburgh region for some compounds exceed the local contribution, whereas for others the local exceeds the regional.

The parallel measurements in the rural satellite site in Holbrook will provide values of the regional PM concentration and composition. These results will be compared with the values measured in the central Supersite to distinguish the regional and local contributions. The PM components that are enriched in the urban area will be quantified. Air trajectories by the Kahl group for the periods of interest will be used to inform this comparison. Measurements from different sites along the same trajectory will be compared for the appropriate time periods.

The University of Delaware team will also quantify the regional or local sources for the various particles. Once the single particle spectra are classified, their spectra will be examined to determine their source and atmospheric processing they have undergone. Typical sources of the condensation nucleus that can be identified include homogeneous sulfuric acid - water and organic nucleation, soot, biogenic materials, metals, and crustal material. The nuclei then undergo atmospheric processing that includes condensation of vapors and cloud processing that increase the particulate mass of secondary compounds. Typical secondary components that can be identified include sulfates, nitrates, and aromatic condensible organics. Both composition and back trajectories will be used to identify the likely source of the nucleus and the secondary species contributions on a particle-by-particle basis.

The estimates based on measurements will be compared with the theoretical predictions of the 3D modeling effort to provide further insights into the two contributions.

5.4 Source-Receptor Relationships

Hypothesis 4.1 A complementary suite of instruments (single particle instruments, continuous composition monitors) and techniques (enhanced organic tracers, inorganic tracers) can directly determine the local air quality contributions from a broad range of sources including a) primary emissions from power plants fired by coal, oil, or gas, diesel- or gasoline-powered transportation, meat cooking, coke plants, biogenics, biomass burning, incineration, and crustal sources and b) secondary compounds emitted from power plants, and transportation systems.

Methods with single particle resolution (RSMS-II, LIBS, SEM), continuous operation (metals) and the availability of a wide range of organic and inorganic tracers provide a unique opportunity to develop the next generation of source-receptor methods that combine all of this information to apportion all the PM components to their sources. For example, it could become possible to identify a specific particle as the product of coal combustion, on which ammonium nitrate and biogenic secondary organic material has condensed. A DOE funded study by the Robinson/Pandis groups on source characterization in the area will provide source-fingerprints for the major local sources (coke ovens, power plants, transportation, and others) using the same instrumentation. The EPA/STAR modeling project will investigate theoretical methods for combining these approaches to provide daily source apportionment for the study period. The result will be daily source-resolved PM, which can be used both by local authorities for SIP development, and by the epidemiological study (see hypothesis 6).

Hypothesis 4.2 *An increase in temporal resolution of elemental constituents of atmospheric aerosol coupled with sulfate and carbon analyses of comparable frequencies will permit (a) unprecedented resolution of sources by receptor modeling techniques, e.g., Factor Analysis (FA), Multi-Linear Regression (MLA), and Chemical Mass Balance (CMB) analyses, (b) resolution of plumes from individual stationary sources impacting the site, and (c) resolution of local and regional sources.*

The hypothesis that higher frequency sampling rates will improve source resolution based on inorganic tracers will be tested by the Ondov group with limited applications of FA and MLR on the most highly resolved data and composited data. Evidence that plumes from stationary sources can be resolved will be tested by comparing time series plots of the elements with wind roses and results of FA and MLR for these periods. The hypothesis that local and regional sources can be resolved will be tested by comparing time series data collected simultaneously at the two sites.

Hypothesis 4.3 *Specific aerosol signatures are associated with transport from specific source regions and along different altitudes.*

The air trajectories calculated by the Kahl group will be statistically compared with the aerosol measurements. This statistical analysis will demonstrate the relationships between the origin and path of the air masses affecting the region and the measured aerosol concentration and chemical composition.

5.5 Aerosol Properties

Hypothesis 5.1 *Visibility in the area can be predicted from RH and size/composition information obtained from aerosol sizing instruments and size-resolved bulk chemistry instruments (MOUDI).*

The scattering measurements of the nephelometer will be compared with the theoretically estimated values using the visibility model of Pilinis (1989). The input to the model will be the measured size/composition of the aerosol (from aerosol number distribution measurements and impactor measurements).

Hypothesis 5.2 *Most particles in the area are liquid throughout the day in both winter and summer.*

The single particle measurements by the University of Delaware will provide qualitative evidence for the existence of water in the ambient particles as a function of RH and chemical composition. The TDMA evaporation experiments (gradually decreasing the RH) by the Pandis group will quantify this liquid water content for the submicrometer particles. A smooth change in size as the RH decreases will indicate the existence of metastable particles existing as supersaturated solutions. If different particles exhibit different size changes after the RH decrease the single particle instrument will be used to quantify their composition. The combination of the two techniques will provide the quantitative link between liquid water content of the particles, RH, and their chemical composition.

Hypothesis 5.3 *Aerosol in the area consists of two groups of particles based on the hygroscopic properties: those consisting mainly of sulfates that grow rapidly with relative humidity and those consisting of mainly carbonaceous material that grow slowly.*

The TDMA growth experiments coupled with the single particle measurements of the RSMS-II will be used to investigate the link between chemical composition of particles and their ability to grow with increasing RH. This unique experiment will measure for the first time the chemical composition of often observed “more” and “less hydrophilic” atmospheric particles.

5.6 Health Effects

Hypothesis 6 *The health effects attributed to PM are due to one of the following characteristics shown in Table 1 or a combination of these.*

All of these characteristics (with the exception of the individual source contribution) will be measured directly during the Supersite Program for 18 months with at least daily resolution by a variety of groups and often using multiple approaches. The measurement program will result in a comprehensive database of PM characteristics for use in epidemiological studies. The Samet group will use this PM characterization together with measurements of health outcomes (mortality, morbidity, and others) to investigate the links between the two.

5.7 Indoor Exposure

Hypothesis 7.1 *There is significant seasonal variability of the contribution of outdoor PM_{2.5} to indoor PM_{2.5} levels.*

The PM_{2.5} measurements in the research house, which will be located near to the central Supersite location, will be performed for a few weeks every season. The measurements will be directly compared to the outdoor measurements to investigate the seasonal variability of indoor to outdoor fine PM concentrations.

Hypothesis 7.2 *Regional housing stock characteristics influence PM_{2.5} penetration.*

The data collected in Pittsburgh houses will be compared to those currently being collected by the LBNL team in houses in the San Joaquin Valley. These results together with analysis of the corresponding house characteristics will be used to investigate the role of regional variations in housing stock on indoor PM exposure.

Hypothesis 7.3 *Sulfate can be used as a tracer for the penetration of ambient PM indoors as a function of size.*

The indoor and outdoor sulfate PM_x concentrations will be compared to establish the relationship between the corresponding concentrations as a function of PM size.

Hypothesis 7.4 *Transport and fate of outdoor PM to and in the indoor environment is size and composition dependent.*

For selected days the indoor and outdoor size-resolved PM concentrations of the major concentrations will be compared. The possibility of significant changes in nitrate and semivolatile organics concentrations as the particles enter the indoor environment will be investigated. We hope to use a second single particle mass spectrometer owned by the Wexler group to perform this comparison for the first time on a single particle basis.

6. RESULTS AND BENEFITS EXPECTED

The following results are expected from the Pittsburgh Supersite program:

- Comprehensive characterization of the PM in the study area. This will include, size distribution, composition as a function of size and for individual particles, temporal and spatial variation, optical and hygroscopic properties.
- Development and evaluation of state-of-the-art instrumentation and measurement approaches (single particle instruments, continuous measurement approaches)
- Apportionment of the measured PM (both primary and secondary) to sources as a function of time. These results should be valuable for SIP development.
- Establishment of links between the PM characteristics and health effects in the study area.
- Quantification of the relationship between indoor and outdoor PM concentrations in the region.
- Development of a dataset (in coordination with the other Supersites) for the evaluation of the approaches used for the description of PM processes in atmospheric chemistry models.

7. GENERAL PROJECT INFORMATION

7.1 Personnel

Twenty different groups from thirteen universities, one national laboratory, two private companies, and one federal agency will be involved in the project. Team members in addition to Carnegie Mellon University include:

Collaborator	Task	Funding
Prof. Anthony Wexler, Prof. Murray Johnston (Univ. of Delaware)	Single Particle Mass Spectroscopy	EPA-DOE
Prof. Wolfgang Rogge (Florida Intern. Univ.)	Organic aerosol speciation	EPA
Prof. Mark Hernandez (Univ. of Colorado)	Biaerosols	EPA
Prof. Jeff Collett (Colorado State Univ.)	Peroxides, cloud and fog composition	EPA
Dr. Suzanne Hering (Aerosol Dynamics)	Real time nitrate and sulfate	EPA
Prof. Jonathan Kahl (Univ. Wisconsin)	Air trajectories	EPA
Prof. Barbara Turpin (Rutgers Univ.)	High-res. OC/EC, FTIR of organics	DOE
Prof. John Ondov (Univ. of Maryland)	Semi-continuous metals	DOE
Prof. Steven Buckley (Univ. of Maryland)	Laser Induced Breakdown Spectroscopy	DOE
RJ Lee Instruments Ltd.	Single particle composition, morphology	DOE
Professor Kevin Crist (Ohio University)	Satellite sites	DOE
Dr. Antonio Miguel (Univ. Calif. Riverside)	PAHs and organic speciation	DOE
Prof. Delbert Eatough (Brigham Young Univ.)	Organic aerosol sampling	DOE
Dr. Urs Baltensperger (Paul Scherrer Institute)	Surface area	Other
Professor Jonathan Samet (Johns Hopkins)	Epidemiological study	Other
Dr. Richard Sextro (Lawrence Berkeley Nat. Lab)	Indoor study	Other
Dr. Thomas Feeley (DOE-FETC)	Site management and coordination	Other

The Carnegie Mellon University team of Professors Spyros Pandis, Cliff Davidson, and Allen Robinson will coordinate and lead the overall effort. Dr. Pandis will direct the measurements of aerosol size distributions, acidity, hygroscopic properties, VOCs, and visibility.

Dr. Davidson will be responsible for the measurements of PM mass concentration and inorganic composition. Dr. Robinson will be responsible for the measurements of OC/EC and data management. Both EPA and DOE/FETC funds will support the work at Carnegie Mellon University.

The project will support 12-15 Ph.D. and approximately 10 undergraduate students who will be advised by the corresponding investigators. The students will be educated in using state-of-the-art sampling and analysis methods. This study is a natural extension of the investigators' research interests and therefore other graduate students in their groups will also be involved.

7.2 Project schedule

A general schedule of key dates for the overall project is given below.

Task	2000				2001				2002				2003			
	W	Sp	Su	F												
Site																
Finalize site location	■															
Site preparation		■	■	■	■											
Site restoration												■	■			
QA/QC																
Finalize QA/QC	■	■														
Qual. Management Plan	■	■														
Sampling																
Baseline						■	■	■	■	■	■					
Intensives						■			■	■						
Data Analysis																
Preliminary analysis						■	■	■	■							
Hypothesis testing									■	■	■	■	■	■	■	
Reporting																
Planning reports	■	■														
Progress reports		■		■	■	■		■	■	■		■	■	■		
Final report															■	■
Additional Studies																
Indoor Study							■	■	■	■						
Epidemiology							■	■	■	■	■	■	■	■	■	■

7.3 Summary of qualifications to conduct the proposed research

We believe that the proposed team can make a strong and innovative contribution to the current understanding of ambient PM characteristics, PM measurement methods and provide the necessary input to regulatory agencies, assisting in their effort to improve air quality at lower costs. The project team has considerable experience in ambient measurements, analysis and modeling of photochemical pollution and aerosol processes. The investigators have had extensive and highly productive interactions in the past with the Environmental Protection Agency (EPA), Department of Energy (DOE), California Air Resources Board (CARB), the South Coast Air Quality Management District (SCAQMD), the Electrical Power Research Institute (EPRI), Coordinating Research Council (CRC), Southern California Edison, and other agencies. The previous projects serve as models of how we intend to carry out the proposed project.

research. In addition, many of the collaborators have budgeted funds to come to planning sessions at Carnegie Mellon University. To facilitate coordination between the different Supersites, the Principal Investigators will attend the twice-annual Supersite review and planning meetings at Research Triangle Park, NC.

Data management: The Carnegie Mellon University team will handle overall data management. Initial data management, such as merging particle mass with flow rate measurement, will be performed by the investigator that is making the measurements. Individual investigators will also be responsible for checks involved in Level 1 validation and quality control test data. The data manager at Carnegie Mellon University will bring the data from all of the investigators together. The data manager will perform Level 2 validation checks and construct the project data archive.

The raw data will be posted on our password-protected web site (a lot of them in real time) to be accessed by the various project groups and our collaborators in EPA. After the quality assurance and quality control has been completed we would like to provide a reasonable time (around one year) to the various participating groups to submit their work for publication. During this period we will try to accommodate as much as possible the various research groups who may want access to parts of the database. We will be very flexible during this transition period and try to share the available information with other supersite teams or other researchers without compromising the intellectual property rights of the various investigators of the Pittsburgh Supersite team and the EPA collaborators. When the papers are accepted for publication or a year after the QA/QC has been completed (whichever comes first) the corresponding data will be available to everybody (scientific community and public) through our web site. We foresee that the whole dataset will be available to the public by the end of 2004.

Site management: Carnegie Mellon University has budgeted funds to hire a site manager for the project. Among the responsibilities of the manager will be to oversee the day-to-day operations of the site.

7.5 Facilities

A location in Schenley Park has been selected by the CMU team for the central sampling site. This is a large grassy area adjacent to the CMU campus, several hundred meters from the nearest heavily traveled street (Forbes Avenue), roughly 50 meters past the end of a dead end street on campus. There are no major sources within several hundred meters of the site. Schenley Park extends more than a kilometer to the south and west, the predominant upwind directions. Discussions are underway with the City Planning Department to obtain permission to locate several trailers with electric power at the site.

The air pollution laboratories in CMU will serve as the center for the preparation, maintenance, and calibration of the monitors. To supplement the existing facilities, the College of Engineering at Carnegie Mellon is developing a new air pollution laboratory to support the Supersite project. The new laboratory space is approximately 1500 square feet. Carnegie Mellon University has pledged to renovate the space at a cost of \$500,000 such that it is appropriate for contamination controlled air pollution. A letter indicating this support is attached

to the end of the proposal. Description of the individual investigator facilities is included as an appendix.

7.6 Reporting

A set of technical reports will be generated over the course of the study. Individual investigators will prepare technical report as they complete their analyses. This material in combination with progress reports will be used to prepare semi-annual progress reports and the final technical report describing the results and findings of the entire project. The results of the study will be presented at technical meetings and published in international peer-reviewed journals. Individual investigators will also prepare papers about detailed aspects of the work. The Pittsburgh Supersite team is committed to making the data from the project available in an easily accessible fashion. The Pittsburgh team will work with EPA and the other Supersites to establish a protocol and framework for reporting the Supersite data.

7.7 Collaboration with EPA Researchers

We intend to keep the Supersite Program open to scientists in the EPA and as much as possible to the rest of the scientific community. Collaboration may include participation in the field campaign (e.g., to test new instruments or technologies, to evaluate additional methods, or to measure additional components), sharing of the data to test additional hypotheses, combination of the supersite results with other studies, etc. We have already identified a number of opportunities for collaboration with various research groups in EPA and we will actively pursue and remain open to additional opportunities.

We will work with the Monitoring and Quality Assurance Group (R. Scheffe, etc.) to coordinate the operation of the Pittsburgh Supersite and its satellite sites with the EPA Speciation and PM networks to provide the best available data set for the area of interest. The collaboration will also include sharing information about the performance of the various PM monitors, our quantification of the various artifacts for the study area, etc. We will continue our collaboration with Bruce Harris (RTP) and his colleagues in developing methods for measurements of ammonia and other semivolatile inorganic aerosol components. Our work on the formation of secondary organic aerosol, its speciation, and properties will be coordinated with the work of E. Edney and colleagues in the National Exposure Research Laboratory. On the modeling front we plan to continue our collaboration with the scientists (R. Dennis, J. Ching, F. Binkowski, etc.) of the Atmospheric Sciences Modeling Division using the Supersite measurements to evaluate and improve atmospheric chemistry models like MODELS-3. We will explore the potential collaboration with the scientists of the National Health and Environmental Effects Research Lab (especially the Human Studies and Toxicology Divisions). This collaboration will ensure that the proposed comprehensive air quality study in Pittsburgh will be accompanied by high quality epidemiology studies and will take advantage of the latest results in PM toxicology. As the epidemiology component of the Pittsburgh Supersite is still evolving, the details of this collaboration have not been discussed yet with the corresponding EPA scientists. Finally, the LBNL group lead by Sextro will continue and expand their collaboration with the EPA researchers working on indoor air pollution, and exposure assessments.

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APPENDICES

APPENDIX 1. LETTERS OF SUPPORT

1. **Department of Energy – Federal Energy Technology Center (DOE/FETC)**
2. **Jonathan Samet** (Johns Hopkins University)
3. **Lawrence Berkeley National Laboratory – Indoor Environment Department (LBNL/IED)**
4. **Jared Cohon** (President, Carnegie Mellon University)
5. **John Anderson** (Dean of Engineering, Carnegie Mellon University)
6. **Richard Ode** (Bayer Corporation)
7. **James Salvagio** (Pennsylvania Department of Environmental Protection)
8. **Roger Westman** (Allegheny County Health Department)

APPENDIX 2.

ADDITIONAL INFORMATION ABOUT PROPOSED APPROACH

2.1 Estimated Annual Average PM concentrations

Pittsburgh is an area influenced by reasonably well-defined local, remote, and biogenic sources (Figure A.1). This will make source-receptor relationships much easier to quantify compared to areas closer to the eastern seaboard where the urban centers interact with each other strongly. The estimated annual average $PM_{2.5}$ concentration for the Supersite location is approximately $20 \mu\text{g m}^{-3}$ (Falke, 1999). The maximum daily average measured PM_{10} concentration in the area in 1998 was approximately $150 \mu\text{g m}^{-3}$.

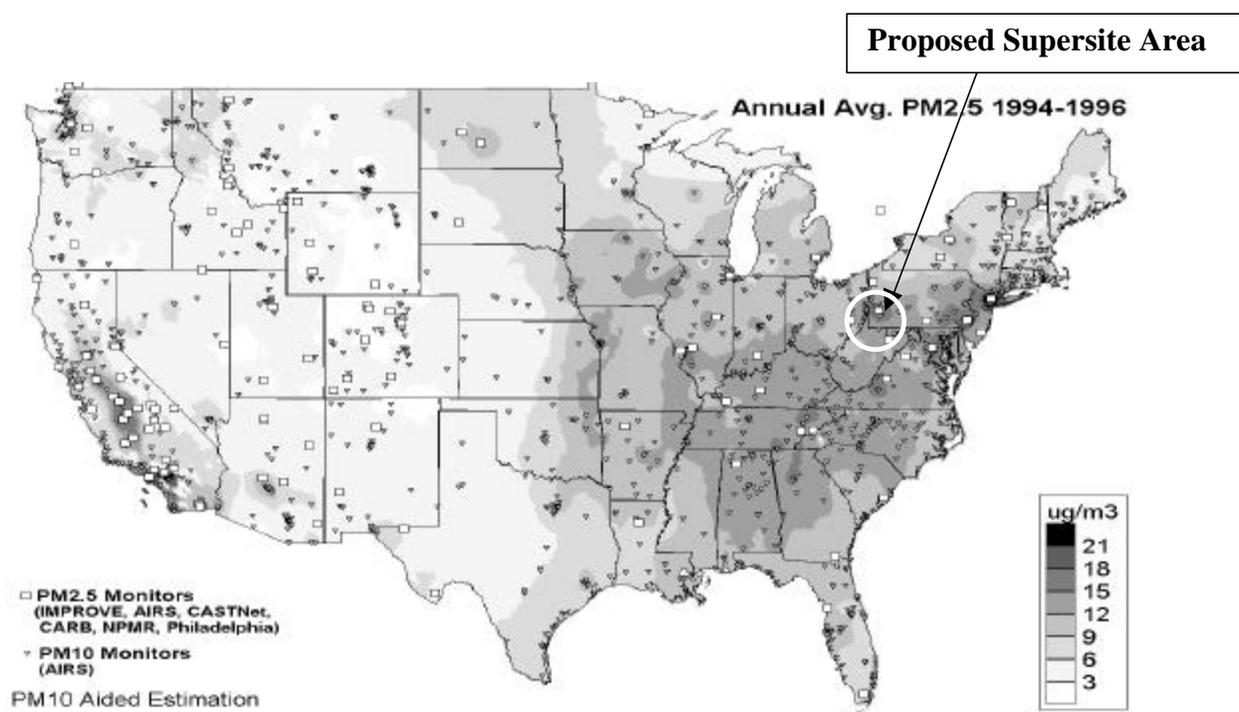


Figure A.1 Annual average $PM_{2.5}$ concentrations (1994-1996) derived from PM_{10} aided spatial estimation, Falke (1999).

2.1 Acronyms

A list of definitions of acronyms for instrumentation (see Table 2) follows:

¹ Ultrafine SMPS: Scanning Mobility Particle Spectrometer (TSI model 3936N25) for 0.003-0.150 μm

² SMPS: Scanning Mobility Particle Spectrometer (TSI model 3934L) for 0.01-1.0 μm

- ³ APS: Aerodynamic Particle Sizer Spectrometer (TSI model 3320) for 0.5-1.0 μm
- ⁴ ELPI: Electrical Low Pressure Impactor (Dekati)
- ⁵ Ultrafine CPC: Ultrafine Condensation Particle Counter (TSI model 3025A) for 0.003-10 μm
- ⁶ FRM: Federal Reference Method PM_{2.5} Sampler
- ⁷ TEOM: Tapered Element Oscillating Microbalance PM_{2.5} Sampler
- ⁸ CMU Sampler: Carnegie Mellon University system shown in Figure 2
- ⁹ LPI: Low Pressure Impactor developed by Susanne Hering
- ¹⁰ MOUDI: Micro-Orifice Uniform Deposit Impactor
- ¹¹ IC: Ion Chromatography
- ¹² ICPMS: Inductively Coupled Plasma Mass Spectrometer
- ¹³ OC and EC: Organic Carbon and Elemental Carbon
- ¹⁴ PC-BOSS: Particle Concentrator-Brigham Young University Organic Sampling System. Analysis is conducted for several species: sulfate and nitrate (IC), NH₄⁺ (spectrophotometry), OC/EC (Temperature Programmed Volatilization analysis), pH and acidity.
- ¹⁵ R&P sampler: Ruprecht and Patashnik sampling system
- ¹⁶ GC-MS: Gas Chromatography-Mass Spectrometry
- ¹⁷ FTIR: Fourier Transform Infrared Spectroscopy
- ¹⁸ MOUDI-PUF system: MOUDI-Polyurethane Foam plug preceded by a cyclone and denuder
- ¹⁹ HPLC: High Performance Liquid Chromatography
- ²⁰ RSMS-II: University of Delaware Single Particle Mass Spectrometer
- ²¹ SEM: Scanning Electron Microscopy
- ²² HFAS/GFAA: High Frequency Aerosol Sampler/Graphite Furnace Atomic Absorption Spectrophotometry
- ²³ TDMA: Tandem Differential Mobility Analyzer
- ²⁴ CCN Counter: Cloud Condensation Nuclei Counter manufactured by DH Associates
- ²⁵ GC-FID: Gas Chromatography-Flame Ionization Detector
- ²⁶ CSU collector: Colorado State University cloudwater collector

2.2 Speciation of Organic Aerosol

The material collected in the denuder, the filter and the PUFs will be analyzed by an improved GC/MS technique developed by the Rogge group for the quantification of the concentrations of individual compounds. The proposed improved technique (for details see section 4.3) will allow the increase of the pool of organic compounds that can be chromatographically separated and made elutable from the gas chromatographic column used. Daily filter samples will be collected throughout the sampling campaign. Collected filter samples will be grouped into biweekly composites and analyzed together, yielding biweekly average ambient fine particle organic compounds concentrations. Each 29th day, XAD-Denuder/Filter/PUF sampling will be conducted and the entire set will be analyzed separately to

obtain additional detailed information about the partitioning of semi-volatile organic compounds between the gas- and particle-phases. During the intensive sampling periods the sampling frequency will be increased to two samples per day (12 hour samples) and the XADs, filters, and PUFs each will be analyzed separately. For 2 days of two intensive campaigns, 4 hours sampling will be conducted and all XADs, filter, and PUFs analyzed separately. The proposed schedule will provide a unique dataset with high temporal and chemical resolution that will broaden the knowledge about the chemical composition of organic particulate matter. This dataset will allow the Rogge group to derive source/receptor relationships using their published organic source profiles together with the collected ambient data.

Each of the samples (XAD, filter, PUF), and composited filter samples will be spiked with 7 deuterated recovery standards before extraction. XAD will be extracted successively four times with a mixture of dichloromethane/acetone/hexane (2:3:5) (Gundel et al., 1995). Quartz fiber filters will be extracted with dichloromethane three times using mild sonication. Similarly, PUF samples will be extracted three times with dichloromethane in a specially designed apparatus that allows to repeatedly compress the PUF foam plug. After extraction, the sample volume will be reduced to about 0.5 to 2.0 ml and divided into two aliquots. One aliquot will be used for derivatization with diazomethane to convert organic acids to their methyl ester analogues and acidic hydroxy compounds to their respective methoxy analogues. After the derivatization, both sample aliquots will be stored in a freezer until analysis by GC/MS. In order to make other polar organic compounds accessible to chromatography, a method will be developed and refined during this project that uses BSTFA [bis(trimethylsilyl)trifluoroacetamide] for compound derivatization by silylation (Simoneit et al., 1999). Furthermore, for selected samples, silica gel column chromatography will be conducted with 8 different eluting solvents, fractionating the sample extract according to compound polarity. Solvent elution sequence includes: (F1) hexane, (F2) hexane/toluene (3:1), (F3) hexane/toluene (1:1), (F4) hexane/ethyl acetate (19:1), (F5) hexane/ethyl acetate (9:1), (F6) hexane/ethyl acetate (6:1), (F7) hexane/ethyl acetate (4:1), and (F8) methanol. In order to obtain quantifiable fractions, a method will be developed that allows to quantitatively track the fractionation and conversion of the polar fractions into GC chromatographic derivatives.

Extract analysis will be accomplished using a Hewlett-Packard Model 5973 quadrupole mass spectrometer coupled with a HP 6890 series gas chromatograph. At least the following compound classes will be searched for and when identified also quantified: n-alkanes, n-alkanoic acids, n-alkanols, n-alkanones, furans, furanones, resin acids, levoglucosan, sterols, PAHs, compounds identified in smog chamber experiments as possible secondary organic atmospheric reaction products, and others. As far as available, high purity standards will be used to aid quantification. Beyond the listed compounds, every effort will be made to identify in a few selected samples everything possible, applying the extract derivatization and fractionation methods to be developed.

2.3 Size-resolved FTIR spectra with solvent rinses

Size-segregated samples will be collected on five impaction stages with cut points between 0.05 and 2.0 μm for 24 hours on ZnSe disks at 1 lpm using a Hering Low Pressure Impactor (LPI) during the three intensive periods. Spectra will be taken of a clean area of the ZnSe disk and of the deposit using a Mattson Research Series 100 FTIR spectrometer, and spectral results

will be presented as the percent of incident light absorbed versus wavenumber. Each spectrum will be an average of 200 spectral scans at 2 cm^{-1} wavenumber resolution. Functional groups will be identified based on spectral libraries and standards. Instrumental sensitivity will be evaluated by daily analysis of a standard thickness polystyrene film and weekly analysis of KBr pellets comprised of mixtures of organic and ammonium sulfate standards. Following initial analysis samples will be gently rinsed with spectral-grade hexane, spectral-grade acetone, and deionized water and reanalyzed after each rinse. The rinse is performed by holding the substrate at a 45° angle and applying 1 ml of solvent to the deposit from a pipet. The solvent is allowed to flow slowly over the deposit for approximately 5-10 seconds. This process will be repeated twice. The substrates are then air dried and reanalyzed by FTIR. Acetone is applied to the sample after the final water rinse to facilitate drying. Spectra are integrated using GRAMS 32 peak integration software and functional group absorbances are quantified relative to sulfate.

2.4 LIBS

Laser-Induced Breakdown Spectroscopy (LIBS) is an optical technique that can be used to detect trace inorganic species and particles at femtogram-picogram levels in combustion products and in the ambient atmosphere. LIBS has been used as an analytical technique for gases, liquids, and solids (Song et al., 1997; Schechter, 1997). Applications of LIBS employ a pulsed laser with a high peak power to form a spark (breakdown) in the medium to be examined.

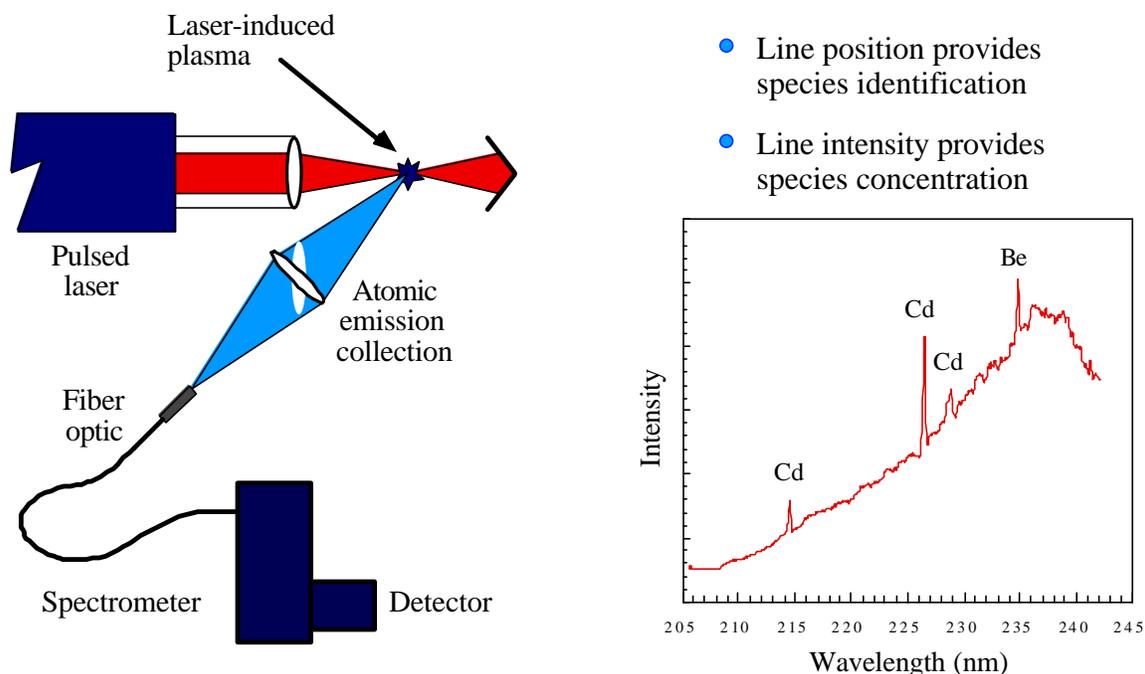


Figure A2: Conceptual illustration of the LIBS system and a sample spectrum.

In gases, the temperature of the resulting plasma is in the range of 10,000 – 15,000 K, hot enough to fragment all molecules into their constituent atoms, and to excite the electrons in the atoms out of the ground state and into excited electronic states. As the plasma cools, excited electrons relax back into their ground states, emitting light at characteristic atomic frequencies. Identification of the atoms present in the sample volume occurs using well-known atomic emission lines, and quantification of the atomic species concentration occurs via quantification of the intensity of the atomic emission lines. A conceptual diagram and sample spectra are illustrated in Figure A2. Sensitivities range from femtograms for some species, such as Be, to well above the picogram level for other species, such as Sb.

LIBS is extremely well suited as a diagnostic for trace inorganic species. The Buckley group has recently been directing a project at Sandia National Laboratories to apply LIBS as a real-time, in situ monitor for toxic metals in combustion systems (Buckley et al., 1999; Hahn et al., 1999). A field detection system has been assembled that can run in an unmanned mode for continuous emissions monitoring (Figure A2). Laboratory experiments suggest that LIBS can be used to measure particles as small as 100-150 nm depending on the species present. With the capability in the software to detect single particle hits, it is possible to do joint composition and sizing analysis of single particles. This ability makes LIBS an excellent diagnostic for trace species in the ambient atmosphere. Laboratory measurements to validate this technique have been accomplished. Ambient measurements have been made at industrial sites and in Livermore, CA.

2.4 Single Particle Mass Spectrometry

There are now a number of groups world-wide who have built single particle instruments and employed them in field campaigns (e.g., Noble and Prather, 1996; Murphy et al., 1998). All of these measurements were performed using the light scattering type of instrument so only examined particles greater than a few hundred nanometers in diameter. From experience with single particle instruments and a large body of literature on laser ablation mass spectrometry, we can summarize the capabilities of the current RSMS-II design that are especially suited for exploring atmospheric aerosols.

1. **External mixing properties** -- atmospheric particles are emitted by a wide range of sources and undergo disparate processing in the atmosphere. This results in particles of a given size having a range of compositions. These compositions can often be grouped into categories or classes of similar composition (e.g., Song et al., 1999).
2. **Composition of fine and ultrafine particles** -- Although there are large numbers of fine and ultrafine particles in the atmosphere, the mass of particles in these size ranges is quite small. As a result of this small mass loading, using conventional techniques to analyze the particles in these size classes necessitates sampling a large volume of air either at a high volume flow rate or over a long sampling period. The single particle technique described here analyzes individual particles so the overall particulate mass in a given size is not a constraint. Wexler and Johnston have demonstrated that single particle analysis is effective down to about 10 nm (Carson et al., 1997) and has good sensitivity to impurities at 50 nm (Ge et al., 1998). This particle size range is extremely important to atmospheric processes such as cloud dynamics and radiative balance.
3. **Size distribution of composition** -- In all the experiments proposed here, RSMS-II will be run in parallel with independent particle sizing instruments (a TSI SMPS and APS) so that

the particle hit rate can be normalized to the actual particle concentration that is sampled. Thus particle-sizing instruments will record the size distribution while RSMS-II will be used to establish the composition of particles analyzed at a given size. The RSMS-II hit rate will be calibrated beforehand using particles that are easy to analyze. Thus the discrepancy in the particle number distribution obtained from RSMS-II and the pure sizing instruments will indicate the percentage of particles either not analyzed or not analyzable.

4. **Speciating inorganic compounds** -- The speciation abilities of the instrument are currently not as varied or quantitative as bulk instruments, but Wexler and Johnston have shown that for instance different sulfur-containing compounds, such as sulfate, methane sulfonates, and hydroxymethane sulfonates, can be distinguished from each other (Neubauer et al., 1996). Elemental and metals analysis has also been demonstrated (Murphy et al., 1998; Ge et al., 1998).
5. **Distinguishing elemental from organic carbon** -- From the laser ablation literature, it is known that elemental carbon particles can be distinguished from organic carbon particles by the pattern of carbon-hydrogen peaks in the mass spectra (DeWaele et al., 1983). The usual laser desorption/ionization single particle analysis is only effective for speciating aromatics and distinguishing organic from elemental carbon. More in-depth single particle organic analysis techniques are described later in this proposal.
6. **Temporal resolution** -- Atmospheric particles often contain labile compounds whose concentration is affected by reactions or condensation/evaporation. Due to the presence of point sources, fronts, and turbulent eddies, the concentrations and compositions of atmospheric particles may exhibit sharp spatial gradients. Single particle analysis is fast compared to bulk analytical techniques. The transit time from sampling to analysis is measured in seconds so that a) rapid gradients in number or composition can be identified and b) labile compounds are not significantly transformed between sampling and analysis. The anticipated hit rate of hundreds of particles per minute will enable rapid transients in composition to be resolved.

Focusing of Aerosol Particles. It has been known for a number of years that passing an aerosol through a sharp or conical orifice where the flow is choked (that is, sonic) focuses certain particles (Dahneke, 1982; Fernandez de la Mora and Riesco-Chueca, 1988 and references therein). The focussed particles have a Stokes number value around one, the exact value depending on the nozzle geometry and the distance from the nozzle to the focal point. The U. of Delaware team employs this principle in their current single particle instrument, a second-generation version called RSMS-II (Rapid Single-particle Mass Spectrometry-II). The instrument focuses only a narrow range of particles sizes to the source region of the mass spectrometer, but this size range can be selected by adjusting the pressure upstream of the nozzle. If we consider a given nozzle geometry, let us term the Stokes number that is focused by Stk_f . Thus we can write

$$Stk_f = (D_p^2 \rho_p u_o / 18 \mu D_n) C_c$$

where D_p is the particle diameter that is focussed, ρ_p is its density, u_o is the velocity through the orifice (which is sonic since the flow is choked), μ is the viscosity of air, D_n is the orifice diameter and C_c is the Cunningham non-slip correction factor. All the terms except D_p and C_c can be combined into an effective diameter, $D_{p,max} = (18 \mu D_n Stk_f / \rho_p u_o)^{1/2}$ giving $(D_p / D_{p,max})^2 = 1 / C_c$. Since the maximum value of C_c is 1, $D_{p,max}$ is the maximum particle aerodynamic diameter than the nozzle can focus. C_c is a function of the particle diameter and pressure. The usual function for the Cunningham correction factor is difficult to manipulate analytically (Seinfeld

and Pandis, 1998), but a simple linear approximation, $C_c = 1 + 1.66 (2\lambda/D_p)$, is close to the more precise equation and has a maximum error of only 10% at $Kn=1$. Using this approximation for C_c gives a quadratic in D_p whose solution is

$$D_p = ((3.32\lambda)^2 + D_{p,max}^2)^{1/2} - 3.32\lambda$$

where λ , the mean free path, is a function of pressure via $\lambda = \lambda_o p_o/p$, where p_o and λ_o are the pressure and mean free path at standard conditions. Since the mean free path is a function of pressure, the particle size focussed in the mass spectrometer can be selected by adjusting the pressure as long as this size is smaller than $D_{p,max}$.

The maximum size that can be focussed, $D_{p,max}$, is a function of properties of air (μ , u_o) and the particle (ρ_p) which are not adjustable. The only adjustable parameter is the nozzle diameter, D_n , and geometric considerations such as the cone angle and distance from the orifice to the focal point, which are incorporated in Stk_f .

It is best to run the orifice choked because this focuses the smallest particles, but this requirement places limits on the orifice diameter in that the vacuum pump driving the orifice must be large enough to choke the flow. A 600 lpm pump is large but reasonably transportable and leads to a 3 mm orifice. The result is that for unit density particles, $D_{p,max}$ is about 2 micron. At low pressures, the focussed diameter is a linear function of pressure but this sensitivity reduces as the focussed diameter approaches $D_{p,max}$. By scanning the pressure from about 300 torr to about 1 torr, the nozzle is able to focus particles ranging from 1 micron to 10 nm in aerodynamic diameter - selecting the pressure is the next step.

One challenge to the design of the instrument is controlling the pressure upstream of the nozzle over a wide dynamic range while efficiently transmitting particles. We use a bank of 10 critical orifices whose flow is controlled by a rotary valve (Valco Instruments <http://www.vici.com>). The area of each orifice is selected to evenly distribute the 10 particle diameters logarithmically over the 10 nm to 2 micron size range. Each flow-control orifice is a sharp hole minimizing particle deposition and associated clogging. After the orifice bank is a section of straight tube where the flow straightens and becomes laminar before it enters the focussing orifice, giving more reliable focussing characteristics. The transmission efficiency of the inlet and the instrument's ability to size and analyze atmospheric particles has been submitted for publication (Mallina et al., 1999).

Standard software in the University of Delaware laboratory will be used to convert the time-based raw spectra to mass-based spectra that can then be interpreted. The pressure will be converted to particle aerodynamic diameter via equation 2. The parameter $D_{p,max}$ is a function of the geometry of the nozzle, which is fixed during each experiment. The pressure governs the mean free path, λ , which then determines the particles size that is focussed. The pressure diameter relationship will be calibrated with standard aerosols selected by a DMA both before and after each sampling period. When aerodynamic techniques are employed to size particles, as RSMS-II does, the particle density and aerodynamic properties contribute to the uncertainty in sizing. The density can be estimated from the particle composition reducing this uncertainty. Likewise, from the relative humidity and composition, the particle shape (e.g., spherical liquid, faceted crystal) can be estimated and used to reduce the uncertainty in converting aerodynamic to physical diameter.

Particle Detection. Particles that are focussed to the source region of the mass spectrometer are detected in one of two ways. Larger particles are detected by light scattering. A CW doubled Nd-YAG laser passes through the particle beam just upstream of the center of the source region. Two PMTs in the source region detect forward scattered radiation at angles of +/- 30 degrees and signal coincidence from these two PMTs is used to trigger the ablation laser (Ohigashi et al., 1994). Tests show that light scattering is effective down to about 200 nm.

For smaller particles, light scattering is not effective so the ablation laser is free fired (Reents et al., 1994; Carson et al., 1997; Ge et al., 1998). Currently we use an MPB PSX-100 laser, which fires at up to 100 Hz. To maintain single particle analysis, it is important to operate the instrument such that most laser shots miss a particle. For instance, if one in 10 shots result is a hit, then 1 out of 100 hits is a double hit, that is, two particles were in the source region. Here the nozzle flow rate characteristics become useful. Generally, the atmosphere contains a great many ultrafine particles and relatively fewer fines. This is somewhat counterbalanced by the flow rate through the nozzle. Larger particles are focussed at higher pressures where the sampling flow rate is higher whereas smaller particles are focussed at lower pressures where the sampling flow rate is lower. Nevertheless, if the hit rate is too high, dilution of particle stream is necessary to maintain single particle analysis. Particles are "detected" by the presence of a spectrum. The technique has been used in the laboratory to analyze particles down to 10 nm (Carson et al., 1997) and we have used it to demonstrate sensitivity to 0.1 mass percent impurities in 50 nm particles (Ge et al., 1998).

Since some particles may not be readily analyzed by RSMS-II and for the smallest particles, the spectrum is used to identify the presence of the particle, the measurements contain some uncertainty as to the number of particles present. As a result, the particle number will be measured simultaneously with an independent instrument (a TSI SMPS). The RSMS-II and standard number concentration measurements will be compared to determine the fraction of the particles analyzed.

Particle Analysis. The source region of the mass spectrometer is specially designed to maximize the probability of a particle hit when the laser is free-fired. First, the excimer laser beam propagates collinear to and in the opposite direction from the particle beam. In most designs these two beams are normal to each other so the overlap region is only a few hundred microns. With collinear beams, the overlap is very large and the source region size is governed by the ion optics in the mass spectrometer. In RSMS-II the ion optics have been designed to allow a 4 cm source region (Carson et al., 1997). The excimer laser beam is focussed to the center of the source region where it has a waist about 0.6 mm in diameter. This widens to about 2mm at the top and bottom of the source region. The particle beam passes through a 1 mm skimmer before it enters the source region of the mass spectrometer. In the center of the source region, 18 cm from the primary orifice, the beam is very well defined and about 4 mm across (measured by impacting oleic acid particles on a glass slide). It is the overlap between the hour-glass-shaped laser beam and the conical particle beam which determines the particle hit-rate probability. The overall particle hit rate is the product of this probability and the volume flow rate sampled.

Data System. The data system consists of a 500 MHz 8-bit A/D converter mounted in a PC (Precision Instruments 9847). The board was customized by the manufacturer so that valid spectra could be detected in firmware on the board -- PCs are not yet fast enough to check in

software each spectrum for validity at 100 Hz. Valid spectra are stored on the PC disk and archived on writeable CD-ROM.

Individual spectra can be viewed in real time in the field and can be used provide feedback to other measurements. Ultimately, a more statistically significant analysis of the data will be performed. Specifically, spectra from each particle each size will be grouped into categories of similar particle type. Two methods will be employed. We have used the CART (Classification And Regression Tree) algorithm successfully to bin laboratory generated particles by composition and quantify the amount of different sulfur compounds in a particle (Neubauer et al., 1996). To quantify, the algorithm must be trained with standards of known composition, which may be impractical for atmospheric applications. Alternatively, a neural network based algorithm has been tested on atmospheric particles and is able to classify them without a priori training (Song et al., 1999). This is clearly advantageous for atmospheric applications. Alternatives to these algorithms will be explored if they fail to classify the spectra.

RSMS-II has a number of advantages over the more conventional designs currently in use.

1. Particle size selection. Particles can be sized and selected over a much wider size range and the particle transmission rate for the selected size is much higher than for nozzles that transmit a broader range.
2. Particle sampling. Instruments that transmit a range of sizes must cope with the dramatic increase in particle number as the particle diameter decreases. Since the vast majority of atmospheric particles are small, significant time will be spent waiting for the larger particles to appear. With the new design, a given size is sampled until a statistically significant number are obtained and then another size is selected.
3. Particle detection. For smaller particles where the atmospheric number concentrations are typically higher, free firing is practical for analyzing particles. The particle number concentration is so low for larger particles that the hit rate becomes prohibitively low so the particles are detected by light scattering.
4. Particle size limits. In free-firing mode, the instrument is not limited by light scattering for particle detection. Thus ultrafine particles can be sized and sampled.
5. Particle analysis. Impactors can be used to obtain aerosol composition but the mass of smaller particles is very low in the atmosphere. Thus a large sampling time is needed to obtain the composition of fine and ultrafine particles for typical atmospheric loadings. Single particle analysis is well suited to analyzing small particles because the analysis is proportional to number not mass.
6. Volume flow rate. The volume flow rate into the instrument is proportional to the pressure upstream of the focussing orifice. As a result this flow rate is higher for larger particles (which are fewer) and lower for smaller particles (which are more plentiful) helping to equilibrate the hit rate over particle size.

2.5 Cloud and fog water collection

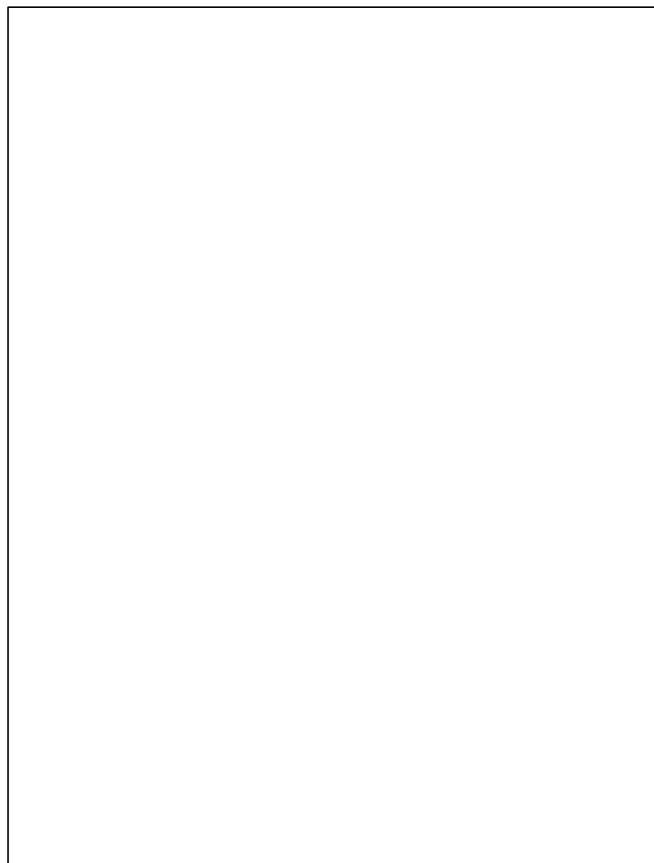
The Colorado State University's CASCC2 collects fog/cloud drops by drawing droplet-laden air at $5.8 \text{ m}^3 \text{ min}^{-1}$ over six banks of $508 \text{ }\mu\text{m}$ diameter Teflon strands. Drops are collected by inertial impaction on the strands. The 50% size cut for the CASCC2 corresponds to a drop diameter of $3.5 \text{ }\mu\text{m}$. Collected drops coalesce and are carried by gravity and aerodynamic drag down into a Teflon sample trough and through a Teflon sample tube to a polyethylene sample

bottle. The collector is cleaned prior to each fog/cloud event and blanks are taken. Operation of the CASCC2 will be automated for this study. Fog/cloud presence will be detected using a Gerber Scientific Model PVM-100 Particulate Volume Monitor. This instrument monitors forward light scattering to determine cloud/fog liquid water content (LWC). When the LWC is sufficiently high to indicate fog presence, the CASCC2 will automatically be turned on. At the same time the PVM-100 will activate a modem to place a call to a pager carried by the individual conducting the fog measurements, notifying her/him that sampling has commenced. The operator will come to the site immediately to ensure equipment is operating properly and to change samples as needed.

2.6 Determination of semi-volatile material

The combination of the technology used in the BIG BOSS sampling system (Tang, 1994) and the Harvard particle concentrator (Sioutas, 1994a,b) has resulted in the Particle Concentrator-Brigham Young University Organic Sample System (PC-BOSS) (Ding 1997, 1999a; Eatough 1999) (Figure A3). The PC-BOSS has five advantages over diffusion denuder systems previously used to determine fine particulate semi-volatile material.

1. Both semi-volatile ammonium nitrate and semi-volatile organic compounds are determined



with the same sampler (Ding 1999b, Eatough 1999).

2. The use of a particle concentrator eliminates the need for the independent measurement of the efficiency of collection of gas phase organic compounds by the diffusion denuder (Ding 1999a; Eatough 1999).

3. The elimination of the independent measurement of denuder breakthrough (Cui 1998; Eatough 1995; Tang 1994) results in a sampler which can be used in routine field operation.

4. The collection of the concentrated particles in a low-volume flow stream simplifies the power requirements of the sampler.

5. The effective high sample flow obtained with the particle concentrator allows for the collection of samples over time periods as short as one hour (Eatough 1999; Pang 1999a,b).

Figure A3. Schematic of the PC BOSS Sampler to be used for the determination of fine PM composition.

The PC-BOSS sampler has been validated in sampling programs completed in Tennessee (July 1997), in Riverside CA (August-September 1997), in Bakersfield CA (February-March 1998) and in Provo

UT (November-December, 1998) (Pang 1999a; Ding 1999b; Pang 1999b). In the experiments completed to date the efficiency of the denuder for the removal of gas phase organic material, nitric acid and SO₂ was shown to be near 100%. Most gas phase ozone, NO₂ and ammonia is also removed by the denuder (Ding 1999b; Eatough 1999; Obeidi 1999). The agreement for fine particulate mass, carbonaceous material, sulfate and nitrate between collocated PC-BOSS samplers was ±8% and agreement for these species between the PC-BOSS and comparable diffusion denuder samplers was ±5-10% (Ding 1999b, Pang 1999a,b). For all studies, the results obtained with the PC-BOSS sampler indicated that from 10 to 50% of the fine particulate mass was not measured with the PM_{2.5} FRM sampler due to the loss of semi-volatile organic material and ammonium nitrate during sampling. The majority of the loss at Riverside and Provo was due to semi-volatile organic material, but at Bakersfield the major species lost was ammonium nitrate.

During the intensive periods samples five samples will be collected and analyzed daily with a PC-BOSS sampler by the BYU team to establish the diurnal pattern of fine particulate chemical species, including semi-volatile nitrate and organic material. Approximately half of the samples collected during the three two-week intensive field sampling programs will be selected for analysis. PM_{2.5} mass will be determined from the material collected on the Teflon filter in the minor channel of the PC-BOSS (Figure A3). This mass will be corrected for the loss of ammonium nitrate and semi-volatile organic material (determined from analysis of the Nylon and charcoal impregnated filter, CIF, in the minor flow channel of the PC-BOSS). Constructed mass will also be determined from the various analyzed species. The concentration of fine particulate sulfate and of nitrate retained by a particle collection filter will be determined by ion chromatographic analysis of ultrasonic aqueous extracts of each quartz and Teflon filter (a total of three filters/sample) of every PC-BOSS collected sample. The concentration of nitrate lost from particles during sample collection will be obtained by ion chromatographic analysis of IC eluent extracts of both the Nylon and CIF filters of the PC-BOSS. The concentrations of ammonium ion in extracts of the minor flow Teflon filter for each PC-BOSS sample will be determined spectrophotometrically. The pH of these extracts will be determined by pH measurement and the acidity obtained as previously described (Koutrakis et al., 1988). The concentrations of organic carbonaceous material and soot retained on each PC-BOSS quartz filter (Figure A3), will be determined by temperature programmed volatilization analysis (TPV) from ambient to 800 EC in a N₂/O₂ atmosphere (Eatough 1993, Ellis 1982). The concentrations of semi-volatile organic material lost from the particles during sampling will be obtained from TPV analysis of the material collected by each CIF of the PC-BOSS in a N₂ atmosphere from ambient to 400 EC (Eatough 1993, Tang 1994).

2.7 Continuous Nitrate, Sulfate, and Carbon Measurements

For particle nitrate the ADI approach has been compared to denuder-filter methods at three different California locations, namely Riverside, Mira Loma and Bakersfield, and has yielded regression slopes of 0.96, 1.00 and 1.07 with correlation coefficients of 0.96. Example data from Bakersfield, California is shown in Figure A4 (Dutcher et al., 1999). Laboratory tests show collection efficiencies of greater than 95% for particles between 0.1-1 μm. Interference testing shows less than 1% response to nitric acid or ammonium ion.

Data from the combined sulfate, carbon nitrate system collected in December 1998 in Marshall, Colorado are shown in Figure A5 (Hering et al, 1999). The data show that the time

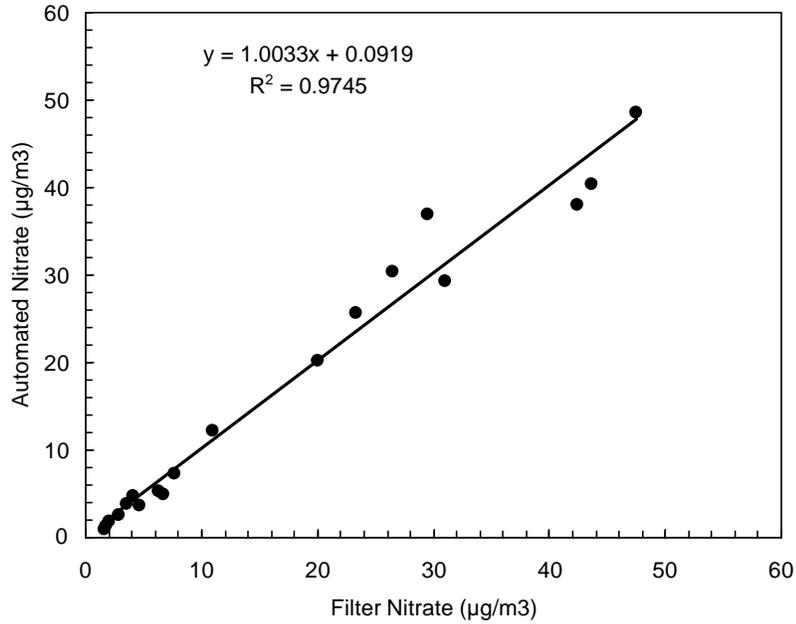


Figure A4. Comparison of nitrate concentrations measured by the automated nitrate monitor with measured by a filter sampler.

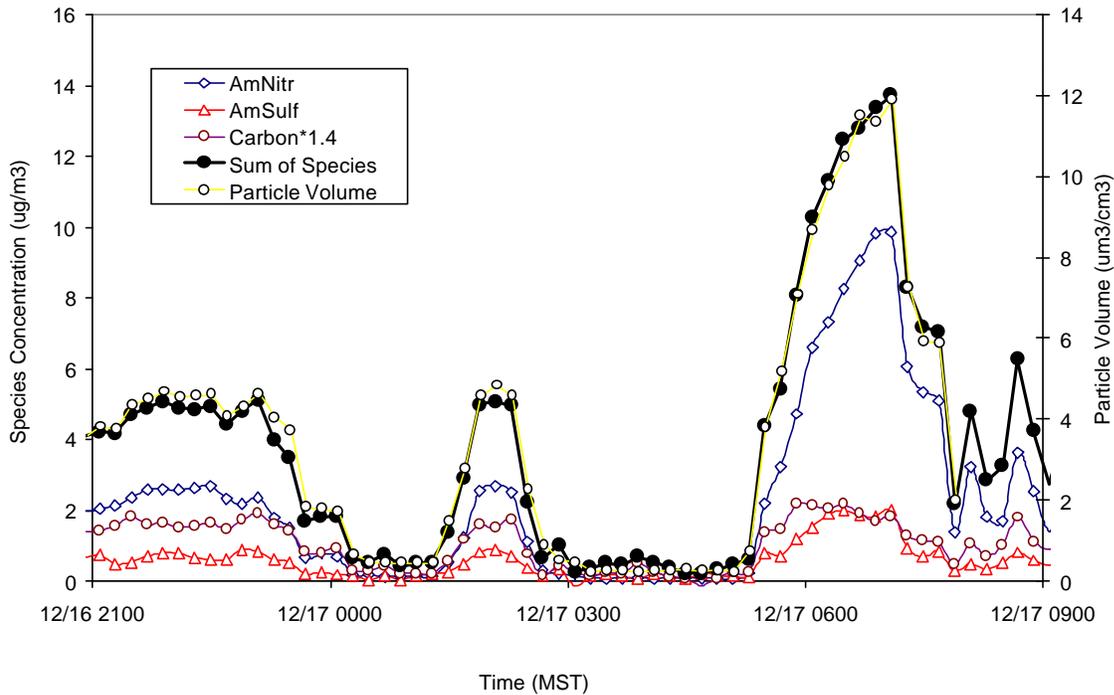


Figure A5. Time series of the automated sulfate, nitrate, carbon measured at Marshall, Colorado, with comparison of the mass sum of species (left hand axis) to optical particle counter volume ($\mu\text{m}^3/\text{cc}$, right hand axis). Sum of species is calculated as $1.29 \cdot \text{nitrate} + 1.375 \cdot \text{sulfate} + 1.4 \cdot \text{carbon}$.

variation in the sum of the nitrate, sulfate, and carbon species measured by these systems tracked the total particle concentration, as indicated by physical size distribution measurements. Additionally, the mass sum is comparable to the measured aerosol volume, with a mass to volume ratio just over 1 g cm^{-3} . Note that the relative proportions of carbon, sulfate, and nitrate vary. Such data are extremely valuable to the proposed atmospheric aerosol modeling for the Pittsburgh Supersite. The combined modeling and measurement effort will provide valuable insights into the sources and formation processes for these particle constituents which comprise the majority of the fine particle mass.

2.8 Bioaerosols

The Hernandez group using direct microscopy and molecular biological analyses will develop and apply rapid, quantitative, aerosol assays to characterize the identity, distribution and activity of microbiological components present in outdoor aerosols. This aerosol microbiology study will focus on bacteria, fungi and their spores. The definition of "microbiological" here does not dictate the necessity to be isolated or quantified by culture. In response to the limitations of conventional microbiological analysis, the Hernandez group will refine accepted (and novel) epifluorescent microscopy practices with genetic-based, molecular biology assays into rapid, *non-culture* based techniques that can directly measure and classify microbiological bioaerosol material in outdoor air. Our sampling approach for characterizing outdoor bioaerosols is to use two different types of common samplers in conjunction with each other: cyclone wet samplers and high volume $\text{PM}_{10\&2.5}$ filter samplers. The wet samplers will be used for culturing, microscopic and genetic analyses, while the total PM samplers will be used for biomass determinations (vs. total mass). Sensitive biological stains and image analyses will be used to directly characterize microbiological aerosols collected by both types of samplers. Image analysis will be used to accurately measure the size and morphology of stained biological particle recovered from outdoor air. Using widely accepted molecular methods, genetic probes, polymerase chain reaction (PCR), and denaturing gradient gel electrophoresis (DGGE) will be used to classify airborne microorganisms on a phylogenic, rather than a culturable basis.

2.9 Meteorology

Atmospheric trajectory analysis has long been used to identify the location of upwind regions that contribute material to samples collected hundreds and even thousands of kilometers downwind. Information contained in modeled trajectories includes the upwind transport pathway corresponding to air arriving at the sampling site and the temperature at each point in the trajectory. This information identifies the transit time from upwind sources, thus aiding in the determination of en route chemical transformation and possible interaction with clouds, among other things. The trajectory model developed by Harris and Kahl (1994) will be applied by the Kahl group to calculate trajectories twice daily for a 1.5 year segment of the project. This model calculates 10-day transport along isentropic surfaces, thus accounting for the adiabatic vertical motions that characterize the basic features of atmospheric transport. The model switches from isentropic to mixed-layer mode when trajectories come close to the earth's surface. In this mode, air parcels are advected using winds averaged throughout the lowest 500 m of the atmosphere. In the isentropic mode the parcels are advected using winds found along a surface of constant potential temperature. The model also features a dynamic "theta-chooser" algorithm, which

calculates the potential temperature surface that corresponds to the desired altitude of trajectory arrival at the receptor.

2.10 Gas-phase measurements

Individual VOC concentrations will be measured chromatographically using the GC-FID and GC/MS techniques. Samples will be collected into 32 L Summa canisters that will be pressurized during sampling to approximately the equivalent of 96 L of air at one atmosphere. The GC-FID method will use an HP gas chromatograph and integrator system with a J&W Scientific DB-1 column. The sample will be loaded through a gas-sampling valve onto a Supelco Carbotrap 300 sorbent trap, at 200 to 300 mL min⁻¹. Residual water will be removed by passing He through the trap at 100 mL min⁻¹ for 7 min. The trapped sample is then desorbed at 340°C for 10 min through a second gas-sampling valve into a loop filled with glass beads. The organics are vaporized by heating the loop at 100°C and cryo-focused onto the head of the column held at -60°C. The column-oven temperature is held for 5 min at -60°C and then increases at 4°C min⁻¹ to 200°C. Using a similar technique Lewis et al. (1999) reported a species quantification limit of about 0.1 µg m⁻³ allowing them to quantify the concentrations of roughly 130 compounds in Atlanta air.

The GC-MS analysis will be similar to the GC-FID. Ambient samples will be loaded onto a multibed Tenax TA-Amborsorb-Charcoal sorbent trap in a Dynatherm Analytical Instruments model 890. The sample will be desorbed at 300°C for 6 minutes to a freeze-out loop immersed in liquid nitrogen. The rest of the analysis will follow the GC-FID protocol.

The Colorado State University (CSU) team will make gas phase measurements of hydrogen peroxide and soluble organic peroxides using a continuous monitor based on the method of Lazrus et al. (1986). This dual-channel instrument, constructed at CSU with the assistance of Drs. Greg Kok and Teresa Campos of NCAR, features a detection limit of ~ 0.1 ppbv. Air is drawn into the instrument through a Teflon sample tube. The first instrument channel scrubs soluble hydroperoxides (including hydrogen peroxide and soluble organic peroxides) from the air into solution where they are reacted to produce a fluorescent dimer, the concentration of which is measured by an on-line fluorimeter. The second instrument channel is identical to the first except that catalase is added to the sample stream to destroy hydrogen peroxide, permitting measurement of residual, organic peroxide concentrations. The hydrogen peroxide concentration is given by the difference between the two channel concentrations. The peroxide analyzer is calibrated by automated injection of aqueous standards. Routine checks are also made to verify efficient transmission of gaseous peroxides through the Teflon sample tube and efficient destruction of hydrogen peroxide by catalase in the second channel. Data will be recorded at 10 minute intervals and averaged to longer periods as needed for use in the cloud/fog study and for tests of the influence of hydrogen peroxide and organic peroxides on health. Expertise and instrumentation for the peroxide measurements will be provided by CSU with on-site assistance from CMU personnel.

2.11 Polar Organics

Polar organic compounds will be detected by an aerosol MALDI experiment. Matrix-assisted laser desorption ionization (MALDI) is widely used to obtain mass spectra of highly polar compounds. The analysis is performed by mixing the analyte with a matrix compound that

strongly absorbs the laser radiation. The matrix-analyte mixture is then irradiated with a pulsed laser beam to eject intact analyte ions without fragmentation. The U. of Delaware group has performed MALDI of bulk and single-particle samples for several years (e.g., Mansoori et al., 1996).

On-line single particle MALDI will be performed as follows. Ambient aerosol will be mixed with a small flow of the hot vapor matrix quickly cooling it to ambient temperature and reducing the vapor pressure. The matrix vapor will condense on existing aerosol particles producing a matrix/analyte mixture like that used in a conventional MALDI experiment. This principle is similar to that of a "mixing-type" condensation nucleation counter (Okuyama et al, 1984) except that a much smaller amount of vapor will be condensed on the particles. The increase in particle size due to matrix condensation is controlled by the relative flow of the matrix vapor and the aerosol. A large body of literature has established the operating parameters (e.g., Willeke and Baron, 1993).

The U. of Delaware team has built a prototype apparatus to condense a very thin film of benzoic acid matrix on ultrafine particles. The goal of this experiment was not to perform MALDI of aerosol organics but rather to study the effect of a thin, absorbing coating on the yield of ions from non-absorbing particles. With this apparatus, it was found that a benzoic acid film corresponding less than a 5% increase in the particle size (the smallest size increase that could be measured with our experimental setup) was sufficient to increase the number of particles analyzed by as much as a factor of two. This increase in the "hit" rate arises from particles that pass through the edge of the laser beam. Because particles near the edge of the laser beam experience a lower laser irradiance than particles in the center of the beam, they may yield too few ions to be detected. Adding a small amount of benzoic acid increases the amount of laser radiation that is absorbed by the particle and increases the yield of ions from the core material. In this way, particles near the edge of the laser beam are detected and the hit rate increases. This experiment underscores the dramatic effect that even a small amount of an absorbing material can have on the laser ablation process.

Based upon conventional MALDI experiments, we expect that no more than a 1:1 mass ratio of matrix to analyte is needed to enhance formation of organic molecular ions. Since particle mass is proportional to the cube of the diameter, a doubling of the particle mass by condensation of matrix vapor will result in a 26% increase in particle diameter. This size change is small relative to the density uncertainty and corresponding size uncertainty for aerodynamically sized particles and therefore should not significantly alter conclusions drawn from correlated size-composition measurements of the transformed particles.

2.12 Semi-continuous metals

The semi-continuous metals sampler of the Ondov group consists of a high-frequency aerosol sampler (HFAS) and state-of-the-art true simultaneous multi-element Graphite Furnace Atomic absorption spectrometer. The HFAS consist of a state-of-the-art dynamic aerosol concentrator. PM 2.5 is sampled at 200 L min⁻¹ and delivered to GFAA system or to a sample fraction collector for on or off-line analyses, respectively. In <10 (for urban air) to 20 (rural air) minutes the U. of Maryland (UMCP) group typically collects enough slurry to permit 4 suites of 4 or 5 elements to be determined, each in triplicate. At the 200 L min⁻¹ sampling rate, analyte masses delivered to the GFAA at the smallest concentrations observed by Ondov in rural Maryland air exceed

instrumental sensitivities (rivaling far more expensive ICP-MS but with far less sample volume requirement) by factors of 2 to >400 for Al, As, Cd, Cu, Fe, Mn, Ni, Pb, Se, V, and Zn. In addition to high temporal resolution, it is of paramount importance that analytical concentration measurements be accurate. Tests with NIST Standard Reference Material 1648 (“Urban Particulate Material”) confirm these results for Cd, Pb, Zn, Se, As, Cr, Mn, Cu, and Ni. Tests for the remaining elements are in progress. Additional field tests of the instrument are being made in College Park, MD, and at the Atlanta Super Site in August, 1999.

The Ondov group will construct and deploy two HFASs, i.e., one at the main site and one at the satellite site. These will be deployed for 2 weeks during each of 3 two-week intensives and will be used to collect samples continuously at a sub-hourly interval to be selected during a pilot field test prior to the first scheduled intensive. To save costs and permit a maximum number of analyses to be performed, samples will be collected in fraction collectors (each holding up to 288 samples) and returned to UMCP for analysis on a (truly) simultaneous Graphite-Furnace Atomic Absorption Spectrometer for 18 elements in the following four groups:

Group 1: As, Cu, Mn, Ni, Cr

Group 2: Cd, Se, Ag, Pb

Group 3: Al, Fe, Zn, Ca, and Bi (Bi is an internal standard),

Group 4: V, Ti, Be, Ba

The elements selected include criteria pollutants (Pb and Be), hazardous air pollutants (known as air toxins; i.e., Cd, Cr, Cu, Ni, As, and Se), first series transition metals either known (V and Zn) or suspected to elicit respiratory inflammation (Ti, V, Cr, Mn, Fe, Ni, Cu, Zn; i.e., all but Sc and Co); essential nutrients (Fe, Zn, Se, Cr), and the aquatic toxin, Al. In addition, most are primary source marker species (i.e., As and Fe, steel; Zn, Cd, Cr, Pb, Ag, incinerators; Ni and V, residual fuel oil combustion; Se, coal combustion; Ti, paint manufacture and applications (fine particles) or crustal dust (coarse particles); Ca limestone/construction material; and Cu, Cd, Zn, respective smelter emissions and/or metals processing.

Until more experience is gained, 3 replicate analyses will be made for each suite of elements. Analysis of each suite about 5 minutes per replicate, so that the time to complete 3 replicates is 15 minutes per suite. The initial target collection rate will be 6 samples per hour, pending ambient concentrations. As the collection rate will far exceed the analytical rate the UMCP group will analyze selected series of samples based on observations made with continuous aerosol mass and particle concentrations, SO₂ concentration, and wind direction. At 200 samples from each intensive will be analyzed. Many more samples can be analyzed if fewer suites are selected, however, the best strategy may be to remove replications as 10 minute sampling times will likely provide for replication, in which case >600 samples would be analyzed per intensive. Note that each fraction collector can accommodate 288 samples, i.e., about 2 days worth.

2.13 Three-Dimensional Modeling Study

In collaboration with Ted Russell in Georgia Tech., the CMU groups have created a comprehensive three-dimensional model for the study of PM_x in the region shown in Figure A6. The model includes a state-of-the-art description of PM processes and describes the complete aerosol size/composition distribution using user-selected chemical and size resolution. The model is also coupled to a sensitivity analysis module so it can calculate directly the sensitivities

of PM concentrations to small changes in source strength. The response to larger changes can be calculated with additional simulations.

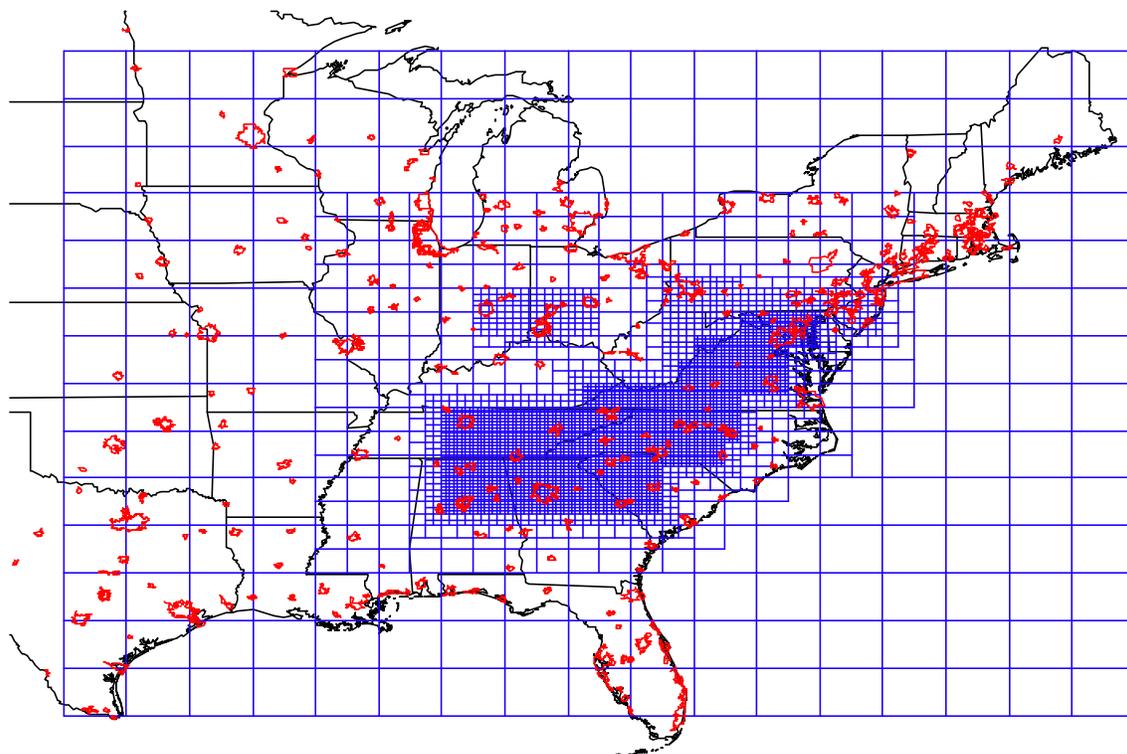


Figure A6. Modeling region used in current simulations of the size/composition distribution of PM in the central and eastern US by the CMU group. The model grid can be adjusted for different applications. High resolution (5x5 km) not shown here will be used in the area surrounding the Pittsburgh Supersite for additional simulations.