

**QUALITY ASSURANCE PROJECT PLAN  
FOR  
PITTSBURGH AIR QUALITY STUDY  
(PAQS)**

**Carnegie Mellon University**

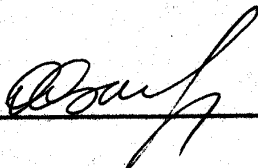
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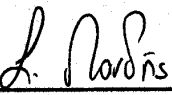
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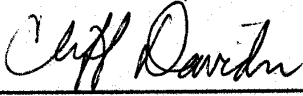
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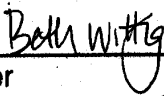
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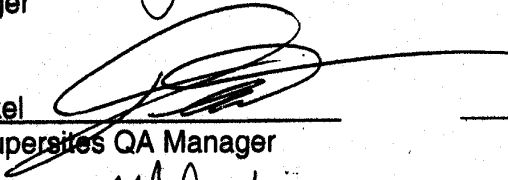
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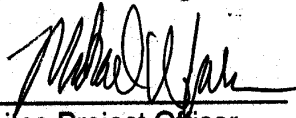
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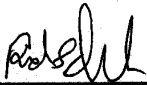
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# QUALITY ASSURANCE PROJECT PLAN FOR PITTSBURGH AIR QUALITY STUDY (PAQS)

## 1. PROJECT PLANNING AND ORGANIZATION

### 1.1. 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 for the morbidity and/or mortality. 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 internal combustion engines and coal combustion 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**

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

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<sub>2.5</sub> mass (FRM PM<sub>2.5</sub>) do not measure most of the aforementioned characteristics. Indicative of the difficulty of making accurate 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 temporal and spatial variability of airborne particles, 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 that 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 Graphite Furnace Atomic Absorption (GFAA) and Laser Induced Breakdown Spectroscopy (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 organic carbon (OC) and elemental carbon (EC) measurements, enhanced organic aerosol speciation by Gas Chromatograph with Mass Spectrometer detector (GC/MS), ultrafine aerosol size distribution measurements, semivolatile organic aerosol partitioning measurements, bioaerosols, and continuous direct surface area measurements.

The poor 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 been 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 are the primary and secondary organic PM fractions? 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<sub>2.5</sub> levels with emissions. The design of these strategies is complicated by the importance of secondary aerosol to PM<sub>2.5</sub> concentrations. Of particular concern are non-linearities between emissions and ambient PM levels. For example, reductions in SO<sub>2</sub> and sulfate can free the associated ammonia in aerosol ammonium sulfate. This additional ammonia can react with available nitric acid vapor to form aerosol ammonium nitrate (Seinfeld and Pandis, 1998). In extreme cases in specific areas in the NE US, SO<sub>2</sub> controls could even 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<sub>x</sub> 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. The study will also determine what reactants control secondary PM formation under certain conditions (e.g., ammonia).

Deterministic modeling with appropriate input data allows for a 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, and continuous measurements) that address the above issues.

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 primary and secondary PM 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.
- 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.

## 1.2. Project Scope and Work 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 number, surface, and volume distributions as a function of particle size; chemical composition as a function of size and on a single particle basis; and 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.) on the PM concentrations in the area.

Combining the ambient monitoring study with the proposed 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 responses of the PM characteristics to changes in these emissions in support of the emission control decision-making in the area (SIP development, etc.)

Table 2 lists the major measurements and Measurement Quality Objectives (MQO) to be achieved during the PAQS. MQOs listed in this table include measurement resolution, Measurement Detection Limit (MDL), precision, accuracy, and data completeness. The measurements are described in detail in the Experimental Design Section of this document. Definitions of Data Quality Indicators (DQI) are given in the corresponding section of this document.

**Table 2. Measurements in the Pittsburgh Supersite Program**

Measurements	Instrumentation	Resolution	MDL	Precision	Accuracy	Completeness	PI
Aerosol number distribution	Ultrafine SMPS, SMPS, APS	10 min	N/A	30%	N/A	70%	Pandis
Aerosol surface distribution	Ultrafine SMPS, SMPS, APS, Epiphaniometer	10 min	N/A	30%	N/A	70%	Pandis
Aerosol volume distribution	Ultrafine SMPS, SMPS, APS	10 min	N/A	30%	N/A	70%	Pandis
PM <sub>2.5</sub> mass	FRM, CMU Sampler, MOUDI	1 day	0.2 µg/m <sup>3</sup> per stage/filter	10%	10%	70%	Davidson, Robinson
	TEOM	10 min	T/D	10%	10%	70%	Davidson, Robinson
PM <sub>10</sub> mass	FRM, CMU Sampler, MOUDI	1 day	0.2 µg/m <sup>3</sup> per stage/filter	10%	10%	70%	Davidson, Robinson
PM <sub>x</sub> mass	MOUDI	1 day	0.2 µg/m <sup>3</sup> per stage/filter	10% per stage	10% per stage	70%	Davidson, Robinson
PM <sub>2.5</sub> ions, elements	CMU Sampler/ IC & ICPMS or AAS	1 day	0.1 µg/m <sup>3</sup>	20%	20%	70%	Davidson
PM <sub>2.5-10</sub> ions, elements	CMU Sampler/ IC & ICPMS, or AAS	1 day	0.1 µg/m <sup>3</sup>	20%	20%	70%	Davidson
HNO <sub>3</sub> vapor	CMU Sampler/ IC	1 day	0.3 µg/m <sup>3</sup>	30%	30%	70%	Davidson
NH <sub>3</sub> vapor	CMU Sampler/ IC	1 day	0.5 µg/m <sup>3</sup>	30%	30%	70%	Davidson
Size-resolved ions and metals	MOUDI/IC and ICPMS or AAS	-	0.1 µg/m <sup>3</sup>	20% per stage	20% per stage	70%	Davidson, Robinson
PM <sub>2.5</sub> OC and EC <sup>13</sup>	Organic sampler/thermal	1 day	0.5 µgC/m <sup>3</sup>	30%	30%	70%	Robinson
	PC-BOSS system	1 day	0.1 µgC/m <sup>3</sup>	5%	5%		Eatough
	In situ carbon analyzer	2 hours	0.3 µg/m <sup>3</sup>	10%	10%	70%	Turpin
PM <sub>10</sub> OC and EC	Organic sampler/thermal	1 day	0.5 µgC/m <sup>3</sup>	30%	30%	70%	Robinson
PM <sub>x</sub> OC and EC	MOUDI/thermal	1 day	0.5 µgC/m <sup>3</sup>	30%	30%	70%	Robinson
Organic speciation	Organic sampler/GC-MS	2 weeks	per stage	T/D	T/D	33%	Rogge
Organic size-resolved characterization	LPI/FTIR	1 day	T/D	T/D	T/D	T/D	Turpin

Measurements	Instrumentation	Resolution	MDL	Precision	Accuracy	Completeness	PI
Polar Organics	RSMS-II	Continuous		T/D	T/D	T/D	Wexler
Single Particle Chemical Composition	RSMS-II	Continuous	T/D	T/D	T/D	33%	Wexler
	Filter/SEM	6 hours	T/D	T/D	T/D	T/D	RJ Lee
	LIBS	Continuous	T/D	T/D	T/D	T/D	Buckley
Semi-continuous metals	HFAS/GFAA	1 hour					Ondov
Continuous nitrate	ICVC	10 min	1 $\mu\text{g}/\text{m}^3$	10%	25%	85%	Hering
Continuous sulfate	ICVC	10 min					Hering
Continuous carbon	ICVC	30 min					Hering
Water soluble ions	Steam sampler	2 hours	0.2 $\mu\text{g}/\text{m}^3$	10%	20%	70%	Khlystov
Bioaerosols	Epi-fluorescent microscopy, Molecular biology assays	1 day	T/D	T/D	T/D	T/D	Hernandez
Visibility	Nephelometer	Continuous	N/A	T/D	T/D	T/D	Pandis
	Visual Range	6 hr	N/A	N/A	N/A	N/A	
Growth with RH CCN concentration	TDMA/RSMS-II	Variable	N/A	T/D	N/A	N/A	Pandis
	CCN Counter	Variable	N/A				Pandis
Wind, Temp, Pres, RH, Precipitation, UV and Solar Radiation Trajectories	Met sensor	10 min	N/A	10%	10%	80%	Davidson
	T/D	1 day	N/A	N/A	N/A	N/A	Kahl
VOCs	GC-FID, GC-MS	6 days	T/D	T/D	T/D	T/D	Pandis
Peroxides	CSU Monitor	1 hr	0.2ppbv	20%	20%	70%	Collett
O <sub>3</sub>	Ozone Monitor	10 min	0.6ppbv	10%	10%	80%	Pandis
NO and NO <sub>2</sub>	NOx Monitor	10 min	0.4ppbv	10%	10%	80%	Pandis
SO <sub>2</sub>	SO <sub>2</sub> Monitor, Filter	10 min	0.4ppbv	10%	10%	80%	Pandis
CO	CO Monitor	10 min	40ppbv	10%	10%	80%	Pandis
Fog and cloud composition	CSU Collector	Variable	T/D	20%	20%	80%	Collett

N/A: not applicable

T/D: to be determined

### 1.3. Project Description

The PAQS is 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 document. 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) 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 air shed.

The ambient monitoring study has been designed to test a set of hypotheses, which are described in a subsequent section. 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 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. Local and state air pollution agencies are also supporting the effort. 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 PM<sub>10</sub> and PM<sub>2.5</sub> mass (both with FRMs and continuously with TEOMs) and standard gas species (O<sub>3</sub>, CO, SO<sub>2</sub>, NO<sub>x</sub>); 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 other 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<sub>2.5</sub>. 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 fifth 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 and a comprehensive modeling 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, although these studies are an important part of the overall research plan.

#### **1.4. Experimental Design**

The PAQS has been designed to test a wide range of complementary hypotheses. The first group of hypotheses falls 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. Finally, health effects data will be collected under funding from other agencies, and when combined with the ambient measurements, will provide a rich data set for the planned epidemiological study. The hypotheses to be tested are briefly summarized 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 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 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, together with meteorological information (e.g. air trajectories) and source-receptor models will allow for

the 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 many of the hypotheses that have been proposed to explain the PM effects on mortality and morbidity.

#### **1.4.1. Overview**

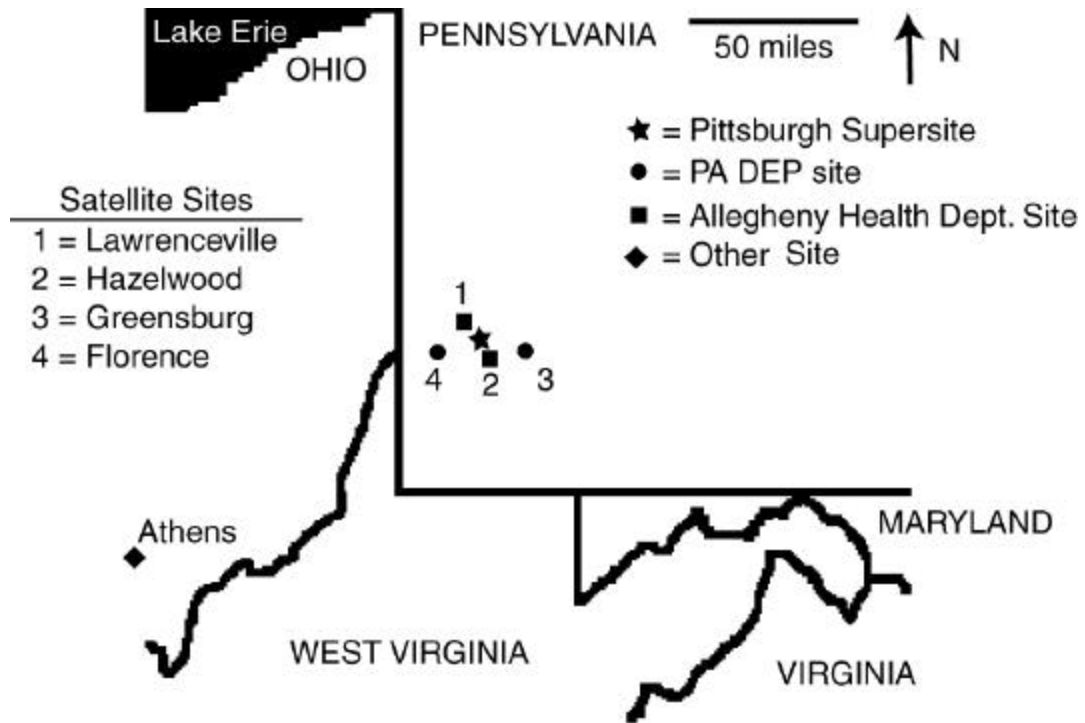
The proposed study consists of the following five components:

- Ambient monitoring at a central Supersite and a set of satellite sites in the Pittsburgh region,
- An instrument development and evaluation study,
- A comprehensive modeling component (currently funded by the STAR program of EPA),
- An epidemiological study (additional funding will be requested by other agencies), and
- A data analysis and synthesis component.

The EPA Supersite Program funds will only be used to support activities of components (1), (2) and (5). DOE funds will also be leveraged to support the same components. The proposed approaches for each of these components are summarized below.

#### **1.4.2. Ambient Monitoring**

The central Supersite will be located next to the Carnegie Mellon University campus near downtown Pittsburgh. Five additional sites will serve as Satellite sites. One satellite site is located in Athens, Ohio. This satellite site is currently being operated and will continue to be operated by FETC as part of their UORVP. Two additional satellite sites are located in Florence, Pennsylvania and Greensburg, Pennsylvania and are existing PM sampling sites of the regulatory network. The final two satellite sites are located in Lawrenceville, Pennsylvania and Hazelwood, Pennsylvania. These sites are ordinarily run by the Allegheny Health Department, which has agreed to increase the frequency of sampling at satellite sites to accommodate the Supersite program. Figure 1 shows the location of the central Supersite, one UORVP satellite site, two Allegheny Health Department satellite sites, and two DEP satellite sites.



**Figure 1. Map of Pittsburgh region showing the approximate location of the Supersite and the five DOE/FETC UORVP/Allegheny County Health Department sampling sites that will be used as satellite 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 14-30 -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 light scattering,
- PM Hygroscopicity,
- Meteorology,
- Gases, and
- Fogs and clouds.

Each of these measurement categories is listed in Table 2 with instrumentation, Measurement Quality Objectives, and the investigator. A brief discussion of each measurement category follows.



#### 1.4.2.1. *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  $\mu\text{m}$ . 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 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.

#### 1.4.2.2. *PM Mass Characterization*

The Robinson group will measure PM mass concentration with a variety of samplers and the gravimetric approach. The  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  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  $\mu\text{m}$  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  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  mass concentrations reflects the concentration in this size range. A Micro-Orifice Uniform Deposit Impactor (MOUDI) will be used to sample  $\text{PM}_x$ , 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. A humidity-controlled chamber will be used for equilibrating the filters according to standard protocol.

#### 1.4.2.3. *PM Chemical Composition*

*Inorganic Components.* The inorganic speciation samplers ( $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ) for the Supersite will consist of a combination of denuders and filters. The samples will be analyzed for major and trace inorganic species using Ion Chromatography (IC) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The sampling frequency will be once per day during the regular period and five times per day during the intensives, with 4-hour samples during the day and 6 hour samples at night. MOUDI impactor samplers will also be analyzed for inorganic chemical composition during the intensive periods.

*Carbonaceous components.* Organic carbon (OC) and elemental carbon (EC) will be measured using a denuder – filter pack system developed at CMU. OC and EC will also be measured by the Turpin group using their improved in situ carbon analyzer during intensive runs and during regular sampling periods. The in situ carbon analyzer collects PM<sub>2.5</sub> 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. Samples collected using a MOUDI will be analyzed for OC and EC by the Robinson group. Samples collected using a Hering Low Pressure Impactor (LPI) will be analyzed by the Turpin group by Fourier Transform Infrared Spectroscopy (FTIR). FTIR will 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<sub>2.5</sub> inlet with a fine particle concentrator, denuder, and several filters (Quartz, Teflon, Nylon, and Charcoal-impregnated). 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, ammonium, pH, and acidity.

#### 1.4.2.4. *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. 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.

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). MALDI is a widely used 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 concurrently the size and 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). This mass information, combined with an assumed density, is used to translate the measurement into an equivalent spherical particle size. Laboratory experiments have shown that this technique works quite well at reproducing known aerosol size distributions with particles from 0.15 – 1  $\mu$ m (Hahn and Lunden, 1999). The LIBS system will be deployed during two of the intensive sampling periods and during 1 month of the baseline-sampling period.

*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. This will yield complementary information about the elemental composition and morphology of individual larger particles that will not be provided by the single particle spectrometer.

#### 1.4.2.5. *Continuous and Semi-Continuous PM Composition*

In addition to the previously mentioned continuous (or semi-continuous) measurements of the aerosol size distribution, OC, 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 the central Supersite. 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  $\mu\text{m}$  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<sub>2</sub>, 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<sub>2</sub>. Because the sample is concentrated, the analyses can be done using proven, robust gas analyzers.

#### 1.4.2.6. *Bioaerosols*

The Hernandez group will coordinate laboratory and field studies to 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  $\mu\text{m}$ . 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  $\mu\text{m}$ ), and (iii) determine the abundance and identity of microbioaerosols (bacteria, fungi, and their spores) using direct microscopy combined with novel molecular biological assays.

#### 1.4.2.7. *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.

#### 1.4.2.8. *PM Hygroscopicity*

The Pandis group will quantify the ability of ambient fine particles to absorb water and grow using the Tandem Differential Mobility Analyzer (TDMA) technique (Zhang et al., 1993). These measurements during the intensive periods will provide the growth factors as a function of particle size and composition. 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 for the

first time the link between chemical composition and hygroscopic properties of individual ambient particles.

#### 1.4.2.9. *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 once 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 altitude of transport and possible source regions, and (iii) an atmospheric transport climatology for the Pittsburgh region.

#### 1.4.2.10. *Gases*

Several gases will be measured continuously during the 18-month period and reported as 1-hour average concentrations. These include O<sub>3</sub>, NO, NO<sub>2</sub>, CO, and SO<sub>2</sub>. 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).

#### 1.4.2.11. *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 whenever it occurs during the 18-month sampling period.

Collected fog 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).

### 1.4.3. **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.

#### 1.4.3.1. *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. The new instrument will have a dual time-of-flight system so that both positive and negative ions are analyzed for each particle. 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, it will automatically refill the laser gas. The instrument will record inlet flow and pressure and store them with each spectrum. The computer will monitor the relationship between flow and pressure. 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 they clog more easily than the larger orifices. 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 from 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 from 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 as many as 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 a 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.

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

#### 1.4.3.2. 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 – APS – RSMS-II
Surface area	Epiphaniometer – SMPS/APS
PM <sub>2.5</sub> and PM <sub>10</sub> mass	FRM – TEOM – Speciation Sampler – MOUDI
PM Elements	Speciation Sampler/ICPMS – HFAS/GFAS – RSMSII – LIBS
PM Sulfate, Nitrate	Speciation Sampler – Steam sampler – ICVC –RSMSII
PM Carbon	Speciation Sampler – Rutgers Sampler – ICVC – PC BOSS –RSMSII
Polar Organics	Detailed Speciation – FTIR – RSMSII/MALDI

#### 1.4.4. Epidemiological Study

The proposed monitoring study with its wide range of epidemiology-relevant measurements, 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<sub>2.5</sub>, PM<sub>10</sub> mass concentration and composition, but also PM<sub>x</sub>, number distributions including the ultrafine size range, surface area (measured directly with the epiphaniometer), surface area distribution, organic speciation and polar organics, and concentrations of aerosols from specific sources 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 time series analysis techniques may be funded with available resources of the Johns Hopkins group. If Samet is not able to do this work due to a lack of funds, collaboration will be sought with another group.



### 1.4.5. 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 at Georgia Tech., these groups have created a comprehensive three-dimensional model for the study of  $PM_x$  in the region. 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 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  $SO_2$  emissions in the modeling domain;
- The sensitivity of the PM in the area to these  $NO_x$ ,  $SO_2$ , and VOC emissions;
- The contribution of primary organic aerosol sources to the OC in Pittsburgh; and
- The contribution of primary and secondary biogenic aerosol to the organic PM in Supersite area.

### 1.5. Personnel Qualifications and Training Required

The project team of the PAQS 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 appropriate PI's will manage the operation and maintenance of the individual research instruments. These PI's will provide SOPs for all responsible users of

the equipment detailing operation, quality assurance functions, and data analysis. It will also be the PI's responsibility to insure that responsible users receive any special training or certification required to operate and/or maintain these instruments. The QA manager for the project will review, comment and approve all SOPs for the program.

## 1.6. Communication Plan

There are three Principal Investigators who will coordinate and lead various aspects of the overall effort: Spyros Pandis, Cliff Davidson, and Allen Robinson (Figure 2). Monthly conference calls and e-mails will be used to coordinate the activities of the individual investigators.

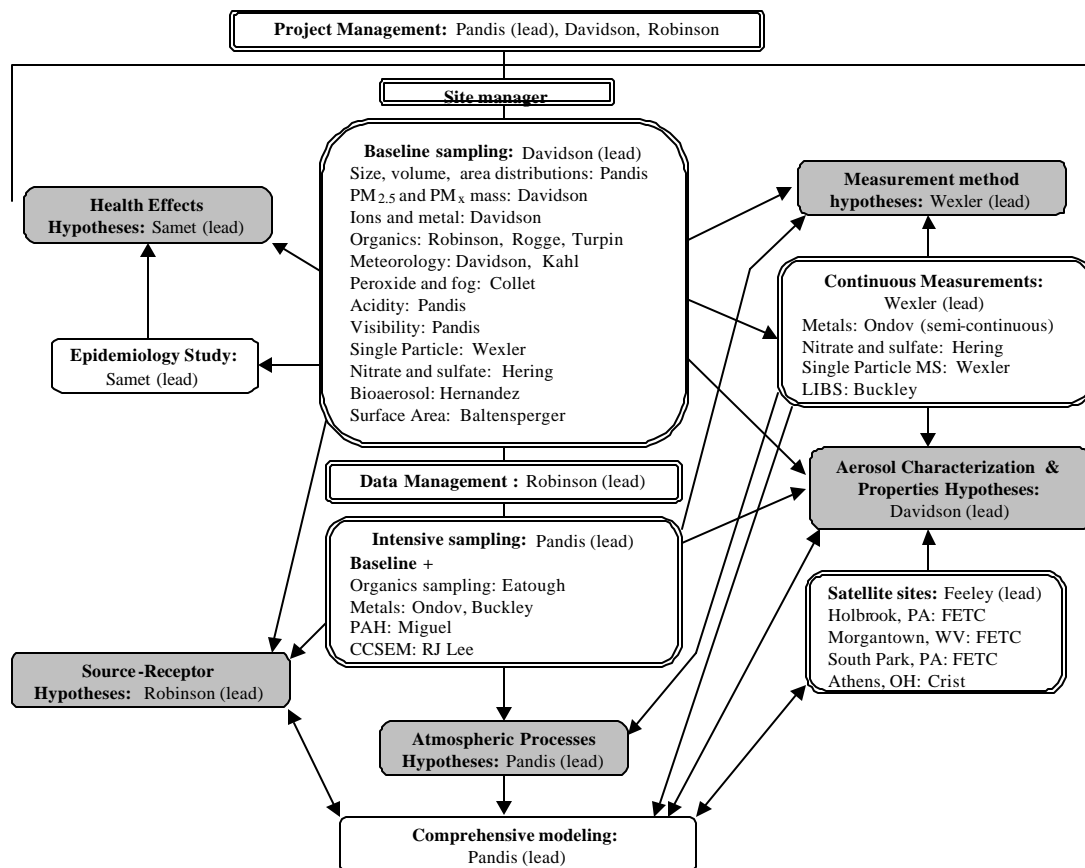


Figure 2. Communication plan for the Pittsburgh Supersite Program

To facilitate evaluation of the progress of the overall project, individual investigators will file progress reports to the Carnegie Mellon University team. Progress reports will be expected on a semi-annual basis. All investigators will write a detailed technical report describing the results and findings of their portion

of the project. All reporting will be done electronically and will form the basis for the semi-annual reports to EPA.

Planning meetings will also be held at technical meetings, such as the AAAR annual meeting, that many of the individual investigators attend in conjunction with their normal 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.

To maximize the effectiveness of the research efforts, data will be shared among the subcontractors, with Allegheny County (Darrell Stern), State of Pennsylvania DEP (Mike Zuvich) and EPA (Paul Solomon). No data will be released or published without prior discussion / agreement among the collaborators.

## **2. PROJECT IMPLEMENTATION**

### **2.1. Project Responsibilities**

Table 4 lists the individuals with responsibility for various aspects of the PAQS Supersite activities. PAQS will be directed by a Project Management Team, consisting of the three PIs: Spyros Pandis, Cliff Davidson, and Allen Robinson; and the site manager: Andrey Khlystov (Figure 3). The Project Management Team will be responsible for budgeting, all communications with the U.S. EPA, coordination with the Science Team, coordination with parallel studies, and supervision of data archiving and site management. The Project Management Team will communicate weekly throughout the course of the project. The team will communicate three times per week during the 3 intensive sampling periods (described later in this document). Occasional conference calls and e-mails will be used to coordinate the activities of the individual investigators.

Spyros Pandis is responsible for overall project management and will oversee the project and coordinate interactions between different groups. Allen Robinson will be responsible for the data management of the project. Andrey Khlystov will be responsible for siting, installation, and operation issues at the central Supersite. Cliff Davidson will be responsible for responding to Quality Assurance (QA) issues raised during the project by the external QA manager, Beth Wittig.

Beth Wittig will be the Quality Assurance manager with the following responsibilities:

- Produce the Quality Assurance Project Plan (QAPP);
- Review Standard Operating Procedures (SOPs);
- Coordinate and perform Technical Systems Audits (TSAs) and performance audits;
- Update the Science Team on any Quality Assurance issues; and
- Produce the Quality Assurance Final Report (QAFR).

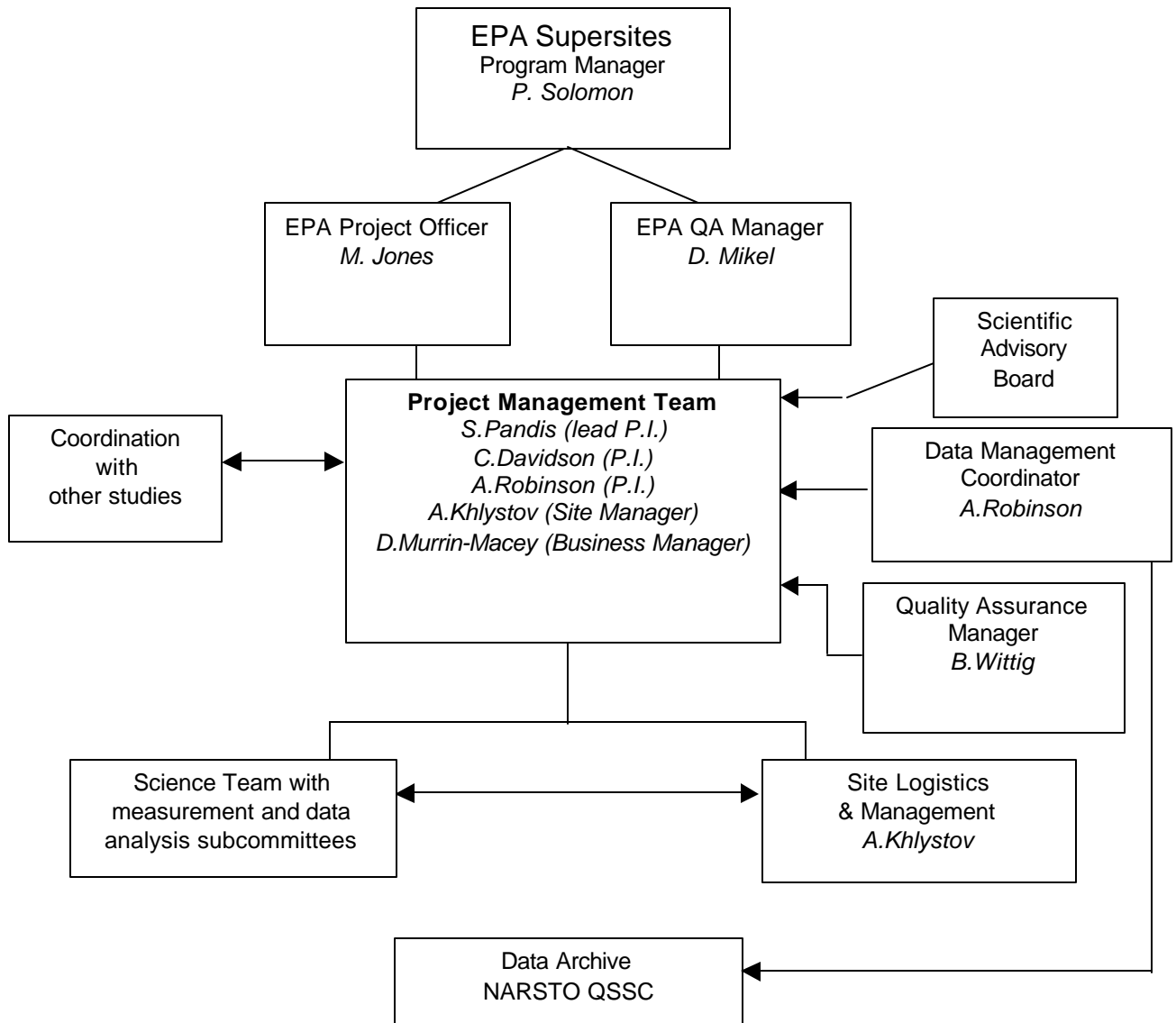


Figure 3. Organizational Chart of PAQS Management Structure

Twenty different groups from thirteen universities, one national laboratory, two private companies, and one federal agency will be involved in the project (Table 4). The individual PIs will be responsible for running and maintaining their portions of the PAQS study as well as performing quality assessment of field and laboratory procedures and operations.

**Table 4. List of collaborators of PAQS and their tasks.**

Collaborator	Task	Funding
Prof. Spyros Pandis, Prof. Cliff Davidson, Prof. Allen Robinson (Carnegie Mellon Univ.)	Overall project management, Aerosol physical and chemical characterization	EPA-DOE
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. Susanne 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
Prof. Delbert Eatough (Brigham Young Univ.)	Organic aerosol sampling	DOE
Dr. Urs Baltensperger (Paul Scherrer Institute)	Surface area	Other
Professor Jonathan Samet (Johns Hopkins) or other investigator	Epidemiological study	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 also direct the measurements of aerosol size distributions, acidity, hygroscopic properties, VOCs, and visibility. Dr. Davidson will also be responsible for the inorganic composition measurements and for responding to QA concerns raised by the QA Manager. Finally, Dr. Robinson will also be responsible for OC, EC, and PM mass measurements, and project data management. Both EPA and DOE/FETC funds will support the work at Carnegie Mellon University.

## 2.2. Project schedule

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

**Table 5. Project Schedule.**

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

## 2.3. Project Design Criteria

### 2.3.1. Site Selection

Variables to be determined when evaluating a site for consideration include: representativeness of an individual site, the distance of the site from point sources and major roadways or other urban sources, and the spatial distribution to assure adequate spatial distribution. Specific criteria for sampler height siting, the siting of samplers away from obstructions and in a location of unrestricted airflow and removal from major roadways will follow U. S. EPA guidelines.

The main monitoring site will be located in Schenley Park close to the downtown Pittsburgh. 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. The location of the site is within the greater Pittsburgh area. Particle monitoring at this site is intended to represent both an urban scale and neighborhood scale for exposure assessment to PM.

### 2.3.2. Sample Collection and Handling

Each PI will prepare a detailed Standard Operating Procedure (SOP) that will describe sample preparation, collecting and handling as well as determine the sampling times, frequencies and sample media.

### 2.3.3. Sample Custody

It is assumed that all investigators and their staff will perform satisfactory sample custody. The Quality Assurance Manager will inspect all sample custody forms, logs and procedures during the TSAs. All SOPs will have detailed text discussing the sample custody. Any deviations will be noted during the TSAs.

## 2.4. Data Quality Indicators

The typical Data Quality Indicators (DQI) associated with measurements are precision, accuracy, representativeness, completeness, minimum detection limits (MDLs) and comparability. These DQIs can be quantified for a majority of the individual instruments, as well as for the project as a whole. The DQIs will be determined to the extent possible for each instrument/system of the project, and will be the responsibility of the individual PIs. Specific values for DQIs will be provided in the individual SOPs and Research Plans (RPs). The Quality Assurance Manager will perform technical systems audits to ensure that DQIs are reported and met by the individual PIs.

### 2.4.1. Precision

Precision is a measure of the repeatability of results or of the agreement among individual measurements of the same parameter under the same prescribed conditions. Precision of the analytical instruments will be performed by repeated analysis of independent traceable standards that are separate from the standards used for instrument calibration. The precision of filter-based methods will be assessed by running collocated samplers. Continuous instruments will be subjected, when possible, to artificially generated analytes. The individual investigators will determine the number of replicate analyses needed to properly assess the precision of each instrument. Replicate analyses will be performed during periods of calibration. For each series of replicate analyses, the precision will be calculated as:

**Equation 2.1**    Precision (%) =  $100 [2 s] / \{x\}$

where s is the standard deviation between the replicate analyses and {x} is the mean of the replicate analyses. DQI values for precision will be stated in the individual SOPs and RPs.

## 2.4.2. Accuracy

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

**Equation 2.2 Accuracy (%) =  $(100 * [s - \{x\}]) / s$**

where  $s$  is the standard value of the authentic traceable standard and  $\{x\}$  is the mean of the instrument responses to the replicate analysis. DQI values for accuracy will be established in the individual SOPs and RPs.

## 2.4.3. Minimum detection limits

The minimum detection limit (MDL) is defined as a statistically determined value above which the reported concentration can be differentiated, at a specific probability, from a zero concentration.

Analytical procedures and sampling equipment impose specific constraints on the determination of detection limits. For the gaseous parameters, MDLs are determined by challenging the instruments with purified zero air. However, for filter-based instruments, the MDLs are determined by blanks. It is recommended that all filter-based instruments perform the field and laboratory filter blank tests. It is a good laboratory practice for the field blank to be a filter that undergoes all the preparation, transportation, storage, and analysis activities as and with the sample filters. The main difference between the field blank and a sample filter is that it is left inside the instrument housing with the filter cover on, but not loaded into the filter mechanism. Laboratory (lab) blanks are filters that undergo all of the same lab processes as the sample filters, and none of the sampling activities, including transportation, storage, and sampling. It is a good laboratory practice to randomly pick a filter and leave it in the weighing room. This filter is then post-weighed and handled in the same manner as all filters arriving from the field. It is recommended that 10% of all filters handled should be lab and field blanks. The actual methodologies for determining MDL will be stated in the individual SOPs and RPs.

Measurement results below MDLs of the instrument should be reported as measured and to the level of precision of the instrument, but flagged accordingly. Data values derived from any MDL data should be flagged appropriately.

The following sections illustrate how MDLs are quantified for filter and non-filter methods.



### 2.4.3.1. *Continuous Measurements*

The configuration of the continuous gas monitors (in particular the ability to introduce standards at the sample inlet) allows for the determination of the MDL for each continuous analyte. The MDL includes all sampling and analytical procedures and therefore represents a detection limit that can be applied to ambient concentrations. The MDL concentration is determined in zero air with a small amount of analyte (estimated MDL) and therefore will not address matrix interferences.

The MDL for each continuous gas monitor will be determined through statistical evaluation of the zero check standard. The following equation will be used to determine the MDL:

**Equation 2.3**  $MDL = t_{(n-1, 0.99)} * s$

where s is the standard deviation of the replicate zero analyses, and t is the student's t-test value for a standard deviation estimate with n-1 degrees of freedom at a 99% confidence level.

### 2.4.3.2. *Discrete Measurements*

The laboratory analytical protocol requires that samples be collected at a location away from analysis. Standards for the determination of detection limits for these laboratory instruments are prepared in the laboratory and therefore are not subject to the same procedures and equipment as the ambient samples. This detection limit is referred to as the instrument detection limit (IDL). The IDL is indicative of the ability of the instrument to differentiate, at a specific probability, between zero and a specific concentration. The IDL standard does not experience the same handling procedures as filter or canister collection, and therefore does not provide information relating to the detection limit at ambient concentrations. The IDL will be determined through statistical evaluation as described in Equation 2.3.

### 2.4.4. **Completeness**

The completeness of the data set will be determined as the percentage of the scheduled sample collections that result in validated ambient observations that meet data quality objectives set forward in the program quality assurance plan.

**Equation 2.4**  $Completeness (\%) = (N \text{ valid measurements} / \text{total } N \text{ measurements}) * 100$

DQI values for completeness will be stated in the individual SOPs and RPs.

## 2.4.5. Comparability

Comparability refers to how confidently one data set can be compared with another. Ideally, two instruments that measure the same parameter would be statistically comparable. One of the objectives of the Supersite is to test new state-of-the-science instruments to see if the values collected are comparable with instruments of well-known and documented accuracy and precision. For a research study that will be testing state-of-the-science instruments and methods, comparability becomes more difficult to estimate. The way to ascertain comparability can be estimated using the following MQOs.

### 2.4.5.1. *Inference of Analysis*

At times, when instruments are used in research projects, such as a Supersite, there may one instrument that measures species that cannot be duplicated or compared against other methods. In this case, the only QA activity would be internal calibrations or maintenance checks. It is recommended that an instrument of known quality be operated and used to evaluate measurements collected from a research instrument. As an example, if a new method for analyzing sulfates in vapor phase is developed, but there are no instruments to compare the results to, it would be recommended that data be used from a speciated particle sampler that captures sulfates. By using phase to particle models, the sulfate data can be compared against the sulfate vapor data and inferences about the quality of the sulfate data can be made. The Quality Assurance Manager must be aware of these types of analyses and perform the final analysis in the QAFR.

### 2.4.5.2. *Trend Analysis*

Trend analysis techniques have been applied successfully to Photochemical Assessment Monitoring Stations (PAMS) measurements. Several trend analyses may be effective indicators of trends in the Supersite measurements. Mean or median concentrations, highest daily maximum, percentile of daily maxima can all be used to test whether hourly data and integrated 24-hour data are following similar trends. The following rules will be applied when performing trend analysis:

- Apply statistics for detecting trends, such as linear regressions of species or tests of variance such as the student's t-test, and
- Apply proper weighting factors that are based upon models using known ratios of parameters in the atmosphere.

The principal investigators and the Quality Assurance Manager will select the analyses used to evaluate trends in the Supersite measurements.

### 2.4.5.3. *Intercomparisons*

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.

The intercomparison between instruments will be performed only for data that meet the data quality objectives for precision, accuracy and completeness. In cases where instruments are used in which comparisons cannot be made, or measurements cannot be duplicated, the only QA will be internal calibration and maintenance checks.

### 2.4.6. **Representativeness**

Generally, representativeness expresses how closely a sample reflects the characteristics of the surrounding environment. This is usually quantified in terms of a spatial scale for monitoring. 40 CFR 58, Appendix D discusses monitoring scale in great detail. In brief, the major components of the Supersite measurements are fine and coarse particles in the Pittsburgh urban area. The fine and coarse particle scale is recommended to be 'neighborhood' scale with a distance on the order of 0.5 to 4.0 kilometers.

Variables to be determined when evaluating a site for consideration include: representativeness of an individual site, the distance from the site to point sources, major roadways, other urban sources, and the immediate local environment. Specific criteria for sampler height siting, the siting of samplers away from obstructions and in a location of unrestricted airflow and removal from major roadways will follow U. S. EPA guidelines.

The main monitoring site is located in Schenley Park in the Oakland district of Pittsburgh. The site is on top of a grassy hill adjacent to the CMU campus, several hundred meters from the nearest heavily traveled street (Forbes Avenue), and fifty meters past the end of a dead end street on campus. There are no major sources within several hundred meters of the site. Schenley Park extends more than a kilometer to the south and west, the predominant upwind directions. The exposure of the surrounding environs represents both an 'urban' and 'neighborhood' scale for particle monitoring.

Once the field portion of the program is completed, the Quality Assurance Manager will prepare a Quality Assurance Final Report (QAFR). The QAFR will summarize the uncertainty of the data sets in terms of the MQOs stated in Section 2.4. This approach will provide a pathway for reconciliation of the Data Quality Objectives as listed in Table 2.

### 3. DATA ACQUISITION AND 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 who is making the measurements. Individual investigators will also be responsible for the evaluation of quality control test data and Level 1 and Level 2 measurement validation. The Data Management Coordinator (DMC), Allen Robinson, will bring the data from all of the investigators together and construct the project data archive (NARSTO QSSC).

#### 3.1. Handling and Custody of Samples

Procedures will be developed to collect, transport and store the samples for analysis that will minimize the possibility of contamination or introduction of artifacts. These procedures will be documented in SOPs. Special care will be taken to prevent the volatilization of semi volatile species from filter samples, as well as to prevent contamination of collected samples from the ubiquitous gaseous air pollutants such as ammonia or formaldehyde.

Specific procedures to ensure the integrity of the collected samples will be outlined in the SOPs and RPs developed for each instrument. However, at a minimum these will include the necessary procedures for ensuring sample integrity during:

- Preparation of sampling material, including procedures for cleaning substrate media, loading substrate media into sampling apparatus, and transporting sampling media to field locations;
- Storage of sampling media after sampling, including sealing procedures and temperature requirements during transport;
- Archiving sampling material before analysis to restrict photochemical decomposition and thermal decomposition; and
- Removing samples from the archive for analysis in such a way that preserves sample integrity.

Sample custody will be documented with sampler log sheets for each substrate material (filter, denuder, impregnated cartridge) that will track the lifetime of the substrate media from preparation and cleaning, deployment to the field location, sampling including verification of sampler operation, retrieval, laboratory archiving until analysis, analysis and data reporting.

Unique sample identification numbers will be assigned to each sample collected to record the sample site, sample collection time, substrate media, and sample collection method. These parameters will be used to track the ambient measurements in the project database. Additional information on sample

duration, data quality validation codes, measurement units and sample error bounds will also be included in the data base structure.

Many of the measurements will be made in real-time, removing the necessity for procedures on media preparation, sample retrieval, archiving and analysis. For these measurements, however, separate procedures will be developed to determine the sample representativeness, accuracy, and precision and to ensure that the data are archived in a manner that preserves data integrity. The data will be stored with a unique identification number, similar to the sample identification number, in that it will record the site of measurement, time of measurement and the duration of sampling to make the measurement.

### **3.2. Data Recording**

The data will be stored on electronic media for continuous and semi-continuous instruments. It is strongly recommended that data be "backed-up" every day or sampling interval. Duplicate CD-ROM or diskettes will be created for data storage.

A sample NARSTO-format data template will be furnished to all principle investigators. It is important for all PIs and co-PIs to use this template. The ambient data as well as secondary (calibration and descriptive data) storage will be the responsibility of the individual PIs. These data will be made available for inspection or review by the QA Manager.

Data obtained from non-automatic devices (e.g. flow meters) will be recorded in a designated lab and field journals. All maintenance procedures and calibration data will also be recorded in designated lab and field journals.

### **3.3. Identification of Data**

All data will have appropriate identification such that is clearly identifiable and traceable to the instrument / method from which the data were produced. This identification and traceability will be maintained throughout the lifetime of the data.

All data will be reported to and ultimately archived by the Data Management Coordinator (DMC), with appropriate time stamping to indicate the time increment of the data. A valid time-averaged data set must contain validated data points for at least 70% of the total possible data points over the time interval. Otherwise, the time-averaged values are flagged and reported using an appropriate validation code.

Data will be reported in Eastern Standard Time, including day, month, and year as formatted as MM/DD/YYYY hh:mm format (e.g., 01/15/2001 10:20). The daily time cycle runs from 00:00 to 23:59 (24:00 is not a valid time). Character values

may not be used to denote sampling or analysis months and leading zeros should be used for day or month entries less than ten (i.e., 08 to represent August, not 8 or AUG).

All data fields should have a value present, either the measured or adjusted data value or a missing value representation. There should be no blank fields. Contributors should report data where possible and use flag codes. All values should be numerical values, not character or alphanumeric values, to aid quality control efforts. Missing values for data parameters should be represented by a value of -9999. Data flag codes should differentiate between valid values, invalid values, estimated values, interpolated values, and MDLs.

All data reporting forms will contain a column for flagging and indicating the validity of quality data. All problematic and missing data points will be highlighted in the form through the insertion of appropriate coded flags. These flags are listed below. Flags beginning with the letter "V" for valid values, "M" for missing values, or "H" for historical data unable to be assessed or validated. No invalid non-missing data will be placed in the Reporting Form to avoid their possible inadvertent use. Additional flags may be incorporated as appropriate to the measurement. The individual PIs will be required to submit comprehensive lists of additional flags used upon submission of data to the archive.

Code Data Quality Flag Definition:

V0	Valid value
V1	Valid value but compromised wholly or partially of below-MDL data
V2	Valid estimated value
V3	Valid interpolated value
V4	Valid value despite failing some statistical outlier tests
V5	Valid value but qualified because of possible contamination (e.g., pollution source, laboratory contamination source)
V6	Valid value but qualified due to non-standard sampling conditions (e.g., instrument malfunction, sampling handling)
M1	Missing value, no value available
M2	Missing value because invalidated by Data Originator
H1	Historical data that have not been assessed or validated

### 3.4. Data Validation

All Supersite data will be validated and classified with a level of validation; ranging from zero (0) to two (2). Level 0 designations will be given to raw data and other research products that have not been audited or peer reviewed. Level 0 data contain all available measurement data and may contain data in the form of quality control checks and flags indicating missing or invalid data. Level 1 data are data generated by project groups. Level 1 data is the designation for data that have been modified in response to audits, adjusted to account for "blank bias" (lab analyses) or "zero drift" (continuous ambient measurements). Level 2

designations are given to data that have undergone interpretative and diagnostic analysis by the individual PIs. To receive this designation, data must have been closely examined by the PIs for consistency with related data sets.

The SOPs or RPs for individual instruments will detail the methods of review, validation and verification of data. The SOP or RP will also contain criteria for accepting, rejecting, or qualifying the data.

### **3.5. Data reduction and transfer**

The SOPs and RPs will describe data reduction procedures. All the raw data, both primary (ambient data) and secondary (e.g. calibration) will be archived without modifications. This will insure that there is no permanent loss of data as a result of problems during data transfer or data reduction. Each data reduction procedure and the transfer of data will be documented in logbooks and/or field forms.

## **4. ROUTINE CONTROLS AND PROCEDURES**

Routine controls and procedures for individual instruments will be carried out according to the individual SOPs and RPs. At minimum, these routine controls will include:

- Checks of the flow rates,
- Leak Checks,
- Calibration, and
- Determination of blanks.

The SOPs and RPs will also include templates for standard forms and checklists, and routine procedures such as acceptance testing of equipment and preventive and corrective maintenance. The maintenance schedule and procedures will be detailed in the SOPs or RPs.

If an audit shows that a system may be out of specifications, the SOPs and RPs will be used to identify and resolve the issue. The instrument or sampler will be considered to be online after normal operation of the system is verified by repeating the audit procedures.

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### APPENDIX 1. LOCATION OF SITE.





West view



View North



View East



View South

**APPENDIX 2. LIST OF ADDRESSES AND THE RESPONSIBLE PERSONS FOR LABORATORIES AND SUPPORTING FACILITIES TO BE USED IN PAQS.**

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## **APPENDIX 3. STANDARD OPERATING PROCEDURES AND RESEARCH PROTOCOLS.**