QUALITY ASSURANCE PROJECT PLAN

for the

BALTIMORE SUPERSITE

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1.0 TITLE AND APPROVAL SHEET

1.1 Preface

This Quality Assurance Project Plan is submitted in fulfillment of the following U.S. Environmental Protection Agency (EPA) quality assurance project plan requirements of EPA Cooperative Agreement number R82806301 (EPA award date: January 15, 2000).

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1.2 Quality Assurance Project Plan Approval Sheet

This plan has been approved by the following individuals.

Baltimore Supersite Lead Principle Investigator — Date: 6/30/01
John M. Ondov

Baltimore Supersite Quality Assurance Manager — Date: 6/23/01
Philip K. Hopke

Ziad Ramadan — Date: 6/27/01
Baltimore Supersite Data Manager

EPA Supersite Quality Assurance Manager — Date: 5/2/01
Dennis Mikel

EPA Supersite Project Officer — Date: 5/2/01
Michael Jones

EPA Supersite Program Manager — Date: 5-29-01
Paul Solomon

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2.3 LIST OF ABBREVIATIONS

CPC - Condensation Particle Counter

EC - Elemental Carbon
EPA - Environmental Protection Agency

FA - Factor Analysis
FRM - Federal Reference Method

HVOS - High-Volume Organic Sampler

LIDAR - LIght Detection And Ranging

MDE - Maryland Department of Environment
MQO - Measurement Quality objectives

OC - Organic carbon
OPC - Optical particle counter
OPS - Operations
OS - Organic Speciation

PI - Principle Investigator

QA - Quality Assurance

RDI - Rotating Drum Impactor
ROS - Reactive Oxygen Species

S- Sub daily
SC - Semi Continuous
SEAS-Sequential Elements in Aerosol Sampler
SPMS - Single Particle Mass Spectrometer

UM - University of Maryland
UMUHVAS - University of Maryland Ultra High Volume Air Sampler

3.0 DISTRIBUTION LIST

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Timothy J. Buckley, Investigator, Johns-Hopkins University

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Marc B. Parlange, Investigator, Johns-Hopkins University

Wolfgang F. Rogge, Investigator, Florida International University

Katherine S. Squibb, Investigator, University of Maryland at Baltimore

Anthony S. Wexler, University of California at Davis (formerly University of Delaware at Newark)

Murray Johnston, University of Delaware at Newark

Ziad Ramadan, Data Manager, Clarkson University

Theodore Erdman, EPA Region III

Fran Pluciennck, Maryland Department of Environment

Richard Wies, Maryland Department of Environment

Dennis K. Mikel, EPA Quality Assurance Manger

Michael Jones, EPA Project Officer

Richard D. Scheffe, Program Manager, EPA Office of Air Quality Planning and Standards

Paul Solomon, Project Officer, EPA office of Research and Development SDOS - Sub-daily Organic Sampler

4.0 QA PROJECT PLAN GOALS

The Baltimore Supersite Project encompasses an enormous number of sophisticated measurements ranging from well specified Federal Reference Method monitoring to research- grade field measurements with new state-of-the art instruments, to innovative new laboratory analysis methods and applications (e.g., short-term *in vitro* toxicology assays). The goals of the QA plan are to document the framework needed to ensure that:

- the measurements to be undertaken will adequately support the project objectives regarding data collection and hypothesis testing,
- data collected are of the highest quality that can be reasonably expected,
- the quality of the data is known,
- the data and its quality are adequately documented, and
- the data are adequately preserved and rendered in available form.

Additionally, this QAPP documents changes in allocation of resources, sampling, and analytical strategies made since the submission of the project proposal.

5.0 PROBLEM DEFINITION AND BACKGROUND

5.1 Overview

Recent epidemiologic studies have shown that short-term increases in urban particulate air pollution are associated with increased mortality and morbidity from respiratory and cardiovascular diseases. The studies suggest that non-accidental death rates in cities correlate with daily levels of respirable aerosol particles, even at particulate concentrations below the current National Ambient Air Quality Standard. Mortality victims tend to be elderly, with pre-existing respiratory disease, and individuals with asthma appear to be at higher risk. Other studies have established a link between levels of airborne particles and respiratory symptoms in children and hospital admissions for bronchitis, asthma and pneumonia. The precise mechanism by which air particles exert their toxic effects is not known. However, recent evidence suggests strongly that particles sufficiently small to reach the alveoli of the lung may directly initiate (or exacerbate) irritation of respiratory tissues by stimulating local cells to release reactive oxygen species (ROS; e.g., hydrogen peroxide and superoxide free radicals) and inflammatory mediators, such as cytokines. Experimental evidence strongly suggests that a release of cytokines and ROS by alveolar macrophage and lung epithelial cells contributes to the toxic effects of particulate air pollutants.

Many components of air particles could play a role in stimulating respiratory cells to produce cytokines and ROS. Possible candidates include endotoxin, mineral oxides, water-soluble metals; diesel soot and/or its components, polar organic compounds (OC, e.g., produced by atmospheric oxidation of volatile OC), and the ultrafine aerosol particles. Recent studies indicate that, of these, water-soluble inorganic compounds seem to exert the most profound effects and demonstrate that cytokine and ROS responses by respiratory cells in culture are good indicators of *in vivo* responses to

particles. These assays, then, provide us with a means of predicting key toxic response one would expect to see in inhalation studies and in humans exposed to these particles. By determining the immuno-reactivity of particles in ambient air, one can begin to identify key sources that should be targeted for regulation to achieve a reduction in health effects of air pollutants.

Primary particulate mass emissions from High Temperature Combustion Sources (HTCSs) are emitted in narrow accumulation aerosol peaks with geometric mean diameters between 0.1 and 0.3 :m, and are observed in this size range in ambient size spectra of their marker elements. Once in the atmosphere, these particles grow by capturing water vapor, sulfur dioxide (which becomes converted to secondary sulfate) and various other materials of secondary origin, including polar organic compounds. Thus, older or more highly-processed aerosol particles are substantially larger, i.e., with geometric mean sizes typically between 0.4 and 1 :m.

Baltimore is a populous and important, mid-Atlantic, industrial deepwater port city, located 50 km north of Washington, DC, and 150 km east of the Appalachian mountains. A mere two hour drive to Philadelphia and four hours to New York, Baltimore is a major transportation thoroughfare between populous southern and norther cities. Baltimore is an excellent choice to study the properties of local, regional, and interregionally transported aerosol emissions affecting urban air quality and investigating hypotheses regarding aerosol age, time-resolved sampling, and toxicological response. Like much of the Northeast, PM air quality in Baltimore is heavily influenced by secondary sulfate formed during transport of sulfur emissions from the heavily industrial Ohio Valley that lies >300 kilometers to the west. Air traveling from the Ohio Valley is orographically projected by the Appalachians which facilitates cloud processing and concomitant heterogeneous conversion of sulfur dioxide to sulfate, providing a more aged/processed aerosol which can be differentiated from local emissions by particle size and by chemical composition.

Baltimore air quality is also influenced by urban emissions in Washington, DC and a cluster of coal-fired power plants, and municipal and sludge incinerators along the Potomac River extending 50 to 90 km southwest of Baltimore. Locally, most of the Baltimore's industry is concentrated in the 125 km^2 area comprising South Baltimore and Dundalk (Figure 5.1), just a few kilometers from the center of the City, and

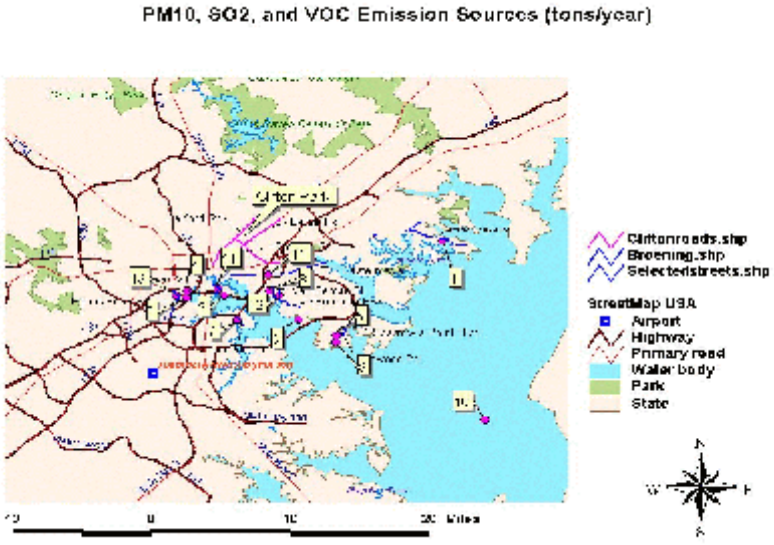

Figure 6.1 Map of the Baltimore region showing the main sources of particulate matter, SO_2, and VOCs.

immediately adjacent to populous neighborhoods. In all, the South Baltimore/Dundalk area contains >40 industrial facilities, including 16 chemical manufacturing plants; 5 bulk materials shipping terminals; 2 medical waste, 1 municipal, and 1 sludge incinerator, 6 land fills for storage of domestic and industrial, including hazardous, waste; the nation's largest Yeast Plant, a rendering plant, an automotive painting plant, and a major Steel plant. In addition to industrial sources, emissions from some 30,000 heavy diesel vehicles using the City's three major toll facilities (Ft. McHenry, Harbor Tunnel, and Key Bridge) each day adds to the area's air pollution problems.

Mean and max PM10 concentrations in south Baltimore (Fairfield) substantially exceed those observed in rural and suburban areas of Maryland by as much as 50% (In 1997, means were31 $\mu g/m^3$ at Fairfield vs. 17 to 20 $\mu g/m^3$; maxima were 86 $\mu g/m^3$ at Fairfield versus 50 to 70 $\mu g/m^3$ at rural and suburban sites. Total aerosol carbon concentrations in summer range from to 2 to 10 $\mu g/m^3$. About 20% of this is elemental carbon while the remainder is characterized as organic carbon by thermal-optical analysis. During the AEOLOS intensive of August, 1995, concentrations of Ca, Cr, Hg, Ti, Cl, Mn, Mo, Sb, and Zn measured in east Baltimore during winds from the direction of the BRESCO municipal incinerator, exceeded those measured upwind of the City by from 10 to >20-fold [Gordon, 1988; Ondov and Wexler, 1998]. In samples influenced by winds from the Bethlehem Steel plant and sources in Hawkins Point, Cr, Fe, Mn, Sb, V, and Zn concentrations exceeded those outside the city by from 2- to 150-fold [Maciejczyk, 2000]. Lastly, 10-fold enrichments in PAH concentrations are observed in the Curtis Creek area, presumably due to the high density of motor vehicles in the area [Baker, 1991]. While there may be other factors, it is, perhaps, poignantly relevant that the percentage of obstructive pulmonary disease deaths in the South Baltimore area is nearly 1.7-fold greater than for the whole of the city [Baltimore City Health Department, 1995].

The problem to be addressed by the Baltimore Supersite Project is to elucidate the contributions of the key sources and key aerosol particle components/metrics responsible for acute human health effects as indicated by *in vitro* inflammatory response measures.

5.2 Objectives

Primary objectives are to i) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques; ii) provide important information on the potential for health effects of particles from specific sources and generic types of sources, iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, v) provide support to existing exposure and epidemiologic studies to achieve enhanced evaluation of health outcome-pollutant and -source relationships, and vi) test the following specific hypothesis:

1. Reduced (i.e., hourly and sub-hourly; three-hourly for organic compounds) sampling/analysis times will immensely improve source attribution.

2. Various health effects of PM are associated with its specific chemical and physical (but mostly chemical) components that, owing to the vast number of these, a source based allocation of air toxins will provide the most useful information for PM standards and control.

3. Different aerosol constituents and properties will have different abilities to elicit the release of cytokines and ROS by cultured cells and that these difference will reflect differences in the extent and types of adverse health effects.

4. Aerosol age affects the size, chemistry, and health effects of PM. Thus spatially distant upwind, industrial area, and center-city aerosols differ significantly in temporal variability and biologically relevant composition.

5. Taken together, detailed sub-hourly information of major, minor, and trace inorganic and organic aerosol constituents, size-resolved aerosol particle concentrations, and cytokine/ROS *in vitro* responses will permit unprecedented resolution of sources of toxic PM components and their toxic effects.

6. 24-hour and short-term concentrations, cytokine and ROS responses, and health effects of potentially toxic aerosol components in areas of Baltimore that are strongly influenced by heavy industry measurably exceed those observed in an urban downtown site that is weakly influenced by industrial sources.

7. Spatial distribution of various fine aerosol particle constituents are highly inhomogeneous due to both variations in sources and regional circulations.

5.3 Project Organization

5.3.1 Project Management and Responsibilities. A project organizational chart is shown in Figure 5.2 and is described as follows. As lead PI, **Dr John Ondov** (UMCP), is responsible for overall project management, integration of individual project components and coordination of the final synthesis of the results. Ondov is assisted by an internal steering committee composed of the individual co-investigators, through frequent telephone conference and email communications; and by an external advisory committee, comprised of air pollution monitoring, epidemiology, toxicology, and policy/regulatory experts from the scientific community at large and EPA. Day-to-day operation of the project is the responsibility of Dr. Thomas Tuch, Senior Aerosol Scientist. Dr. Patrick Pancras has been hired to serve as project analytical chemist and is responsible for coordination and day-to-day performance of analytical work. Drs. Tuch and Pancras are assisted by a Graduate Research Assistant, Jennifer Moore (UMCP), and Markus Pahlow, graduate research assistant at JHU, during intensive sampling campaigns.

Drs. Anthony S. Wexler (UC Davis) and **Murray V. Johnston** (Univ. Delaware) are responsible for fielding the 3nd generation automated single-particle mass spectrometer system for near-real time constituent analysis. **Dr. Philip Hopke** (Clarkson Univ.) is responsible for hypothesis testing, and will serve as project quality assurance officer, and will perform the QA/QC audits. Dr. Hopke will be assisted by Dr. Ziad Ramadan, who will be responsible for data base management, and an external contractor who is responsible for development of the database system. **Dr. Katherine Squibb** (UM, Baltimore) is responsible for conducting cytokine/ROS response assays on $PM_{2.5}$ samples. **Dr. Timothy J.. Buckley** (Johns-Hopkins Univ.) is responsible for coordination of Baltimore Supersite activities with community sites measurements. Dr. Buckley will also serve as a liaison between Supersite project investigators and epidemiology, toxicology, and exposure researchers at the Johns Hopkins School of Public Health. **Dr. Marc B. Parlange** (Johns Hopkins Univ.) is responsible for deployment and operation of an advanced 3-wavelength scanning LIDAR system for mapping of relative PM concentrations. **Dr. Wolfgang Rogge** (Florida International Univ.) is responsible for organic compound analysis for source identification.

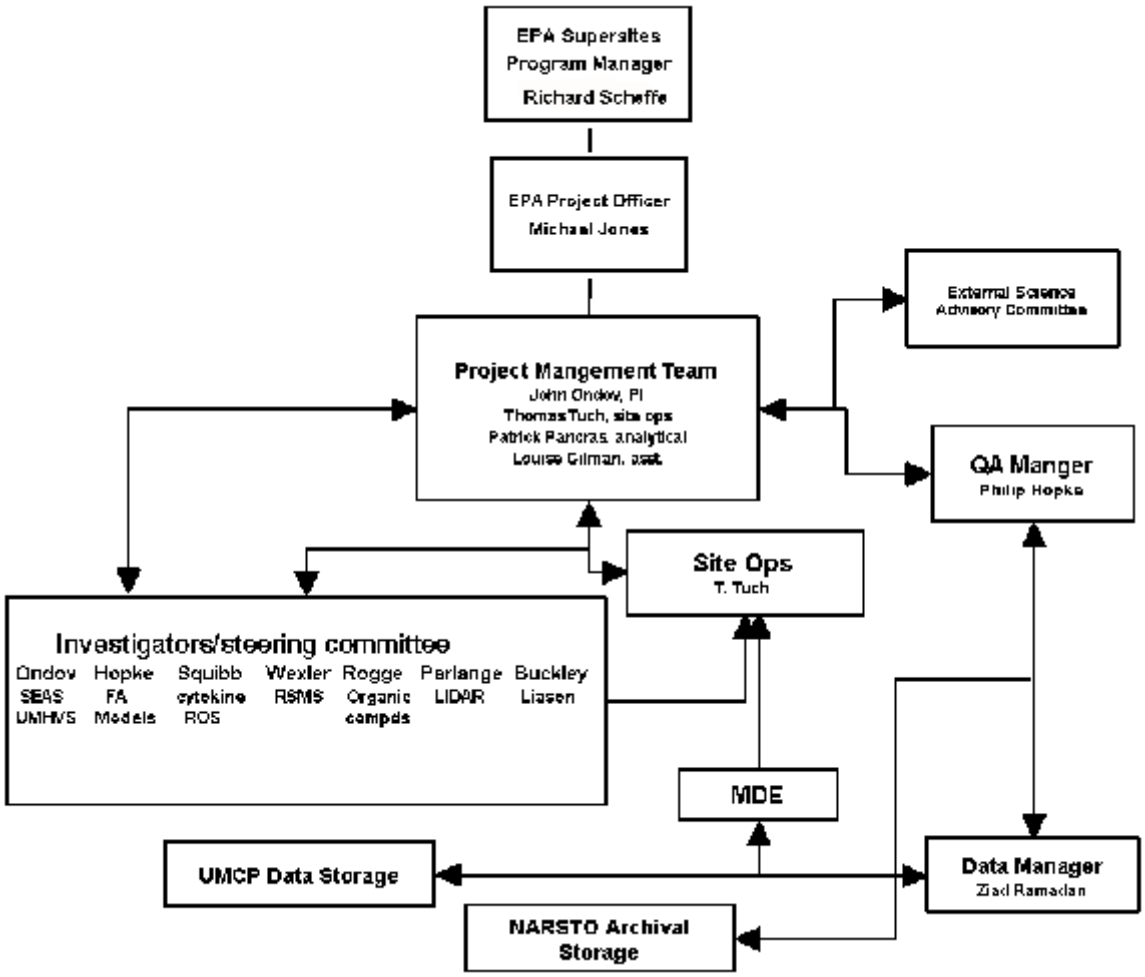

Figure 6.1 Organizational chart for the Baltimore Supersite project.

The Maryland Department of Environment will supply the following measurements on a 1-in-3-day basis during the routine field measurement phase at the Clifton Park supersite: FRM mass, PM2.5 speciation, semicontinuous aerosol mass (TEOM), VOC (ozone season only), CO, and NOx. The MDE will also provide instruments to be used by UMCP for daily FRM and speciation measurements during the intensive sampling campaigns.

The various members are listed in Table 5.1 along with their addresses and contact information.

Table 5.1 Baltimore Supersite Organization

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5.4 Project Schedule

The project period is Jan 1, 2000 to Dec 31, 2003. The first 18 months are dedicated to purchase, calibration, and construction, and installation of instruments, and data base management program construction. The first field campaign, i.e., a (nominally) 30 day intensive study will be initiated on or about May 1 2001, at the South Baltimore site. The equipment will be moved to Clifton Park immediately afterward and setup for initiation of the summer intensive campaign on July 1, 2001.

Routine field measurements will ensue for the next 11 months at Clifton Park. The second (nominally 30-day) intensive field campaign will be initiated on or about January 2nd, 2002. Projected dates for reporting, data base construction/data delivery, and reporting are indicated in Figure 5.3a and b. Additionally, critical dates are listed in Table 5.2. As indicated, we plan to host a data analysis workshop in the second part of the measurement period, and again early in the 4th year of the project. The last 16 months of the project will be dedicated to data interpretation, synthesis, and developing a final project report.

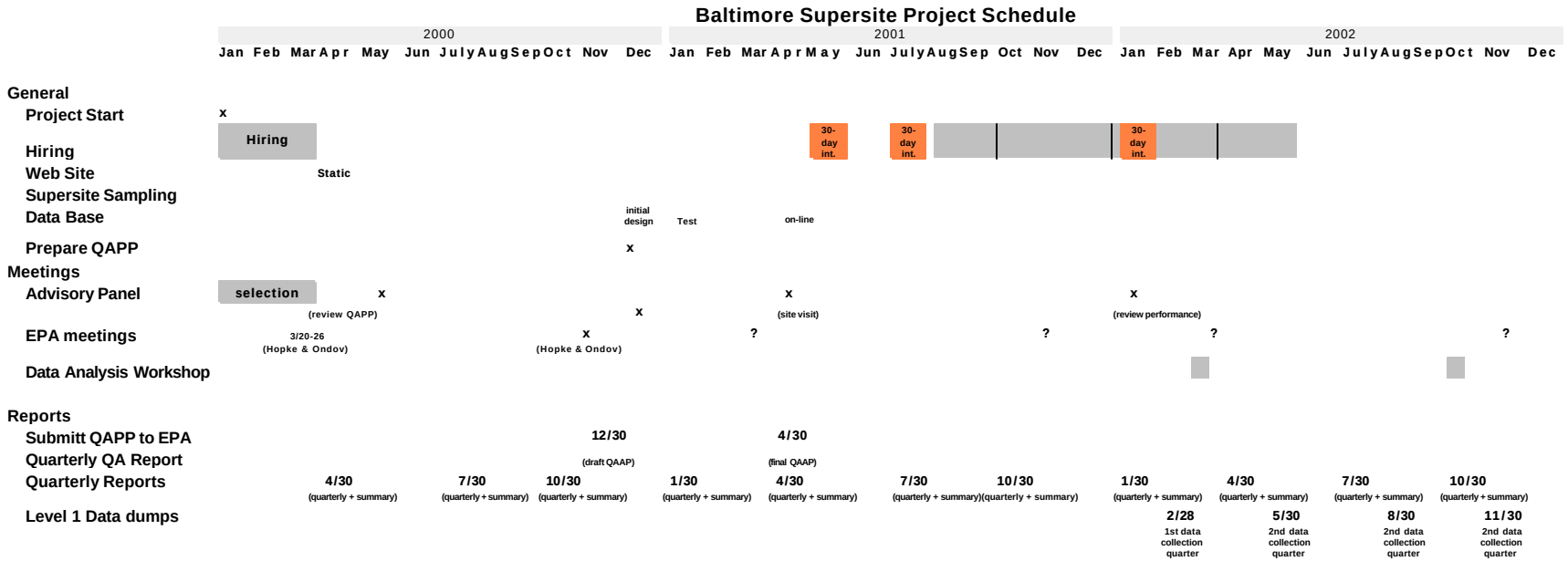

Figure 5.3a. Baltimore Supersite Project Schedule

Baltimore Supersite Project Schedule

2003

	Jan	Feb	Mar	Apr	May	Jun	July	Aug	Sep	Oct	Nov	Dec
Meetings												
Advisory Panel								x (review results)				
EPA meetings												
PI meetings				x				x				
Data Analysis Workshop												
Reports												
Quarterly QA Report												
Quarterly Progress Reports	1/30			4/30			7/30			10/30		12/30
Final Report												12/30

Figure 5.2b. Baltimore Supersite Project Schedule, continued

Table 5.2 Baltimore Supersite Project Schedule

January 15, 2000	Project Start Date
March 22-24, 2000	Eastern Supersites PI meeting 1, Ondov & Hopke
April 30, 2000	Quarterly Progress Report + Quarterly Rept. Summary Due
May 11, 2000	1st PI Teleconference
July 30, 2000	Quarterly Progress Report + Quarterly Rept. Summary Due
October 30, 2000	Quarterly Progress Report + Quarterly Rept. Summary Due
December 1, 2000	Draft QAPP prepared for PI review
December 30, 2000	QAPP to be forwarded to EPA for review
January 30 2001	Quarterly Progress Report + Quarterly Rept. Summary Due
April 30, 2001	Quarterly Progress Report + Quarterly Rept. Summary Due Final QAPP to be forwarded to EPA and all PIs
May 1, 2001	Start 30-day (Nominal) Sampling Intensive, South Baltimore
July 1 2001	Start Sampling Intensive,Clifton Park, Start of 11-month Clifton Park Measurement Period
July 30, 2001	Quarterly Progress Report + Quarterly Rept. Summary Due
October 30, 2001	Quarterly Progress Report + Quarterly Rept. Summary Due
January 1, 2002	Second 30-day Intensive, Clifton Park
January 30, 2002	Quarterly Progress Report + Quarterly Rept. Summary Due
February 28, 2002	Level 1 validated data to be forwarded to limited access EPA Supersite Progam data web or FTP site (for 1st data collection quarter)
April 30, 2002	Quarterly Progress Report + Quarterly Rept. Summary Due
May 30, 2002	End Field Measurements Level 1 validated data to be forwarded to limited access EPA Supersite Program Web or FTP site (for 2nd data collection quarter)
July 30, 2002	Quarterly Progress Report + Quarterly Rept. Summary Due
August 30, 2002	Level 1 validated data to be forwarded to limited access EPA Supersite Program Web or FTP site (for 3rd data collection quarter)
October 30, 2002	Quarterly Progress Report + Quarterly Rept. Summary Due
November 30, 2002	Level 1 validated data to be forwarded to limited access EPA Supersite Program Web or FTP site (for 4nd data collection quarter)
January 30, 2003	Quarterly Progress Report + Quarterly Rept. Summary Due
April 30, 2003	Quarterly Progress Report + Quarterly Rept. Summary Due
July 30, 2003	Quarterly Progress Report + Quarterly Rept. Summary Due
October 30, 2003	Quarterly Progress Report + Quarterly Rept. Summary Due
December 31, 2003	Quarterly Progress Report + Quarterly Rept. Summary Due
December 31, 2003	Final Project Report + Executive summary Report Quality Assurance Final Report (QAFR) due

6.0 PROJECT TASK DESCRIPTION

Principle tasks are as follows: i) field measurements, ii) laboratory sample analysis, iii) data base entry, iv) QA/QC, v) data reduction/analysis in support of project objectives and testing of stated project hypotheses, vi) reporting, and vii) submission of data for archival storage.

6.1 Sampling Sites

The Baltimore Supersite Project encompasses measurements to be conducted serially at two core sites: i.e., Clifton Park, an urban site located 2 km north west of downtown Baltimore and surrounded by residential neighborhoods; and a South Baltimore site situated in the midst of industrial sources. Measurements will be made at Clifton Park will include two, nominally, 30 day intensive sampling campaigns and 9 additional months of routine measurement activities. Measurements at the South Baltimore site will be conducted for a period not to exceed 30 days. All measurements are designed to support the project objectives and hypotheses listed above. We have received approval to use property owned by the FMC Corporation in South Baltimore, a site currently used by MDE for routine aerosol monitoring. More than 18 substantial point industrial and municipal sources are located along a, roughly, 225° arc extending west from the Fairfield/East Brooklyn communities on the Patapsco River/Curtis Bay inlet, south through Brooklyn along Curtis Bay/Curtis Creek, and east through Hawkins Point (Figure 6.1). These sources are positioned to allow us to test the ability of highly-time resolved monitoring to permit resolution of sources and evaluation of the toxic potential in support of hypotheses 1-6, and achieve spatial characterization objectives for this highly-polluted neighborhood; one that is typical of many Northeastern cities.

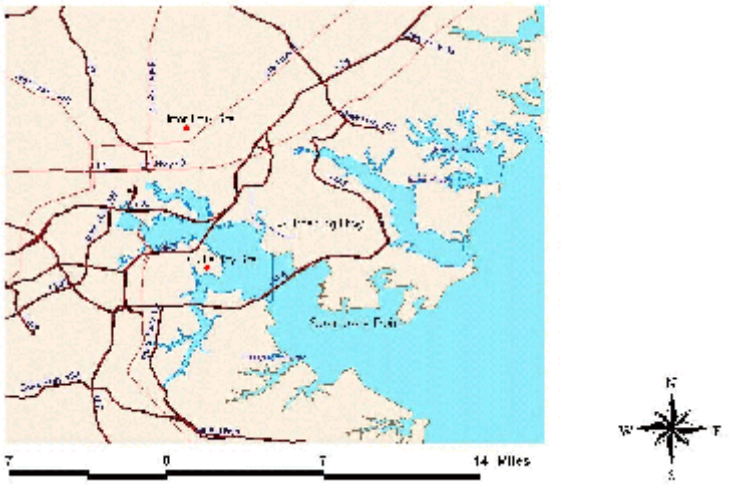

Figure 6.1 Map of the Baltimore area showing the primary sampling site at Clifton Park and the site for the intensive study in South Baltimore at Curtis Bay.

6.2 Measurements

Baltimore supersite measurements encompass the measurements listed below. For each measurement system, there are individual standard operating procedures (SOPs). Additional measurements will be made available by MDE at the Clifton Park site (i.e., continuous mass via TEOM, ozone, CO, NOx, and VOC), by neighboring authorities (e.g., Pennsylvania DEP, Washington, DC; and IMPROVE sites at Shenandoah National Park), and by EPA collaborators.

Quality assurance plans for measurements made by MDE, State agencies, and EPA collaborators are discussed in their own QAPPs.

Commercially Available and Standard Methods

i) Semi/continuous mass, sulfate, nitrate, and EC/OC;
ii) Semi/continuous Aerosol Number vs Size distribution with Scanning Mobility Particle Sizer (SMPS) and a TSI Aerodynamic Particle Sizer (APS);
iii) Meteorological parameters: Temperature (2 heights), wind direction, wind speed, sigma theta, and solar insolation.
iv) FRM mass and Speciation sampling (performed by MDE except during intensives)
v) Filter/PUF sampling for organic compound determinations

Special Measurements and Measurements employing Advanced Technology

vi) Bulk PM2.5 collections with the UMUHVAS
vii) 30-min fine particle measurement of elemental constituents (SEAS-Sequential Elements in Aerosol Sampler/retrospective analysis)
viii) 30-min fine particle collections for cytokine/ROS response assays
ix) Single Particle Mass Spectrometer (RSMS III)
x) LIDAR measurement of particle fields and mixing height
xi) Drum Impactor collections (5 and 8 size intervals)

The frequency of the various measurements at the Clifton Park and South Baltimore sites are listed in Table 6.1.

Table 6.1 Summary of Baltimore Supersite Measurements by Variable (or measurement domain)

Measurement	Size range/max size	Instrument	Sites	Frequency	Duration	Group
Commercial Continuous/Semicontinuous Monitors						
Ultrafine/near accumulation aerosol number-size distribution, indoor @<70%	0.02 to 0.5 :m	Scanning Mobility Particle Spectrometer	1,2	5 min	12 months	UMCP
Far accumulation aerosol/coarse size spectrum, outdoor ambient	0.5 to >44 :m	Forward Scanning Laser Spectrometer,				
Far accumulation aerosol/coarse size spectrum	0.5 to >10 :m	Optical Particle Counter	1,2	5 min	12 months	UMCP
Accumulation aerosol vs aerodynamic size spectra	0.5 to 20 :m	Aerodynamic Particle Spectrometer	12	5 min	Intensives	UMCP
Mass concentration	PM2.5	TEOM, 1400A	12	5 min	12 months	MDE
Sulfate concentration	PM2.5	R&P	1,2	10 min	12 months	UMCP
Nitrate concentration	PM2.5	R&P	1,2	10 min	12 months	UMCP
EC/OC	PM2.5	R&P Series 5400-99-004-743-00 25	1,2	30 to 60 min	12 months	UMCP
Temp (2 heights), RH, wind speed and direction, sigma theta, barometric pressure, solar insulation		RM Young/Campbell Sci. met station	1,2	10 s	12 months	UMCP
Sensible heat and momentum fluxes		3-D SONIC ANEMOMETER	1,2	1 s	intensives	JHU
Ozone		**TECO**	1	5 min avg.	12 months	MDE
NOx, NO2, NO		TECO	1	5 min avg.	12 months	MDE
SO2		TECO	1*	5 min avg.	12 months	MDE

VOC		Hewlet Packard GC	1	30 min avg.	ozone season	MDE
Special Measurements						
As, Cu, Mn, Ni, Cr, Cd, Se, Ag, Pb, Al, Fe, Zn, Ca, V, Ti, Be, Ba (choice of elements may change as data are gathered).	<1.2 :m	UMCP SEAS, retrospective analysis	1,2	30 min	12 months 1000 samples	UMCP
Single particle classification by composition and size (Most metals, e.g., Na, Mg, K, Cr, Cu, Zn, Cd, Cs, La, Pb, some valence information, NH4SO4, sulfites, hydroxymethane sulfonic acid, methane sulfonic acid, EC/OC, polynuclear aromatic hydrocarbons)	<1.5 :m*	UDE/UCDRSMS III	1,2	continuous	12 months	UDE
Relative Aerosol Concentration and Mixing Height						
Time domain scan (8 km range)		JHU 3-wavelength Lidar	area	1 scan every 6 days	12 months	JHU
Time domain scan		JHU 3-wavelength Lidar	area	1 scan every hour during daylight	Intensives	JHU
Collections for Off-Line Analyses						
FRM Mass Conc.,	<2.5 :m	RAAS2.52.5-100	1,2	1 in 3 day, 24 hr	12 months	MDE
FRM Mass Conc	<2.5 :m	RAAS2.52.5-100	1,2	daily 24 hr	intensives	UMCP

Speciation Sampler (for elemental, sulfate, p-nitrate, and EC/OC analysis)	<2.5 :m	RAAS2.52.5-400*	1	1 in 3 day, 24 hr	12 months	MDE
Speciation Sampler (for elemental and EC/OC analysis)	<2.5 :m	RAAS2.52.5-400*	1,2	daily 24 hr	intensives	UMCP
Size Segragated Aerosol	<0.69 to 10 :m	5-STAGE RDI	1	1 in 3 day, 24 hr	12 months/analyze 4 per month	UMCP
Highly-Size Resolved Size Segregated Aerosol	<0.069 to 10 :m	8-STAGE RDI	12	24-hr, hrly resolution	Intensives/analyze 10 sets of 12 one-hourly divisions	UMCP
PM2.5 for Cytokine/ROS response assays	<1.2 :m	UM HFAS	1,2	1 hr	12 months	UMCP
Bulk PM	<2.5 :m	UMUHVAS	1	1 week	12 months	UMCP
Organic Compounds, 24 hours	<1.2 :m	100 LPM sampler	1	24 hr	40 per 2 intensives	UMCP
Organic Compounds, short term	<1.2 :m	5-HP HVS	1,2	3 hrs	220 per 2 intensives	UMCP

[1]Site 1 = Urban Residential Supersite; Site 2 = Urban Industrial Supersite. Asterisk (*) indicates information specified is subject to change

6.2.1. Program Specific Data/Sample Acquisition Objectives. The Data Quality Objectives (DQOs) and the related Measurement Quality Objectives (MQOs) are described in detail in the Appendix to this plan. As discussed below, instrument-specific Data Quality Objectives are described in detail in the project SOPs. In this section, we delineate and describe the measurement tasks to be conducted in support of project objectives/hypothesis testing, and describe the data/sample acquisition objectives associated with each task. These tasks are defined in Table 6.2, where they are correlated with the specific project objectives and hypotheses. Brief technical descriptions of the measurements are provided below along with the investigating team responsible for them. More detailed descriptions are provided in the investigator's SOPs/RPs. The individual SOPs/RPs also include sample handling procedures, the individual measurement QC processes including the field and corrective actions for the individual measurements, instrument testing and inspection guidelines, the consumables and supplies needed for the individual measurements, and the health, safety and training issues for each measurement.

6.2.1.1 Task 1. Perform Highly time-resolved aerosol measurements for source attribution using advanced factor analysis methods

Purpose/Intended Use: The purpose of this task is to acquire data on PM constituents to permit determination of their sources. The intended use of the data is exploration with multivariate statistical techniques including multilinear regression, principle components analysis, chemical mass balance, and, most importantly, advanced factor analysis methods. These data are further intended to evaluate the hypothesis that shorter sampling/analysis times will benefit resolution of sources by statistical methods. The data are also to be used to investigate differences between urban and industrial airsheds within the City. Generally, measurements should be made over times comparable to changes in meteorological variables and source strengths, or at maximum feasible temporal resolution to provide maximum resolving power via statistical methods.

Measurements Required: Quantitative measurements of elemental and organic source marker species are required for source attribution. Single particle mass spectrometry data are to be used to further identify sources and regional vs local origin of aerosol. Time-resolved size distributions for elemental aerosol constituents can aid in identification of sources, resolution of source profiles (especially for high-temperature combustion sources), and aid in resolving local vs distant sources of PM and its constituents. Short term measurements of major aerosol constituents, i.e., EC/OC, aerosol mass, sulfate, and nitrate, are required as source markers and species needed to reconcile aerosol mass with measured species mass. Relative aerosol concentration and mixing height and number vs particle size spectral are ancillary measurements that will aid in the resolution of sources and identification of source fingerprints. Programmatic objectives dictate that hundreds of valid measurements be made of short-term concentrations of elemental marker species via quantitative methods, making automated semi-continuous methods

the methods of choice.

Table 6.2 Relationship Between Data/Sample Aquisition Tasks, and Project Objectives/Hypotheses

Task #		Task Description and Project Objective or Hypothesis to be tested	Required Measuerments	Ancillary Measurements	Required Sites/Duration	Number or duration of samples/ analyses required
1		**Perform highly-time, size, and compositionally-resolved aerosol measurements for Source Attribution using advanced Factor Analysis methods**	* SC element markers, SPMS, SCSO4, SCmass, SCEC/OC, short-term organic speciation	time resolved elemental size distributions, number vs size distributions, LIDAR relative aerosol concentration and mixing height	Urban Residential/12 months (intensives for OS)	hundreds
	O1	Provide entended, high-quality, highly-time resolved data set				12 months worth
	H1	Reduced sampling/analysis times will measurably improve source attribution				several days worth
	HO8	Spatial distributions of FP constituents vary due to local sources and regional circulations	* SC element markers, SPMS, SCSO4, SCmass, SCEC/OC, short-term organic speciation, LIDAR wind and particle fields	time resolved elemental size distributions	Urban Residential + Industrial site intensive	12 months worth
2		**Characterize relative aerosol concentration and mixing height in Baltimore**	LIDAR		Urban Residential + Industrial site intensive	several months of weekly observations
3		**Highly-time-resolved sample collection for Cytokine/ROS Response Assay**	TASK 1 measurements + retrospective cytokine, ROS response assays + aerosol particle number distribution spectra	time resolved elemental size distributions	Urban Residential/12 months (intensives for OS)	hundreds

O2	Provide information on potential health effects of aerosol from sources				hundreds
H02	Immuno-inflammatory driven Health Effects of PM are associated with particles emitted from specific sources	TASK 1, Cytokine/ROS response assays, time-resolved elemental size distributions		Urban Residential + Industrial site intensive	hundreds
H03	Different aerosol constituents and properties will elicit different responses in cytokine/ROS response assays	TASK 1, Cytokine/ROS response assays		Urban Residential/12 months	hundreds
H04a	Aerosol age affects the size, chemistry, and health effects of PM	time resolved elemental size distributions + Task 1 measurements + cytokine, ROS response assays		Urban Residential/12 months	several weeks worth
H04b	Spatially distant upwind, industrial area, and center-city aerosols differ in temporal variability and biologically relevant composition	Time - resolved elemental size distributions + TASK 1 measurements		Urban Residential + Industrial site intensive	several weeks worth
H05	Combined multivariate data from the array of semi-continuous and short-term measurements will permit attribution of the immuno-inflammatory metric among sources	TASK 1, Cytokine/ROS response assays	time-resolved elemental size distributions	Urban Residential + Industrial site intensive	hundreds
H06	Pollutant concentrations and immuno-inflamatory response metrics in the industrial sector exceed those in the urban residential sector	TASK 1, Cytokine/ROS response assays	time-resolved elemental size distributions	Urban Residential + Industrial site intensive	several weeks worth
HO7	Acute health responses are more closely associated with elevation of short term exposure than with 24 hr averages	TASK 1, Cytokine/ROS response assays	Community site Measurements	Urban Residential + Industrial site intensive	several days worth
HO8	Spatial distributions of FP constituents vary due to local sources and regional circulations	TASK 1 measurements + LIDAR		Urban Residential + Industrial site intensive	several days worth

4	**Bulk PM collection**					
	O3	Provide bulk PM for archival storage, and retorspective analyses and testing	Ultra High-volume Fine Particle collections		Urban Residential/12 months	several grams
5	**Detailed organic characterization**					
	O4	Provide detailed information on nature and sources of OC	Short-term and 24-hr OC collections and detailed compound analyses, requires only combined, not separate, Filter and PUF analyses	bulk PM from UMUHVS	Urban Residential + Industrial site intensive	1 mo. summer, 1 mo. winter

6	O5	**Support existing exposure and epidemiologic studies**	TASK 1, 2, 3 measurments	Community site Measurments	Industrial site intensive	several days worth
	HO7	Acute health responses are more closely associated with elevation of short term exposure than with 24 hr averages	TASK 1, 2, 3 measurments	Community site Measurments	Industrial site intensive	several days worth

Program Specific Quality Standards, Criteria, and Objectives. Programmatic quality objectives are to obtain data with accuracy and precision of sufficient quality to be of value in the statistical models. The data should be accompanied by realistic uncertainties, and sufficient numbers of measurements need to be made to permit solutions to the multivariate models. Specific data quality objectives for each type of measurement are provided in the standard operating procedures for each instrument or analytical procedure.

Data Records/Reports Required. Electronic data reports of average flow rate during sample collection, sample ID, and QSSC flags pertaining to sample collection. Analytical results shall include analyte concentrations, uncertainty estimate, information on detection limit, and appropriate QSSC flags. Chain of custody records are to be maintained.

Technical Descriptions and Measurement Personnel

1. Semi-Continuous Elemental Marker Species
   - Investigating Team: University of Maryland, College Park
   - Method: SEAS (Semi-Continous Elements in Aerosol System). Collection of ambient aerosol in aqueous slurry after steam injection and dynamic aerosol concentration followed by elemental analysis by Graphite Furnace Atomic Absorption and/or inductively-coupled plasma mass spectrometry [Kidwell *et al.*, 1998; Kidwell and Ondov, 2001].

2. Single Aerosol Particle Constituents
   - Investigating Team: University of Delaware/University of California Davis
   - Method: Single Particle Mass Spectrometer. Laser ionization of particles followed by Time-of-Flight mass analyses for positive and negative ions [Ge *et al.*, 1998].

3. Semi-continuous Nitrate, Sulfate, EC/OC, and aerosol Mass.
   - Investigating Team: University of Maryland, College Park
   - Method: Mass based on Tapered Element Oscillating Microbalance (TEOM)
     EC/OC (R&P Model 5400)
     Nitrate: R&P model 8400N based on method of Stolzenburg and Hering [2000]
     Sulfate: R & P model 8400S, based on method of Stolzenburg and Hering [2000]

6.2.1.2 Task 2. Characterize relative aerosol concentration and mixing heights in Baltimore

area.

Purpose/Intended Use: The purpose of this task is to acquire data on wind and particle fields, and mixing height needed to understand local circulations and transport of aerosol particles and constituents from local sources and to assess regionally transported material from air aloft. It is further intended that the data be used to characterize transport during identifiable meteorological and seasonal regimes. Measurements need to be collected during intensive periods in an attempt to document fumigation of the measurement site by particle containing plumes from industrial sources. Measurements need to be conducted to evaluate seasonal differences.

Measurements Required: Programmatic objectives dictate that several months of valid measurements be made of wind and particle fields over the study domain. These should be made on a weekly basis, making an automated remote sensing method the methods of choice.

Program Specific Quality Standards, Criteria, and Objectives. Programmatic quality objectives are to obtain data with a spatial resolution of 100 m or better in both horizontal and vertical directions and that the extent of the measurements be sufficient to observe plumes from industrial sources. A range of 8 km (3 wavelength system) will permit observation of plumes in the Clifton Park/Brooklyn-Curtis Bay study area. Specific data quality objectives for each type of measurement are provided in the standard operating procedures for each instrument or analytical procedure.

Data Records/reports Required. Electronic data reports of data for all instruments are required from each PI/instrument operator and for all instruments.

Technical Descriptions and Measurement Personnel

1. LIDAR

Investigating Team:	Johns Hopkins University
Method:	3-wavelength LIDAR. A pulsed laser is used as the light source. In elastic LIDAR, the light scattered back toward the instrument from molecules and particles in the atmosphere is collected by a telescope and measured with a photodetector. The signal is digitized and analyzed by a computer in order to obtain relative concentration of aerosols and the mixing height.

2. Sonic Anemometer

Investigating Team:	Johns Hopkins University
Method:	3-dimensional sonic anemometer mounted at a height of approximately

5 m. Wind speed and the speed of sound is measured on three non-orthogonal axes and transformed into orthogonal wind components u_x, u_y, u_z and the air temperature. From the turbulent wind fluctuations, momentum flux is calculated. By finding the covariance between the vertical wind speed fluctuations, and temperature fluctuations the sensible heat flux is computed.

6.2.1.3 Task 3. Highly time-resolved sample collection/Assays for Cytokines/ROS Response.

Purpose/Intended Use: The purpose of this task is to acquire data to permit investigation of important relationships between PM, PM constituents and properties, and the ability of PM to stimulate cells to produce mediators of inflammation. The intended use of the data is exploration with multivariate statistical techniques including multilinear regression, principle components analysis, chemical mass balance, and, most importantly, advanced factor analysis methods. These data are further intended to evaluate hypotheses that aerosol from different generic sources, local vs distant, industrial vs urban, fresh vs aged sources induce quantifiably different immuno-inflammatory responses. And, additionally that physical aerosol characteristics, e.g., particle no., area, or mass size distributions influence these metrics. The aerosol particle collections for these measurements should be made to coincide with the other short term measurements outlined in Task 1.

Measurements Required: Short term fine particle sample collections suitable for *in vitro* response assays. Quantitative *in vitro* assays of the release of ROS and cytokines involved in mediating the inflammatory response *in vitro* are required using cultured cell lines. Particle sample endotoxin concentrations are needed to determine if bacterial contamination may be affecting the *in vitro* response measurements. The latter are needed to determine if bacterial exposure/contamination may be affecting the former. Programmatic objectives dictate that hundreds of valid measurements be made of short-term aerosol samples making the University of Maryland High-Frequency Aerosol Sampler the method of choice. Time- and highly-size-resolved distributions of aerosol particles and their element constituents are required to evaluate hypotheses regarding physical aerosol properties and aerosol age/degree of atmospheric processing. These require measurements with particle spectrometers capable of sizing particles ranging in diameter from 30 nm to 10 μm. The size domain for time- and size-resolved elemental constituent measurements should be nominally 70 nm (lower limit for currently available time-resolved device) to 10 μm.

Program Specific Quality Standards, Criteria, and Objectives. Programmatic quality objectives are to obtain data with accuracy and precision of sufficient quality to be of value in the statistical models. The data should be accompanied by realistic uncertainties, and sufficient numbers of measurements need to be made to permit solutions to the multivariate models. Specific data quality objectives for each type of measurement are provided in the standard operating procedures for each

instrument or analytical procedure.

Data Records/Reports Required. Electronic data reports of the data for all assays are required. Data reports shall include assay concentrations, information on detection limits, and appropriate QSSC flags. Chain of custody records required.

Technical Descriptions and Measurement Personnel

1. Aerosol slurry samples
   Investigating Team: University of Maryland, College Park - Sampling

   Method: University of Maryland High-Frequency Aerosol Sampler Collection of ambient aerosol in aqueous slurry after steam injection and dynamic aerosol concentration followed by automated storage in individual glass vials via XY fraction collector []Kidwell *et al.*, 1998].
2. Cytokine assays
   Investigating Team: University of Maryland, Baltimore - Assays

   Method: Incubation of aqueous particle slurries with appropriate test cells followed by cytokine assay with commercially available ELIZA kits, and cytotoxicity tests by measuring lactate dehydrogenase release. Assays for endotoxin are made using Limulus Polyphemus amebocytic assay. ROS assays will be performed by measuring fluorescent intensity of dichlorodihydrofluorescein diacetate in cells exposed to particles. [Becker *et al.*, 1996; Kobzik *et al.*, 1990].

3. Particle Number-Weighted Size Distributions
   Investigating Team: University of Maryland, College Park

   Method: 30 nm to 0.5 μm with TSI Scanning Mobility Particle Spectrometer (SMPS); 0.5 to >44 μm with PMS Forward-Scattering Laser Spectrometer (FSLS) at ambient outdoor conditions; 0.3 to >10 μm at (dry) indoor conditions with Climet OPC; 0.5 to 20 μm at (dry) indoor conditions with TSI Aerodynamic Particle Sizer (APS).

4. Time- and Size-Resolved Elemental Aerosol Constituents, Sampling
   Investigating Team: University of Maryland, College Park

   Method: 5- and 8-stage Rotating Drum Impactors (RDI) loaded with mylar,

teflon, or mylar and aluminum or Teflon and aluminum foils. [Raabe et al. 1988; Cahill and Wakabayashi, 1993]

5. Time- and Size-Resolved Elemental Aerosol Constituents, Analyses

Investigating Team: DELTA Group, University of California, Davis

Method: Synchrotron X-ray Fluorescence. Fluorescence of characteristic X-rays by excitation with extremely bright Synchrotron radiation to achieve very low detection limits [Cahill et al., 2001].

6.2.1.4 Task 4. Bulk PM Collection.

Purpose/Intended Use: The purpose of this task is to acquire bulk fine PM for use in methods development, analytical investigations, biologic/toxicological testing, and archival storage. Records of shipments to users to be maintained.

Measurements Required: Several Weekly collections of bulk PM.

Program Specific Quality Standards, Criteria, and Objectives. Programmatic quality objectives are to obtain gram quantities of PM with an established large particle cut off size, free from contamination that will affect assays and analyses for effects/determinations of inorganic constituents. Specific data quality objectives for each type of measurement are provided in the standard operating procedures for each instrument or analytical procedure.

Data Records/Reports Required. Electronic data reports shall include flow rates and sampling times.

Technical Descriptions and Measurement Personnel

1. Bulk PM Collector

Investigating Team: University of Maryland, College Park
Method: University of Maryland Ultra High-Volume Aerosol Sampler. Cyclone preseparator followed by collection on Teflon filter media in a filter enclosure containing ten modified 8" x 10" high-volume filter holders.

6.2.1.5 Task 5. Detailed Organic Compound Characterization.

Purpose/Intended Use: The purpose of this task is i) to investigate the nature of compounds present in Baltimore air, with emphasis on acquiring information on compounds potentially useful as inherent source tracers. Additionally, ii) data are to be collected to permit source attribution modeling with a range of multivariate statistical methods including advanced factor analysis methods.

Measurements Required: Several 24-hour combined filter/PUF samples need to be collected to provide sufficient sample for exploring organic matter composition. Additionally, a minimum of 50 short-term (e.g., 3-hr) filter/PUF samples need to be collected for use in multivariate statistical models. None of the filter/PUF samples need be extracted or analyzed separately for this task. Lastly a few bulk PM samples should be analyzed. However, the sampling technology for bulk sampling is designed to provide samples for elemental analyses and their integrity for organic sampling cannot be assured.

Program Specific Quality Standards, Criteria, and Objectives. Programmatic quality objectives are to obtain data with accuracy and precision of sufficient quality to permit positive identification of compounds in a variety of compound classes and to be of value in the statistical models. The data should be accompanied by realistic uncertainties, and sufficient numbers of measurements need to be made to permit solutions to the multivariate models. Specific data quality objectives for each type of measurement are provided in the standard operating procedures for each instrument or analytical procedure

Data Records/Reports Required. Electronic data reports shall include flow rates and sampling times. Organic compound analysis data shall include the compound name, CAS number, concentration, a reliable estimate of the uncertainty in the value, detection limit information, and QSSC standard flags indicating the validity of the data. Chain of custody records are required.

Technical Descriptions and Measurement Personnel

1. Short - Term Organic Sample Collection

Investigating Team:	University of Maryland, College Park
Method:	University of Maryland built sampler comprised of a grease-free coarse-particle preseparator, 62-mm teflon coated aluminum filter holder loaded with quartz fiber filters followed by 4-inch diameter glass PUF container all operating at 500 LPM.

2. 24-hour Organic Sample Collection

Investigating Team:	University of Maryland, College Park
Method:	University of Maryland built sampler comprised of a grease-free coarse-particle preseparator, 62-mm teflon coated aluminum filter

holder loaded with quartz fiber filters followed by 4-inch diameter glass PUF container all operating at 110 LPM.

3. Sample Storage/Delivery

Investigating Team: University of Maryland, College Park
Method: On-site freezer storage, followed by cold transfer to UMCP freezer storage prior to cold shipment to FIU.

3. Organic Compound Analyses

Investigating Team: Florida International University
Method: Solvent extraction followed by Gas-Chromatorgraphy-Mass spectrometry. Polar oxygenated organic compounds analyzed after derrivitization. [Rogge et al., 1991]

6.2.1.6 Task 6. Support JHU Exposure and Epidemiologic Studies.

The Baltimore Supersite will be providing data collected at the South Baltimore and main Supersite at Clifton Park to JHU for use in achieving the objectives and testing hypotheses indicated for this task in Table 6.1. Measurements in common to the Supersites and some or all JHU sites (residential and community sites) will include PM2.5 mass, XRF elements, particle no. vs size measurements, meteorologic parameters (wind speed, wind direction, temperature, and RH), and criteria gases (O_3, CO, NOx). The JHU measurements are being made under funding from other projects and are discussed in the their own QAPPs. The JHU workplan, encompassing the types of measurements to be made at the various sites, will be posted on the Baltimore Supersite's website ((www.chem.umd.edu/supersit).

7.0 DATA HANDLING AND ARCHIVING

7.1 Data Acquisition

The purpose of this section is to document the procedures to be used in the management and archiving of data gathered during the Baltimore supersite program. It is assumed that data will be stored on electronic media for continuous and semi-continuous instruments as indicated previously. Specific procedures are provided in the individual SOPs. The data will be "backed-up" every day. Separate CD-ROM will be created for data storage. For data resulting from subsequent chemical analysis of samples, it is required that the responsible PIs backup their data for each batch of samples analyzed.

A sample electronic data template will be furnished to all principal investigators. It is important for all PIs and co-PIs to use this template.

7.2 Formatting of Data

All data will be reported to and ultimately archived by the Data Manager (DM), 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 90% of the total possible data points over the time interval. Otherwise, the time-averaged

values are flagged and reported using an appropriate validation code. Validation codes will be taken from the standard listing of codes approved by the Supersites Data Managers' group for use with the archiving of data through the NARSTO Quality Systems Science Center (see section 7.6)

7.3 Date and Time Formats

Data will be reported in Eastern Standard Time, including day, month, and year as formatted as MM/DD/YYYY format (e.g., 08/15/2000 14:25). For those instruments were greater time resolution is essential (aerosol mass spectrometer, for example), the time should include seconds. The daily time cycle runs from 0000 to 2359 (2400 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). It should be noted that the sampling day will begin at 01:00 during the period when daylight savings time is in effect.

7.4 Reporting Missing Data

All data fields should have a value present, either the measured or adjusted data value or a missing value representation. There should not be blank fields. Contributors should report data where possible and use flag codes to describe the data quality (see section 7.6 Documentation of Data Quality). 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, and MDLs.

7.5 Reporting Calibration Values and Uncertainty Estimates

The calibration values and estimates of precision and minimum detection limit for all measurements will be maintained by the research organizations and reported to the Data Manager. All data quality indicators, including calibrations, standards, and adjustments, will be submitted to the Quality Assurance Manager. Access to calibration values is crucial for many quality assurance, analytical, and modeling exercises. All of the ancillary data such as calibration, maintenance, repair, and other QA data will be collected and retained as metadata files connected to the primary stored data. Notebooks should be scanned and the resulting electronic image files submitted to the Data Manager as part of the measurement metadata at the time of submission of the validated data.

Uncertainty estimates should be reported for all parameters for which it is possible to do so. These estimates should be provided either in the measurement method information table or in the primary data tables as separate data fields. Uncertainty estimates should not be offered in a separate file nor should they be inferred as part of a flag code. The metadata that accompanies the data file should describe the investigator's method of calculating uncertainty for each parameter.

7.6 Initial Documentation of Data Quality

All data reports will contain a column for flagging to indicate the validity of data. All problematic and missing data points will be identified in the report through the insertion of appropriate coded flags. Since these

data will have to be submitted to NARSTO in their format, it is desirable to use the NARSTO flag convention. Table 7.1 lists and defines these flags.

Table 7.1. Data Validity Flags

Data qualification flag codes	Definition
V0	Valid value
V1	Valid value but comprised 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, sample handling)
M1	Missing value because no value is available
M2	Missing value because invalidated by Data Originator
H1	Historical data that have not been assessed or validated

All data submitted to the NARSTO Quality Systems Science Center must be validated and classified with a level of validation; ranging from zero (0) to two (2). The process is summarized in Table 7.2

Table 7-2. Summary of the Data Validation, Documentation, and Access Process

	Data Status at Validation Levels 0, 1, 2, and 3.			
	Level 0	Level 1	Level 2	Level 2 (Submitted)
Review Status	Raw Data	QA'd Data	Data Analyses Completed	Continuous Use in Analysis and Modeling
Processing and Reviews Performed by	PIs	PIs	Data Manager	QSSC
Metadata Records	Incomplete	PIs	Data Manager	QSSC
Access	PIs, Data Manager, QA Manager	Project	Project	QSSC
Time to Data Distribution	Continuous: Within 1 week	Continuous: Within 1 month	Within 6 months of submission for Level 2 validation.	QSSC
	Laboratory: not submitted	Laboratory: Within 3 months		
Source	PIs	Project	Project	LaRC DAAC
Format	Project Database	Project Database	QSSC Format	LaRC DAAC format
Change Control Point of Contact	Data Manager	Data Manager	Data Manager	QSSC

7.7 Data Management and Archive

Principal Investigators will be responsible for transmitting all data to the Data Manager within the time frames following data collection as outlined in Table 7.2. These data will be quality assured and archived in the Baltimore Supersite permanent data archive and will be transmitted for final storage at the NARSTO Permanent Data Archive. It is expected that the individual principal investigators will store their raw data and associated files (calibrations, comments, etc) in electronic format for at least five years.

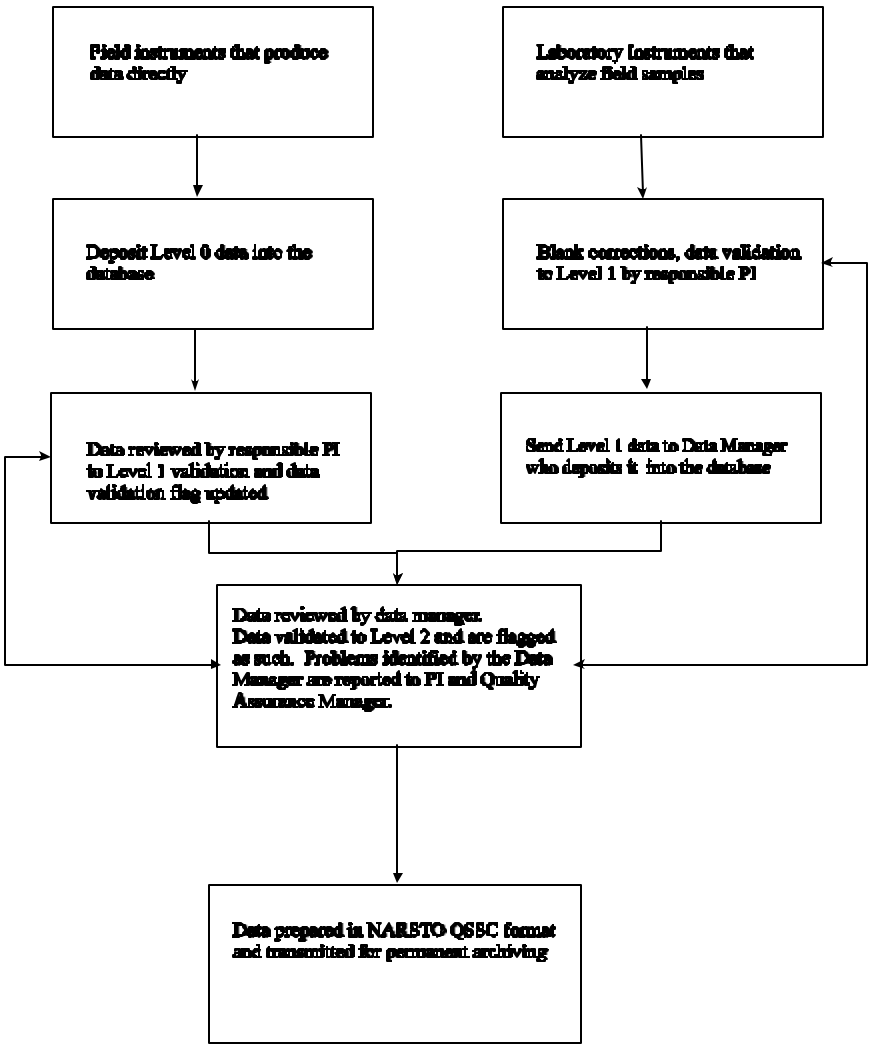

Figure 7.1. Schematic diagram of data flow in the Baltimore Supersite Project.

The data flow diagram is shown in Figure 7-1. A data tracking system will be implemented to document any modifications. The data will be subjected to quality assurance checks (outlier screening, date and time/flag/units checks, and statistical analysis) by the QM prior to submission to the NARSTO QSSC. A separate SOP for data management will be developed for the Baltimore Supersite.

7.8 Analysis of Samples or Data Collected

The analytical procedures for each proposed measurement are briefly described in Section 6. The detailed procedures and the necessary steps to ensure data validity are included in the SOPs prepared by the individual investigators.

All data collected by the Baltimore Supersite program, as well as data collected in parallel by any of the cooperating states and other monitoring operations, will be archived. The data archive will conform to the NARSTO formatting guidelines to represent a single point of reference of the physical and/or chemical characterization of fine PM at the core and peripheral sites.

7.9 Data Preservation

To protect the integrity of the database, it is being stored on a secure server to which there will be limited password-protected access. The data are to be stored on a RAID5 storage system that will provide considerable redundancy and ability to reconstruct any losses from individual hard disk malfunctions. In addition we will have the original data CDs that will be available. There will also be a secondary data archive at Clarkson on a RAID1 system. Thus, we are confident that we can ensure against data loss in the data management process.

7.10 Instrument Calibration and Performance Evaluation

Each investigator will be responsible for generating procedures for the calibration of analytical instruments and metrics for evaluating the performance of these instruments to the extent possible. The QA manager will make performance audits to ensure the accuracy of data collected as well as audits of the QA records of each investigator. A QA audit SOP will be prepared to detail the processes to be employed in these audits. Our primary approach will be a technical systems audit that will be conducted during the initial intensive sampling period in May 2001.

For discrete monitors that use collection of particulate matter or atmospheric gases on sampling media over an integration time, the sample collection equipment (monitors of air flows, pressure, temperature) will be calibrated before and after deployment to the field, and will be routinely checked against independent measurement devices as well as being subject to verification by the QA manager. Analysis of samples will only occur after the analytical equipment has been calibrated according to procedures put forward in the SOP and instrument performance has been deemed acceptable. The criteria to determine the acceptability of analytical instrument response will be developed by the investigators and included in the SOP. Analysis of separate traceable standards that are not used in instrument calibration will be used to determine the adequacy of the instrument performance and precision.

7.11 Data Reduction and Reporting

Data reduction and reporting will be the responsibility of each of the individual investigators. The SOP for each and every measurement should include the steps taken in the reduction of the data taken in the program. The SOP must be prepared before analysis, approved by the Quality Assurance Manager, and posted to the Baltimore Supersite webpage before any measurements are made.

The data will be reported to and archived by the University of Maryland at College Park in an appropriate format designed into the project database within 6 months of the field measurements. The data will be formatted according to NARSTO formatting guidelines with standardized measurement units, sample collection time, site location and time increment of the data. For all data entries, a value will be reported. A negative number (-9999) will be used to indicate missing values. Additionally, validation codes will be reported with each data point to indicate whether the data are validated or invalidated according to the data quality objectives. This will allow for information that is questioned to be included in the overall database and yet excluded from certain analyses where the reason for invalidation is relevant. The data will be delivered to the NARSTO QSSC as per the terms and agreements of the Cooperative Agreement between EPA and the University of Maryland at College Park.

7.12 Data Assessment

All data will be critically assessed during and after collection to ensure the quality of the data. These assessments will include independent performance audits, data processing audits, as well as external review of the technical systems used to collect the data. Each investigator will be required to address data assessment in the preparation of his/her SOP.

7.13 Use of Data

Table 6.1 lists the expected results of the project as a series of hypotheses that will be tested. Once the data are validated and archived in a database, the analysis of the data will test the hypotheses. Techniques to be used in source apportionment include advanced factor analysis and trajectory-based methods. Comparisons of instrument performance will be made using multivariate calibration including partial least squares, neural network analysis.

7.14 Quality Assurance

The management of the Baltimore Supersite includes a Project Management Team as well as a separate External Scientific Advisory Committee. Within the Project Management Team, the Quality Assurance Manager and the Data Manager will review the SOPs for their completeness in dealing with quality control and data assessment issues. This review will be completed before the initiation of field measurements.

8.0 ASSESSMENT OF DATA/CORRECTIVE ACTIONS

Assessment of data during the intensives and 9-month monitoring study will be made on several levels. First, each of the investigators is responsible for quality control of the data set collected. This will include verifying operational condition of the research equipment as well as checking for consistencies in the data collected as well as performing the needed quality control calibrations and adjustments. This will be of particular importance during the intensive study periods. Informal meetings among the PIs will also provide the opportunity to discuss data validity.

During the 9-month study, a more complete data assessment will be made by the Quality Assurance

Manager (QAM) with the assistance of the Data Manager. These evaluations will look for anomalies among the measurements between the core and satellite sites and inconsistencies between the discrete and continuous measurements. For example, one such assessment may look at the results from the near real-time concentrations of sulfate, nitrate, and carbon and compare these results to the mass obtained by the TEOM and the 24-hour integrated values of these variables obtained using the chemical speciation sampler. Size distributions of PM can also be compared to total PM mass. Evaluations of the continuous data from the 9-month study will be performed two times per week. The validity of discrete measurements can be assessed in comparison to near real time measurements. Since discrete samples, such as filter samples, will be returned in batches, their validity will be ascertained when samples are returned and flagged if they are inconsistent with continuous data.

If the reviews by the QAM indicate a possible problem, the investigator will be contacted for further information. If the QAM is not satisfied with the results of the review, the Lead Principal Investigator will be contacted and it will be determined whether the data will remain in the Baltimore Supersite database. The PI will be informed of any data removal or invalidation that occurs in the database.

9.0 Quality Assurance Final Report

In accordance with the terms and agreements, a Quality Assurance Final Report (QAFR) will be prepared at the end of the project that reviews the QA processes and results for the Baltimore Supersite measurement program.

REFERENCES

Baker, J. (1999) University of Maryland Chesapeake Bay Laboratory, Private communication.

Baltimore City Health Department (1995) *Mortality Statistics*. City of Baltimore Health Department.

Becker, S., Soukup, J.M., Gilmour, M.I. and Devlin, R.B. (1996) Stimulation of human and rat alveolar macrophages by urban air particulates: Effects on oxidant radical generation and cytokine production. *Toxicol. Appl. Pharmacol.* 141:637-648.

Cahill, T. A., Wakabayashi, P. (1993) Compositional analysis of size-segregated aerosol samples. Chapter 7, *Measurement Challenges in Atmospheric Chemistry*, L. Newman, Ed.; pp. 211-228, ACS, Washington, D.C.

Ge, Z., Wexler, A. S., Johnston, M. V. (1998) Laser desorption/ionization of single ultrafine multicomponent aerosols. *Environ. Sci. Technol. 32*:3218-3223.

Gordon, G. E. (1988) Receptor Models. *Environ. Sci. Technol. 22*:1132-1142.

Kidwell, C. B., Ondov, J. M., Sioutas, C., Koutrakis, P. (1998) Ambient Aerosol Concentration by Condensation and Virtual Impaction for Collection and Chemical Analysis. J. Aerosol Sci. 29:S1039

Kidwell, C. B., Ondov, J. M. (2001) Development and Evaluation of a Prototype System for Collection of Sub-Hourly Ambient Aerosol for Chemical Analysis. Accepted for publication in Aerosol Sci. Technol.

Kobzik, L., Godleski, J.J., and Brain, J.D. (1990) Oxidative metabolism in the alveolar macrophage: Analysis by flow cytometry. *J. Leukocyte Biol.* 47:295-303.

Maciejczyk, Polina Borgoul (2000) Atmospheric Fate and Dry Deposition of Particles Bearing Trace Elements and Soot in the Baltimore Area. Ph.D. Thesis, University of Maryland, College Park.

Ondov, J. M., Wexler, A.S. (1998) Where do particulate toxins reside? An improved paradigm for the structure and dynamics of the urban mid-Atlantic aerosol. *Environ Sci. Technol.32*:2547-2555.

Raabe, O. G., Braaten, D. A., Axelbaum, R. L., Teague, S. V., Cahill, T. A. (1988) Calibration studies of the DRUM Impactor. *J. Aerosol Sci. 19*:183-195.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., (1991) Sources of Fine Organic Aerosol: 1. Charbroilers and Meat Cooking Operations. *Environ. Sci. Technol. 25*:1112-1125.

Stolzenburg MR, Hering SV (2000) Method for the Automated Measurement of Fine Particle Nitrate in the Atmosphere, *Environ. Sci. Technol. 34*: 907-914.

APPENDIX

DATA QUALITY OBJECTIVES AND MEASUREMENT QUALITY OBJECTIVES FOR THE BALTIMORE SUPERSITE

Data Quality Objectives/indicators

It is the policy of the Baltimore Supersite that all ambient air quality monitoring and research measurement data generated for internal and external use shall meet specific qualitative requirements, referred to as Data Quality Objectives. The DQO process is detailed in US-EPA's "Guidance for the Data Quality Objectives Process, EPA QA/G-4 (1994). Measurement Quality Objectives (MQOs) are the set of objectives for each individual instrument that is utilized during the study. These vary from instrument to instrument. For some instruments, i.e., the $PM_{2.5}$ Federal Reference Method samplers and most gaseous instruments, the MQOs are known due to the extensive testing that has been performed. However, there will be many instruments employed during the study where the MQOs will not be known. It will be part of the principle investigators' and the Quality Assurance Manager's responsibility to attempt to determine the individual MQOs.

Data Quality Objectives

Activities are necessary for effective environmental protection. It is the goal of EPA and the Baltimore Supersite to minimize expenditures related to data collection by eliminating unnecessary, duplicative, or overly precise data. At the same time, the data collected should have sufficient quality and quantity to support defensible decision-making. The most efficient way to accomplish both of these goals is to establish criteria for defensible decision making before the study begins, and then develop a data collection design based on these criteria. By using the DQO Process to plan environmental data collection efforts, EPA and the Baltimore Supersite can improve the effectiveness, efficiency, and defensibility of decisions in a resource-effective manner.

DQOs are qualitative and quantitative statements derived from the outputs of the first six steps of the DQO Process that: clarify the study objective; define the most appropriate type of data to collect; determine the most appropriate conditions from which to collect the data specify tolerable limits on decision errors, which will be used as the basis for establishing the quantity and quality of data needed to support the decision.

The DQOs are then used to develop a scientific and resource-effective data collection design. It provides a systematic procedure for defining the criteria that a data collection design should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision errors for the study, and how many samples to collect. By using the DQO Process, the EPA and Baltimore Supersite will assure that the type, quantity, and quality of environmental data used in decision making will be appropriate for the intended application. In addition, the Agency will guard against committing resources to data collection efforts that do not support a defensible decision.

Optimize the Design for Obtaining Data

The DQO Process consists of seven steps. The output from each step influences the choices that will be made later in the Process. During the first six steps of the DQO Process, the planning team developed the decision performance criteria that were used to develop the data collection design. The final step of the Process involves developing the data collection design based on the DQOs. Every step should be completed before data collection begins.

The seven steps of the DQO process are:

- State the Problem
- Identify the Decision
- Identify the Inputs to the Decision
- Define the Study Boundaries
- Develop a Decision Rule
- Specify Tolerable Limits on Decision Errors
- Optimize the Design

Each of these steps will be examined in the following section. Each of these steps has been performed to ensure a maximized project.

Iteration of the DQO Process

State the Problem: The toxicity of aerosol components as affected by age, industrial vs urban character, and seasonal differences in source terms and atmospheric chemistry are not well understood. Another problem is the intercomparison of the state-of-the-science aerosol characterization instruments and the determination of their reliability, accuracy and sensitivity relative to conventional measurement techniques..

Identify the Decision: The EPA solicited proposals to establish and operate supersites based on a series of defined hypotheses that were to be tested using the advanced methods to be deployed at the supersites. The specific hypotheses for the Baltimore supersite are given in Table 6.2. The decisions are then the tests of these hypotheses.

Identify the Input to the Decision: Several inputs can be identified as inputs to the decision. These are the existing knowledge base that led to the posing of the various hypotheses. This base of information used to define these hypotheses is outlined in Section 5.1.

Define the Study Boundaries: The sampling locations are described in Section 6.1. They were chosen to provide a site at which source composition data could be obtained during a limited intensive sampling campaign (FMC Site) and to provide a site that was representative of community exposure and typical concentration patterns downwind of central Baltimore (Clifton Park). The Clifton Park site has been used as the community monitoring site in a panel exposure study in Towson, MD and was previously

shown to be representative of the outdoor aerosol composition in the region (Williams *et al.*, 2001).

Develop a Decision Rule: The purpose of the Decision rule is to weigh the parameters of interest and specify the action level. Integration of previous DQO outputs are used here to describe the logical basis upon which the final decision is made.
Specify Tolerable Limits on Decision Errors: The EPA and Supersite investigators are interested in knowing the true nature of the urban atmosphere in the Baltimore area. Since data can only estimate, decisions that are based on measurement data could be in error (decision error). The goal of the investigators was to develop a data collection design that reduces the chance of making a decision error to a tolerable level. There are two reasons why the true value of the atmosphere is for the most part, poorly characterized:

The atmosphere almost always varies over time and space. Limited sampling will miss some features of this natural variation because it is usually impossible or impractical to measure. Sampling design error occurs when the sampling design is unable to capture the complete extent of natural variability that exists in the true state of the environment.

Analytical methods and instruments are never absolutely perfect, hence a measurement can only estimate the true value of an environmental sample. Measurement error refers to a combination of random and systematic errors that inevitably arise during the various steps of the measurement process (for example, sample collection, sample handling, sample preparation, sample analysis, data reduction, and data handling).

The combination of sampling design error and measurement error is called total study error, which may lead to a decision error. Since it is impossible to eliminate error in measurement data, basing decisions on measurement data will lead to the possibility of making a decision error. In this approach, the data are used to select between one condition of the environment (a *null hypothesis*, H_o) and an alternative conditions (an *alternative hypothesis*, H_a). The null hypothesis is treated like a baseline condition that is presumed to be true in the absence of strong evidence to the contrary.

In terms of the Baltimore Supersite study, the null hypotheses are listed in Table 6.2 along with the associated measurements being made to provide the data that will serve as a basis for decisions.

Optimize the Design: The purpose of optimizing the design is to identify the most resource-effective data collection regime. As part of the planning that went into writing the successful peer-reviewed proposal, a research design was outlined in terms of types of measurements to be made. These original ideas have been refined to produce the listing of measurements provided in Table 6.2.

MQO Indicators

The MQO indicators for the Baltimore Supersite Experiment will be determined in the usual way for a research project. The typical MQO indicators associated with data measurements are: Precision, Accuracy, Representativeness, Completeness, Estimation of Bias, Minimum Detection Limits (MDLs) and Comparability. Many of these MQOs can be measured on most of the instrument and the

project as a whole. The MQOs will be determined for each individual instrument/system. However, some of the experimental instruments perform analyses that are not easily reproducible or cannot be compared against conventional analyzers. There will not be an opportunity for running duplicate instruments of many of the newer and more costly instruments such as the continuous sulfate, nitrate, and OC/EC instruments nor the aerosol time-of-flight mass spectrometer. Therefore, the Supersite study provides an interesting scenario in terms expanding the relationship of quality assurance and data quality. It is also concievable that some MQOs will be developed during the course of the study. The typical MQOs can be used as indicators of error or bias in a data set. However, there are a number of additional indicators that can be documented and can assess the data qualitatively. These are: Inference of Analysis, Intercomparison and Trend Analysis. By using all indicators, the following statements can be made about the quality of the data set:

Attempts will be made to quantify the error of the data generated. This shall be accomplished by performing performance audits against accuracy flow checks and Technical System Audits. The QA data collected will be used to document accuracy, precision and bias.

Data generated shall be of sufficient quality to facilitate intercomparison with differing methodologies measuring the same parameters. The QAM and principle investigators will perform statistical evaluation of data. Intercomparisons should only be performed on Field Analyses data.

All researchers shall strive to provide the maximum quantity of data possible for the duration study to allow for a robust intercomparison of data.

Communication will be encouraged throughout the study. Sharing of Level 0 data is encouraged but not required. The definitions of data validation levels are given in Table 7.2, Level 0 intercomparisons may clue different investigators into whether their instruments are operating correctly.

Each of the MQOs are discussed in detail below.

Accuracy

The accuracy of the continuous gas monitors will be determined from performance audits of the individual gas phase instruments. The performance audit will challenge the instrument with standards, from an independent, NIST traceable source not used for calibration, encompassing the operational range of the instrument. A minimum of three data points, including zero will be used to conduct the performance audit. The following equation will be used to estimate the slope, intercept and correlation coefficient. The following equation is be employed:

$$y = mx = b \qquad \text{Equation 1}$$

where the audit standard concentration is the independent (x) variable, the instrument reading is the dependent (y) variable, m is the slope, and b is the y intercept, will be used to assess accuracy.
For gravimetric and speciated fine particle samplers, the accuracy will be defined as a accuracy flow check. The estimation of accuracy for this method is:

$$\%\text{Accuracy} = \left[\frac{Q_a - Q_m}{Q_a} \right] x100 \qquad \text{Equation 2}$$

where Q_a is the flow rate measured using a NIST traceable flow device, Q_m is the flow rate measured by investigator.

Bias

Due to the unique research nature of many of the measurements to be conducted by SuperSite, the situation may arise where primary standards are unavailable to determine bias. In addition, bias of the discrete methodologies can only be determined for the analytical instruments, and does include effects introduced by sample collection and transport. In these instances the determination of bias is the correct action. Bias will be calculated under three distinct situations:

- a primary standard does not exist to determine instrumental accuracy
- the comparison of two discrete methodologies using ambient data
- comparison two discrete methodologies using ambient data, one of which is a Federal reference method.

When a primary standard method is not available, bias will be calculated using the equation:

$$\text{Bias} = \frac{1}{n} \sum_{i=1}^{n} \left[\frac{s - x_i}{s} \right] \cdot 100 \qquad \text{Equation 3}$$

where s is the standard value and x_i is the instrument results of the ith measurement of the standard.

For comparison of two methodologies, neither of which is considered a reference standard, bias will be calculated by the equation:

$$\text{Bias} = \frac{1}{n} \sum_{i=1}^{n} \frac{\left[\frac{m1_i - m2_i}{m1_i + m2_i} \right]}{2} \cdot 100 \qquad \text{Equation 4}$$

where $m1_i$ and $m2_i$ are the ith measurement of the two methodologies (m1 and m2) being subjected to comparison. The use of the average of the two methodologies in computing bias recognizes that a primary standard is not available.

If the results of a particular methodology are being compared to a primary standard then the following equation:

$$\text{Bias} = \frac{1}{n} \sum_{i=1}^{n} \left[\frac{m1_i - m2_i}{m1_i} \right] \cdot 100 \qquad \text{Equation 5}$$

where the numerator has been replaced with the ith measurement of the primary standard will be used

to determine bias.

Precision

Precision of the continuous gas monitors will be determined from replicate analyses of calibration standards, instrument span check standard and/or precision check standard records. Precision for the GC/FID and GC/MS system will be determined using multiple analyses of a 5 component mixture supplied by NCAR. A minimum of 5 data points should be used for the precision to be calculated. Precision should be determined for data time periods between calibrations or other major maintenance periods that may effect the operation performance of the instrument. Precision for filter based instruments will be performed by comparing the percent difference between similar methods. Precision will be determined from the standard deviation using the following equations.

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2} \qquad \text{Equation 6}$$

where x_i is the experimentally determined value for the i^{th} measurement, n is the number of measurements performed, and $\overline{X}$ is the mean of the experimentally determined values.

The precision will be determined as percentage of the average concentration of the span check standard or precision check standard using the following equation.

$$Precision = \{x\}_{avg} +/- 1.96*s \qquad \text{Equation 7}$$

where $\{x\}_{avg}$ is the average of the span or precision measurements, s is the standard deviation of the replicate span check standard or precision check standard data. The upper and lower 95% probability limits are set using this statistical test.

Minimum Detection Limits

The 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 following filter blank tests: field blanks and laboratory blanks. Field blanks are defined as a filter that travels with the filters that will be utilized in sample collection. The filter should be treated in the same manner as any other filter with the exception of begin loaded into the filter mechanism. It is a good field practice to take the field blank up to the sampler and leave it inside the instrument housing with the filter cover on. When the sample filters are removed after the sample run, the field blank is also removed and processed in the same manner as all filters. It should also travel in the same carry case as all filters. Storage and handling should be as identical to all processed filters. Laboratory (lab) blanks are filters that are pre-weighed and processed in the same

manner as all filters. 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 following sections will illustrate how MDLs are quantified for filter and non-filter methods.

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 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;

$$MDL = t_{(n-1,1-a = 0.99)} * s \qquad \text{Equation 8}$$

where s is the standard deviation of the replicate zero analyses, t is the students t value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom, will be used to determine the method detection limit[7].

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 subjected 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 at a specific concentration. The IDL standard does not experience the same handling procedures; collection on filter medium and denuders for HPLC analysis or canister collection for GCMS analysis; and therefore does not provide information relating to the detection limit at ambient. The IDL for each HPLC and GCMS analyte will be determined through statistical evaluation as described in equation 8.

Completeness

Completeness will be determined from the data generated using the following equation:

$$\text{Completeness} = (D_x - D_c)/D_c \times 100 \qquad \text{Equation 9}$$

where D_x is the number of samples for which valid results are reported and D_c is the number of samples that are scheduled to be collected and analyzed during the year.

Representativeness

Generally, representativeness expresses how closely a sample reflects the characteristics of the surrounding environment. This is usually quantified in terms of monitoring scale. It is not the scope of this manual to discuss monitoring scale in detail, however, monitoring scale must be understood for the project. The main component of the Supersite is fine particles. Fine particle scale is recommend to be neighborhood scale, which is defined as representing an area in the order of 0.5 to 4.0 kilometers. The Supersite project will primarily be conducted in Clifton Park. The site was previously used for an EPA exposure panel study (Williams *et al.*, 2001). The location of the site is within the greater Atlanta area. The exposure of the surrounding environs does represent at least a neighborhood scale for particle monitoring. For more details on the location and site layout, please refer to Section 6.1

References

Environmental Protection Agency (EPA) (1994) *Guidance for the Data Quality Objectives Process*, EPA QA/G-4, EPA report EPA/600/R96/055, Washington, DC, September 1994

Williams, R., Suggs, J., Zweidinger, R., Evans, G., Creason, J., Kwok, R., Rodes, C., Lawless, P., Sheldon, L., 2000a. The 1998 Baltimore particulate matter epidemiology-exposure study: part 1 - comparison of ambient, residential outdoor, indoor and apartment particulate matter monitoring. Journal of Exposure Analysis and Environmental Epidemiology, in press.