QUALITY ASSURANCE PROJECT PLAN

for the

GULF COAST AEROSOL RESEARCH AND CHARACTERIZATION PROGRAM (GC-ARCH): HOUSTON 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 contract number R-8280621 (Gulf Coast Aerosol Research and Characterization Program (GC-ARCH) - EPA award date January 15, 2000).

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1.2 Quality Assurance Project Plan Approval Sheet

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2.0 TABLE OF CONTENTS

2.3 List of Abbreviations

A
AM – human alveolar macrophage
ASACA – Assessment of Spatial Aerosol Composition in Atlanta

B
BDL – below detection limit

C
CMB – chemical mass balance
CNC – condensation nucleus counter

D
DOE – Department of Energy
DMA – differential mobility analyzer
DQO – data quality objectives

E
EC – elemental carbon
EPA – Environmental Protection Agency

F
FRM – Federal Reference Method

G
GC-ARCH – Gulf Coast Aerosol Research and Characterization Program

H
HRM – Houston Regional Monitoring Network

I
IDL - instrument detection limit

L
LIDAR – laser imaging detection and radar

M
MDL – minimum detection limit
MQO – measurement quality objectives

N
NBS – National Bureau of Standards
NMDS – Nafion membrane diffusion scrubber
NOAA – National Oceanic and Atmospheric Administration

O
OC – organic carbon
OPC – optical particle counter

P
PAH – poly aromatic hydrocarbon
PAMS – photochemical assessment monitoring stations
PI – principal investigator
PLS – partial least squares
PM – particulate matter
PMF – positive matrix factorization
PRESS – prediction residual sum of squares

Q
QA/QC – quality assurance/quality control
QAM – quality assurance manager
QAPP – quality assurance project plan

R
RP – research protocol

S
SCCAPM – Southern California Center for Airborne Particulate Matter
SCISSAP – Southern Center for the Integrated Study of Secondary Air Pollutants
SEARCH – Southeastern Aerosol Research and Characterization Study

T
TexAQS – Texas Air Quality Study-2000
TNRCC – Texas Natural Resource Conservation Commission

U
UT-HHSC – University of Texas, Houston Health Science Center

V
VOC – volatile organic compounds

3.0 PROJECT DESCRIPTION AND MANAGEMENT

3.1 Overview

Statistical associations between elevated concentrations of fine particulate matter and increased mortality and morbidity have recently been established (as summarized in the final rule for the National Ambient Air Quality Standard for fine particulate matter, Federal Register, July 18, 1997). While considerable uncertainty remains regarding the causal links between ambient particulate matter and health effects, there are a number of candidate hypotheses relating the physicochemical properties of ambient particulate matter to health effects. Some of the particulate matter properties that may be related to health effects include (Health Effects Institute/NOAA, 1998) particulate matter mass concentration, the size distribution of particulate matter, ultra-fine particle concentration, metal concentrations, acid concentrations, organic compound loading, sulfate and nitrate salt concentrations, peroxide concentrations, elemental carbon concentrations, and cofactors.

This range of fine particulate matter physical and chemical properties that may be related to health outcomes encompasses virtually all of the measurable properties of fine particulate matter (fine PM). Finding associations between these myriad properties and health outcomes will be difficult unless organizing or simplifying principals can be identified. One logical organizing principal is to classify fine PM into source categories. The number of significant PM source categories is much smaller than the number of PM physical and chemical properties that may influence human health. Therefore, carefully examining PM source categories, in conjunction with PM exposure and toxicity studies, has the potential to improve our understanding of the relationships between human health and fine PM.

The Gulf Coast Aerosol Research and Characterization (GC-ARCH) Program will examine the concentration, composition, and sources of fine particulate matter in Houston, Texas. There are several reasons for choosing Houston as a location for fine particulate matter studies. First, the entire Southeastern Texas region experiences annual average concentrations of fine PM (specifically PM less than 2.5 μm in aerodynamic diameter, or $PM_{2.5}$) in the range of 10-12 $\mu g/m^3$. Superimposed on these background concentrations are regions in which industrial and urban emissions drive the annual average concentrations of fine PM to 16-18 $\mu g/m^3$. These high background concentrations with local hot spots, located in a region of high population density (Houston is the fourth most populous city in the United States), result in high exposures to fine PM. A recent report, performed by Sonoma Technologies, Inc., under contract to the City of Houston, estimated that approximately 2.5 million people in the Houston area may be exposed to annual average PM concentrations in excess of 15 $\mu g/m^3$ (Lurmann, et al., 1999).

In addition, Southeast Texas has a mix of industrial, natural and urban emissions that are not duplicated in other regions of the country. Finally, the high temperatures, high

humidity and complex coastal meteorology of Southeast Texas are likely to lead to particulate matter formation processes unique to the region.

The overall goals of the Gulf Coast Aerosol Research and Characterization Program are to characterize the composition and identify the sources of particulate matter in Southeastern Texas, to develop and test new methods for characterizing fine particulate matter, and to collect data on the physical and chemical characterization of fine particulate matter that can be used to support exposure and health effects studies.

The analyses preformed under the Houston Supersite (GC-ARCH) study, TexAQS, and by the TNRCC will generate a comprehensive air quality data set for Texas. Specific activities funded by the EPA Supersite program are detailed in this QAPP. For the sake of clarity and overview of the TexAQS and TNRCC efforts are also described in this report and their relationship to the Supersite objectives are described.

3.2 Objectives

The objectives of the GC-ARCH study are:

1. to collect physicochemical data on fine PM over a 16 month period, use the data to identify sources, and to characterize spatial and temporal variability in fine PM source contributions and composition in Southeastern Texas
2. to characterize spatial and temporal variability in fine PM source contributions and composition throughout the southeastern United States, and
3. to examine the physical and chemical process that govern PM formation and transformation in Southeastern Texas

Three additional objectives will be addressed by integrating the measurements made in this program with measurements to be made in separately funded studies. These objectives are:

4. to develop a combined database on PM, gas phase air pollutants and meteorological variables suitable for testing models of the formation and fate of fine PM; this objective will be achieved by coordinating with a large, integrated ozone and PM field study planned by the Southern Oxidants Study for the summer of 2000. This study will be referred to as the Texas Air Quality Study, or TexAQS.
5. to examine exposures to fine PM from specific source categories in Southeastern Texas; this objective will be achieved by coordinating with an exposure study currently underway in Houston, funded by the Mickey Leland National Urban Air Toxics Research Center, and
6. to relate the physicochemical data on fine particulate matter to mammalian tissue responses; this objective will be achieved by coordinating with an EPA funded project currently underway at the University of Texas Houston Health Science Center.

The Houston Supersite is specifically defined as any investigations preformed under GC-ARCH. All other studies noted in this Quality Assurance Project Plan are not funded by the EPA under the Houston Supersite grant.

The overall goals of the GC-ARCH program (and all of the Supersites) are to characterize particulate matter and its sources, support health effects and exposure research, and to conduct methods testing, evaluating different methods of characterizing PM. Table 3.2-1 describes how the six objectives of the GC-ARCH program will address each of these goals and summarizes hypotheses that will be tested.

Table 3.2-1. Expected Results and Benefits

Supersite Program Objective	***GC-ARCH Objective and hypotheses to be tested***
Characterize particulate matter and its sources	*Objective 1: Collect physicochemical data on fine PM that can be used to characterize spatial and temporal variability in fine PM source contributions and composition, in Southeastern Texas; test the following hypotheses:* • Source profiles of PM in an upwind site, a site downwind of a heavily industrialized region and a site downwind of the urban core will be substantially different, and spatial gradients in fine PM concentrations will be greatest in the Ship Channel (industrial) region. • Maximum fine PM concentrations in Southeast Texas will be observed in the summer, when secondary PM generation peaks. • Variations in fine PM concentration and composition on a 10-15 minute time scale will be substantial and this temporal variability will be related to, but will not identically track, variability in ozone concentrations. • FRM mass monitors and 24-hour speciation monitors correspond to time integrated near-real time measurements of PM mass, sulfate and nitrate.
	Objective 2: Characterize spatial and temporal variability in fine PM source contributions and composition, throughout the southeastern United States; test the following hypotheses: • Source profiles of PM in Southeastern Texas will be substantially different than those in the Southeastern U.S., east of the Mississippi River. Spatial gradients in fine PM concentrations and composition will be greater in the Houston area than in Atlanta. • Maximum fine PM concentrations will be observed in the summer, when secondary PM generation peaks.
	Objective 3: examine the physical and chemical process that govern PM formation and transformation in Southeastern Texas; test the following hypotheses: • In regions of high PM concentration gradients, increases in PM mass are primarily due to condensation onto existing PM, rather than formation of new particles. • Rates of condensation of organics onto hydrophobic and hydrophilic PM will vary, and the condensation rates will depend on the hydrophobic surface area available for condensation.

	• Rates of PM growth will be highly correlated with concentrations of semivolatiles, peroxides, and acid gases and gas/particle partitioning ratios for organics will depend on the hydrophobic surface area available for condensation. • Rates of PM growth will differ for fresh and photochemically aged PM.
	Objective 4: Develop a combined database on PM, gas phase air pollutants and meteorological variables, suitable for testing models of the formation and fate of fine PM; test the hypotheses listed under objective 3.
Support health effects and exposure research	Objective 5: examine exposures to fine PM from specific source categories in Southeastern Texas; test the following hypotheses: • PM characteristics measured at ambient air quality measurement sites may be representative of ambient concentrations outside of homes, depending on the land cover surrounding the homes. • Source strengths for fine PM indoors and outdoors differ. • Indoor penetration of PM is a strong function of PM size
	Objective 6: relate the physicochemical data on fine particulate matter to mammalian cell responses; test the following hypotheses: • Human alveolar macrophage (AM) response depends on source contributions and PM composition.
Conduct methods testing, evaluating different methods of characterizing PM	Included as part of objectives 1-5

3.3 Project Schedule

Data collection will occur during a 16-month period beginning in August 2000. During the first six weeks of sampling, intensive measurements will be collected in coordination with the Texas Air Quality Study (TexAQS). Logistical preparations for the sampling program will rely extensively on the preparations that are already underway for TexAQS. An overall timeline for the project is given in Table 3.3-1.

Table 3.3-1 Project Schedule

Date	Task
December 1999	Study coordinators for TexAQS develop web site, and begin site selection and preparation
November 1999	Project planning meeting for TexAQS, including site evaluation.
January 2000	Funding awarded for GC-ARCH; Final site selection for GC-ARCH core sampling locations
April 2000	Project planning meeting for TexAQS and GC-ARCH
April 15, 2000	End of first quarter
May 15, 2000	First quarter report due
May 2000	Detailed site plans, investigator assignments and site layouts established
July 15, 2000	End of second quarter
August 15, 2000	Second quarter report due
August-September 2000	Six-week intensive sampling program
October 15, 2000	End of third quarter
November 15, 2000	Third quarter report due
January 15, 2000	End of fourth quarter
February 15, 2000	Fourth quarter report due
February 2001	Data analysis meeting for six-week intensive, quality assurance reports completed; data analysis projects associated with six-week intensive begin analysis of data
April 2001	Preliminary data on six-week intensive sent to central website
June 2001	Submission of interim progress report to U.S. EPA
December 2001	Scientific manuscripts on six-week intensive measurements and data analysis prepared/presented; additional data analysis manuscripts prepared in 2002
August 2000 – November 2001	16-month field sampling
February 2002	Data analysis meeting, quality assurance reports completed

	for 16 month sampling program
April 2002	Preliminary data on 16 month sampling program sent to central website
June 2002	Submission of interim progress report to U.S. EPA
November 2002	GC-ARCH data submitted to NARSTO QSSC
December 2002	Scientific manuscripts on measurements and data analysis prepared/presented; additional data analysis manuscripts prepared in early 2003
June 2003	Final project report prepared and submitted to U.S. EPA

3.4 Project Organization

The Gulf Coast Aerosol Research and Characterization Program (or the Houston Supersite) involves researchers from the University of Texas at Austin, Rice University, Texas A&M University, Texas Tech University, the Georgia Institute of Technology, Clarkson University, the University of Delaware, and Aerosol Dynamics, Inc.. The management structure for GC-ARCH is summarized in Figure 3.4-1 and Table 3.4-1.

GC-ARCH is directed by a Program Management Team, consisting of the PI, the co-PI, and the program manager. The PI is David Allen from the University of Texas; the co-PI is Matt Fraser from Rice University. The PI and co-PI are responsible for budgeting, all communications with the U.S. EPA, coordination with the Science Team, coordination with parallel studies, supervision of data archiving and site management, and communication with the Scientific Advisory Board. The program manager, Vincent Torres, is responsible for day-to-day administration of the program and its budgets. The Program Management team will communicate weekly throughout the course of the project. The team will communicate three times per week during the 6-week intensive sampling program (described later in this document).

The Science Team consists of all investigators receiving support from GC-ARCH. The specific responsibilities of each member of the Science team are described later in this document. The Science team consists of sub-committees on measurements and data analysis.

A data archiving and quality assurance team (including an independent quality assurance officer funded to perform quality assurance systems and performance audits and to review QA plans) will report directly to the program management team. Quality assurance is managed by Gary McGaughey of the University of Texas. The Quality

Assurance Manager (QAM) is responsible for performing technical audits on all data. These audits include assessing the quality of data submitted to the Data Management Coordinator (DMC) as well as reviewing the data before it is submitted to the archive. Data archiving is managed by Elena McDonald-Buller from the University of Texas. It is the DMCs responsibility to organize all data submitted by the individual PIs, as well as submit the data to the data archive (NARSTO QSSC).

The individual PIs are responsible for running and maintaining their portions of the GC-ARCH study as well as performing quality assessment of field and laboratory procedures and operations.

A Scientific Advisory Board consists of representatives from all of the collaborating institutions, plus other stakeholders. The board will meet semi-annually.

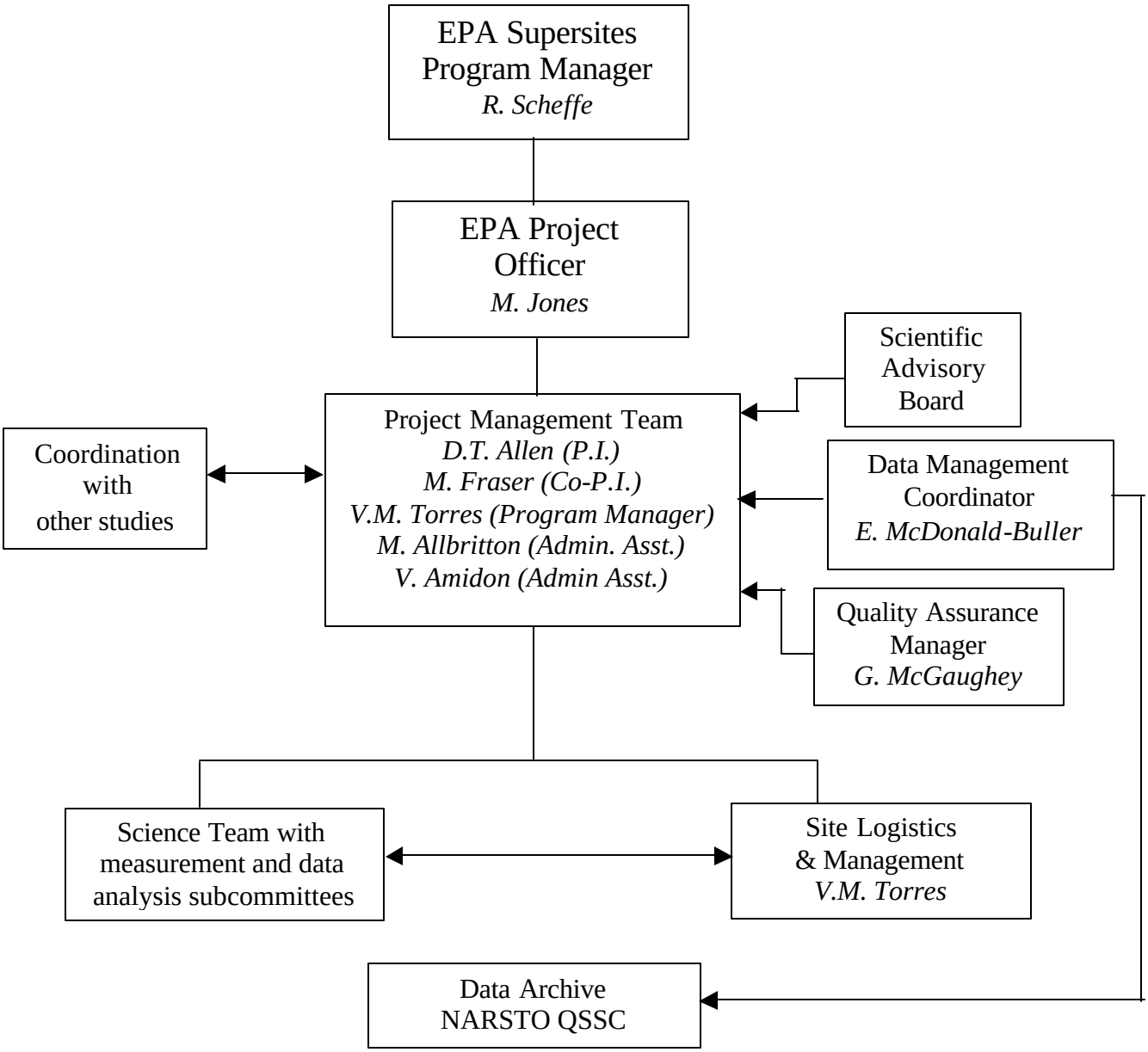

Figure 3.4-1. Organizational Chart of GC-ARCH Management Structure

Table 3.4-1. GC-ARCH/Houston Supersite Organization

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Additional Collaborating Institutions:
Assessment of Spatial Aerosol Composition in Atlanta (ASACA)
City of Houston, Office of the Mayor
Department of Energy, Atmospheric Chemistry Program (DoE)
Houston Regional Monitoring Network (HRM)
Mickey Leland National Urban Air Toxics Research Center
National Oceanographic and Atmospheric Administration
Southeastern Aerosol Research and Characterization Study (SEARCH)
Southern California Center for Airborne Particulate Matter (SCCAPM)
Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP)
Texas Air Quality Study (TexAQS)
Texas Hazardous Substance Research Center
Texas Natural Resource Conservation Commission (TNRCC)
University of Texas, Houston Health Science Center (UT-HHSC)

Listed below are short descriptions of the responsibilities of the collaborating organizations.

Texas Natural Resource Conservation Commission
The Texas Natural Resources Conservation Commission (TNRCC) will provide extensive, ongoing measurements of fine PM characteristics. These measurements are detailed in section A4 (Project/Task Description) of this QAPP.

SEARCH/SCISSAP/ASACA
GC-ARCH, in collaboration with the Southeastern Aerosol Research and Characterization Study (SEARCH), the Assessment of Spatial Aerosol Composition in Atlanta (ASACA) and the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP), will examine sources, spatial variability in PM mass and composition over a region extending from Texas to Georgia. Databases assembled in the GC-ARCH, SEARCH, ASACA, SCISSAP and related networks will be compared and contrasted and this coupled sampling network will allow investigators to characterize

differences in particle size and composition across the Southeastern quadrant of the United States.

TexAQS Field Study

The measurements to be made during the six week intensive sampling period described in Section 4 of this QAPP will be coordinated with an air quality study being organized by the State of Texas and investigators affiliated with the Southern Oxidants Study. TexAQS will bring to Southeast Texas 5-10 radar profilers capable of measuring wind fields aloft, multiple aircraft equipped with air quality instrumentation, a LIDAR capable of profiling vertical distributions of PM and ozone, particle size measurement equipment with rapid time resolution mounted on a P3 aircraft, PM composition (sulfate, nitrate and carbon) analysis equipment with rapid time resolution mounted on a P3 aircraft, and other instrumentation.

Mickey Leland Center

The Mickey Leland National Urban Air Toxics Research Center will be funding investigators to perform PM exposure measurements at a total of approximately 100 homes in the Houston area. Measurements will be made indoors, outdoors and with personal monitors. The measurements of PM physicochemical properties made through the Houston Supersite will compliment these ongoing activities.

UT-HHSC

A study being performed by the University of Texas Houston Health Science Center (UT-HHSC), funded by the U.S. EPA, is examining the responses of human alveolar macrophage (AM) to both model and ambient PM. Samples collected at the GC-ARCH sites will be used in the AM response testing by the UT-HHSC.

Texas Hazardous Substance Research Center

The Texas Hazardous Substance Research Center is a consortium of Lamar University, Texas A&M University, the University of Houston and the University of Texas at Austin, based at Lamar University. The Center has recently received an appropriation of air quality research funding from the Texas State legislature. A portion of these funds has been committed to the combined TexAQS study and GC-ARCH. These funds will support measurement and data analysis activities related to TexAQS and GC-ARCH.

Houston Regional Monitoring Network

The Houston Regional Monitoring Network is a group of privately funded air quality monitoring sites in Southeastern Texas. These are among the best instrumented sites in the region. The HRM network adds substantial capabilities to the Houston Supersite network of sites.

City of Houston, Office of the Mayor

The City of Houston has a record of supporting the collection and analysis of air quality data, including a study that has estimated fine PM exposures in the Houston area (Lurmann, et al., 1999). The City also funds an air quality monitoring network. The city

of Houston network adds substantial capabilities to the Houston Supersite network of sites planned for both the 6 week and 16 month sampling programs. All data collected at the City sites during the sampling programs will be made available to GC-ARCH.

Southern California Center for Airborne Particulate Matter (SCCAPM)
The GC-ARCH program will develop a formal collaboration with the SCCAPM. Initially the collaboration will involve experts in epidemiology and toxicology from the UCLA Center serving on the advisory board for GC-ARCH.

3.5 Project Documentation Organization

This QAPP is one of several documents that discusses and describes the Houston Supersite Study. The QAPP includes a discussion of the Data Quality Objectives (DQOs), as well as Measurement Quality Objectives (MQOs).

The individual investigators (members of the Science Team performing measurements, listed in Table 3.4-1) are each responsible for preparing a Standard Operating Procedure (SOP) for each instrument deployed during the program. The SOPs will be followed for routine collection of data to reduce uncertainty in the resulting measurements. Non-routine procedures and study protocols for sampling periods and data labeling will be covered by an accompanying research protocol (RP). Both the SOPs and RPs will contain concise and clear descriptions of the measurement activities. A consistent format for the SOPs and RPs will be used by all investigators on the project to prevent misunderstandings between operations. In some cases, as with new experimental designs, the procedures have not been formalized. In these cases, written procedures will be submitted to the Project manager for review. SOPs and RPs will discuss data spikes, duplicate data, laboratory and field blanks, as well as surrogates and other indicators in detail. In addition, all SOPs and RPs will discuss instrument testing and inspections, calibrations and their frequency, inspection of consumables and supplies, data acquisition and management. The SOPs and RPs will also specifically define quality objectives for their experiments.

The individual PIs are responsible for all record keeping and document control in the field. This information shall be specified in the respective SOPs and RPs. Records shall include raw data, chain of custody logs, field logs, sample preparation and analysis logs, printouts, and calibration and QC checks.

Following the end of the project, an independent Quality Assurance Auditor will provide the EPA with a final Quality Assurance Final Report as an appendix to the final project report. This section of the final report will include a critical evaluation of whether or not the quality objectives were met during the project. A peer review of all documents will occur per guidelines established by the EPA.

4.0 TASK DESCRIPTION

The Gulf Coast Aerosol Research and Characterization (GC-ARCH) program will be conducted in Houston, Texas (the Houston Supersite). Houston was chosen as a Supersite location due to its unique combination of industrial and urban emissions. Houston has the largest concentration of petrochemical manufacturing facilities in the United States, and as a consequence the industrial source signatures for PM and PM precursors are strong, particularly for organics. In addition, Houston is the fourth most populous city in the United States. In the Houston region approximately 2.5 million people may be exposed to annual average PM concentrations in excess of 15 $\mu g/m^3$. Emissions from typical urban anthropogenic sources and biogenic sources are also significant. In addition, exposure studies, toxicological studies, and a large ambient air quality field study are planned for the summer of 2000. These studies will provide valuable data sets that can be combined with the data to be collected by the program.

The objectives of the GC-ARCH study are to:

1. Collect physicochemical data on fine PM, in Southeastern Texas, over a 16 month sampling period; use the data to identify sources and to characterize spatial and temporal variability in fine PM source contributions and composition
2. Characterize spatial and temporal variability in fine PM source contributions and composition, throughout the southeastern United States
3. Examine the physical and chemical processes that govern PM formation and composition in Southeastern Texas
4. Develop a combined database of PM, gas phase air pollutants and meteorological variables, suitable for testing models of the formation and fate of fine PM; this objective will be achieved by coordination with a large, integrated ozone and PM field study planned for the summer of 2000
5. Examine exposures to fine PM from specific source categories in Southeastern Texas; this objective will be achieved by coordinating with an exposure study currently underway that will continue through 2000
6. Relate the physicochemical data on fine PM to mammalian cell responses; this objective will be achieved by coordinating with an EPA funded project currently underway.

4.1 Sampling Site Locations and Measurements

A 16 month field sampling program (August 2000 – November 2001) for the Houston Supersite will be undertaken at three core sampling sites (Aldine, Deer Park, and HMR#3) jointly operated by GC-ARCH, HRM and TNRCC. These three core sites are locations of the EPA funded Houston Supersite. In addition, approximately 20 peripheral sampling sites will be operated by TNRCC in a separate effort not funded by the Houston Supersite program. The locations of the core and peripheral sites are shown in Figure 4.1-1. The three sites were chosen to best represent Houston's industrial and urban areas.

The Aldine site is downwind of the urban area. Deer Park/La Porte is typical of an industrial region and is upwind of the Ship Channel area. The HRM#3 site is located directly within the Ship Channel region. Detailed maps of the three core sites are available from the TexAQS web site (http://www.utexas.edu/research/ceer/texaqs).

The measurements listed in Table 4.1-1 will be made at three core sites in the Houston area over the 16-month investigation period (August 2000 –November 2001). The entity responsible for each measurement (TNRCC, HRM or GC-ARCH) is identified in Table 4.1-1. A group of approximately 20 peripheral sites to be operated by TNRCC will provide additional information. The particulate matter measurements to be made at the peripheral sites are shown in Table 4.1-2. Parallel gas phase measurements will also be made at these sites.

In addition to the 16-month field study, a six week intensive study will also be undertaken. A summary of the measurements to be made at the three core sites during the six week intensive sampling period is given in Tables 4.1-3 and 4.1-4.

Figure 4.1-1. Core and peripheral PM monitoring sites. A dot on a site indicates that the Federal Reference Method sampler for fine PM will be operated at the site. An S indicates that speciation measurements (trace metals, inorganic ions and organic/elemental carbon) will be made. The core sites are a privately operated site (HRM Site #3) near Clinton, Deer Park, and Aldine.

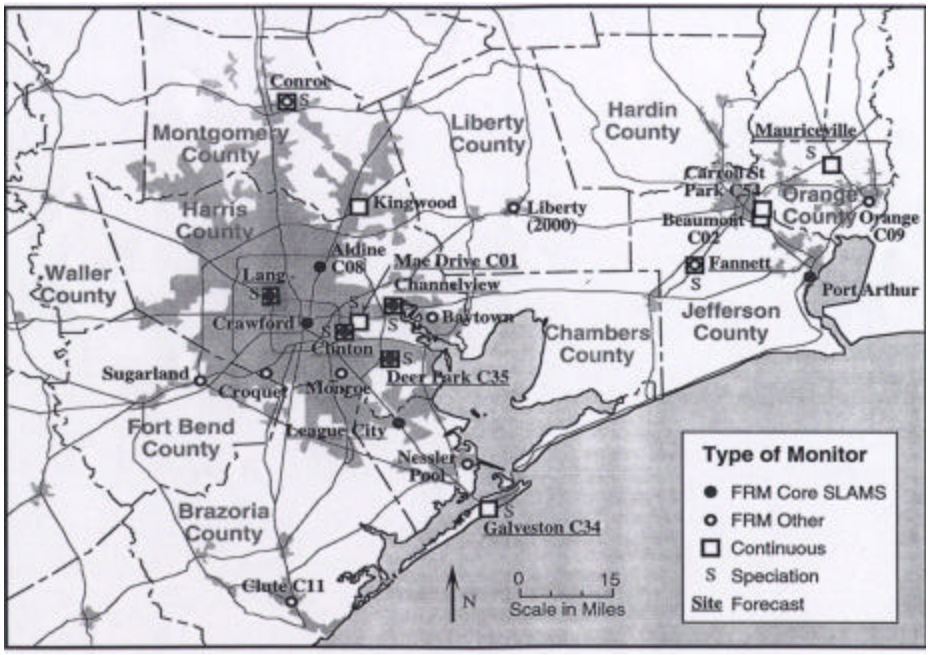


Table 4.1-1. Measurements to be made at the core sites over 16 month field study

Measurement	***Houston Regional Monitoring (HRM) Network Site 3 (downwind industrial)***	***Deer Park/La Porte (upwind industrial)***	***Aldine (downwind urban)***
PM measurements			
Federal Reference Method (FRM)	Every sixth day PM_{10} and $PM_{2.5}$ (HRM)	Every third day PM_{10} and $PM_{2.5}$ (TNRCC)	Every third day PM_{10} and $PM_{2.5}$ (TNRCC)
Continuous PM Mass (TEOM)	HRM	TNRCC	TNRCC
Inorganic ions	Every third day at nearby TNRCC site (TNRCC)	Every third day (TNRCC)	Every third day (TNRCC)
OC/EC	Every third day at nearby TNRCC site (TNRCC)	Every third day (TNRCC)	Every third day (TNRCC)
Trace metals	Every third day at nearby TNRCC site (TNRCC)	Every third day (TNRCC)	Every third day (TNRCC)
Near real time sulfate	HRM using Aerosol Dynamics instrument	Aerosol Dynamics, (ADI)-GCARCH	Aerosol Dynamics, (ADI)-GCARCH
Near real time nitrate		ADI -GCARCH	ADI-GCARCH
Near real time carbon	HRM (R&P instrument)	ADI -GCARCH	ADI –GCARCH
Molecular characterization of organic fractions	Selected dates from filter samples collected every third day (Rice-GCARCH)	Selected dates from filter samples collected every third day (Rice-GCARCH)	Selected dates from filter samples collected every third day (Rice-GCARCH)
Gas measurements			
Ozone, CO	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO, NO_x	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO_y	Continuous (TNRCC)	Continuous (TNRCC)	Continuous (TNRCC)
Denuder HNO_3	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)
Denuder NH_3	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)
SO_2	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
PAMS hydrocarbons	Auto-GC (HRM)	Auto-GC (TNRCC)	Auto-GC (TNRCC)
Carbonyls	On forecast (HRM)	Third day (TNRCC)	Third day (Rice-GCARCH)
Meteorological Data*	HRM	TNRCC	TNRCC

*Meteorological data includes wind speed, wind direction, relative humidity and solar radiation

Table 4.1-2. Data to be collected at peripheral sites (all data to be collected by the TNRCC).

Site	FRM	TEOM	Inorganic Ions	Trace Metals	OC/EC	Met. Data*
Aldine	Daily					X
Baytown	Every sixth day					X
Channelview	Daily	X	X	X	X	X
Clinton	Daily	X	X	X	X	X
Clute	Every sixth day					X
Conroe	Every third day	X	X	X	X	X
Crawford	Every third day					X
Croquet	Every sixth day					X
Galveston						X
Kingwood		X				X
League City	Every third day					X
Liberty	Every sixth day					X
Mae Drive		X	X	X	X	X
Monroe	Every sixth day					X
Nessler Pool	Every sixth day					X
Sugarland	Every sixth day					X
Beaumont		X				X
Carroll St. Park		X				X
Fannett	Every third day	X	X	X	X	X
Mauriceville		X	X	X	X	X
Orange	Every sixth day					X
Port Arthur	Daily					X

*Meteorological data includes wind speed and wind direction at all sites and relative humidity and solar radiation at selected sites

Table 4.1-3 Particulate phase measurements to be performed at core sites during six week intensive study.

Measurement	***HRM Site #3 (downwind industrial)***	***Deer Park /La Porte (upwind industrial)***	***Aldine (downwind urban)***
Particulate matter measurements			
FRM	Every sixth day PM_{10} and $PM_{2.5}$ (HRM), Daily at nearby TNRCC site (TNRCC)	Daily $PM_{2.5}$ (TNRCC)	Daily $PM_{2.5}$ (TNRCC)
Continuous PM Mass	HRM	TNRCC	TNRCC
Inorganic ions	Every third day at nearby TNRCC site (TNRCC)	Daily sample collection; selected samples analyzed (TNRCC)	Daily sample collection (TNRCC)
OC/EC	Every third day at nearby TNRCC site (TNRCC)	Every third day (TNRCC)	Every third day (TNRCC)
Trace metals	Every third day at nearby TNRCC site (TNRCC)	Every third day (TNRCC)	Every third day (TNRCC)
Near real time sulfate	HRM using Aerosol Dynamics instrument, Texas Tech instrument	Aerosol Dynamics, (ADI)-GCARCH	Aerosol Dynamics, (ADI)-GCARCH
Near real time nitrate	Texas Tech Instrument	ADI -GCARCH	ADI-GCARCH
Near real time carbon	HRM	ADI -GCARCH	ADI –GCARCH
Molecular characterization of organic fractions	Selected dates from filter samples collected every third day (Rice-GCARCH)	Selected dates from filter samples collected every third day (Rice-GCARCH)	Selected dates from filter samples collected every third day (Rice-GCARCH)
Size distributions	TAMU-GCARCH	TAMU-GCARCH	TAMU-GCARCH
Single particle MS	Univ. Del. (GC-ARCH)		
Organic compound classes of size resolved PM	Daily (UT-GCARCH)	Daily (UT-GCARCH)	Daily (UT-GCARCH)
Additional PM measurements, ground based and aircraft	Year 2000 Field Study	Year 2000 Field Study	Year 2000 Field Study

Table 4.1-4. Gas phase measurements to be performed at core sites during six week intensive study.

Measurement	***HRM Site #3 (downwind industrial)***	***Deer Park /LaPorte (upwind industrial)***	***Aldine (downwind urban)***
Gas phase measurements			
Ozone, CO	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO, NO_x	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO_y	Continuous (TNRCC)	Continuous (TNRCC)	Continuous (TNRCC)
Denuder HNO_3	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)
Denuder NH_3	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)
Acid gases: SO_2, HCl, HONO, HNO_3		Semi-continuous (TTU-GCARCH)	
NH_3		Semi-continuous (TTU-GCARCH)	
SO_2	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
PAMS hydrocarbons	Auto-GC (HRM)	Auto-GC (TNRCC)	Auto-GC (TNRCC)
Carbonyls	Selected dates (HRM)	Selected dates by TNRCC (TNRCC)	Selected dates by TNRCC (Rice-GCARCH)
Semivolatiles		Selected dates from samples collected by EPA	
Peroxides		Semi-continuous (TTU-GCARCH)	
Additional gas phase measurements, ground based and aircraft	Year 2000 Field Study	Year 2000 Field Study	Year 2000 Field Study
Meteorological Data*	TNRCC	TNRCC	TNRCC

*Meteorological data includes wind speed, wind direction, relative humidity and solar radiation

4.2 Approach

Each objective consists of scientific hypotheses that will be tested. The relationship between the hypotheses and the overall Supersite Program Objectives is shown in Table 3.2-1. The relationship between the hypotheses to be tested and the measurements to be made are summarized in Table 4.2-1

Table 4.2-1. Relation between hypotheses to be tested and measurements to be made as part of the Supersite program.

Objective	Hypothesis to be tested	Required Measurements
Objective 1	Source profiles of PM in an upwind site, a site downwind of a heavily industrialized region and a site downwind of the urban core will be substantially different, and spatial gradients in fine PM concentrations will be greatest in the Ship Channel region.	• FRM mass measurement • Fine PM speciation (ions, metals, elemental and organic carbon) • Molecular characterization of organic fraction of fine PM
Objective 1	Maximum fine PM concentrations in Southeast Texas will be observed in the summer, when secondary PM generation peaks.	• FRM mass measurement • Near-real time fine PM mass measurements • Fine PM speciation (ions, metals, elemental and organic carbon)
Objective 1	Variations in fine PM concentration and composition on a 10-15 minute time scale will be substantial and this temporal variability will be related to, but not identically track, variability in ozone concentration.	• Near-real time fine PM sulfate • Near-real time fine PM nitrate • Near-real time fine PM carbon • Ozone and other secondary indicators of photochemistry (i.e. carbonyls)
Objective 1	FRM mass monitors and 24-hour speciation monitors correspond to time integrated near-real time measurements of PM mass, sulfate and nitrate.	• FRM mass measurement • Fine PM speciation (ions, metals, elemental and organic carbon) • Near-real time fine PM mass measurements • Near-real time fine PM sulfate • Near-real time fine PM nitrate • Near-real time fine PM carbon
Objective 2	Source profiles of PM in Southeastern Texas will be substantially different than those in the Southeastern US east of the Mississippi River. Spatial gradients in fine PM concentrations and composition will be greater in Houston than in Atlanta.	• FRM mass measurement from SEARCH network • Fine PM speciation (ions, metals, elemental and organic carbon) from SEARCH network • Molecular characterization of organic fraction from SEARCH network
Objective 2	Maximum fine PM concentrations will be observed in the summer, when secondary PM generation peaks.	• FRM mass measurement from SEARCH network • Near-real time fine PM mass measurements from SEARCH network • Fine PM speciation (ions, metals, elemental and organic carbon) from SEARCH network
Objective 3	In regions of high PM concentration	• Real-time measurements of particle

	gradients, increases in PM mass are primarily due to condensation onto existing PM, rather than formation of new particles.	size distributions • Near-real time fine PM mass measurements • Near-real time fine PM sulfate • Near-real time fine PM nitrate • Near-real time fine PM carbon
Objective 3	Rates of condensation of organics onto hydrophobic and hydrophilic PM will vary and the condensation rates will depend on the hydrophobic surface area available for condensation.	• Near-real time fine PM mass measurements • Organic compound classes of size resolved PM • Real-time measurements of particle size distributions • Semivolatile organic compounds • Fine PM speciation (ions, metals, elemental and organic carbon) • Single particle analysis by mass spectrometry
Objective 3	Rates of PM growth will be highly correlated with the concentrations of semivolatiles, peroxides, and acid gases and gas-particle partitioning ratios for organics will depend on the hydrophobic surface area available for condensation.	• Near-real time fine PM mass measurements • Fine PM speciation (ions, metals, elemental and organic carbon) • Near-real time fine PM sulfate • Near-real time fine PM nitrate • Near-real time fine PM carbon • Semivolatile organic compounds • Semi-continuous peroxide measurements • Semi-continuous measurements of SO_2, HCl, HONO, HNO_3 and NH_3 • PAMS Hydrocarbons and carbonyls • Organic compound classes of size resolved PM • Single particle analysis by mass spectrometry
Objective 3	Rates of PM growth will differ for fresh and photochemically aged PM.	• Near-real time fine PM mass measurements • Fine PM speciation (ions, metals, elemental and organic carbon) • Near-real time fine PM sulfate • Near-real time fine PM nitrate • Near-real time fine PM carbon • Organic compound classes of size resolved PM • Single particle analysis by mass spectrometry
Objective 5	PM characteristics measured at ambient air quality measurement	• Real-time measurements of particle size distributions

	sites may be representative of ambient concentrations outside homes, depending on the land cover surrounding the homes.	• Molecular characterization of organic fraction of fine PM
Objective 5	Source strengths for fine PM indoors and outdoors differ.	• Real-time measurements of particle size distributions
Objective 5	Indoor penetration of PM is a strong function of PM size.	• Real-time measurements of particle size distributions
Objective 6	Human alveolar macrophage response depends on source contributions and PM composition.	• FRM mass measurement • Fine PM speciation (ions, metals, elemental and organic carbon) • Molecular characterization of organic fraction of fine PM

4.3 Sampling Activities: Objective 1

Objective 1: Collect physicochemical data on fine PM, in Southeastern Texas, over a 16-month sampling period; use the data to identify sources and to characterize spatial and temporal variability in fine PM source contributions and composition

4.3.1 Task 1a

Task 1a: Collect a 16 month time series of near real time particulate matter data and test the following hypotheses:

- *Spatial gradients in fine PM concentrations will be greatest in the Ship Channel (industrial) region.*
- *Maximum fine PM concentrations in Southeast Texas will be observed in the summer, when secondary PM generation peaks.*

Measurements identified by the notation TNRCC and HRM in Tables 4.1-1 and 4.1-2 will be performed by these agencies, respectively. The data collection activities to be performed by GC-ARCH are listed below and are identified in Table 4.1-1 by the notation GC-ARCH. Only brief technical descriptions of the measurements to be performed by GC-ARCH are given here. More detailed measurement descriptions are provided in the SOPs.

GC-ARCH will perform the following measurements:

- *Near real time sulfate, nitrate and aerosol carbon*
  Investigating Team: Aerosol Dynamics, Inc.
  Method: Semi-continuous measurements of nitrate, sulfate and carbon will be made using instruments based on the method of Stolzenburg and Hering (1998, 1999).

- *Molecular characterization of extractable organics from filter samples*
  Investigating Team: Rice University
  Method: Filter samples will be collected every third day at each of the three core sites, resulting in approximately 500 samples; these samples will be stored and up to 100 will be selected for detailed molecular characterization of the extractable organics. Analysis will be accomplished using methods described by Fraser, et al., (1998a,b).

- *Ammonia and nitric acid from denuders*
  Investigating Team: Rice University
  Method: Measurements of gaseous ammonia and nitric acid will be collected on glass denuders before collection of particulate matter on a Teflon filter. The denuders will be coated with sodium carbonate (for nitric acid) and citric acid (for ammonia) over a 24-hour integration period. Additionally, volatilization of ammonium nitrate during the 24-hour sample period will be determined using an impregnated backup filter behind the sodium carbonate denuder. Denuder samples will be collected every third day at each of the core sites resulting in approximately 500 samples. Quantification of nitrate and ammonium ions will be done at Rice University and will rely on ion chromatography.

- *Carbonyls*
  Investigating Teams: TNRCC (Deer Park core site), Rice University (Aldine core site)
  Method: Measurement of carbonyl compound concentrations will be taken every three days and employ 2,4-dinitrophenyl-hydrazine (DNPH) sampling techniques. Cartridge preparation methods have been described by Trapp and de Serves (1995); the detection methods have been described by Grosjean and Grosjean (1995) and Grosjean, et al., (1996). DNPH cartridge samples will be collected every third day at two of the core sites resulting in approximately 350 samples. Measurements at one of the core sites will be performed by TNRCC. Rice University will perform measurements at the other core site.

- *Canister sampling for VOC analysis*
  Investigating Team: TNRCC and HRM (all three core sites), University of Texas at Austin (sites throughout Southeastern Texas)
  Method: All of the three core sites will have automatically operated gas chromatographs (Auto-GC), run by the TNRCC and

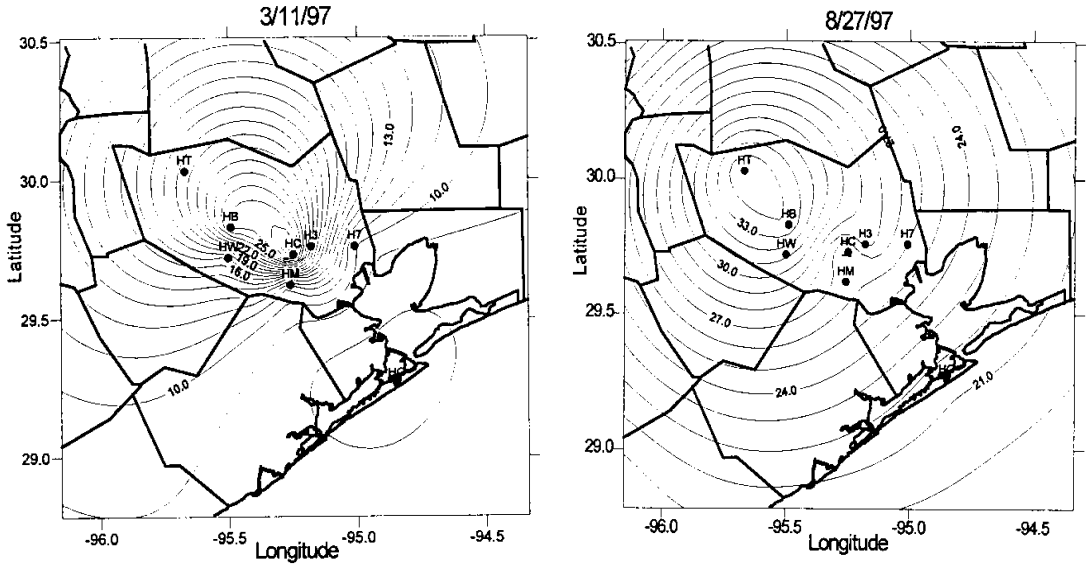
HRM, which will analyze air samples for hydrocarbons. The University of Texas will collect source dominated samples from throughout Southeastern Texas using canisters. The samples will be cryofocussed and analyzed by gas chromatography with flame ionization detection (U.S. EPA, 1989). In addition, some of the canister sampling (approximately four canisters per month) will be conducted at the Deer Park and HRM 3 sites to ensure comparability between Auto-GC and canister analyses.

- *Spatial mapping*
  Investigating Team: The University of Texas at Austin
  Method: UT will create mappings (similar in format to Figure 4.3.1-1) of the spatial distributions of particulate matter mass, sulfate, nitrate, organic carbon and elemental carbon concentrations, based on the data collected every third day.

Samples collected or analyzed using GC-ARCH funding for Task 1a will be retrieved from each of the core sites at least once every third day. The samples will be returned to Rice University. Rice University will be responsible for delivery of the samples to the chemical analysis teams, or archiving the samples for later analysis. The site managers will also be responsible for maintaining continuously operating instrumentation.

The activities listed above will enable the GC-ARCH program to collect and archive the data described in Tables 4.1-1 and 4.1-2, over a period of 16 months. The resulting data set will include a core set of continuous measurements (PM mass at three core sites and six peripheral sites; sulfate and PM carbon at three core sites; aerosol nitrate at two core sites; gas measurements at core and most peripheral sites), and a more extensive set of measurements made every third day.

Figure 4.3.1-1. Concentrations of fine $PM_{2.5}$ in the Houston area. The particulate matter isopleths shown in these plots were estimated (Lurmann, 1999) based on $PM_{2.5}$ monitoring done at 8 locations in the Houston area (shown as dots in the Figure) between March 1997 and March 1998 (Tropp, et al., 1998). The data for 3/11/97 show high $PM_{2.5}$ concentrations (isopleths are in $\mu g/m^3$) in the Ship Channel (industrial) area. The data for 8/27/97 show $PM_{2.5}$ concentrations conditions when the peak concentrations are observed downwind of the urban core.



4.3.2 Task 1b

Task 1b: Use the data collected during the 16-month field study to identify sources and to characterize spatial and temporal variability in fine PM source contributions and composition; test the following hypothesis:

- *Source profiles of PM at an upwind site downwind of a heavily industrialized region and a site downwind of the urban core will be substantially different*

The extensive data collected as part of the 16-month field program will be subjected to three levels of data analysis for source resolution:

- *Spatial distributions of the daily averages of fine PM mass, fine PM sulfate, fine PM nitrate, fine PM organic carbon and fine PM elemental carbon*
  Investigating Team: The University of Texas at Austin
  Method: Isopleths, similar to those shown in Figure 4.3.1-1, will be created for each sampling day based on data from the three core sites and the peripheral sites. These spatial mappings will be used to qualitatively assess the importance of

various sources in specific geographical regions. The mappings may also be of use in assessing potential PM exposure patterns and in identifying data anomalies.

- *The use of molecular and atomic tracers to identify source contributions.*
  Investigating Team: The University of Texas at Austin
  Method: These analyses will rely on trace metal concentrations and the concentrations of organic, molecular tracers. Chemical Mass Balance (CMB 8) techniques (Friedlander, 1973; Watson, et al., 1991, 1998) will be used to identify sources, some of which are listed in Table 4.3.2-1. Since source allocation data will be available for a variety of sites, the source strengths can be mapped in a manner analogous to that shown in Figure 4.3.2-1.

- *Neural networks*
  Investigating Team: Clarkson University
  Method: The back-propagation neural network method of Song and Hopke (1996) will be used to solve the chemical mass balance problem, incorporating non-linearities into the system.

Table 4.3.2-1. Representative tracer species to be used in source attributions

Source	Tracer species	Reference
Road Dust	Si, Al	Watson et al (1998)
Wood Smoke	Levoglucosan	Simoneit et al (1999)
Vehicle Exhaust	Hopanes and Steranes	Schauer et al (1999b),Fraser et al (1998b),Rogge et al (1993)
Diesel Vehicles	Elemental Carbon	Schauer et al (1999b); Rogge et al (1993)
Meat Cooking	Unsaturated Fatty Acids	Schauer et al (1999a); Rogge et al (1991)

4.3.3 Task 1c

Task 1c: Perform methods intercomparisons and statistical analyses of the data sets; test the following hypotheses:

- *Variations in fine PM concentration and composition on a 10-15 minute time scale will be substantial and this temporal variability will be related to, but will not identically track, variability in ozone concentrations.*
- *FRM mass monitors and 24-hour speciation monitors correspond to time integrated near-real time measurements of PM mass, sulfate and nitrate.*

Task 1c compares methods for characterizing fine PM. The problem in performing the comparisons is relating the measurements of PM components using highly time resolved

and chemical specific instrumentation (such as single particle mass spectroscopy) to the measurements obtained from 24-hour chemical speciation monitors and to the 24-hour FRM mass concentrations. This is a problem for which multivariate calibration methods (including partial least squares, PLS) are ideally suited:

- Intercomparison of Data
  Investigating Team: Clarkson University
  Method: Intercomparisons will be performed using multivariate calibration methods, including partial least squares (PLS; Lober et. al., 1987; Thomas and Haaland, 1990; Martens and Naes, 1991). Positive matrix factorization (PMF) will be used in handling missing and below detection limit (BDL) values.

4.4 Sampling Activities: Objective 2

Objective 2: Characterize spatial and temporal variability in fine PM source contributions and composition, throughout the southeastern United States; test the following hypotheses:

- *Source profiles of PM in Southeastern Texas will be substantially different than those in the Southeastern U.S., east of the Mississippi River. Spatial gradients in fine PM concentrations and composition will be greater in the Houston area than in other southern cities. ASACA has been designed to characterize spatial PM gradients in Atlanta. Preliminary results suggest that Atlanta has relatively small spatial variations in PM mass and composition within the city, though levels are significantly higher than the rural background.*
- *Maximum fine PM concentrations will be observed in the summer, when secondary PM generation peaks.*

The 16-month sampling program will be used to characterize spatial and temporal variability in PM, sources, mass and composition in Southeast Texas (as described under Objective 1). In addition, GC-ARCH, will put these findings in context by comparing data collected in Southeast Texas to similar data collected by the Southeastern Aerosol Research and Characterization Study (SEARCH), the Assessment of Spatial Aerosol Composition in Atlanta (ASACA) and the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP). These PM networks are examining sources and spatial variability in PM mass and composition over a region extending from Texas to Georgia. In addition to these special studies, a number of other routine PM measurements are being made by individual states and by the IMPROVE program.

Investigating Teams: Georgia Institute of Technology and
The University of Texas at Austin

Method: Data bases assembled in the GC-ARCH, SEARCH, ASACA, SCISSAP and related networks will be compared and contrasted, allowing investigators to characterize

differences in particle size and composition across the Southeastern quadrant of the United States. Data analysis procedures will partially mirror those used in Objective 1. A variety of analysis tools will be used to develop a spatial and temporal understanding of particulate matter source characteristics over the Southeast. Molecular and atomic tracers will be used to identify source contributions. These analyses will rely on trace metal concentrations and the concentrations of organic, molecular tracers. Chemical Mass Balance techniques will be used to identify sources, some of which are listed in Table 4.3-1. Kriging and other spatial correlation/time series analyses will be used to provide a view of the PM dynamics around the Gulf States, and will tie in results of the SEARCH, SCISSAP, ASACA, SOS, IMPROVE and individual state networks. A summary of the SEARCH, ASACA and SCISSAP measurements and measurement locations is given in Table 4.4-1.

Table 4.4-1. Measurements made in the SEARCH and SCISSAP networks

	SEARCH Network	*SCISSAP Network*	*ASACA Network*
Measurement Locations	A total of 4 rural and 4 urban sites in Georgia, Florida, Alabama and Mississippi	Six sites that augment existing rural and urban networks	Four urban sites that complement the SEARCH/Supersite in Atlanta
Particulate Measurements	• FRM • Continuous particulate mass • Semicontinuous measurement of nitrate, sulfate, ammonium, OC and EC • 24 hour measurement of metals, nitrate, sulfate, ammonium, OC and EC	• FRM • Multi-channel denuder-filter pack systems	• Continuous particle mass • Multi-channel denuder-filter pack systems
Gas phase Measurements	• Ozone • SO_2 • CO • Nitric acid, ammonia • $NO/NO_2/NO_y$	• Nitric acid, ammonia • $NO/NO_2/NO_y$	

4.5 Sampling Activities: Objective 3

Objective 3: Examine the physical and chemical processes that govern PM formation and composition in Southeastern Texas

Task 3: Data Collection and Intercomparison; Six week intensive sampling

A major objective of GC-ARCH is to examine the physical and chemical processes that govern particulate matter formation in Southeastern Texas. These processes will be examined through measurements made during a six-week intensive sampling period during the summer of 2000. The measurements funded by GC-ARCH during the intensive period will focus on the core sites. Note that one of the core sites (Deer Park) may be temporarily moved to a location in the City of LaPorte that is capable of hosting the extensive ground based measurements that will be made during TexAQS.

These physical and chemical data on fine PM will be subjected to intercomparisons, using the methods described in Task 1c. The data will also be used to examine the processes that lead to the rapid photochemical processing of particulate matter in the industrial (Ship Channel) region of Houston and to examine the heterogeneous organic chemistry leading to particulate matter formation and transformation in Houston. The following hypotheses will be tested:

- *In regions of high PM concentration gradients, increases in PM mass are primarily due to condensation onto existing PM, rather than formation of new particles.*
- *Rates of condensation of organics onto hydrophobic and hydrophilic PM will vary, and the condensation rates will depend on the hydrophobic surface area available for condensation.*
- *Rates of PM growth will be highly correlated with concentrations of semivolatiles, peroxides, and acid gases and gas/particle partitioning ratios for organics will depend on the hydrophobic surface area available for condensation.*
- *Rates of PM growth will differ for fresh and photochemically aged PM.*

A summary of the measurements to be made at the core sites during the six week intensive sampling period is given in Tables 4.1-3 and 4.1-4. Specifically, the following enhancements to the 16-month measurements will be undertaken:

- *Increase sampling frequency for filter and cartridge based samples*
  Investigating Team: Rice University
  Method: The frequency of filter and cartridge collection at the core sites will be increased from every third day to daily. While these filters and cartridges, suitable for mass, inorganic ion, OC/EC, trace metal, semivolatile, and carbonyl analyses will be collected, not all will be analyzed. The filters will be archived and samples from selected days will be analyzed.

- *Measurements of size distributions*
  Method: To compliment the detailed aerosol chemical analysis, aerosol size distributions will be continuously measured at the HRM and Deer Park locations. Multiple instruments are required for this measurement. For this study a differential mobility analyzer (DMA) will be used for

classification of particles between ~0.01 and ~0.5 μm, while an optical particle counter (OPC) will size particles in the ~0.15 to ~ 4 μm range. Rather than using only a condensation nucleus counter (CNC) as a detector for the DMA, as is common, a fraction of the particles will be measured by the OPC. Stolzenburg et al. (1998) most recently demonstrated the effectiveness of this approach, which both reduces errors in DMA measurements due to multiply charged particles, and reduces errors in OPC data resulting from uncertainties related to particle index of refraction. Through the use of automated solenoid valves, both the CNC and OPC will intermittently sample the aerosol prior to classification by the DMA. This will provide more statistically representative data for the supermicrometer particles measured by the OPC, as well as a total aerosol concentration to which the integral of the recovered size distribution can be compared. The complete measurement sequence is expected to take approximately ten minutes. The necessary components of the instrumentation will be maintained at ambient temperature to enable sampling of particles at equilibrium with the outside relative humidity. During every other sampling sequence, a desiccant-lined inlet will be used to permit characterization of the dry aerosol to provide details of its hygroscopicity. Complete automation will permit 24 hour sampling at two of the core sites.

- *Daily measurements of the organic compound classes in size resolved PM*
  Investigating Team: The University Of Texas at Austin
  Method: Collection of aerosol using a Hering low pressure cascade impactor coupled with analysis by Fourier Transform infrared spectroscopy (method developed by Allen et al., 1994).

- *Measurements of semivolatiles*
  Investigating Team: Len Stockburger, EPA.
  Method: Cartridge samples will be collected at one of the core sites, using denuders and afterfilters.

- *Single particle mass spectroscopy*
  Investigating team: University of Delaware
  Method: An on-line single particle analysis technique will be used to measure particle-by-particle size and composition over the size range from 10 nm to 2 microns. The instrument is

described in more detail in Carson et al. (1997) and Ge et al. (1998).

- *Add semi-continuous measurement of ammonia and acid gases*
  Investigating team: Texas Tech University
  Method: Measurements of ammonia and acid gases will be made using the automated wet denuder system developed by Texas Tech University. This system was deployed during the 1999 Atlanta Supersite inter-comparison study.

- *Add a second semicontinuous method for particulate sulfate and nitrate*
  Investigating Team: Texas Tech University
  Method: The Texas Tech system for acid gas analysis can also be used for PM constituents.

- *Add semicontinuous measurements for peroxides and formaldehyde*
  Investigating Team: Texas Tech University
  Method: Atmospheric H_2O_2 will be measured using the Texas Tech Diffusion Scrubber method. Texas Tech will also provide a near-continuous measurement for formaldehyde, based on a diffusion scrubber fluorometric method.

4.6 Sampling Activities: Objective 4

Note: This objective is not funded by EPA under the Supersites Program.

Objective 4: Develop a combined database on PM, gas phase air pollutants and meteorological variables, suitable for testing models of the formation and fate of fine PM; this objective will be achieved by coordinating with a large, integrated ozone and PM field study planned for the summer of 2000;

Investigating Teams: GC-ARCH, HRM and the TNRCC (described in Tables 4.1-3 and 4.1-4).

The intensive sampling funded through the GC-ARCH program will be timed to coincide with a large, integrated ozone and PM sampling program currently planned for the summer of 2000, which will be referred to as the Texas Air Quality Study (TexAQS). TexAQS will bring to Southeast Texas 5-10 radar profilers capable of measuring wind fields aloft, aircraft equipped with air quality instrumentation, a LIDAR capable of profiling vertical distributions of PM and ozone, particle size measurement equipment with rapid time resolution mounted on a P3 aircraft, and other instrumentation. The instrumentation available on the aircraft is described in the technical attachments. The measurements made during TexAQS, coupled with the measurements made by GC-

ARCH, will create a data set powerful enough to rigorously test models of PM formation and fate.

The GC-ARCH program will convene a modeling group prior to and at the conclusion of the six-week intensive sampling period. As demonstrated in prior field experiments, involving data analysts (including modelers) in the study design is critical to ensuring maximum utility of the efforts. Shortly after the conclusion of the intensive sampling period, the modeling team will select up to three multi-day episodes suitable for modeling. The GC-ARCH program then will assemble and quality assure meteorological, gas phase air pollutant and PM data for these episodes from all available sources (GC-ARCH, TexAQS, TNRCC, and others), and will work with the relevant agencies and industries to collect and archive day specific emissions. This activity will include individuals from Georgia Tech TNRCC and modelers from other interested agencies and industries (e.g., from the EPA Models3 group, EPA Region 6, etc.).

4.7 Sampling Activities: Objective 5

Note: This objective is not funded by EPA under the Supersite Program.

Objective 5: Examine exposures to fine PM from specific source categories in Southeastern Texas; this objective will be achieved by coordinating with an exposure study currently underway that will continue through 2000

The following hypotheses will be tested:

- *PM characteristics measured at ambient air quality measurement sites may be representative of ambient concentrations outside of homes, depending on the land cover surrounding the homes.*
- *Source strengths for fine PM indoors and outdoors differ.*

Both the 16-month and six-week sampling program will be coordinated with an ongoing study of fine PM exposures in Southeastern Texas, which is funded by the Mickey Leland National Urban Air Toxics Research Center.

Investigating Team:	Mickey Leland Center
Method:	Investigators funded by the Mickey Leland Center will measure indoor concentrations and outdoor concentrations of PM, trace metals, organic carbon, elemental carbon, aldehydes, PAHs and VOCs, as well as personal exposures to $PM_{2.5}$ mass, at approximately 100 homes in the Houston area. Sampling times for most of the analyses will be either 24 or 48 hours. These data will allow the researchers in the Leland study to examine the relationships between outdoor concentrations and indoor concentrations of $PM_{2.5}$ and $PM_{2.5}$ components. GC-ARCH will coordinate sampling

with the Mickey Leland Study (sampling at the core and peripheral sites on the same days as the exposure measurements). In addition, it is desirable to obtain indoor/outdoor partitioning ratios as a function of particle size. Therefore the particle size distribution measurements, described under Objective 3, will also be performed in parallel with the Leland study measurements at 15 houses (30 days of measurements).

4.8 Sampling Activities: Objective 6

Note: This objective is not funded by EPA under the Supersite Program.

Objective 6: Relate the physicochemical data on fine particulate matter to mammalian cell responses; this objective will be achieved by coordinating with an ongoing EPA funded project.

A study being performed by the University of Texas, Houston Health Science Center (UT-HHSC) funded by the U.S. EPA, is examining the responses of human alveolar macrophage (AM) to both model and ambient PM. A description of the project is given in the attachments. Samples collected at the GC-ARCH core sites will be used in the AM response testing by the UT-HHSC. Samples collected on days with varying distributions of source strengths will be provided to the UT-HHSC researchers. These data will help test whether human AM response depends on source contributions and PM composition.

5.0 DATA AND MEASUREMENT QUALITY OBJECTIVES FOR MEASUREMENT DATA

The management team of the GC-ARCH Program is committed to achieving and maintaining the highest level of quality possible throughout the performance of the project. All data collected in this project shall meet specific qualitative conditions required by any project that receives EPA/governmental funding. These requirements are referred to as the Data Quality Objectives (DQOs) and are quantitatively met through Measurement Quality Objectives (MQOs). MQOs are the set of objectives for each of the individual instruments that are implemented during the study. Both the DQOs and MQOs will 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 extensive testing that has been performed. However, for many of the research instruments used in this study, DQOs and MQOs are not known. It will be the tasks of the individual PI's and the Quality Assurance Manager's to attempt to determine the respective DQOs and MQOs throughout the course of the study.

5.1 Data Quality Objectives (DQOs)

The DQOs for this project are presented in Table 4.2-1.

5.2 Measurement Quality Objectives (MQOs)

The typical Measurement Quality Objective (MQO) indicators associated with data measurements are precision, accuracy, representativeness, completeness, minimum detection limits (MDLs) and comparability. These MQOs can be measured on most of the instruments, and on the project as a whole. The MQOs 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 MQOs will be provided in the individual SOPs and RPs. It is the responsibility of the Quality Assurance Manager to perform technical audits to insure that MQOs are reported and followed by the individual PIs.

5.2.1 Precision

Precision is a measure of the repeatability of the results or of the mutual agreement among individual measurements to 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 required number of replicate analysis to properly determine the precision of each instrument will be determined by the individual investigators. The precision of each instrument will be determined between periods of calibration (not

immediately following calibration). For each series of replicate analysis, the precision will be calculated as:

Precision (%) = 100 [2 σ] / {x} (1)

Where σ is the standard deviation between the replicate analyses and {x} is the mean of the replicate analyses. MQO values for precision will be established in the individual SOPs and RPs.

5.2.2 Accuracy

Accuracy (bias) is the closeness of a measurement to a reference value, and reflects the systematic distortion of a measurement process that causes error in one direction. To the extent possible, accuracy will be determined from replicate analysis 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 number of required challenges will be determined in the program quality assurance plan. The instrument responses for these challenges will be recorded, the accuracy of the instrument will be determined by:

Accuracy (%) = (100 * [s – {x}]) / s (2)

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

5.2.3 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.

Completeness (%) = (# of valid measurements/total # of measurements) *100 (3)

Completeness goals of 75% will be set for the following instruments:

- Filter-based samplers
- Near-real time sulfate (ADI)
- Near-real time nitrate (ADI)
- Near-real time carbon (ADI)
- Low pressure impactors
- Aerosol sizing system.

MQOs values for completeness for all other samplers will be established in the individual SOPs and RPs.

5.2.4 Summary of Sampling Activities/Intercomparability

A summary of the gas-phase and particulate matter measurements to be made during the GC-ARCH study is given in Table 5.2.4-1. The intercomparison between instruments will be performed only for data that meet the data quality objectives for precision, accuracy and completeness. In cases in which instruments are used in which comparisons cannot be made, or measurements cannot be duplicated, the only QA will be internal calibration and maintenance checks.

5.2.5 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 non-zero known concentration. Analytical procedures and sampling equipment impose specific constraints on the determination of detection limits. MDLs for specific instrumentation are provided in the 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 (e.g., averages) derived from any MDL data should be flagged as specified in section 7.2.5 below.

5.2.6 Representativeness

Measurements will be made at three core locations in Southeast Texas with a peripheral network of approximately 20 monitoring locations. The three core locations were chosen based on isopleths of $PM_{2.5}$ concentrations determined from measurements made between March 1997 and March 1998. The analysis of these isopleths resulted in the scientific hypothesis that the source profiles of PM in an upwind site, a site downwind of a heavily industrialized region and a site downwind of the urban core are substantially different and that spatial gradients of fine PM concentrations will be greatest near the industrial regions.

The criteria for locating a core sampling site followed siting requirements of the U. S. EPA. 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 air-flow and removal from major roadways will follow U. S. EPA guidelines.

The peripheral network of measurement locations, including approximately 20 additional sites to be operated by the TNRCC, were sited to meet regulatory requirements and to examine community exposure to fine PM, fine PM transport, and fine PM concentrations in source regions. The initial siting plan was modified slightly by the TNRCC after consultation with the PI and co-PI to better fit the scientific objectives of this program.

The SEARCH network includes four urban and four rural sampling locations in Georgia, Florida, Alabama and Mississippi designed to determine sources and spatial variability in PM mass and composition. At these locations, a suite of particulate characterizations will be made that is comparable to those made at locations in Southeastern Texas, allowing the analysis to be broadened over the entire Southeastern United States.

Table 5.2.4-1. Summary of Gas-Phase and Particulate Matter Measurements to be made during the GC-ARCH Study

Parameter	Method	Investigator	Site	Time Period*
Gas-Phase Measurements				
O_3	CAMS method	HRM	HRM	C
	CAMS method	TNRCC	Deer Park, Aldine	C
CO	CAMS method	HRM	HRM	C
	CAMS method	TNRCC	Deer Park, Aldine	C
NO, NO_x	CAMS method	HRM	HRM	C
	CAMS method	TNRCC	Deer Park, Aldine	C
NO_y	CAMS method	TNRCC	HRM, Deer Park, Aldine	C
Denuder HNO_3	Ion chromatography	Rice-GCARCH	HRM, Deer Park, Aldine	T
Denuder NH_3	Ion chromatography	Rice-GCARCH	HRM, Deer Park, Aldine	T
		TTU-GCARCH		SC
Acid Gases: SO_2, HCl, HONO, HNO_3	Texas Tech method	TTU-GCARCH	HRM	SC
SO_2	CAMS method	HRM	HRM	C
	CAMS method	TNRCC	Deer Park, Aldine	C
NH_3	Texas Tech method	TTU-GCARCH	HRM	SC
PAMS hydrocarbons	Auto-GC	HRM	HRM	SC
	Auto-GC	TNRCC	Deer Park, Aldine	SC
Carbonyls	2,4-dinitrophenyl-hydrazine (DNPH) sampling techniques	HRM	HRM	SD
	DNPH techniques	TNRCC	Deer Park	I
	DNPH techniques	Rice-GCACRH	Aldine	T
Semivolatiles		EPA	Deer Park	SD
Peroxides		TTU-GCARCH	Deer Park	SC
Additional gas phase measurements, ground based and aircraft		Year 2000 Field Study	HRM, Deer Park, Aldine	SD

Parameter	Instrument	Investigator	Site	Time Period*
PM Measurements				
Federal Reference Method (FRM)	Standard reference method	TNRCC	HRM, Deer Park, Aldine	I
	Standard reference method	HRM	HRM	S
Continuous PM Mass	TEOM	TNRCC	Deer Park, Aldine	C
	TEOM	HRM	HRM	C
Inorganic ions	EPA Speciation Network	TNRCC	HRM	I
	EPA Speciation Network	TNRCC	Deer Park, Aldine	T
OC/EC	EPA Speciation Network	TNRCC	HRM, Deer Park, Aldine	T
Trace Metals	EPA Speciation	TNRCC	HRM, Deer Park, Aldine	T
Near real time sulfate	Method of Stolzenburg & Hering (1998, 1999).	HRM	HRM	SC
	Method of Stolzenburg & Hering (1998, 1999).	ADI-GCARCH	Deer Park, Aldine	SC
Near real time nitrate	Texas Tech method	TTU-GCARCH	HRM	SC
	Method of Stolzenburg & Hering (1998, 1999).	ADI-GCARCH	Deer Park, Aldine	SC
Near real time carbon	R & P instrument	HRM	HRM	SC
	Method of Stolzenburg & Hering (1998, 1999).	ADI-GCARCH	Deer Park, Aldine	SC
Molecular characterization of organic fraction	Gas chromatography/ mass spectroscopy	Rice-GCARCH	HRM, Deer Park, Aldine	SD
Size distributions	DMA/CNC	TAMU-GCARCH	HRM, Deer Park, Aldine	SC
Single particle MS	Rapid single particle mass spectrometer	U-Del – GCARCH	HRM	SC
Organic compound classes of size resolved PM	LPI/FTIR	UT-GCARCH	HRM, Deer Park, Aldine	I
Additional Measurements				
Meteorological Data	CAMS method	HRM		C
	CAMS method	TNRCC		C

* H = hourly, C = continuous, I = 24-hour integrated, S = every six days, SC = semi-continuous, SD = selected dates, T= every third day.

6.0 SPECIAL TRAINING REQUIREMENTS/CERTIFICATION

Operation and maintenance of the individual research instruments will be managed by the PI's in charge of their implementation. 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.

7.0 DATA ACQUISITION AND MEASUREMENTS

This section discusses data acquisition and measurements with respect to handling and custody of samples, analysis of samples/data collected, instrument calibration and performance evaluation, data reduction and reporting, and data assessment.

7.1 Handling and Custody of Samples

A procedure will be developed to collect, transport and store the samples for analysis that will minimize the possibility of contamination or introduction of artifacts. Special care will be taken to prevent the volatilization of semivolatile 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 developed for each instrument. However, at a minimum these will include the necessary procedures for ensuring sample validity during:

- *preparation* of sampling material, including procedures to clean substrate media, loading substrate media into sampling apparatus, and transport of sampling media to field locations
- *storage* of sampling media once removed from sampling location including sealing procedures and temperature requirements for transportation from field locations to laboratory
- *archiving* of sampling material until the analysis can be performed including restrictions of photochemical decomposition and temperature requirements
- *requirements* for removing samples from archive for analysis 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. A duplicate log will be maintained inside the laboratory to track media during deployment. When the sample is returned to the laboratory, the sampler log sheet will be reconciled against the laboratory duplicate log to ensure the information recorded on the media preparation.

Unique sample identification numbers will be assigned to each sample collected to record the sample site, sample collection time, substrate media, and sample collection means. These parameters will be used to report the ambient measurements into the project data base. 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.

7.2 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 GC-ARCH program. It is assumed that 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. It is also recommended that separate CD-ROM or diskettes be created for data storage.

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

7.2.1 Formatting of 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 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 (see section 7.2.5 Initial Documentation of Data Quality).

7.2.2 Date and Time Formats

Data will be reported in Central Standard Time, including day, month, and year as formatted as MM/DD/YYYY format (e.g., 08/15/2000 14:25). 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).

7.2.3 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 be no blank fields.** Contributors should report data where possible and use flag codes (see section 7.2.5 Initial 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, estimated values, interpolated values, and MDLs.

7.2.4 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 Office. 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.

Uncertainty estimates should be reported for as many parameters as possible. 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.

7.2.5 Initial Documentation of Data Quality

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. Table 7.2.5-1 lists and defines these flags. 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.

Table 7.2.5-1. Data Qualification Flags

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

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). 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 has 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 QAM for external consistency when compared to other data sets.

7.2.6 Data Management and Archive

Principal investigators will be responsible for transmitting all data to the Data Management Coordinator within six months of the date when the data are collected. These data will be quality assured and archived on the GC-ARCH permanent data archive and will transmitted for final storage at the NARSTO Permanent Data Archive, pending EPA guidance. It is expected that the individual principal investigators will store their data in electronic format for at least five years.

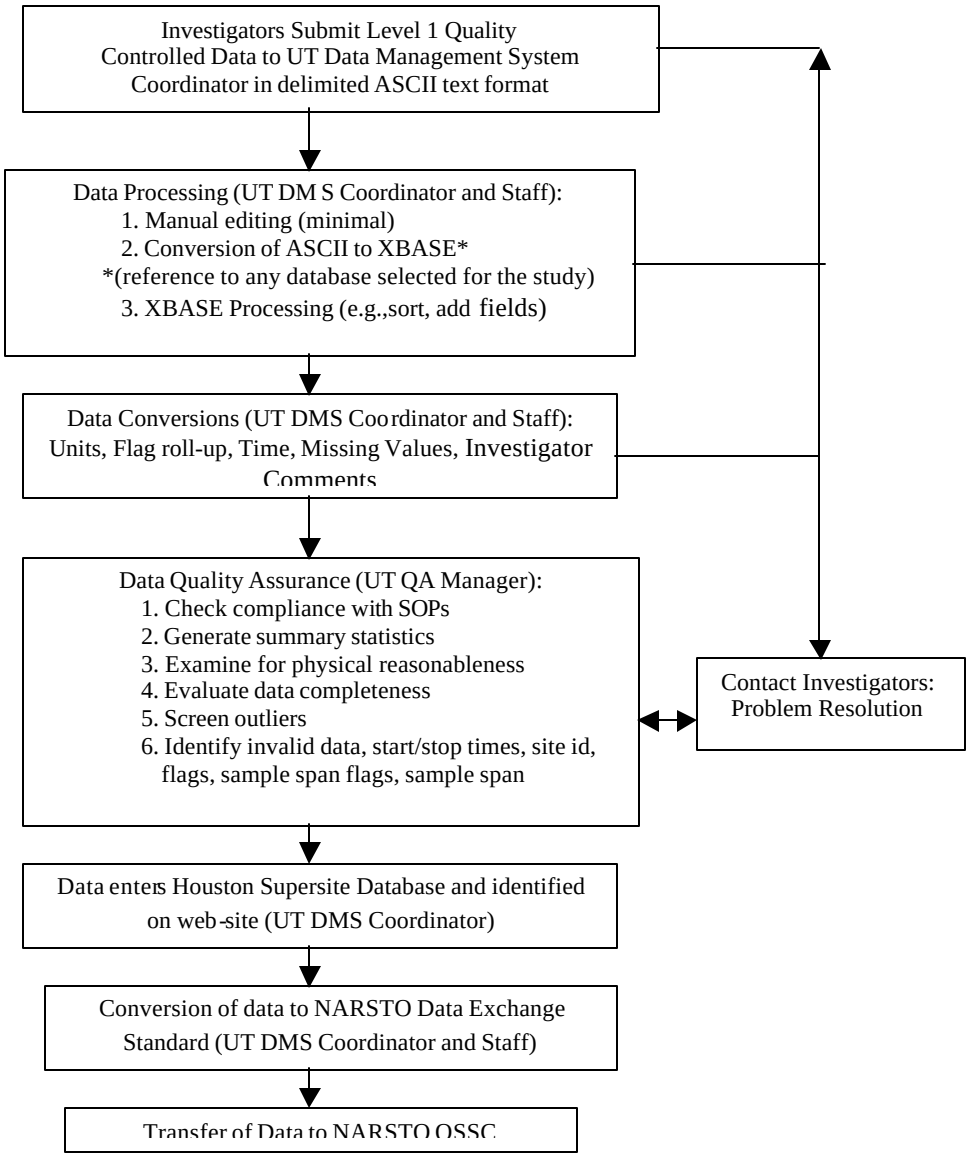
The Data flow diagram is shown in Figure 7.2.6-1. A data tracking system will be implemented to document any modifications. The data will be subjected to quality assurance checks (outlier screening, date and time/flag/units checks, and statistical analysis) by the QAM prior to submission to the NARSTO QSSC. A separate SOP for data management will be submitted to GC-ARCH.

7.3 Analysis of Samples or Data Collected

The analytical procedures for each proposed measurement are briefly described in Section 4. 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 GC-ARCH program, as well as data collected in parallel by the TNRCC 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.

Figure 7.2.6-1 Data Flow Diagram for GC-ARCH Project



7.4 Instrument Calibration and Performance Evaluation

Each investigator will be responsible for generating procedures for calibration of analytical instruments and metrics for evaluating the performance of these instruments to the extent possible. In addition, the program has allocated funds in the Project Management budget for an independent QA monitor of performance audits to ensure the accuracy of data collected.

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 independent QA monitor. 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 not used in instrument calibration will be used to determine the continued adequate instrument performance and instrument precision.

7.5 Data Reduction and Reporting

Data reduction and reporting will be the responsibility of each of the individual investigators. The SOP for data reduction will be prepared before analysis and submitted to the program quality assurance plan for external review.

The data will be reported to and archived by the University of Texas in a uniform format 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 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.

7.6 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.

7.7 Use of Data

Table 3.2-1 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 include chemical mass balancing techniques, neural net analysis to estimate source strengths and predictive models to transform one sampler response into a suitable intercomparison variable for a separate sampler.

7.8 Quality Assurance

The management of the GC-ARCH will include a Project Management Team as well as a separate Scientific Advisory Board. Funds have been reserved in the Project Management budget to support an external review of the project quality assurance plans, which will include the relationship between measurements and objectives and the SOPs for ambient samplers.

8.0 ASSESMENT OF DATA/CORRECTIVE ACTIONS

Assessment of data during the six-week intensive and 16-month studies 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 six-week intensive study. Informal meetings among the PIs will also provide the opportunity to discuss data validity.

During the 16-month study, a more complete data assessment will be made by the Quality Assurance Manager (QAM). These evaluations will look for anomalies among sites and inconsistencies between continuous and discrete 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 those obtained by TEOM. Size distributions of PM can also be compared to total PM mass. Evaluations of the continuous data from the 16 month study will be performed approximately 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 Project Manager will be contacted and it will be determined whether the data will remain in the GC-ARCH database. The PI will be informed of any data removal or invalidation that occurs in the database.

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