

## GULF COAST AEROSOL RESEARCH AND CHARACTERIZATION PROGRAM

### INTRODUCTION

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. A list of some of the particulate matter properties that may be related to health effects includes (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 principles can be identified. One logical organizing principle 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 objectives of the research program described in this proposal will be

1. to 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
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 will be:

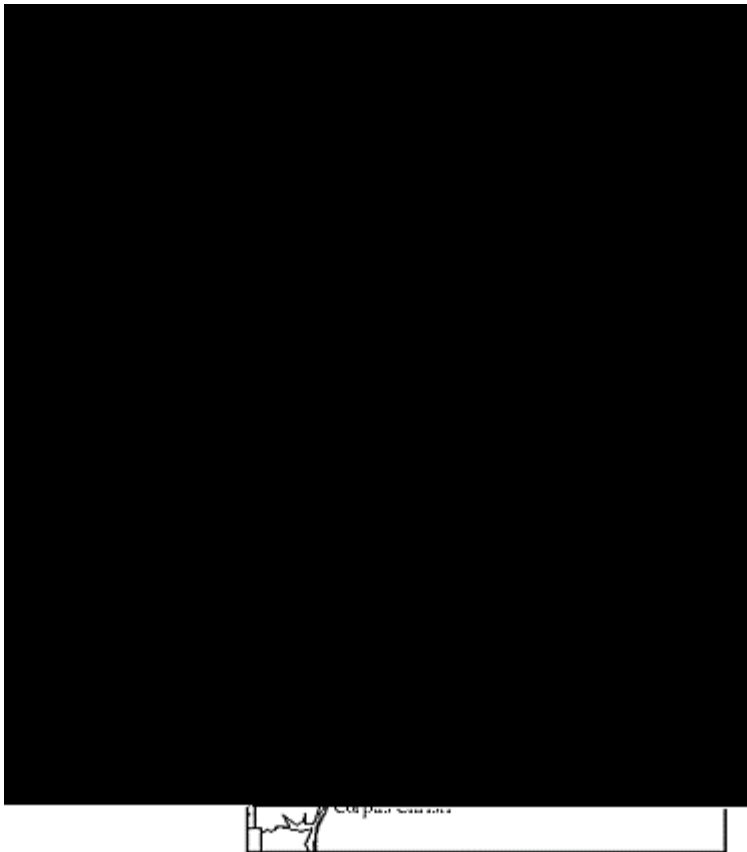
4. to develop a combined database on PM, gas phase air pollutants and meteorological variables, suitable for testing models of the formation and fate of fine PM; this objective will be achieved by coordinating with a large, integrated ozone and PM field study planned by the Southern Oxidants Study for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

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### SITE SELECTION

There are several reasons for choosing Southeastern Texas as a sampling location. First, the entire region experiences annual average concentrations of fine PM (specifically PM less than 2.5  $\mu\text{m}$  in aerodynamic diameter, or  $\text{PM}_{2.5}$ ) in the range of 10-12  $\mu\text{g}/\text{m}^3$ . Superimposed on these background concentrations are regions in which industrial and urban emissions drive the annual average concentrations of fine PM to 16-18  $\mu\text{g}/\text{m}^3$ . 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  $\mu\text{g}/\text{m}^3$  (Lurmann, et al., 1999). Typical isopleths of fine PM concentrations in the Houston area, together with a map of the region, are shown in Figures 1 and 2. A mapping of the spatial distribution of estimated PM exposures (based on conservative estimates of indoor-outdoor partitioning) is given in Figure 3.

*Figure 1: Southeastern Texas and the Houston metropolitan area*



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Figure 2. 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  $mg/m^3$ ) 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.

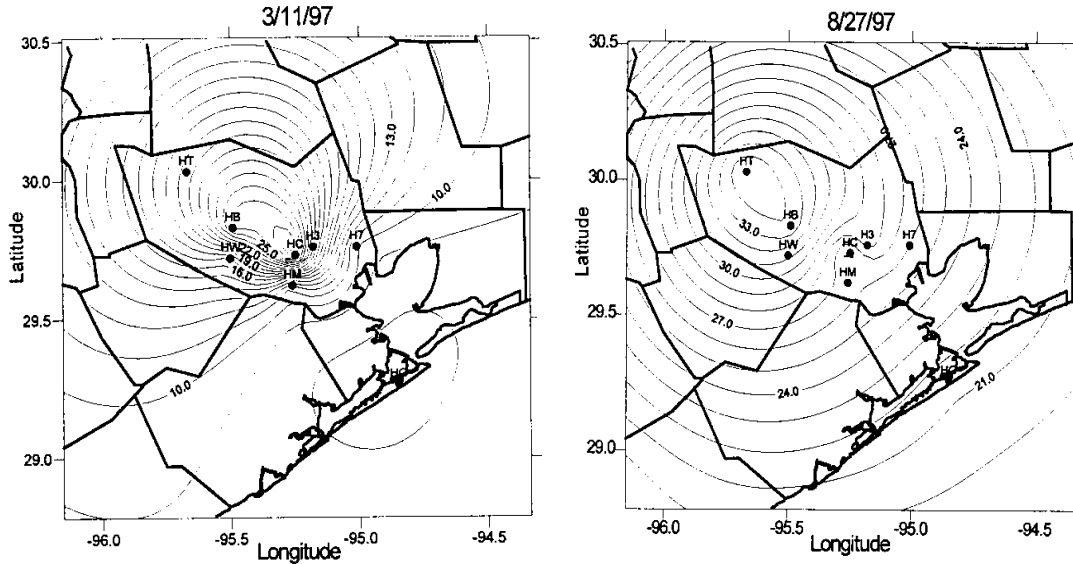
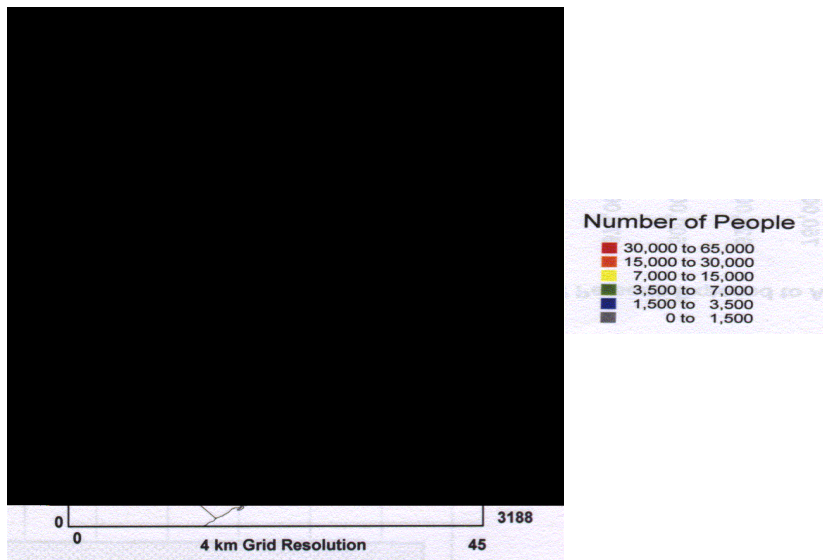


Figure 3. Predicted spatial distribution of  $PM_{2.5}$  exposures in the Houston area. Interpolations based on the  $PM_{2.5}$  measurements made in 1997 and 1998 were combined with census data, an exposure model, and ratios of 1996 emissions to predicted 2007 emissions to produce the anticipated exposure distributions for  $PM_{2.5}$  in 1998 and 2007 (Lurmann, et al., 1999). The estimated exposure pattern for 2007 is shown. Current data indicate that more than 2.5 million people may be exposed to annual average  $PM_{2.5}$  concentrations greater than  $15 \mu g/m^3$ .



Figures 2 and 3 illustrate the magnitude and spatial distribution of fine particulate matter exposures that can be expected in the Houston area. It is anticipated that these exposures will be broadly representative of particulate matter exposures throughout the western Gulf Coast and southeastern United States. While data are not yet available for fine particulate matter concentrations

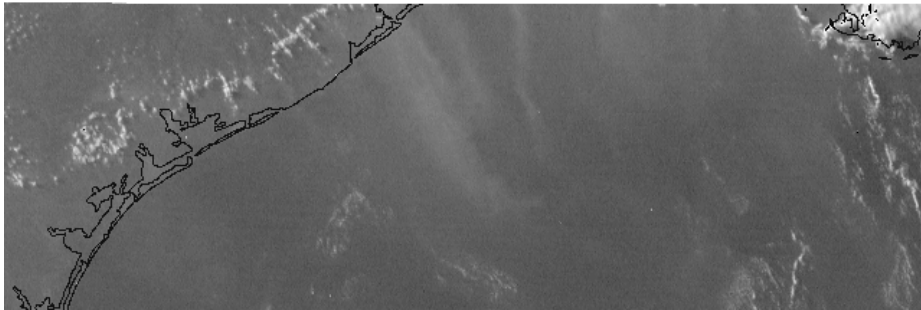
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throughout this region, satellite images convey the spatial extent of elevated particulate matter. Figure 4 shows plumes of particulate matter emerging from the Houston, Beaumont and Lake Charles regions on a summer day. The plumes extend for over a hundred kilometers into the Gulf. Elevated ozone concentrations (up to 200 ppb) were measured near the particulate matter plume shown in Figure 4. Figure 5 shows predicted ozone concentrations for a typical summer episode for the western Gulf Coast, with elevated ozone concentrations predicted for the entire region (Allen, 1999). It is anticipated that elevated particulate matter concentrations will show a similar geographic extent.

An additional reason for choosing Southeastern Texas as a sampling location is the mix of emission sources located in the region. The emissions in Southeast Texas are due to a complex mix of typical urban anthropogenic sources, biogenic sources, and significant industrial emissions. The Houston area is home to the largest concentration of petrochemical manufacturing facilities in the United States, and as a consequence the industrial source signature in Southeastern Texas will be strong, particularly for organics. Thus, data collected in the Houston area would be relevant to other cities along the Gulf Coast and to sites with extensive industrial, petrochemical emission sources.

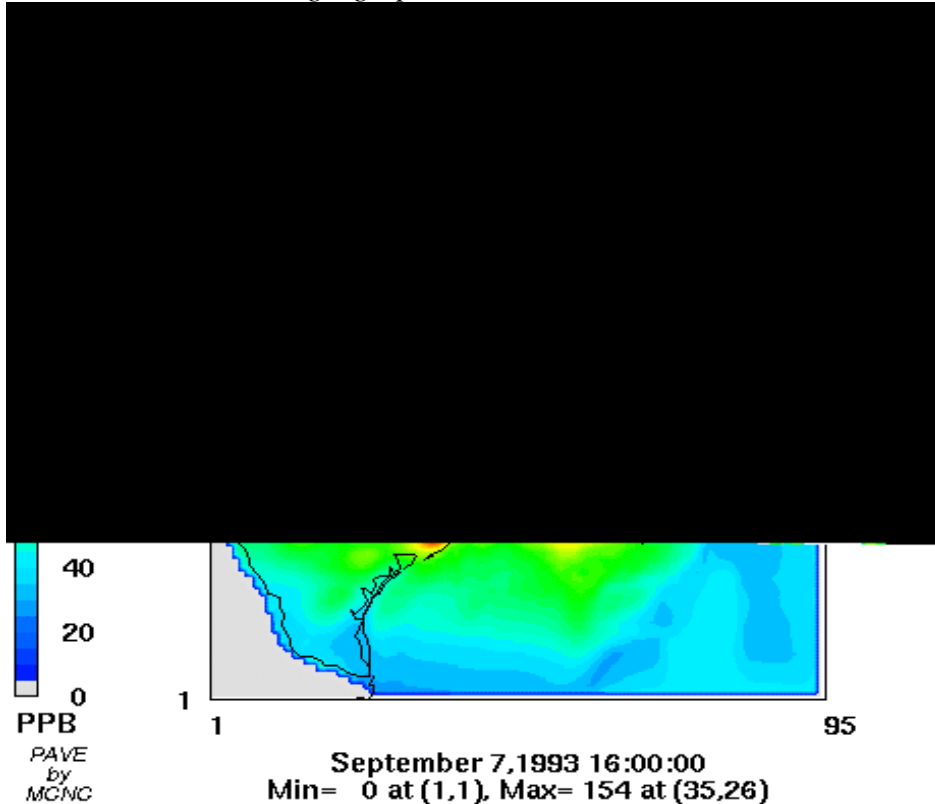
Finally, as described later in this proposal, exposure studies, toxicological studies, and a large ambient air quality field study are planned for the summer of 2000 in Southeastern Texas. These studies will provide valuable data sets that can be combined with the data to be collected by the program described in this proposal.

*Figure 4. Particulate matter plumes over the Gulf of Mexico, observed by satellite during a summer photochemical episode. The center of the Figure is the Texas-Louisiana border. The plumes track winds blowing offshore from Houston, Beaumont/Port Arthur and Lake Charles.*



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Figure 5. Ozone concentrations predicted for a summer episode; note the spatial extent of the elevated ozone concentrations. It is anticipated that particulate matter concentrations will be elevated over a similar geographical area.



### OBJECTIVES

The major objectives of the proposed Gulf Coast Aerosol Research and Characterization Study (GC-ARCH or the Houston PM Supersite), and the hypotheses that will be tested in the program, are summarized below.

**Objective 1: Collect physicochemical data on fine PM over a 16 month sampling period in Southeastern Texas; use the data to identify sources and to characterize spatial and temporal variability in fine PM source contributions and composition** A 16-month field sampling program (June 2000 – September 2001) will be undertaken. Three core sites, jointly operated by GC-ARCH, the Houston Regional Monitoring Network (HRM), and the Texas Natural Resources Conservation Commission (TNRCC), and approximately 20 peripheral sites, operated by the TNRCC, will be employed. The data will be archived using protocols established by NARSTO (NARSTO, 1999). The data will be used to generate isopleths of the concentrations of fine PM and fine PM components, as illustrated in Figure 2 and as described in the Approach section of this proposal. In addition, source contributions for the fine PM components will be estimated, and the spatial distribution of fine PM source strengths will be determined. Data analysis will focus on testing 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.

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- 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 (and other gas phase pollutant) concentrations.
- FRM mass monitors and 24-hour speciation monitors correspond to time integrated near-real time measurements of PM mass, sulfate, nitrate and carbon.

**Objective 2: Characterize spatial and temporal variability in fine PM source contributions and composition, throughout the southeastern United States** Sampling at the 3 core sites and approximately 20 peripheral sites located in the Houston area will be compared and contrasted with sampling sites operated by the Southeast Aerosol Research and Characterization (SEARCH) network, the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP), and other networks. The combined network will cover the entire southeastern United States, from the southern Atlantic seaboard to the western Gulf coast. As in objective 1, the spatial distribution of source contributions will be estimated. Data analysis will focus on testing 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.
- 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** The physical and chemical process that govern PM formation and transformation in Southeastern Texas will be probed through measurements made during a 6 week intensive sampling period during the summer of 2000. Three core sites jointly operated by GC-ARCH, HRM and the TNRCC and approximately 20 peripheral sites operated by the TNRCC will be involved in PM data collection. The focus of the studies will be on organic gas-particle partitioning and the role of heterogeneous chemistry in PM transformation. Data analysis will focus on testing 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; this objective will be achieved by coordinating with a large, integrated ozone and PM field study planned for the summer of 2000** 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 – 2000 (TEXAQS 2000). TEXAQS 2000, performed through the Southern Oxidants Study, 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 sulfate, nitrate and carbon analysis equipment with rapid time

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resolution, and other instrumentation. The measurements made during TEXAQS 2000, coupled with the measurements made by GC-ARCH, will create a data set powerful enough to rigorously test integrated models of ozone and PM formation and fate. In addition, the combined data set data will be used to examine PM formation and transformation processes and hypotheses described under Objective 3.

**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** Both the 16 month and the 6 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. The Leland Center study will measure indoor concentrations, outdoor concentrations and personal exposures for PM and a number of PM components at approximately 100 homes in the Houston area. GC-ARCH will coordinate measurements at the core sampling sites with these exposure measurements and a limited suite of near real time measurements will be performed by GC-ARCH at some of the homes where exposure is being assessed. Data analysis will focus on testing 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; this objective will be achieved by coordinating with an EPA funded project currently underway** 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 core sites will be used in the AM response testing by the UT-HHSC. Data analysis will focus on testing the following hypotheses:

- Human AM response depends on source contributions and PM composition.

### APPROACH

**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**

*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.*

A 16 month field sampling program (June 2000 – September 2001) will be undertaken, with 3 core sites jointly operated by GC-ARCH, HRM and TNRCC and approximately 20 peripheral sites operated by TNRCC. Over the 16 month period (June, 2000 – September 2001), the measurements listed in Table 1 will be made at 3 sites in the Houston area. The sites include a site upwind of the Ship Channel (industrial) area, a site within the Ship Channel region, and a site

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downwind of the urban area. The entity responsible for each measurement (TNRCC, HRM or GC-ARCH) is identified in Table 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 2. Parallel gas phase measurements are also available at these sites. Gas phase measurements made in the Houston area are described in the technical attachments to this proposal. The locations of the core and peripheral sites are shown in Figure 6.

*Table 1. Measurements to be made at the core sites*

<i>Measurement</i>	<i>Houston Regional Monitoring (HRM) Network Site 3 (downwind industrial)</i>	<i>Deer Park (upwind industrial)</i>	<i>Aldine (downwind urban)</i>
<i>PM measurements</i>			
Federal Reference Method (FRM)	Every sixth day PM <sub>10</sub> and PM <sub>2.5</sub> (HRM)	Every third day PM <sub>10</sub> and PM <sub>2.5</sub> (TNRCC)	Every third day PM <sub>10</sub> and PM <sub>2.5</sub> (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	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)
<i>Gas measurements</i>			
Ozone, CO	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO, NO <sub>x</sub>	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO <sub>y</sub>		Continuous (TNRCC)	Continuous (TNRCC)
Denuder HNO <sub>3</sub>	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)
Denuder NH <sub>3</sub>	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)
SO <sub>2</sub>	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
PAMS hydrocarbons	Auto-GC (HRM)	Auto-GC (TNRCC)	Canister (UT-GCARCH)
Carbonyls	On forecast (HRM)	Third day (TNRCC)	Third day (Rice-GCARCH)
Met. Data*	HRM	TNRCC	TNRCC

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



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Figure 6. 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.

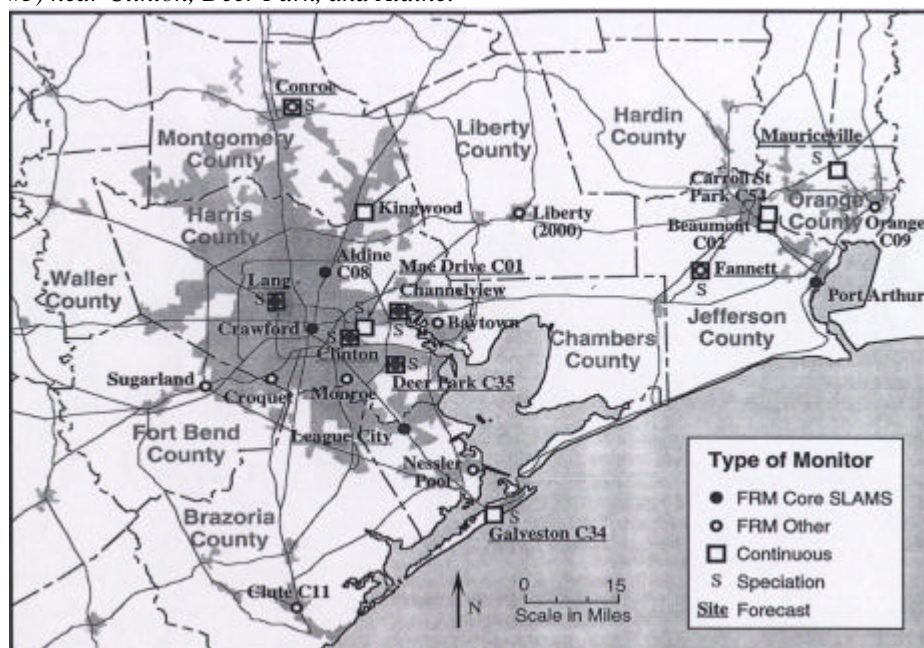


Table 2. Data to be collected at peripheral sites (all data to be collected by the TNRCC)

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

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The proposed measurements are extensive and the complete suite of measurements could not be funded exclusively through the Supersites program. Fortunately, the Texas Natural Resources Conservation Commission (TNRCC) and the Houston Regional Monitoring Network (HRM) provide extensive, ongoing measurements of gas phase pollutants and fine PM characteristics. Specifically, all of the peripheral site measurements will be made by the TNRCC. In addition, the measurements labeled as TNRCC in Table 1 will be made by the TNRCC and those labeled HRM will be made by HRM. These extensive, core measurements will allow GC-ARCH resources to be focussed on the collection of supplemental data. The supplemental data and data collection activities to be funded by GC-ARCH are listed below and are identified in Table 1 by the notation GC-ARCH. Due to space limitations, only brief technical descriptions of the measurements to be funded by GC-ARCH are given.

GC-ARCH will fund the following activities:

- *near real time sulfate, nitrate and aerosol carbon* Semi-continuous measurements of nitrate, sulfate and carbon will be made by Aerosol Dynamics, Inc., using instruments based on the method of Stolzenburg and Hering (1998, 1999). Particles are collected by a humidified impaction process and analyzed in place by flash vaporization. The approach is based on the manual method that has been used for over twenty years to measure the size distribution of sulfate aerosols (Hering and Friedlander, 1982). The difference is that the particle collection and analysis have been combined into a single, integrated collection and vaporization cell, allowing the system to be automated. Particles are humidified prior to impaction to eliminate the rebound of particles from the collection surface without the use of grease (Winkler, 1974 and Stein et al 1994). Interference from vapors such as nitric acid is minimized by use of a denuder upstream of the humidifier. The flow system is configured such that there are no valves on the aerosol sampling line. Analysis is done by flash-vaporization with quantification of the evolved gases. For sulfate the evolved gases are analyzed for SO<sub>2</sub>, as described by Roberts and Friedlander, (1976). For nitrate the evolved vapors are analyzed for nitrogen oxides (Yamamoto and Kosaka,1994). Carbon is detected through quantification of the evolved CO<sub>2</sub>. Because the sample is concentrated, the analyses can be done using proven, robust gas analyzers. For particle nitrate the semi-continuous, flash volatilization approach has been compared to denuder-filter methods at three different California locations, and has yielded regression slopes of 0.96, 1.00 and 1.07 with correlation coefficients 0.96. The combined sulfate, carbon nitrate system was first operated in Marshall Colorado. The data collected by the semi-continuous, flash volatilization systems tracked the total particle concentration, as indicated by physical size distribution measurements. Additionally, the mass sum was comparable to the measured aerosol volume, with a mass to volume ratio just over 1 g/cm<sup>3</sup>. These measurements planned for the Houston Study will provide valuable insights into the time and spatial variation in sources and formation processes for these particles that comprise the majority of the fine particle mass.
- *molecular characterization of extractable organics from filter samples* Filter samples will be collected every third day at each of the 3 core sites by Rice University, 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 by Rice University. Analysis will be accomplished using methods described by Fraser, et al., (1998a,b). The particles are collected on annealed quartz fiber filters, and particulate organics are extracted, by either sonication or Soxhlet techniques using high purity organic solvents. The organic extract is

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then concentrated to the point where trace level organic compounds can be detected by gas chromatography/mass spectrometry. Organic acids will be derivatized to their corresponding methyl esters with diazomethane allowing GC-MS analysis. Extraction and concentration losses are monitored by perdeuterated recovery standards spiked onto the filters before extraction and quantified along with the particulate organic compounds by GC-MS. Authentic standards are used to identify the individual particulate-phase organics, and to calibrate the response of the GC-MS.

- *Ammonia and nitric acid from denuders* 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 a 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* Measurement of carbonyl compound concentrations will employ 2,4-dinitrophenylhydrazine (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. Measurements at the other core site will be performed by Rice University.
- *Canister sampling for VOC analysis* Two of the three core sites will have automatically operated gas chromatographs (Auto-GC), installed and operated by HRM and the TNRCC, which will analyze air samples for hydrocarbons. The third site (Aldine) does not have an Auto-GC, so the University of Texas will deploy a canister sampling at the site. Every third day, 4 hourly samples and one field blank will be collected and returned to the University of Texas for analysis. The 650 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 4 canisters per month) will be conducted at the Deer Park and HRM 3 sites to ensure comparability between Auto-GC and canister analyses.
- *Site management* – Samples collected or analyzed using GC-ARCH funding will be retrieved from each of the core sites at least once every third day. The samples will be returned to Rice University. Rice will be responsible for delivering 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.
- *Data archiving and spatial mapping* – The University of Texas will create a data archive for the 16 month field study. The data archive will include not only the measurements funded through the GC-ARCH Program, but also all of the PM physicochemical data collected by the TNRCC and HRM at the core and peripheral sites. The data archive will conform with NARSTO (NARSTO, 1999) formatting guidelines and will represent a single point of reference for PM physicochemical data associated with the core and peripheral sites. Details of the database structure and associated website are discussed in the Quality Assurance section of the proposal. In addition to archiving the data, the University of Texas will create mappings (similar in format to Figure 2) of the spatial distributions of particulate matter mass,

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sulfate, nitrate, organic carbon and elemental carbon concentrations, based on the data collected every third day. Isopleths of source strengths will also be determined, as described below.

The activities listed above will enable the GC-ARCH program to collect and archive the data described in Tables 1 and 2, over a period of 16 months. The resulting data set will include a core set of continuous measurements (PM mass at 3 core sites and 6 peripheral sites; sulfate and PM carbon at 3 core sites; aerosol nitrate at 2 core sites; gas measurements at core and most peripheral sites), and a more extensive set of measurements made every third day.

*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 in an upwind site, a 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. At the most basic level, 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 will be mapped. Isopleths, similar to those shown in Figure 2, will be created for each sampling day based on data from the 3 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.

A second level of data analysis will involve the use of molecular and atomic tracers to identify source contributions. 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 3. 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 2. This data analysis will be performed by the University of Texas.

Neural networks will also be used to estimate source strengths. The back-propagation neural network of Song and Hopke (1996) will be used to solve the chemical mass balance problem, incorporating non-linearities into the system. Although the mass balance problem is normally thought to be a purely linear problem, the addition of errors into the measurement of both ambient concentrations and source profiles effectively introduces non-linearity into the system. The approach adopted by Song and Hopke (1996) first divides the elemental concentrations by the total measured sample mass. This converts the source contributions to mixing fractions that range from 0 to 1. Then, training sets are created for the neural net model that span the domain created by a reasonable number of sources. When the model is trained with more source profiles than are actually active in the data set, it is able to determine only those sources that are actually contributing to the sample compositions. This approach was able to resolve sources in the NBS data sets that were too collinear to be able to calculated using the CMB or other models. The method is promising as a tool for accurately estimating source contributions when the source profiles are known. Source profiles and a training set for the Houston area have been assembled by Wittig (1998) and will be available for the analysis. This task will be performed by Clarkson University.

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*Table 3. Representative tracer species to be used in source attributions*

<i>Source</i>	<i>Tracer species</i>	<i>Reference</i>
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)

\*other tracer species will be examined, but were not listed due to space limitations

*Task 1c. Perform methods inter-comparisons 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.*

One of the purposes of the Supersites program is to compare 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. Consider, for example, comparing the single particle analysis system with bulk aerosol sample measurements. The single particle analyses are classified into particle types using neural networks. The frequency of occurrence of the particle types should then be compared to the PM compositions measured using traditional speciation methods. This is a problem for which partial least squares (PLS) is ideally suited.

The procedure that will be used to perform the inter-comparison of the data set will be to divide the data set into blocks. Predictive models will be developed for transforming one type of sampler response (e.g, near real time particulate sulfate and nitrate, and real time PM mass) into the response of integrative samplers (e.g., 24-hour FRM and chemical speciation). The more detailed measurements can be designated as the X block, while the dependent sampler data (speciation sampler or FRM) will be denoted as the Y block. The problem is to develop models that will predict a vector of y values given a new input vector of measured compositions,  $\mathbf{x}$ . This problem will be solved using multivariate calibration methods including partial least squares (Lorber, et al., 1987; Thomas and Haaland, 1990; Martens and Naes, 1991). The basic idea in PLS is to find a set of latent variables in the measurement variable space (X) that have a maximum covariance with the dependent variable space (Y). To obtain the PLS model with the best predictive performance, the optimal number of PLS components to be used in the model needs to be determined. The performance criterion is the prediction residual sum of squares (PRESS). That is, within the training set, all of the objects are divided into several subgroups (called validation sets). For a problem such as this one, at least 10 validation sets would be created. Each validation set is left out of the training set and predicted by the model built from the remaining training objects. The process is repeated until all of the validation sets are predicted, and the overall PRESS value is calculated. The number of PLS components corresponding to the

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minimum PRESS is then used to build the final model to predict the additional new test objects. The final PLS model can then be used in the prediction of the values of the Y matrix. By looking at the PLS relationships between measurements, the response of the speciation or FRM sampler to various composition aerosols can be understood. The same methodology can be used to understand the response of one instrument, like total particulate mass, to other appropriately time resolved data, including gas phase measurements.

An additional issue that arises in the data analysis that will be addressed is missing data. One of the questions that typically arises with large sampling campaigns is the handling of missing and below detection limit (BDL) values. BDL values are often replaced with a fixed value such as DL/2 or left as "missing." Treating data as "missing" means that the information that the value is low has been excluded from the analysis. Thus, the information content of the data set is diminished. To use a fixed fraction of the detection limit can induce false correlations in the data if there are two or more variables that have a large number of below detection limit values. A better approach is estimation of the BDL values. One approach to estimating BDL values is to develop statistical estimates of the distributions of possible values and make multiple draws from that distribution to estimate the values and their associated uncertainties (Hopke, et al., 1999). A second approach uses factor analysis, in which individual BDL data points are estimated based on factors, along with an estimate of uncertainty. This method, called Positive Matrix Factorization (PMF), has proved very effective in handling BDL values in ambient aerosol data. In one study (Polissar, et al., 1998), estimates for sea salt aerosol were obtained in spite of over 80% of the Cl values being below detection limits. Using the PMF process, data values with corresponding uncertainties can be estimated for each of the missing or BDL values. These data handling methods provide statistically valid, complete data sets for further analysis.

Task1c will be performed by Phil Hopke of Clarkson University.

### **Objective 2: Characterize spatial and temporal variability in fine PM source contributions and composition, throughout the southeastern United States**

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. A summary of the SEARCH, ASACA and SCISSAP measurements and measurement locations is given in Table 4. 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. In particular, the following hypotheses will be addressed:

- 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

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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.

Industrial, petrochemical sources of PM and PM precursors are far more prevalent in the GC-ARCH sampling region than in the SEARCH sampling region, and the Atlanta domain is more heavily impacted by mobile sources. In addition, the distribution of agricultural activity in the two regions is different. It is anticipated that these differences in source profiles will lead to significant differences in PM composition, even though both regions experience high humidity and have some common PM sources and PM precursor sources.

*Table 4. Measurements made in the SEARCH and SCISSAP networks*

	<i>SEARCH Network</i>	<i>SCISSAP Network</i>	<i>ASACA Network</i>
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	<ul style="list-style-type: none"> <li>• FRM</li> <li>• continuous particulate mass</li> <li>• semicontinuous measurement of nitrate, sulfate, ammonium, OC and EC</li> <li>• 24 hour measurement of metals, nitrate, sulfate, ammonium, OC and EC</li> </ul>	<ul style="list-style-type: none"> <li>• FRM</li> <li>• Multi-channel denuder-filter pack systems</li> </ul>	<ul style="list-style-type: none"> <li>• Continuous particle mass</li> <li>• Multi-channel denuder-filter pack systems</li> </ul>
Gas phase measurements	<ul style="list-style-type: none"> <li>• ozone</li> <li>• SO<sub>2</sub></li> <li>• CO</li> <li>• Nitric acid, ammonia</li> <li>• NO/NO<sub>2</sub>/NO<sub>y</sub></li> </ul>	<ul style="list-style-type: none"> <li>• Nitric acid, ammonia</li> <li>• NO/NO<sub>2</sub>/NO<sub>y</sub></li> </ul>	

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 3. 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. This task will be performed at the University of Texas and the Georgia Institute of Technology. At Georgia Tech, the effort will be led by Ted Russell. The work at the University of Texas will be led by David Allen and will be performed by the group working on data archiving and source resolution.

In addition to the comparison of GC-ARCH data with existing SEARCH, SCISSAP, and ASACA data, several augmentations will be made to the SCISSAP network. Specifically, the SCISSAP Mobile Laboratory (which is currently outfitted with a three-channel filter/denuder Particle (PM<sub>2.5</sub>) Composition Monitor and continuous monitors for gas-phase O<sub>3</sub>, SO<sub>2</sub>, CO, and

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NO<sub>y</sub>, NO<sub>x</sub>, NO and meteorology) will be augmented by the addition of semi-continuous instrumentation for PM<sub>2.5</sub> mass, inorganic and organic composition and with a single-particle mass spectrometer system.

With the augmented SCISSAP Mobile Laboratory, a mini-repeat of the 1999 Atlanta Supersite Experiment will be conducted at a site in Atlanta and at a rural site in south Georgia during the Summer of 2000 and Winter of 2001. In addition, daily sampling of PM<sub>2.5</sub> composition will be continued in the Atlanta area through September at a network of PCMs (e.g., the ASACA network). Continuous sampling of PM<sub>2.5</sub> mass will be taken at three sites in Atlanta, and an additional TEOM will be deployed in central Georgia, downwind of Atlanta, to capture the Atlanta plume and how the Atlanta plume evolves during transport.

All of this additional sampling will be conducted by the Georgia Institute of Technology.

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

#### *Task 3a. Data Collection*

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 6-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. A summary of the measurements to be made at the core sites during the 6-week intensive sampling period is given in Tables 5 and 6. Specifically, the following enhancements to the 16-month measurements will be undertaken:

- *Increase sampling frequency for filter and cartridge based samples* – 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.
- *Add measurements of size distributions*



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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 10 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.

- *Add daily measurements of the organic compound classes in size resolved PM* – Infrared spectroscopy will be used to estimate concentrations of organic and inorganic compound classes, as a function of particle size. The method developed by Allen, et al., (1994), employs a Hering Low Pressure Impactor (LPI) to segregate the aerosol into 8 size fractions. The aerodynamic cut-off diameters for the 8 size fractions are 0.05, 0.076, 0.12, 0.26, 0.5, 1.0, 2.0 and 4.0  $\mu\text{m}$ . The impactor is equipped with ZnSe impaction surfaces. The use of these ZnSe impaction disks allows the use of FTIR transmission spectroscopy in the analysis of the PM deposits, which are approximately 3 mm in diameter. Spectra taken of the aerosol deposits typically show strong absorbances due to ammonium sulfate, ammonium bisulfate, nitrate ions, aliphatic carbon-hydrogen bonds, nitroaromatic, organonitrate and carbonyl groups. These absorbances can be converted into concentrations of organic compound classes and inorganic ions in the 8 size fractions. Detection limits depend on the component being analyzed, but extend into the picogram region (Palen and Allen, 1989). The method has been extensively tested in the field and results from the Southern California Air Quality Study and a field study in the Smoky Mountains have been reported (Allen, 1995; Dekermenjian, 1998). Samples will be collected over 24 hours, daily, at each of the core sites. All samples will be analyzed. These measurements will allow chemical composition to be characterized as a function of particle size, particularly for organic compound classes.
- *Add measurements of semivolatiles* Cartridge samples will be collected at one of the core sites, using denuders and afterfilters. These samples will be collected and analyzed by Len Stockburger, an EPA scientist collaborating with GC-ARCH.
- *Add single particle mass spectroscopy* 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. Particles of a narrow size range are focused aerodynamically to the source region of a mass spectrometer. The size that is focused can be selected from 10 nm to 2 microns by adjusting the upstream pressure. An excimer laser beam colinear with the particle beam is periodically fired. If a particle is in the beam, it is desorbed and ionized. The ions are analyzed in a time-of-flight mass spectrometer. Spectra from each particle are recorded and stored on a PC. The instrument is described in more detail in Carson et al. (1997) and Ge et al. (1998). The instrument can analyze for inorganics such as metals and metal oxides, refractory crustal materials such as silicon dioxide, and electrolytic compounds such as sulfates and nitrates. The instrument can also analyze for aromatic organic compounds, and can distinguish elemental from organic carbon. The analysis is surface selective for larger particles at low laser power but samples the bulk of smaller particles (Ge et al., 1998). These measurements will be performed by Tony Wexler of the University of Delaware.
- *Add semi-continuous measurement of ammonia and acid gases* – Measurements of ammonia and acid gases will be made using the automated wet denuder system developed by Texas

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Tech University which is being deployed during the 1999 Atlanta Supersite inter-comparison study. In the Texas Tech system, coarse particles are first removed with a cyclone (50% cut point of 2.5  $\mu\text{m}$  mass median aerodynamic diameter). The sample then enters a parallel plate wetted denuder. A suitable scrubber liquid such as dilute  $\text{H}_2\text{O}_2$  flows down the opposing faces of two closely spaced parallel plates while the sample gas flows upwards at flow rates up to 10 L/min. Soluble gases such as  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HONO}$ ,  $\text{HNO}_3$  are collected efficiently by the denuder liquid. The collection efficiency can be theoretically computed based on the diffusion coefficient of the analyte gas and agrees closely with experimental observations. The liquid is withdrawn at the bottom of the denuder by a peristaltic pump and this effluent contains the collected gaseous analytes in the form of their corresponding characteristic anions. The effluent liquid is concentrated on a preconcentrator column in an ion chromatograph. While one such column is being loaded a second one is chromatographed, the columns are switched every 8-15 min, thus producing analytical results on the collected samples in near real-time (Simon and Dasgupta, 1995a). The sensitivity of the technique using suppressed anion chromatography results in detection limits for most soluble gases in the sub parts per billion (in favorable cases in the sub-parts per trillion) range. Gaseous ammonia is also collected by the denuder and can be determined in the denuder effluent by a cation chromatograph. However, since ammonium is virtually the only cation of interest, a simpler, more compact and more affordable determination system is based on the fluorometric determination of ammonium as the intensely fluorescent 1-sulfonatoisindole.

- *Add a second semicontinuous method for particulate sulfate and nitrate* The Texas Tech system for acid gas analysis can also be used for PM constituents. The analytical system for the PM constituents is essentially the same as that for the gas phase constituents. After the gases are removed by the wet denuder, the aerosol is collected. The capabilities of the parallel plate wet effluent diffusion denuder (WEDD) - vapor condensation particle collection system (VCPCS) - ion chromatographic analyzer has been previously described (Simon and Dasgupta, 1995a). A single ion chromatograph can be time shared between the wet denuder effluent (bearing the gaseous analytes) and the aerosol collection system effluent. The simultaneous measurement of gaseous  $\text{HONO}$  and  $\text{HNO}_3$  and particulate nitrate and nitrite has been described (Simon and Dasgupta, 1995b). The detection limit for soluble anionic constituents of the aerosol is in the low-sub-ng/ $\text{m}^3$  range. The system has been field tested at the Atlanta supersite in the summer of 1999. Based on the experience in Atlanta, the system will be deployed in Houston with duplicate analysis systems serving both the gas and the aerosol phase analytes separately. Also, a liquid chromatography-mass spectrometric detection system will be deployed along with the traditional analysis system. The LC-MS system will allow a number of new aerosol phase components to be detected, including a variety of organic acids.
- *Add semicontinuous measurements for peroxides and formaldehyde* Atmospheric  $\text{H}_2\text{O}_2$  will be measured using the Texas Tech Diffusion Scrubber method. Of the two most commonly used for the in-situ measurement of atmospheric  $\text{H}_2\text{O}_2$ , an international intercomparison by de Serves (1994) found the TTU diffusion scrubber based method superior to the glass coil scrubber method. Currently two approaches are used to measure atmospheric  $\text{H}_2\text{O}_2$ . Both methods use a Nafion membrane diffusion scrubber (NMDS) with a water scrubber as a collector for  $\text{H}_2\text{O}_2$ . Such a collection method discriminates against organic peroxides because of their lower diffusion coefficient and poorer Henry's law solubility relative to  $\text{H}_2\text{O}_2$ . In

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addition, both analytical methods yield lower signals for organic peroxides relative to  $\text{H}_2\text{O}_2$  when identical amounts are introduced to the analytical system, regardless of collection efficiency. Taking into account significantly lower concentrations of organic peroxides relative to  $\text{H}_2\text{O}_2$  that occur in the atmosphere, the methods are essentially specific for  $\text{H}_2\text{O}_2$ . However, the technique can be modified to separately measure  $\text{H}_2\text{O}_2$  and organic peroxides. The scrubber is oversized to collect organic peroxides as well and the peroxides in the mixture are differentiated by a catalytic bed containing granular  $\text{MnO}_2$  which selectively destroys  $\text{H}_2\text{O}_2$ . Texas Tech will also provide a near-continuous measurement for formaldehyde, based on a diffusion scrubber fluorometric method. This method has been field tested and validated in intercomparison studies (Gilpin, et al., 1997). These measurements will provide much better temporal resolution of this important carbonyl compound than the DNPH method.

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.

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*Table 5. Particulate phase measurements to be performed at core sites during 6 week intensive*

Measurement	HRM Site #3 (downwind industrial)	Deer Park /LaPorte (upwind industrial)	Aldine (downwind urban)
<i>Particulate matter measurements</i>			
FRM	Every sixth day PM <sub>10</sub> and PM <sub>2.5</sub> (HRM), Daily at nearby TNRCC site (TNRCC)	Every third day PM <sub>10</sub> and PM <sub>2.5</sub> (TNRCC)	Every third day PM <sub>10</sub> and PM <sub>2.5</sub> (TNRCC)
Continuous PM Mass	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, 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	GC-ARCH	ADI -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

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*Table 6. Gas phase measurements to be performed at core sites during 6 week intensive*

Measurement	HRM Site #3 (downwind industrial)	Deer Park /LaPorte (upwind industrial)	Aldine (downwind urban)
<i>Gas phase measurements</i>			
Ozone, CO	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO, NO <sub>x</sub>	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO <sub>y</sub>		Continuous (TNRCC)	Continuous (TNRCC)
Denuder HNO <sub>3</sub>	Third day (Rice-GCARCH)	Third day (Rice)	Third day (Rice)
Denuder NH <sub>3</sub>	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)	Third day (Rice-GCARCH)
Acid gases: SO <sub>2</sub> , HCl, HONO, HNO <sub>3</sub>		Semi-continuous (TTU-GCARCH)	
NH <sub>3</sub>		Semi-continuous (TTU-GCARCH)	
SO <sub>2</sub>	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
PAMS hydrocarbons	Auto-GC (HRM)	Auto-GC (TNRCC)	Canister (UT-GCARCH)
Carbonyls	Selected dates (HRM)	Selected dates from samples collected daily by TNRCC (TNRCC)	Selected dates from samples collected daily by TNRCC (Rice-GCARCH)
Semi-volatiles		Selected dates from samples collected daily 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
Met. Data	TNRCC	TNRCC	TNRCC

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

*Task 3b Utilize the data collected in Task 3a to examine the rapid photochemistry occurring in the industrial (Ship Channel) region of Houston* Rapid atmospheric photochemistry may lead to elevated levels of fine particulate matter and acid aerosols in Houston and these locally elevated levels of particulate mass and acidity may lead to adverse health impacts. Analysis of historical ozone data for Houston shows that peak ozone concentrations are often measured at monitoring locations near the major industrial sources in the Houston Ship Channel. Ozone concentration time series during these episodes show rapid ozone formation during morning hours, rather than the slow build-up of ozone concentrations with downwind transport of air parcels that is observed in other urban areas (e.g. Los Angeles). Both these observations suggest that rapid atmospheric radical formation and photochemistry in the Ship Channel area dominates ozone and possibly particulate matter formation during these episodes.

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Initial results of PM<sub>2.5</sub> monitoring in Houston (Tropp, et al., 1998) show that the highest fine PM concentrations are observed at monitoring locations in the Ship Channel area where the Deer Park and HRM core sites are located. Data on fine PM composition suggest that rapid atmospheric photochemistry in the Ship Channel area may contribute to high fine PM concentrations (see Figure 2). Rapid particle formation in the Ship Channel region was also observed in airborne measurements of PM, gaseous particle precursors and ozone. Through analysis of data collected using fast response instruments, Tropp et al. (1981) report that in Houston, elevated PM concentrations aloft are often associated with elevated ozone concentrations, suggestive of secondary particulate matter formation. Thus, rapid photochemistry producing locally elevated concentrations of fine particulate matter, has the potential to create local regions of high exposure in Southeast Texas. The processes that lead to these particulate matter hot spots will be characterized using ground based measurements performed by GC-ARCH, HRM and the TNRCC (described in Tables 5 and 6). Parallel, separately funded measurements, will be performed as part of the TEXAQS 2000 field study, described in the section on collaborating institutions. Specific questions that these measurements will test are listed below.

- *What PM components are produced rapidly in the Ship Channel region?* Preliminary data, described above, indicate that much of the PM mass generated rapidly in the Ship Channel region is ammonium sulfate and daily average concentrations can be elevated by approximately 5 - 10  $\mu\text{g m}^{-3}$ . These measurements, however, are based on 24-hour measurements. Short term fluctuations may be much more substantial than 5 - 10  $\mu\text{g m}^{-3}$ . In addition, since denuders were not used in all of the measurements, much of the aerosol neutralization may have occurred on the filters. Short term samples may reveal much greater concentrations of acids than the 24-hour samples and may provide insights into the dynamics of the PM acid neutralization.
- *Ultrafine particle formation* The rapid increases in particulate mass that occur in the Ship Channel region may result in rapid growth of hydrophobic particles, rapid growth of hydrophilic particles, or the formation of new particles. Since the Ship Channel area experiences high concentrations of particulate matter, surfaces are available for PM growth by condensation. This may suppress particle nucleation (Weber, et al., 1996, 1999). Particulate size distributions made upwind and downwind of the Ship Channel will allow the relative rates of condensation and nucleation to be characterized. In addition, the chemical characterization of the PM will allow the dependence of condensation and nucleation processes on PM composition to be examined.
- *What cofactors are associated with rapid PM formation?* Gas phase oxidants associated with rapid formation of fine PM will be assessed. In particular, it is known that peroxides can play a significant role in the oxidation of SO<sub>2</sub> to sulfate, so the semicontinuous measurements of sulfate and nitrate concentrations will be compared with the semicontinuous measurements of peroxides and other gas phase species.

### *Task 3c Utilize the data collected in Task 3a to examine the heterogeneous organic chemistry in Houston*

Preliminary monitoring of fine particulate matter composition in Southeast Texas indicates that a large fraction of the particulate matter is organic (Tropp, et al., 1998). Further, because organic constituents in fine PM may be responsible for some of the health effects associated with fine

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particles, and because of the extensive emissions of organic particulate matter precursors in Southeastern Texas, this component of particulate matter is especially important in this region. Therefore, processes that lead to the formation of organic particulate matter should be characterized, especially the processes that convert organic, gaseous precursors into particulate matter (secondary organic aerosol).

Heterogeneous chemistry has long been known to affect the rate of conversion of gaseous precursors into atmospheric PM (e.g. conversion of SO<sub>2</sub> to fine particle sulfate). Additionally, there is a growing awareness that the absorption of semi-volatile organic material to non-volatile carbon affects the ambient concentration measurements of fine particulate matter. To investigate the importance of heterogeneous chemistry on precursor oxidation and the vapor/particle partitioning, several hypotheses concerning the role of heterogeneous chemistry in contributing to fine PM formation in Houston and along the Gulf Coast will be investigated.

- *Does the surface area of fine PM and the composition of the surfaces influence the production of secondary organic aerosol?*. It has been shown that the yield of secondary organic aerosol in smog chamber experiments is dependant on the organic particulate matter concentration, since the secondary organic products in the photo-oxidation of volatile organic compounds require absorption sites on preexisting particles (Odum et al., 1997). With increased organic particle concentrations and increased sorption sites, the particle yield from oxidation of gas phase hydrocarbons should increase. It is less clear whether other absorption sites will effect secondary organic aerosol yields. PM measurements upwind and downwind of the Ship Channel area, where rapid photochemistry occurs, will provide an opportunity to examine these phenomena. Measurements of volatile organics, and carbonyls, as well as molecular and functional group characterizations of the organics in the particulate phase, will allow gas-particle partitioning to be quantitatively assessed. Comparisons between organic partitioning ratios upwind and downwind of the Ship Channel, where sharp gradients in PM surface area are expected, will allow the effect of surface area on gas-particle partitioning to be assessed.
- *Does the chemical aging (oxidation) of organic PM influence the processing of gaseous precursors into secondary fine particulate matter?*. Primary emissions of particulate matter and secondary particulate matter formed in the atmosphere are subject to reactions both within the particles and at the gas-particle interface. For carbonaceous particles, these reactions may have a substantial effect on the nature of the surfaces that are available for condensation of gas phase aerosol precursors. Houston offers an ideal environment to study whether changes in the chemical nature of aerosol surfaces will lead to changes in the production of secondary aerosol – particularly secondary organic aerosol. In Houston, the predominant wind flow pattern is off the Gulf of Mexico. This air mass is subject to rapid photochemistry as it passes over the Ship Channel region. As the air mass first passes over the Ship Channel, secondary aerosol is formed and aerosol surfaces subject to oxidation are likely to be oxidized. Frequently, the flow off the Gulf stalls in late afternoon and reverses,

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well as molecular and functional group characterizations of the organics in the particulate phase.

**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;**

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 – 2000 (TEXAQS 2000). TEXAQS 2000 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, a second mass spectrometer capable of obtaining spectra of single particles (in addition to the University of Delaware instrument funded by GC-ARCH), 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. The instrumentation available on the aircraft are described in the technical attachments. The measurements made during TEXAQS 2000, 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 6 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 3 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 – 2000, 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.).

In addition to providing data suitable for testing PM models, selected analyses performed through TEXAQS-2000 will be used to probe the rapid photochemistry and the heterogeneous chemistry discussed under Objective 3. One specific example of such analyses will involve the single particle mass spectrometry data. During TEXAQS – 2000, NOAA will bring a second single particle mass spectrometer to the study, allowing upwind and downwind spectra to be collected. These data can be used to characterize the types of individual particles that result from rapid



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### **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**

Both the 16 month and the 6 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. A description of the project is given in the attachments. The Leland Center study 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<sub>2.5</sub> 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<sub>2.5</sub> and PM<sub>2.5</sub> 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). 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.

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).

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

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 the following hypothesis:

- Human AM response depends on source contributions and PM composition.

### **COLLABORATION (letters of commitment for all leveraging opportunities are attached)**

*Texas Natural Resource Conservation Commission* The measurements proposed for the 16-month and 6-week sampling programs are extensive and the complete suite of measurements could not be funded exclusively through the Supersites program. Fortunately, the Texas Natural Resources Conservation Commission (TNRCC) provides extensive, ongoing measurements of fine PM characteristics. Specifically, all of the peripheral site measurements described in Table 2 will be made by the TNRCC. In addition, the measurements labeled as TNRCC in Table 1 will be made by the TNRCC. The value of these in-kind measurements is estimated to be in excess of \$2,500,000.

In addition to making measurements as an in-kind contribution, the TNRCC has and will contribute funding that will directly benefit GC-ARCH. TNRCC has already funded two study

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coordinator positions for the TEXAQS-2000 study. These individuals will also support site logistics for GC-ARCH. The TNRCC has also set aside funds for web site development, office space and other infrastructure needs; these resources will directly benefit both TEXAQS-2000 and GC-ARCH.

**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. Data bases 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 - 2000 field study** The measurements to be made during the 6 week intensive sampling period will be coordinated with an air quality study being organized by the State of Texas and investigators affiliated with the Southern Oxidants Study. TEXAQS 2000 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, a mass spectrometer capable of obtaining spectra of single particles, 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. The in kind value of these measurements is estimated to be \$5-10,000,000.

**Mickey Leland Center** In parallel with the measurements of PM physicochemical properties, 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. This project is part of a 3 city study with a total budget in excess of \$1,000,000.

**UT HHSC** A study being performed by the University of Texas Houston Health Science Center (UT-HHSC), funded by the U.S. EPA at a level of \$674,288, is examining the responses of human alveolar macrophage (AM) to both model and ambient PM. Samples collected at the GC-ARCH core 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; \$100,000 of these funds have been committed to the combined TEXAQS 2000 study and GC-ARCH. These funds will support data analysis activities related to TEXAQS-2000 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. A summary of the measurements made at the sites is given in attachments to this proposal. The network adds substantial capabilities to the network of sites planned for both the 6 week and 16 month sampling programs, especially the measurements at site 3, described in the letter of support attached to this proposal.

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*City of Houston* 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 (Luhmann, et al., 1999). The City also funds an air quality monitoring network. A brief summary of the measurements made at the sites is given in attachments to this proposal. The network adds substantial capabilities to the 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 proposed 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.

**EXPECTED RESULTS AND BENEFITS**

The three primary objectives of the Supersites program, as described in the Request for Applications, 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 7 describes how the GC-ARCH program will address each of these objectives and summarizes hypotheses that will be tested. Specific deliverables of the program will be a quality assured database (described in the QA section) and scientific publications and reports on measurements and data analyses.

*Table 7. Expected Results and Benefits*

<b><i>Supersite Program Objective</i></b>	<b><i>GC-ARCH Objective and hypotheses to be tested</i></b>
Characterize particulate matter and its sources	<p><i>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:</i></p> <ul style="list-style-type: none"> <li>• 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.</li> <li>• Maximum fine PM concentrations in Southeast Texas will be observed in the summer, when secondary PM generation peaks.</li> <li>• 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.</li> <li>• FRM mass monitors and 24-hour speciation monitors correspond to time integrated near-real time measurements of PM mass, sulfate and nitrate.</li> </ul>
	<p><i>Objective 2: Characterize spatial and temporal variability in fine PM source contributions and composition, throughout the southeastern United States; test the following hypotheses:</i></p> <ul style="list-style-type: none"> <li>• 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.</li> <li>• Maximum fine PM concentrations will be observed in the summer, when secondary PM generation peaks.</li> </ul>

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	<p><i>Objective 3: examine the physical and chemical process that govern PM formation and transformation in Southeastern Texas; test the following hypotheses:</i></p> <ul style="list-style-type: none"> <li>• 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.</li> <li>• 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.</li> <li>• 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.</li> <li>• Rates of PM growth will differ for fresh and photochemically aged PM.</li> </ul>
	<p><i>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.</i></p>
Support health effects and exposure research	<p>Objective 5: examine exposures to fine PM from specific source categories in Southeastern Texas; test the following hypotheses:</p> <ul style="list-style-type: none"> <li>• 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.</li> <li>• Source strengths for fine PM indoors and outdoors differ.</li> <li>• Indoor penetration of PM is a strong function of PM size</li> </ul>
	<p><i>Objective 6: relate the physicochemical data on fine particulate matter to mammalian cell responses; test the following hypotheses:</i></p> <ul style="list-style-type: none"> <li>• Human AM response depends on source contributions and PM composition.</li> </ul>
Conduct methods testing, evaluating different methods of characterizing PM	Included as part of objectives 1-5

**GENERAL PROJECT INFORMATION**

**Facilities and Personnel.** The proposed research will involve 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.. Listed below are short descriptions of the lead investigators and facilities at each of these institutions. The coordination between the institutions is described in the sub-section describing project management.

The lead investigator at the University of Texas and the PI for the program is David Allen. Dr. Allen is the Henry Beckman Professor in Chemical Engineering and the Director of the Center for Energy and Environmental Resources at the University of Texas at Austin. His area of research is tropospheric chemistry, particularly the organic chemistry leading to secondary organic aerosol formation. Dr. Allen leads the University of Texas’ activities in emission inventory development, ambient air quality monitoring and air quality modeling. His laboratories are equipped with smog chambers, gas chromatography/mass spectrometry with cryofocussing, infrared microscopy, canister sampling capabilities (with over 100 electropolished canisters),

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adsorbent tube analysis capabilities, and low pressure impactors. His labs have sufficient air quality monitoring equipment (ozone, NO<sub>x</sub>, canister autosamplers, meteorological data collection equipment, sheds and trailers) for multiple field stations. For the past four years he has run multiple air quality sampling programs in Texas. He has participated in the Southern California Air Quality Study and other large field programs, and he has served as director of a DoD environmental center and associate director of an NSF Engineering Research Center.

The lead investigator at Rice University and the Co-PI for the program is Matthew Fraser. Dr. Fraser is an assistant professor in the Environmental Science and Engineering Department at Rice University. His area of research is the speciation of organic gases and particulate matter in the urban atmosphere with an emphasis on analysis to determine photochemical potentials, source contributions and atmospheric fate of organic compounds. The laboratories under Dr. Fraser's direction at Rice University are equipped with gas chromatography/mass spectrometry, high pressure liquid chromatography, thermal-optical organic carbon and elemental carbon detectors and an electronic microbalance. Additional facilities available at the University include liquid chromatography-mass spectrometry, and ion-coupled plasma spectrometry.

The lead investigator at Texas Tech University is Purnendu Dasgupta. Dr. Dasgupta is the Paul Whitfield Horn Professor in Chemistry at Texas Tech University. His area of research is the ultratrace atmospheric analysis, particularly using capillary and membrane based separation methods. He has published over two hundred papers in primary research journals and he has been a participant in numerous air quality field studies, including the 1999 Atlanta Methods Intercomparison Supersite. Dr. Dasgupta's group maintains a mobile air quality research laboratory that he will bring to Houston. The mobile lab will include facilities for ultratrace analysis of acids, peroxides, and PM sulfate and nitrate.

The lead investigator at Texas A&M University is Don Collins. Dr. Collins will join the Atmospheric Sciences Department at Texas A&M University in the fall of 1999. He is currently completing his doctoral dissertation at the California Institute of Technology under the supervision of John Seinfeld and Richard Flagan. His thesis research has utilized advanced differential mobility analyzers and optical particle counters to characterize particulate matter size distributions during air quality field campaigns. His laboratory at Texas A&M will include these particle size measurement capabilities.

The lead investigator at Clarkson University is Phil Hopke. Dr. Hopke is the R.A. Plane Professor of Chemistry at Clarkson University; he has been involved in multivariate statistical analyses of atmospheric data for more than 25 years. He has published extensively on PM source allocation and he has served on 6 National Research Council panels, including the current, Congressionally mandated panel that is examining research priorities for atmospheric particulate matter. He is a member of the EPA Clean Air Science Advisory Committee and chairs its technical subcommittee on PM monitoring.

The lead investigator at the Georgia Institute of Technology is Ted Russell. Dr. Russell is the Georgia Power Distinguished Professor of Environmental Engineering. At Georgia Tech, his research examines the dynamics of ozone and particulate matter at urban and regional scales. Dr. Russell has served on multiple National Research Council committees on air quality; he is also a member of the EPA FACA Subcommittee on Ozone, Particulate Matter and Regional Haze, the North American Research Strategy for Tropospheric Ozone and California's Reactivity Science Advisory Committee.

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The lead investigator at the University of Delaware is Tony Wexler. Dr. Wexler is a Professor of Mechanical Engineering department at the University of Delaware. His research focuses on atmospheric aerosols and uses theoretical, numerical, and experimental techniques to approach these problems. For the past 8 years he has been collaborating with Dr. Murray Johnston to develop single particle techniques suitable for characterizing atmospheric aerosol particles in-situ.

The lead investigator at Aerosol Dynamics, Inc. is Susanne Hering. Dr. Hering is founder and president of Aerosol Dynamics Inc., a research firm specializing in the development of measurement methods for fine, airborne particles. In collaboration with Dr. Mark Stolzenburg of Aerosol Dynamics Inc., she developed an automated system for the high-time resolution measurement of fine particulate nitrate and sulfate. Previously she designed a low-pressure impactor for size resolved aerosol sampling, and a two-week integrated sampler for ambient and microenvironmental measurements of fine particle mass and ionic species. Her instruments have been used in multiple field studies.

**Project Schedule.** Intensive data collection will occur during a 16-month period beginning in June, 2000. Logistical preparations for the sampling program will rely extensively on the preparations that are already underway for the TEXAQS 2000 air quality study, scheduled for the summer of 2000. Logistics for the TEXAQS 2000 project are being managed by study coordinators (funding for these positions has been provided by the TNRCC). The work of the study coordinators will allow the aggressive schedule outlined below to be met.

*August 1999:* Study coordinators for TEXAQS 2000 develop web site, and begin site selection and preparation

*November 1999:* Project planning meeting for TEXAQS 2000, including site evaluation; funding awarded for GC-ARCH

*December 1999:* Final site approval for GC-ARCH core sampling locations

*March 2000:* Project planning meeting for TEXAQS 2000 and GC-ARCH

*May 2000:* Project planning meeting for TEXAQS 2000 and GC-ARCH; detailed site plans, investigator assignments and site layouts established

*August-September 2000:* 6-week intensive sampling program

*February 2001:* Data analysis meeting for 6-week intensive, quality assurance reports

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**Project Management** The management structure for GC-ARCH is summarized in the organizational chart shown below. GC-ARCH will be directed by a Program Management Team, consisting of the PI, the Co-PI, and the program manager. The PI will be David Allen from the University of Texas; the co-PI will be Matt Fraser from Rice University. The PI and co-PI will be 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 will be responsible for day-to-day administration of the program and its budgets. The Program Management team will meet weekly, throughout the course of the project. The team will meet daily during the 6-week intensive sampling program.

The Science Team will consist of all investigators receiving support from GC-ARCH. The specific responsibilities of each member of the Science team are described in the proposal. The Science team will consist of sub-committees on measurements and data analysis. Meetings of the full Science Team and subcommittees will follow the schedule given on the previous page. 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. The QA/QC practices are described in the quality assurance section.

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

