Solicited Proposal

Environmental Justice Saturation Monitoring of Selected Pollutants in Wilmington

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August 19, 2005

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STATEMENT OF SIGNIFICANCE

The characterization of a community's exposure to air pollutants is essential in assessing cumulative health impacts. However, the costs of traditional monitoring technologies pose significant limitations on the number of monitoring locations that can be established for exposure studies. This raises concerns about the adequacy of such assessments because exposures to toxic air contaminants can vary substantially in space and time due to variations in proximity to sources of emissions, magnitude and specific mix of emissions and meteorological conditions. These variations are also accompanied by changes in the chemical and physical nature (e.g., particle size distribution) of the mixture of pollutants during transport in the atmosphere. The potential for disproportionate impacts to certain communities due to their proximity to pollutant sources have caused policy maker to consider whether current regulatory practices allow greater air pollution exposures in some communities compared to others.

While the plausibility of environmental inequity in California and the likelihood that these patterns may play a role in disparate health and other outcomes have been established, previous work generally do not account for both socioeconomic status (SES) and cumulative exposure to hazardous air pollutants or deal effectively with issues of spatial clustering and scale. In order to address these issues, an EJ project entitled "Air Pollution and Environmental Justice: Integrating Indicators of Cumulative Impact and Socioeconomic Vulnerability into Regulatory Decision-making" (Pastor et al., 2004) was recently developed and funded by the ARB and the California Energy Commission (CEC). The project is intended to develop a framework that takes into account cumulative exposures, a comprehensive model of vulnerability at the community level including environmental, demographic and SES factors, and a screening tool for regulators and other to identify areas in need of special policy attention and community outreach. This integrated database will include air quality and census data from federal, state, local agencies, and local case studies.

Urban and regional air monitoring programs in U.S. typically consist of a relatively limited number of widely spaced monitoring stations within a given airshed. While these monitoring networks are generally adequate to characterize the spatial variations of secondary pollutants such as ozone, nitrogen dioxide, and nitrate and sulfate particles, they are less useful for determining the range of exposure to directly emitted pollutants such as CO, diesel PM and other toxic air contaminants. Because of the limitation on the number of monitoring locations that can be established for exposure studies using traditional measurement methods, the spatial resolution of most air quality data is relatively coarse (a single monitor for tens of square miles) compared to the spatial resolution of the social economic status (SES) data that will be compiled by the Pastor study. Additional air quality data of finer spatial resolution are needed to complement the Pastor et al. project.

ABSTRACT

The community of Wilmington, near Los Angeles, is the focus of a major study being developed by the ARB involving various measurement and modeling objectives. Wilmington is located in one of the largest industrial and commercial areas of Southern California and the potential for disproportionate health impacts to this community has drawn considerable interest from policy makers and community advocates. Wilmington has several large refineries and the intermodal container transfer facility and associated Alameda corridor, is located just north of the Ports of Los Angeles and Long Beach, and is surrounded by freeways with the greatest concentration of diesel traffic in the Los Angeles metropolitan area.

The Desert Research Institute offers to conduct a field measurement program to characterize exposures to selected pollutants in the Wilmington area. The study will be conducted in three phases. In the initial phase, we will evaluate the precision, accuracy, sampling rates and validity of passive sampling methods in the laboratory using a flow through chamber with known pollutant concentrations. In phase 2, all sampling methods that are proposed for the saturation monitoring program will be tested in Wilmington prior to initiation of the full field study. Measurements will likely include passive monitors for O_3, NO, NO_2, NOx, SO_2, BTEX (benzene, toluene, ethylbenzene, xylenes), formaldehyde, and acrolein, odor-causing sulfides, and low-volume aerosol sampler for fine particulate matter mass and light absorption. The field operations plan and the quality assurance program plan (QAPP) will also be prepared during this pilot study phase. Phase 3, saturation monitoring, will be conducted over a period of one year starting in the summer of 2006 and will consist of a two tiered approach. Tier 1 will consist of four consecutive weeks of monitoring during each quarter of the year at up to twenty sites to establish seasonal average variations in neighborhood-scale exposures among the various census tracts in Wilmington and at various mobile and stationary source hot spots. Tier 1 will consist of one-week integrated passive and low-volume aerosol samples. Tier 2 measurements will supplement the Tier 1 saturation monitoring program with daily sampling for PM and BTEX and continuous CO, VOC and $PM_{2.5}$ mass measurements at selected hotspot locations during two-week sampling periods in both summer and fall/winter. This proposed saturation monitoring program will be coordinated with complementary studies by other investigators of the pollutant gradients in the areas using a mobile monitoring platform and a second study of exposures to ultrafine particles.

Specific objective of the project include: 1) provide an air quality data set that is of comparable spatial resolution as socioeconomic status (SES) data for EJ analysis (Pastor et al., 2004); 2) collect spatially resolved data in order to identify hot spots of selected pollutants, their magnitude and spatial extent, and relative importance compare to a regional background; 3) collect data of sufficient spatial and temporal resolution to allow comparison with fine-scale modeling results; and 4)demonstrate the use of low-cost monitoring technologies such as passive monitors in EJ studies.

1. INTRODUCTION

The characterization of a community's exposure to air pollutants is essential in assessing cumulative health impacts. However, the costs of traditional monitoring technologies pose significant limitations on the number of monitoring locations that can be established for exposure studies. This raises concerns about the adequacy of such assessments because exposures to toxic air contaminants can vary substantially in space and time due to variations in proximity to sources of emissions, magnitude and specific mix of emissions and meteorological conditions that affect dispersion and transport. These variations are also accompanied by changes in the chemical and physical nature (e.g., particle size distribution) of the mixture of pollutants during transport in the atmosphere. The research project described in this proposal will evaluate the use of low cost monitoring techniques for characterizing neighborhood-level exposures to air pollutants in an Environmental Justice (EJ) community.

1.1   Background

The disproportionate impacts that may be experienced by certain communities due to their proximity to pollutant sources have caused policy maker to consider whether current regulatory practices allow greater air pollution exposures in some communities compared to others. The concept of environmental justice (EJ) is intended to address this concern and the need for clearer guidelines for assessing air pollutant impacts at the neighborhood scale. Several programs are underway in California to evaluate tools for assessing such exposures. The California Air Resources Board (ARB) established the Neighborhood Assessment Program (NAP) in order to develop guidelines for evaluating neighborhood air pollution impacts and reduction strategies. In response to Senate Bill 25, ARB is conducting special studies in six communities around the state at locations where children are typically present, such as schools and daycare centers, and near sources of air pollution, including busy highways and industry. In 1986, the South Coast Air Quality Management District (SCAQMD) conducted its first basin-wide study to determine exposure levels and risks associated toxics air contaminants. This initial study of ten toxic air contaminants was followed by a second study in 1998 of 40 toxic air contaminants. The third study in this series, Multiple Air Toxics Exposure Study–III (MATES-III), is currently underway and calls for a two-year sampling program for air toxics beginning in February 2004. The overall objective of these and other related monitoring programs and research studies is to characterize the ambient air toxic concentrations and potential exposures within communities and to certain susceptible populations. In addition to ambient measurements, these projects typically include development of toxics emission inventories and air dispersion modeling to estimate ambient levels and potential health risks of air toxics. The results of these studies are being used to determine the spatial concentration pattern of hazardous air pollutants within the community, assess the effectiveness of current air toxic control measures, provide trend data of air toxic levels, and to update and develop appropriate control strategies for reducing exposures to toxics associated with significant public health risk.

While the plausibility of environmental inequity in California and the likelihood that these patterns may play a role in disparate health and other outcomes have been established, previous work generally do not account for both socioeconomic status (SES) and environmental vulnerability or deal effectively with issues of spatial clustering and scale. In order to address these issues, an EJ project entitled "Air Pollution and Environmental Justice: Integrating Indicators of Cumulative Impact and Socioeconomic Vulnerability into Regulatory Decision-

making" (Pastor et al., 2004) was recently developed and funded by the ARB and the California Energy Commission (CEC). The project is intended to develop a framework that takes into account cumulative exposures, a comprehensive model of vulnerability at the community level including environmental, demographic and SES factors, and a screening tool for regulators and other to identify areas in need of special policy attention and community outreach. This integrated database will include air quality and census data from federal, state, local agencies, and local case studies.

Urban and regional air monitoring programs in U.S. typically consist of a relatively limited number of widely spaced monitoring stations within a given airshed. While these monitoring networks are generally adequate to characterize the spatial variations of secondary pollutants such as ozone, nitrogen dioxide, and nitrate and sulfate particles, they are less effective for determining the full range of exposure to directly emitted pollutants such as CO, diesel PM and other toxic air contaminants. The costs of traditional monitoring technologies also pose significant limitations on the number of monitoring locations that can be established for exposure studies. Therefore, the spatial resolution of most air quality data is relatively coarse (a single monitor for tens of square miles) compared to the spatial resolution of the social economic status (SES) data that will be compiled by Pastor. To complement the Pastor et al. project, additional air quality data of finer spatial resolution that capture real exposure in the community and are compatible with SES data are needed.

The community of Wilmington, near Los Angeles, is the focus of a major study being developed by the ARB involving various measurement and modeling objectives. Wilmington is located in to one of the largest industrial and commercial areas of Southern California and the potential for disproportionate health impacts to the community has drawn considerable interest from policy makers and community advocates. Wilmington has several large refineries, the intermodal container transfer facility and the associated Alameda corridor, and is located just north of the Ports of Los Angeles and Long Beach, and is surrounded by some of the most heavily traveled freeways in the Los Angeles metropolitan area. The California Air Resources Board selected Wilmington for the location of a saturation monitoring study because of its proximity to many stationary, area and mobile sources, existing detailed inventory of emissions (Sax, 2004), recent community-scale monitoring by the ARB (ARB, 2003), and both near-source dispersion and regional air quality modeling of for the area (Isakov, 2004; Venkatram, 2004). Additionally, the South Coast Air Quality Management District measured elemental carbon intermittently during 1997 to 2003 at several sites in the Long Beach/Wilmington area as part of the implementation Rule 1158 and is currently conducting the Multiple Air Toxics Exposure Study–III (MATES-III). The Health Effects Institute funded Desert Research Institute to conduct a field measurement program during MATES-III to characterize and assess exposures to air toxics in microenvironments dominated by mobile sources. These measurements included sites in the Wilmington area.

1.2   Purpose and Objectives

The technical objectives of the study are as follows.

1. Provide an air quality data set that is of comparable spatial resolution as socioeconomic status (SES) data for EJ analysis (Pastor et al., 2004);

2. Collect spatially resolved data in order to identify hot spots of selected pollutants, their magnitude and spatial extent, and relative importance compare to a regional background.

3. Collect data of sufficient spatial and temporal resolution to allow comparison with fine-scale modeling results.

4. Demonstrate the use of low-cost monitoring technologies such as passive monitors in EJ studies.

5. Plan, coordinate, and provide field management for three other related studies that will be conducted along with the saturation monitoring study.

These technical objectives may be rephrased into the following specific testable hypotheses.

1. Passive monitor methods can be used to measure cumulative exposures to selected pollutants over a time period of a week with comparable sensitivity and precision as data obtained by conventional monitoring methods that are averaged over the same period.

2. There are gradients in pollutant concentrations within Wilmington that results in measurable variations in cumulative exposures that can be related to proximity to emissions from either stationary or mobile sources.

3. Seasonal variations in transport related to changes in meteorology affect the pattern and magnitude of cumulative exposures.

4. The existing air quality monitoring in Wilmington is not adequate to characterize the spatial variations in cumulative exposure within the community.

5. Magnitude of light absorption is correlated to proximity to truck traffic and day-of-week variations in diesel truck traffic volume.

2.   TECHNICAL PLAN

The Desert Research Institute proposes to conduct a field measurement program to characterize exposures to selected pollutants in Wilmington, CA. The study will be conducted in three phases. In the initial phase, we will evaluate the precision, accuracy, sampling rates and validity of passive sampling methods in the laboratory using a flow through chamber with known pollutant concentrations. In phase 2, all sampling methods that are proposed for the saturation monitoring program will be tested in Wilmington prior to initiation of the full field study. The field operations plan and the quality assurance program plan (QAPP) will also be prepared as part of this pilot study phase. Phase 3, saturation monitoring, will be conducted over a period of one year starting in the summer of 2006 and will consist of a two tiered approach. Tier 1 will consist of four consecutive weeks of monitoring during each quarter of the year at up to twenty sites to establish seasonal variations in neighborhood-scale exposures and within mobile and stationary source hot spots. In Tier 2, saturation monitoring program (i.e, Tier 1) will be supplemented with daily sampling during two-week sampling periods during both summer and fall/winter. This section describes the specific tasks and the approach that will be used to meet the objectives and hypotheses of the proposed study. It also describes each of the proposed sampling and analytical methods and DRI laboratory facilities.

2.1   Statement of Work and Approach

The Desert Research Institute of the Nevada System of Higher Education (NSHE) will provide the necessary facilities, materials, and personnel to accomplish the following tasks. The work statements are in italic and the approach is described in regular text. The cost proposal is included in the appendix.

2.1.1   Task 1 – Laboratory evaluation of passive monitoring methods.

Evaluate passive monitors for O_3. NO, NO_2, NOx, benzene, toluene, ethylbenzene, xylenes, formaldehyde, and acrolein in the laboratory under controlled conditions to verify the precision, accuracy, sampling rates and validity of measurements for periods extending up to seven days. Prepare a summary of the results and findings for review.

The evaluations will be conducted at DRI during January-April 2006. The proposed measurements that will be evaluated and the number of samples that will be collected and analyzed are summarized in Table 1. The passive samplers will be evaluated using a Teflon indoor chamber of approximately 1 m^3 volume. Figure 1 shows such a chamber with the passive monitors inside the chamber. This chamber is a model of the 200 m^3 outdoor European Environmental Chamber (EUPHOR) in Valencia, Spain, that we recently employed for our atmospheric transformation of diesel emissions study (project funded by the HEI). It was used by the Spanish researchers to evaluate passive VOC samplers. Although our indoor chamber is likely to look a little different, the principle of the operation will be the same: the passive samplers are exposed to known concentrations of pollutants of interest under controlled conditions of temperature and humidity over prolonged time periods. The concentration of pollutants is monitored continuously using appropriate sampling ports and monitoring methods. The following passive monitors will be evaluated:

1. Ogawa Passive Samplers for monitoring O_3, NO, NO_2, and NOx. The exposure times for these samples typically range from a day to two weeks, and can extend as long as one

month. Since we anticipate 7-day sampling periods, the samplers would be exposed up to one week. The sampler collects NO_2 and NOx on separate pads and the NO concentration is computed by subtracting the NO_2 results from the NOx value. The passive NO, NO_2, and NOx data will be compared to a continuous NO/NOx analyzer. Singer et al. (2004) recently reported very good precision and accuracy for these passive samplers.

2. Radiello (Centro di Riserche Ambientali, Padova, Italy, www.radiello.com) diffusive samplers for passive sampling of benzene, toluene, ethylbenzene and m, o-, and p-xylenes (BTEX). These samplers have been used extensively in Europe in several major studies (e.g., Monitoring of Atmospheric Concentrations of Benzene in European Towns and Homes, MACBETH, http://pc4.fsm.it:81/padova/homepage.html ; RESOLUTION – High Spatial Resolution Urban Pollution Monitoring, http://pc4.fsm.it:81/padova/resweb/homepage.html). Additional references are listed on the Radiello web site. The radial design of the Radiello samplers allows the diffusive surface to be located very close to a small sorbent volume, resulting in high sensitivity and consistent sampling rate. VOC are adsorbed in a stainless steel mesh cylinder packed with Carbograph 4 and thermally desorbed and analyzed by GC with MS detection. The samplers have very good minimum detection limits (0.01-0.1 ug/m^3) for BTEX over a sampling period of one week. Once thermally desorbed, the adsorbent is reusable after baking. We will evaluate the use of these passive samplers for measuring 1,3-butadiene as well.

3. A cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated florisil (Radiello) will be evaluated for passive collection of carbonyl compounds. The hydrazones are extracted and analyzed by HPLC with UV detection. Detection limits for the carbonyl compounds of interest range from 0.1 to 0.3 ug/m^3 for a sampling period of one week. We will evaluate the possible interference from the presence of higher concentrations of ozone. According to Radiello (www.radiello.com), the ozonolysis of dinitrophenyhydrazones becomes appreciable only if ozone concentration, averaged over the whole exposure time interval, is higher than 100 ppb. This is rather unlikely under ambient conditions. However, if there is an evidence of such high average ozone concentration, corrected sampling rate values should be used. We will evaluate the validity of this statement.

4. Solid Phase Microextraction (SPME). We used the SPME method extensively for short-term microenvironmental BTEX sampling during our project "Section 211(b) Tier 2 High-End Exposure Screening Study of Baseline and Oxygenated Gasoline", which is described in the section on relevant experience (see also Ceballos et al., 2005). The method does not require solvent extraction and the fiber samples can be analyzed in the field, using a portable gas chromatograph with photoionization detector, by thermal desorption method. SPME devices will be used as a time-weighted average (TWA) sampler for gas-phase analytes including BTEX, by retracting the coated fiber a known distance into its needle housing during the sampling period. Martos and Pawliszyn (1999) tested this sampling method for time ranges from 15 min to 16 hrs, and we will evaluate extending the sampling time for 24 hrs. We will also evaluate the use of SPME method

for carbonyl sampling, using fibers impregnated with a derivatizing agent, *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) hydrochloride.

We will use continuous sampling techniques to monitor the concentration of pollutants in the chamber. Horiba NO/NOx analyzer will be used for NO/NO_2/NOx measurements, KORE MS-200 continuous mass spectrometer for BTEX measurements and Alpha Omega continuous formaldehyde analyzer (modified by DRI) for formaldehyde.

Chamber exposures will be carried out for both 3 and 7 day periods to evaluate the linearity of passive monitors with the concentrations of pollutant bracketing expected ambient concentrations (i.e. minimum and maximum). The exposures will be made in triplicate to evaluate the precision. Two sets of experiments will be conducted to evaluate the potential effects of temperature and relative humidity at moderate (e.g., 25 C and 50%) versus high conditions (35 C and 75%). Minimum detection limit (MDL) will be established for all pollutants. We will also evaluate the effect of humidity (by changing the RH in the chamber) for VOC measurements and the presence of ozone for formaldehyde measurements. Table 1 lists all passive methods that will be evaluate during Task 1 and their stated MDL.

Figure 1. Indoor environmental chamber used for passive monitoring method evaluation

Table 1. Summary of Sampling Plan for Wilmington Saturation Monitoring Project

Species measured	Sampling Methods	Instrument/Analysis Methods	Integration period	MDL	Task 1- Eval.		Task 2 - Pilot		Task 3 - Tier 1		Task 3 - Tier 2	
					No. of Reps	Total Samples	No. of Reps	Total Samples	No. of Sites	Samples Per Site	No. of Sites	Samples Per Site
				Duration	2 weeks		2 weeks		16 weeks		4 weeks	
Passive Time-Integrated Sampling Methods												
NO and NOx	Ogawa passive sampler	colorimetry for nitrite	7 days		3	12	3	6	20	320		
SO2	Ogawa passive sampler	IC for sulfate	7 days				3	6	20	320		
Ozone	Ogawa passive sampler	IC for nitrate	7 days		3	12	3	6	20	160		
BTEX	Radiello passive sampler	thermal desorption onto GC/MS	7 days		3	12	3	6	20	320		
HCHO	Radiello passive sampler	HPLC/UV	7 days		3	12	3	6	20	320		
BTEX	Supelco SPME	thermal desorption onto GC-PID	24 hour		3	6					8	224
BTEX	Supelco SPME	thermal desorption onto GC-PID	24 hour		3	6						
Active Time-Integrated Sampling Methods												
$PM_{2.5}$ mass	Personal aerosol sampler at	gravimetry	7 days				3	6	20	320		
$PM_{2.5}$ light absorption	2 lpm on Teflon	light absorption					3	6	20	320		
$PM_{2.5}$ mass	Airmetric mini-vol	gravimetry	48 hours				1	7			8	224
$PM_{2.5}$ light absorption	samplers at 8 lpm on	light absorption					1	7			8	224
Sulfides	silco canisters	GC/MS									4	40
speciated toxic VOC	DRI OAL 3-channel can sampler	GC/MS	48 hours	0.1 ppbC			1	7				
speciated aldehydes	DRI OAL 3-channel DNPH sampler	HPLC-UV	24 hours	0.1 ppbV			1	14				
Continuous Monitoring Methods												
CO	NDIR		1 min/I hour	50 ppb			1	SCAQMD				
CO/CO_2	NDIR	TSI 8554	10 min				4	4			4	
NO and NOx	chemiluminescent		1 min/1 hoour			1	1	SCAQMD				
SO2			1 hour				1	SCAQMD				
total VOC (estimated)	photo-ionization	RAE systems ppbRAE	1 min	30 ppb		1	4	4			4	
black carbon	photoacoustic	DRI portable PA	1 min	1 ug/m3			1	1				
$PM_{2.5}$ mass (estimated)	light scattering	TSI DustTrak	1 min				4	4			8	
BTEX	Portable GC/MS	Horiba Kore MS200	1 min			1						
HCHO	Continuous HCHO	Modified Alpha Omega	1 min			1						
Temperature, RH	Portable T and RH sensor		1 hour				SCAQMD 3	DRI				

1. Two sets of experiments at two T and RH conditions in triplicate for two time integrations (12 samples total).

2.1.2   Task 2 – Pilot study.

Evaluate the precision, accuracy, sampling rates and validity of passive monitors for O_3, NO, NO_2, NOx, SO_2, benzene, toluene, ethylbenzene, xylenes, formaldehyde, and acrolein, and low-volume aerosol sampler for collection of fine particulate matter under actual ambient conditions. Develop a sampling plan for the saturation monitoring program using information provided by surveys of the Wilmington area conducted by UCLA researchers with their mobile monitoring platform, available emission inventory data and previous modeling efforts. Develop a quality assurance program plan (QAPP) for the saturation monitoring program.

Following the laboratory evaluation phase, the passive and active monitoring techniques will be tested under field conditions in the Wilmington – Long Beach area during May – June, 2006, time period. We propose to conduct the pilot study in the SCAQMD monitoring station in Long Beach for a period of 2 weeks. This site is situated not far from Wilmington area and it is equipped with the number of continuous monitoring methods, including O_3, NO/NOx, SO_2, CO, temperature, RH, wind speed and direction, etc. The proposed measurements for this task are summarized in Table 1. All passive methods listed above will be evaluated by comparison with either continuous measurements (for O_3, NO/NOx, and SO_2) or with traditional "reference" measurement methods (i.e. canisters for BTEX and DNPH-impregnated SepPack cartridges for carbonyl compounds). Canisters and DNPH cartridges will be collected over periods ranging from 48 to 72 hours. Passive samplers will be exposed over two 7-day periods.

We will also compare the following measurements methods during this task:

1. Ogawa Passive Sampler for SO_2 monitoring will be compared with the continuous SO_2 analyzer. Passive sampler will be exposed over two 7-day periods.

2. Personal Environmental Monitors (PEMs) from MSP Corporation (or from SKC, Inc.) for particle sampling for periods up to one week. This monitor consists of a single stage impactor to remove particles above the 50% cut-point of 2.5 um in aerodynamic diameter (PM10 impactor is also available), filter holder, pump and flow controller. Particles are collected on 37 mm filters that can be analyzed gravimetrically for mass and optically for black carbon. A small pump provides the airflow of 2, 4 or 10 L/min. We will use 2 L/min for 7 day's sampling period (i.e. 20 m3 total volume). We will equip the samplers with a 10w solar panel to enable sampling over a period of six days. The PEM monitor will be compared with daily Teflon filter samples for gravimetric mass analysis and light absorption, collected using a $PM_{2.5}$ Airmetrics minivol sampler at 5 L/min.   In addition, a photoacustic instrument for continuous black carbon measurements will be employed for comparison with optical black carbon measurements.

3. Portable CO monitors (battery-powered passive electrochemical unit Langan T15 and TSI 8854) that will be used during Tier 2 monitoring will be compared with each other and with the reference NDIR instrument operated by the SCAQMD.

4. RAE Systems Model PGM-7240 (ppbRAE) portable PID monitors, will be evaluated for continuously monitoring ambient VOC levels. The monitor is equipped with a 10.6 eV photoionization (PID) detector and responds to organic and inorganic gases that have an

ionization potential of less than 10.6 eV, which includes most compounds of interest in this study. It does not respond to light hydrocarbons such as methane, ethane, propane or to acetylene, CO, or formaldehyde. The four PID monitors that will be used during Tier 2 monitoring will be compared to each other and with canister samples.

5. Several TSI DustTrak nephelometer, used to monitor fine particle concentrations, will be compared with gravimetric mass measurements. The laser diode used by the DustTrak has a wavelength of 780 nm, which limits the smallest detectable particle to about 0.1 μm. The scattered light is also dependent upon the index of refraction and light absorbing characteristics of the particles. For the recent PM split study (Fujita et al, 2005) the DustTrak was found to exceed gravimetric mass concentrations of the mobile ambient samples by a factor of 2.24 with an R^2 of 0.75. We will confirm this factor for the Long Beach – Wilmington area.

The results of the pilot study will be summarized in a report that will be submitted to the ARB for review. This report will be accompanied by a draft operational plan for the saturation monitoring program and a quality assurance program plan. The sampling plan will be based on the results of our laboratory and field evaluations and information provided by surveys of the Wilmington area conducted by UCLA researcher's with their mobile monitoring platform, available emission inventory data and previous modeling efforts.

2.1.3 Task 3 – Saturation Monitoring Program.

Conduct saturation monitoring starting in the summer of 2006 for four consecutive weeks during each quarter of the year at twenty sites to establish seasonal variations in neighborhood-scale exposures and within mobile and stationary source hot spot (Tier 1). Supplement the saturation monitoring program with daily integrated and continuous monitoring during two two-week intensives during summer (mid-August to early September) 2006 and fall (November) 2006 to provide additional data for comparison with fine-scale modeling results (Tier 2). Sampling locations for tier 1 and 2 measurements will be selected in consultation with ARB staff and with input from the community of Wilmington.

Tier 1 measurements consist of the Ogawa passive samplers for O_3, NO_2 and NOx and SO_2, Radiello diffusive samplers for speciated VOC and carbonyl compounds, and low-volume particle samplers for gravimetric mass and light absorption. Samples will be collected over a sampling period of 7 days at twenty sites for four consecutive weeks during each of four seasons with the exception of ozone, which will be measured during two seasons only. Tier 1 measurements and the number of samples that will be analyzed are summarized in Table 1. All samples will be collected on a weekly schedule starting on the same day.

Tier 1 measurements represent the base saturation monitoring program and address the first two project objectives in Section 1.3. The actual sampling locations will be specified in the operational plan for the saturation monitoring, which will be prepared and submitted as part of Task 2. Site selections will be based on the following rationale and criteria, which will be refined in the operational plan.

- One sampling site will be located in eight separate census tracts within the Wilmington area to provide cumulative exposure data with comparable spatial resolution to the community-level socioeconomic status data that will be collected in a separate study by Pastor et al. (2004). Two of these sampling sites will have collocated samplers to provide

data on measurement precision. These sampling locations will be selected to represent neighborhood scale exposure levels. Therefore these sites should not be located near emission sources that could cause higher exposure microenvironment.

- In contrast to the first set of sampling sites, measurements are also needed to determine the magnitude and spatial extent of the pollutant concentrations that are associated with the hotspots and to determine their importance compared to regional background levels. Three pairs of sampling sites will be located at mobile source hotspots. One site will be at the roadway while the other will located at a downwind location within 200 km from the roadway. Four sampling sites will be located at stationary source hotspots. The mobile sampling data obtained by UCLA will be used to identify candidate hotspot sampling locations.

Tier 2 measurements address the third project objective (see Section 1.3) to collect data with sufficient spatial and temporal resolution to allow comparison with fine-scale modeling results, especially near emission hotspots. Tier 2 measurements will be conducted during two-week periods during the summer 2006 and fall 2006 seasons. Tier 2 will supplement the Tier 1 network with the daily integrated PM and VOC sampling at eight sites using Airmetric mini-vol and Solid Phase Microextraction (SPME) fiber samplers, respectively. SPME devices will be used as a time-weighted average (TWA) sampler for gas-phase analytes including BTEX, by retracting the coated fiber a known distance into its needle housing during the sampling period. The method does not require solvent extraction and the fiber samples will be analyzed in the field, using a portable gas chromatograph with photoionization detector by thermal desorption. Tier 2 measurements will include continuous measurements at four sites using Portable CO monitors (Langan T15 and TSI 8854), RAE Systems Model PGM-7240 (ppbRAE) portable PID monitors, and TSI DustTrak nephelometers. These measurements will be made at and near mobile source hotspot locations. The Tier 2 measurements and the numbers of samples that will be collected and analyzed are summarized in Table 1.

Tier 2 measurements will also include measurements of odor-causing sulfide compounds using silicosteel canisters. Twenty samples will be collected over a maximum period of six hours at locations to be determined in consultation with ARB staff and the Wilmington community.

Tier 2 measurements will be coordinated with the deployment of UCLA's mobile sampling van. DRI's data will provide temporal resolution continuously over a two-week period at eight locations that will be selected to provide a coarse resolution in the spatial gradients from emission hotspots. UCLA's data will provide highly resolved spatial data, but for relatively short time intervals. The complementary nature of the two data sets can be enhanced by coordinating measurement times and locations between the two projects.

2.1.4 Task 4 – Data Analysis and Reporting

Compile the results of the Phase 1 Laboratory Evaluations and Phase 2 Pilot Study and compare the accuracy precision and validity of passive measurement methods compared to traditional monitoring methods. Quantify significant measurement biases due to variations in environmental conditions such as temperature and relative humidity. Perform level 1 and 2 validations of the data collected during the Phase 3 saturation monitoring and estimate the measurement uncertainties associated with each measured value. Provide a validated database of concentration measurements for selected pollutants in the form compatible with the database

that will be compiled by Pastor et al. study and for use in evaluating the results of fine-scale modeling. Perform analysis of the assembled data to test each of the study hypotheses in Section 1.2.

The data validation process consists of procedures that identify deviations from measurement assumptions and procedures. We will apply the following tests to evaluate the internal, spatial, temporal, and physical consistency of each data set and identify invalid data and outliers. DRI will compile the data perform the following validation checks.

- Determine the bias among the following collocated measurements during the pilot study at the North Long Beach monitoring station.

  - Four each of the following portable analyzers - CO, PID and DustTrak PM

  - Passive NO, NOx, SO2 with SCAQMD analyzers.

  - Passive BTEX with canister measurements.

  - Passive HCHO with DNPH cartridges

  - Gravimetric mass from personal aerosol sampler and Airmetric mini-vol with DustTrak and SCAQMD PM_{10} TEOM

  - Black carbon concentrations estimated from light absorption measurements of the Teflon filters from the personal aerosol sampler and Airmetric mini-vol with the DRI photoacoustic instrument.

- Derive summary statistics (mean, maximum, standard deviation) for all species, sort the concentrations and note any unusually high or low concentrations.

- Compare Tier 1 passive measurements of O_3, NO, NOx and SO_2 with time-integrated averages of the corresponding data from nearby SCAQMD monitoring stations (e.g., North Long Beach). Determine degree of correlation using scatterplots and seasonal time-series.

- Compare seasonal variations and ranges in concentration of the Tier 1 passive measurements of BTEX and formaldehyde with data from the air toxic monitoring at North Long Beach and the Long Beach/Wilmington MATES-III sampling site.

- Compare the gravimetric mass measurements form the low-volume aerosol samples with averages of the Tier 2 daily Airmetrics mini-vol samples.

Following compilation and validation of the database, we will perform descriptive and statistical analysis to address the following hypotheses.

1. Passive monitor methods can be used to measure cumulative exposures to selected pollutants over a time period of a week with comparable sensitivity and precision as data obtained by conventional monitoring methods that are averaged over the same period.

2. There are gradients in pollutant concentrations within Wilmington that results in measurable variations in cumulative exposures that can be related to proximity to emissions from either stationary or mobile sources.

3. Seasonal variations in transport related to changes in meteorology affect the pattern and magnitude of cumulative exposures.

4. The existing air quality monitoring in Wilmington is not adequate to characterize the spatial variations in cumulative exposure within the community.

5. Magnitude of light absorption is correlated to proximity to truck traffic and day-of-week variations in diesel truck traffic volume.

DRI will prepare and submit separate interim reports that summarize the results of the laboratory evaluation and pilot study. Quarterly progress report will be submitted after initiation of the saturation monitoring. At the conclusion of the field study and data analysis, DRI will prepare manuscript(s) for submission to peer reviewed scientific journals and a draft report. We will make necessary revision in response to comments from the ARB and submit the final report. The schedule for the various deliverables is indicated in Section 3.

2.1.5 Task 5 – Planning, Coordination, and Field Management of the Wilmington Air Toxics Monitoring Study

In addition to the saturation monitoring study described in Tasks 1-4, the ARB expects to fund the following research studies as part of the Wilmington air toxics monitoring study.

- Characterization of pollution concentrations and concentration gradient using a mobile measurement platform.

- Determination of the community-scale spatial variations of ultrafine particles.

- Characterization of the relationship between indoor and outdoor PM concentrations.

It is anticipated that separate research groups will be funded to carry out the major components of the study. In addition, on-going monitoring effort by the South Coast Air Quality Management District and ARB will provide additional relevant data. Close coordination of the conceptual, operational, quality assurance and data management aspects of the various study components will be needed to ensure that the study objectives are met to the fullest extent possible. This task addresses a need in the Wilmington Air Toxics Monitoring Study for a comprehensive study plan, coordination and documentation of field operations, quality assurance, data validation, and an overall summary of study findings and conclusions. This planning and coordination tasks will involve the following subtasks.

TASK 5a: Preparation of the Study Plan Volume 1 - Conceptual Plan

1. Update current bibliography, and review and summarize relevant literature.

2. Review available emission inventory data and characterize the spatial and temporal variations in pollutant emissions from mobile, stationary and area sources. Identify potential hot spots in emissions of PM and toxics air contaminants.

3. Review and summarize available data on relevant speciation profiles for major sources of PM and air toxics.

4. Review existing air quality data for the Wilmington area and characterize the spatial and temporal (diurnal and seasonal) variations in ambient concentrations of PM and toxic air contaminants.

5. Characterize the average diurnal variations by season in the meteorological conditions in Wilmington that may affect local transport and dispersion of pollutants.

6. Review results of past modeling and data analysis of the cumulative exposures to PM and TACs in the Wilmington area.

7. Base on items 1-5, develop a preliminary conceptual model of the spatial and temporal variations in the exposure to PM and TAC in the Wilmington area.

8. Meeting with ARB staff in Sacramento to discuss the components and objectives of the Wilmington Study within two weeks of contract initiation.

9. Prepare a concise statement of the problem in context with relevant past measurement and modeling efforts and the objectives of the new ARB study.

10. Formulate specific questions to be answered by the field measurement program based on the technical objectives and hypotheses to be address in each of the major components of the Wilmington Air Toxics Monitoring Study. List measurement methods and the analyses that are planned for each study component. Specify measurement times, frequencies, and durations. Relate each measurement to its intended use in a modeling and/or data analysis activity.

11. Compile a list of existing monitoring resources (air quality and meteorology) that will be available during the study to support study objectives.

12. Identify and characterize the limitation of the Wilmington Air Toxics Monitoring Study as currently proposed with respect to the study objectives. Consider the need for additional air quality and meteorology data beyond those that are currently planned to support alternative modeling and data analysis approaches.

13. Create a schedule of milestones for execution of the field measurement program.

14. Submit a draft study plan within two months after initiation of the contract.

15. Meet with the Air Resources Board staff within two weeks after submitting draft conceptual study plan to discuss the draft report and the operational details of the study.

16. Finalize the study plan and submit report in PDF format within two week of receipt of comments.

TASK 5b: Preparation of the Study Plan Volume 2 - Operational Plan

The second volume study plan is the operational plan (Volume II). This plan represents the design for the field measurement program and specifies the details which will allow the study plan to be executed.

1. Summarize the experimental approach and technical objectives.

2. Assemble information on existing and new sampling sites, including site identification codes, site names, site addresses, coordinates, and elevations. Create maps of existing network and proposed supplemental measurement sites.

3. Evaluate measurement methods with respect to needed averaging times, detection limits, accuracy, precision, and cost-effectiveness.

4. Compile specifications for accuracy, precision, validity and completeness (i.e., data recovery and extent of chemical speciation) of field measurements.

5. Identify opportunities for collection of collocated data among the research groups that could be used in Level 2 data validation. These comparisons could include the measurement of same parameter with the same or comparable method or related parameters that are known to correlate systematically with each other.

6. Specify variable-naming conventions, units, formats, and file-naming conventions for data to be submitted by investigators.

7. Specify the elements needed for data management which will facilitate the receipt, tracking, organization, and dissemination of data acquired in this project.

8. Update the schedule of milestones and create a critical path diagram (Gantt Chart) showing which operational tasks must be completed prior to undertaking other operational tasks and the identity of groups responsible for each task.

9. Submit a draft operational plan within five months from approval of the conceptual program plan.

10. Submit the final operational plan.

TASK 5c: Coordination and Field Management Support

The most important aspects of the field management effort are field operations protocol, siting, communications, oversight of measurements and QA activities, and documentation of measurements and activities. Key elements of this task include:

1. Organize and conduct a one-day workshop in early May, 2006 in Sacramento with ARB and SCAQMD staff, measurement contractors, and other study participants to orient them to the elements in the plan. Review the draft field operations protocol with the project team, and reconcile any discrepancies between the protocol and measurements planned by study participants. Confirm schedules and protocols, and identify potential logistical problems and develop appropriate action plans for their resolution.

2. Coordinate the efforts of measurement groups during the field study. This includes monitoring their accomplishments against the milestones in the program plan, identifying impediments to attaining those milestones, and creating liaisons among project participants to remove those impediments.

3. Provide coordination, as necessary, with the South Coast Air Quality Management District, and other stakeholders such as the Wilmington Community.

4. Coordinate collocated measurements that are made among study participants for the purposes of data validation. Ensure that appropriate QA/QC plan protocols are in place. Confirm that the planned quality assurance program is implemented, measurement plans are followed, and corrective action is taken immediately as problems arise.

5. Retrieve and archive relevant meteorological data during the field study.

TASK5d: Data Validation and Management

1. Review measurement comparison data and provide level 2 validation of selected data sets.

2. If the participants are willing, DRI will compile relevant data sets into a relational database for use in data analysis and to support of model evaluations of by ARB, EPA and others.

TASK 5e: Project Report

1. Submit quarterly progress report on study activities during the field study and subsequent data validation and analysis.

2. Upon completion of the field study, prepare and submit a draft report summarizing the field monitoring activities and meteorological conditions during each intensive study period and describe the data sets that are available from each study participant. Include a summary of the major findings and conclusions of the study with respect to each study objective.

3. Incorporate comments on the draft report and submit the final report.

2.2   Methods

2.2.1   Passive Sampling and Analysis Methods

Ogawa Passive Sampling Systems (Rupprecht and Patashnick Co., Inc.) will be used for monitoring O_3, NO_2, NOx and SO_2. O_3, NO_2, NOx and SO_2 will be collected over weeklong periods using precoated 14.5 mm sampling pads, deployed in personal sampling bodies. NO concentrations will be calculated by subtracting NO_2 from NOx concentrations. Sampling and analysis will be performed according to manufacturer protocols (Ogawa & Co., USA, Inc., http://www.rpco.com/assets/lit/lit03/amb3300_00312_protocolno.pdf). Briefly, the Ogawa NO_2 and NOx pads will be extracted and mixed with a solution of sulfanilamide and N-(1-Naphthyl)-ethylenediamine dihydrochoride to produce a colored nitrite solution which will be analyzed on a Technicon (Tarrytown, NY) TRAACS 800 Automated Colorimetric System (AC). The Ogawa SO_2 pads will be extracted in 8 ml of deionized-distilled water (DDW), 1.75% hydrogen peroxide will be added and sulfate will be measured with the Dionex 2020i (Sunnyvale, CA) ion chromatograph (IC). The filters for ozone are coated with a nitrite-based solution. Ozone oxidizes the nitrite to nitrate. After exposure, the filter is extracted with ultrapure water and the filter extract is analyzed by ion chromatography to determine the nitrate ion concentration, which is used to calculate the total amount of ozone collected. These analyses will be performed by the Environmental Analysis Facility (EAF) of DRI. Detailed SOPs for these analytical methods are available upon request.

Radiello diffusive samplers will be used for passive sampling of benzene, toluene, ethylbenzene, xylenes (BTEX) and possibly 1,3-butadiene (if quantitative measurement of this compound is confirmed during laboratory evaluations). VOC will be collected over weeklong periods using stainless steel net cylinders (3x8 um mesh, 4.8 mm diameter x 60 mm length) packed with Carbograph 4 (350 mg) and deployed in the diffusive sampling bodies, according to the manufacturer instruction (http://www.rediello.com). The Radiello diffusive sampling cartridges will be analyzed by the thermal desorption-cryogenic preconcentration method, followed by quantification of individual hydrocarbons with high resolution gas chromatography/mass spectrometry (GC/MS) method. The Chrompack Thermal Desorption-Cold Trap Injection (TCT) unit (Chrompack International BV) interfaced to Hewlett Packard

5890 II GC with 5979 MSD will be used for sample desorption and cryogenic preconcentration. Once thermally desorbed, the adsorbent is reusable after baking.

We will also used Radiello diffusive samplers to passively collect carbonyl compounds. A stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated florisil (Code 165) will be used. Carbonyl compounds react with 2,4-DNPH forming corresponding 2,3-dinitrophenylhydrazones. The hydrazones are extracted and analyzed by HPLC with UV detection (Waters 2690 Alliance System with 996 Photodiode Array Detector).

The VOC and carbonyl compound analyses will be performed by the Organic Analytical Laboratory (OAL) of DRI. The detailed SOPs for these methods are available upon request.

2.2.2 Personal Environmental Monitor for Particle Sampling

Personal Environmental Monitors (PEMs) from MSP Corporation (or from SKC, Inc.) will be used for particle sampling for up to one week sampling periods. This small, light-weight personal sampler consists of a single-stage impactor followed by a 37 mm filter to collect aerosol particles that can be analyzed gravimetrically for mass and optically for black carbon. The impactors of D50 diameters of 2.5 and 10 um are available for PM2.5 or PM10 sampling and flow rates of 2, 4 or 10 L/min can be specified. We will use 2.5 um impactor and 2 L/min sampling rate. We will equip the samplers with a 10w solar panel to enable sampling with a small pump over one-week long sampling period.

Gravimetric Analysis

Unexposed and exposed Teflon-membrane filters are equilibrated at a temperature of 20 ±5 °C and a relative humidity of 30±5% for a minimum of 24 hours prior to weighing. Weighing is performed on a Sartorius SE2 electro microbalance with ±0.0001 mg sensitivity. The charge on each filter is neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance is calibrated with a 20 mg Class M weight and the tare is set prior to weighing each batch of filters. After every 10 filters are weighed, the calibration and tare are re-checked. If the results of these performance tests deviate from specifications by more than ±5 mg, the balance is re-calibrated. If the difference exceeds ±15 mg, the balance is recalibrated and the previous 10 samples are re-weighed. At least 30% of the weights are checked by an independent technician and samples are re-weighed if these check-weights do not agree with the original weights within ±0.015 mg. Pre- and post-weights, check weights, and re-weights (if required) are recorded on data sheets as well as being directly entered into a data base via an RS232 connection. All PM2.5 and PM10 Teflon filters will be analyzed for mass. All weights are entered by filter number into the DRI aerosol data base.

Light Absorption

Light transmission through the Teflon filter will be measured using a Tobias TBX-10 Densitometer. This instrument is used to measure optical density (O.D.):

$$O.D. = \log_{10} (-1/T)$$

where T = light transmitted through a particle filter. The instrument is adjusted so T = 1.0 (O.D. = 0.0) when no filter is present. The O.D. measurement (no units) are converted to babs values (units of 1/Mm) by:

$$b_{abs} = \frac{(2.303)(ODfinal - ODinitial)(10^6)}{pathlength}$$

where

$$pathlength = \frac{sample\ volume\ (m^3)}{deposit\ area\ (m^2)}$$

The two above equations may be combined as:

$$b_{abs} = \frac{(2.3.3)(OD_f - OD_i)(deposit\ area\ in\ cm^2)(10^2)}{sample\ volume\ in\ m^3}$$

Light absorbing carbon concentrations can be estimated from b_{abs} by dividing the absorption efficiency factor (typically 10 m²/g) of black carbon. This factor will be evaluated by comparison with the black carbon concentrations measured by the photoacoustic instrument during the pilot study.

2.2.3 Time-Integrated Air Sample Collection and Analysis

VOC by collection in canisters followed by analysis by EPA Method TO-15.

Prior to sampling, the canisters will be cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six repeatable cycles of evacuation to ~0.5 mm Hg absolute pressure, followed by pressurization with ultra-high-purity (UHP) humid zero air to ~20 psig are used. The differences between the DRI procedure and the EPA recommended method are that, in the DRI method, canisters are heated to 140°C during the vacuum cycle and more cycles of pressure and vacuum are used. According to our experience and that of others (Rasmussen, personal communication), heating is essential to achieve the desired canister cleanliness. At the end of the cleaning procedure, one canister out of 12 in a lot is filled with humidified UHP zero air and analyzed by the gas chromatograph/flame ionization detection (GC/FID) method. The canisters are considered clean if the total non-methane organic compound (NMOC) concentration is less than 20 ppbC. The actual concentrations of blank-check canisters are typically below 10 ppbC.

Canister samples will be analyzed for speciated VOC concentrations promptly upon receipt of samples from the field, using gas chromatography with mass spectrometric detection (GC/MS) according to the EPA Method TO-15. Briefly, an Entech 7100 preconcentrator is used for sample collection and concentration, and a Varian 3800 gas chromatograph interfaced to a Varian Saturn 2000 ion trap mass spectrometer is used for sample analysis. Calibration of the system is conducted with a VOC mixture (purchased from AiR Environmental) that contained the most commonly found hydrocarbons (including BTEX and 1,3-butadiene).

Blanks will be performed once daily, while performance standards will be executed three times per week. Our analysis plan and data processing standards call for the replicate analysis of approximately 10% of the samples. For canisters the replicate analysis is conducted at least 24 hours after the initial analysis to allow re-equilibration of the compounds within the canister. The replicate analyses are flagged in our database and the programs we have for data processing extract these replicates and determine a replicate precision. Replicate analysis is important

because it provides us with a continuous check on all aspects of each analysis, and indicates problems with the analysis before they become significant. A detailed SOP is available upon request.

BTEX by SPME Sampling followed by Thermal Desorption GC/PID Analysis.

Solid Phase Microextraction (SPME) is a passive method, thus the rate of the fiber uptake is controlled by the diffusion rate of the analytes to the fiber. SPME devices will be used as a time-weighted average (TWA) sampler for gas-phase analytes including BTEX, by retracting the coated fiber a known distance into its needle housing during the sampling period (Martos and Pawliszyn 1999).   75 μm Carboxen/poly(dimethylsiloxane) (CAR/PDMS) fibers will be used for 24-hour BTEX sampling. Prior to sampling, the pre-cleaned fibers will be kept at ambient temperature with an activated charcoal protector. This storage method has been tested in the laboratory and we have not seen any increases in the BTEX background up to 48 hours of storage following cleaning (the longest tested period). After sampling, fibers are kept in sealed Mylar bags inside a cooler with dry ice. Samples are run after an average of 4-10 hours post-sampling, with a minimum of 1 hour and a maximum of 20 hours between sampling and analysis.

All SPME samples are analyzed in a mobile laboratory with a Model 8610C SRI Instruments GC equipped with a heated injection port suitable for SPME desorption and a CP-Sil 5 (Varian, Inc.) capillary column (60m, 0.32mm i.d.) and a PID. The heated flash vaporization injector is maintained at 250 C and PID at 150 C. The column temperature program was 60°C for 2 min, 8 C/min to 165 C and held for 1 min, and then 45 C/min to 240 C and held for 2 min. Helium carrier gas flow rate was 3 ml/min.

Blanks and calibration checks are performed daily on the SRI GC in order to determine the performance of the instrument and quality of the data. Fibers are kept in the injector port throughout the sample run to guarantee that the entire sample was desorbed and to begin the conditioning of the fiber. In addition, fibers are cleaned in a fiber conditioner at 300 C for at least one hour. One fiber per batch of 5 is checked for purity after conditioning. The fiber conditioner consisted of a 70 cm x 16 cm stainless steel box with 5 ports machined to fit the needle size and a Watlow heater/temperature controller capable of maintaining the temperature in the 200-300 C range. A helium flow of approximately 10 ml/min is maintained during fiber conditioning. Testing showed that the same fiber can be subsequently reused up to 40 times for collecting additional samples, unless breakage of the fiber or failure of the mechanism occurs.

SRI GC is calibrated with 1 μl injection of liquid standards prepared in pentane with BTEX at different concentrations (1, 5, 10, 20, 40, 50, and 100 ng/μl). Carboxen/PDMS fibers are calibrated by introducing the SPME for a defined time to a standard gas containing the calibration component, which loads a known mass of standard onto the fiber. The fiber is then introduced to the analytical instrument for calibration. SPME gas calibrations are done initially and throughout the study when necessary. BTEX calibration is performed with certified gas standards at different concentrations (20, 80, 100 and/or 200 ppbv for each compound).

We will test the formaldehyde passive collection method using poly(dimethylsiloxane)/ divinylbenzene (PDMS/DVB) fibers impregnated with a derivatizing agent, *O*-(2,3,4,5,6-

pentafluorobenzyl)-hydroxylamine (PFBHA) hydrochloride (Martos and Pawliszyn, 1999). After exposure, the fibers will be analyzed by GC/PID, as described above.

Carbonyl compounds.

Formaldehyde and acetaldehyde will be collected with Sep-Pak cartridges which have been impregnated with an acidified 2,4-dinitrophenylhydrazine (DNPH) reagent (Waters, Inc), according to the EPA Method TO-11A. When ambient air is drawn through the cartridge, carbonyls in the air sample are captured by reacting with DNPH to form hydrazones, which are separated and quantified using HPLC in the laboratory (Fung and Grosjean, 1981). Depending on the type of sorbent (C18, or silica gel, (Si)) in the cartridge, the ambient measurement results are subject to various artifacts due to interaction with ozone, thus the ozone denuder is recommended for sample collection. After sampling, the cartridges will be eluted with acetonitrile. An aliquot of the eluent will be transferred into a 1-ml septum vial and injected with an autosampler into a high performance liquid chromatograph (Waters 2690 Alliance System with 996 Photodiode Array Detector) for separation and quantitation of the hydrazones (Fung and Grosjean 1981). The same method will be used to analyze the Radiello diffusive carbonyl samples. A detailed SOP is available upon request.

Sulfide compounds.

Silicosteel canisters will be used to collect odor causing reduced sulfur compounds (e.g., hydrogen sulfide, carbonyl sulfide, and carbon disulfide) and analyzed by gas chromatography with mass spectrometry. Reduced sulfur compounds are associated with wastewater treatment, petroleum refining, landfills and composting activities. Many sulfur compounds are not stable in steel canisters and must be collected in either Tedlar bags or canisted lined with non-reactive glass-like substances. Due to the unstable and reactive nature of many sulfur compounds, sample will be collected for a maximum of 6 hours and shipped the same day back to DRI's laboratory and analyzed the following day.

2.2.4 Continuous Measurements

Carbon Monoxide. CO will be monitored continuously by a TSI Model 8854 CO_2/CO monitor. This portable, passive sampling instrument has a resolution of 0.1 ppm and accuracy of 3% or 3 ppm from 0 to 500 ppm for CO. The instrument records CO, temperature and RH at intervals from 1 sec to 1 hour. Changes in ambient temperature can results in calibration shifts of up to 0.5 % per degree C. The temperature dependence of the CO monitor will be evaluated along with the passive monitors during phase 1. In addition, a similar portable, battery-powered passive electrochemical unit (Langan T15) will be also used. CO will also be monitored continuously using an NDIR instrument at the Long Beach monitoring station during the phase 2 pilot study.

NO/NOx. Nitric oxide (NO) is continuously measured by the chemiluminescence nitric oxide-ozone method (OCM). This method is based on the gas-phase chemical reaction of NO with ozone. In this method an ambient air is mixed with a high concentration of ozone so that any NO in the air sample will react and thereby produce light. The light intensity is measured with a photomultiplier and converted into an electronic signal that is proportional to the NO concentration. To measure NOx concentrations, the sum of NO and NO_2 (nitrogen dioxide), the air sample is first reduced to NO, either by a heated catalyst (molybdenum or gold in the presence of CO) or chemically using $FeSO_4$, adding to the NO already present in the sample,

then into the reaction chamber for measurement as described above. The NO_2 concentration is derived by subtracting the NO concentration measurement from the NOx concentration measurements. Standard sensitivity instruments have detection limits of about 0.5 to 3 ppb (60 sec averaging times) and are suitable for air quality monitoring in urban and suburban areas.

<u>$PM_{2.5}$ Mass.</u>

Nephelometers measure light scattered by aerosol introduced into their sample chamber. Nephelometers can be fairly simple and compact instruments with excellent sensitivity and time resolution. The TSI DustTrak nephelometer (DT) monitors forward light scattering that is interpreted as PM mass. The DustTrak Aerosol Monitor is a portable, battery-operated, laser-photometer that measures 90° light scattering (different from the total light scattering measured by an integrating nephelometer) and reports it as PM mass concentration. The laser diode used by the DustTrak has a wavelength of 780 nm, which limits the smallest detectable particle to about 0.1 μm. The reported PM mass concentration is factory-calibrated using the respirable fraction of an Arizona Road Dust standard (ISO 12103-1, A1). The mass scattering efficiency depends on particle shapes, size distribution, and composition (index of refraction). The ISO 12103–1, A1 standard consists of primarily silica particles (70%) that are provided with some particle size specifications. By volume, the standard consists of 1–3% particles with diameter less than 1 μm, 36–44% with diameter less than 4 μm, 83–88% with diameter less than 7 μm, and 97–100% with diameter less than 10 μm. This standard contains a larger quantity of coarse (>2.5 μm) particles than are usually found in ambient aerosol. $PM_{2.5}$ has a higher mass scattering efficiency, so the DustTrak overestimates $PM_{2.5}$ for smaller, chain aggregate soot particles (20). During the Gasoline/Diesel PM Split Study, the DustTrak was found to exceed gravimetric mass concentrations of the mobile ambient samples by a factor of 2.24 with an R^2 of 0.75.

<u>Photoacoustic Black Carbon Analyzer.</u>

The photoacoustic instrument has been developed at DRI and has been described in several publications (Arnott, Moosmüller et al. 1999; Arnott, Moosmüller et al. 2000). Briefly, light from a 1047 nm laser is power-modulated at the operating frequency of an acoustical resonator. Sample air is continuously drawn through the resonator at a flow rate of 1 – 3 lpm. Light absorbing aerosol (black carbon) will absorb some of the laser power, slightly heating the aerosol (typically much less than 1 C). The heat transfers very rapidly from the aerosol to the surrounding air, and the local pressure increases, contributing to the standing acoustic wave in the resonator. The acoustic wave is measured with a microphone as a measure of the light absorption. For the operating conditions of the resonator, and the laser wavelength used, the light absorption measurement is linearly proportional to the mass concentration of the black carbon aerosol in the sample air. The constant of proportionality has been inferred from correlations of black carbon measurements with elemental carbon as determined by the TOR method, and an efficiency factor of 5 square meters per gram is used to go from aerosol light absorption to estimated black carbon mass concentration. No filters are needed for the photoacoustic measurement, and the flow rate is not used in the calculation of aerosol mass concentration. The flow rate must only be sufficient to adequately sample the air with minimal particle loss in the instrument and sample lines. The resolution of the instrument for a 3 second averaging time is usually 2.5 inverse Mm for light absorption, corresponding to 0.5 microgram per cubic meter for black carbon mass concentration. The resolution scales as the square root of sampling time, so for example, a resolution of 0.25 micrograms per cubic meter can be obtained for a 9 second averaging time. The photoacoustic measurement does not receive interference from exhaust

gases, in our experience so far, and it is a zero-based measurement when no light absorbing aerosols are present.

Portable PID Monitor for estimates of total VOC.

A RAE Systems Model PGM-7240 (ppbRAE) portable PID monitor will be used to continuously monitor ambient VOC levels. The monitor is equipped with a 10.6 eV photoionization (PID) detector and responds to certain organic and inorganic gases that have an ionization potential of less than 10.6 eV, which includes aromatic hydrocarbons, olefins, and higher molecular weight alkanes. It does not respond to light hydrocarbons such as methane, ethane, and propane or to acetylene, formaldehyde or methanol. The monitor has < 5-second response and lower detection limit of 1 ppb. Because the total response of the PID depends upon the specific mix of VOC's, the response must be calibrated to the expected mix of VOC. Isobutylene is the calibration gas and the PID response can be adjusted to one of several specific VOC species or a standard mixtures of VOC such as gasoline. We have develop empirical relationships between the PID response to urban air and the sum of VOC species from the canister VOC data.

Kore MS-200 Portable Mass Spectrometer.

This portable, battery-operated converging, annular, time-of-flight (CAT) mass spectrometer is produced by Kore (England). It is not equipped with a GC; sample gases are drawn through a heated inlet system by a pump and enter the CAT source via membrane assembly. Typical analysis time is under one minute, and the membrane assembly allows a ppb sample detection limit to be achieved for many compounds.

Temperature and RH Sensors.

A Dickson TK500 will be used to monitor temperature and RH at up to twelve of the passive monitoring sites. The sensor has a range of -20 to 70 C and 0 to 95% RH with an accuracy of ± 1 C and ± 2% RH at 25 C. Averaging time can be adjusted to 10 sec to 24 hours. The sensor can store 7936 data points (330 days @ 1 hour average) and has a battery life of approximately 1 year.

2.3 Desert Research Institute Facilities

2.3.1 DRI, Division of Atmospheric Sciences, Organic Analytical Laboratory Facility (OAL)

This laboratory established and directed by Dr. Barbara Zielinska since 1989, is equipped with state-of-the-art instrumentation providing a full range of analytical capabilities for identifying and quantifying trace organic contaminants in ambient air, including particulate, volatile and semi-volatile organic compounds and hazardous air pollutants. The organic laboratory operations, quality assurance, data management and validation (both level 1 and univariate level 2) are integrated into an interactive process that occurs through the field measurement and analytical programs. To achieve this integration, the software has been developed to automate the data processing and reporting functions. The laboratory also designs and fabricates air samplers to meet varying project needs using components time-tested for reliability, durability, and cleanliness.

The instrumentation includes:

- Horiba-Kore MS-200 continuous mass spectrometer. Ely, Cambridgeshire, UK

- Varian 3400 GC with Entech 7100 preconcentrator and Model 7016CA canister autosampler. Walnut Creek, CA and Simi Valley, CA

- Shimadzu GC-17A with Methanizer MTN-1 for CO/CO_2 analysis capability by reduction of CO and CO_2 to methane and analysis by FID. Columbia, MD

- Two Hewlett-Packard 5890 Series II gas chromatographs (GC) equipped with flame ionization detectors (FID) and one with electron capture detector (ECD). Palo Alto, CA

- Cryogenic trap for injection of gaseous samples from stainless steel canister or sampling bags. Palo Alto, CA

- Varian Galaxie chromatographic data acquisition system, capable of collecting data from four different GC detectors simultaneously. The software performs data acquisition, peak integration and identification, hardcopy output, post-run calculations, calibrations, and user program interfacing. Walnut Creek, CA

Solid Adsorbent Samples Analysis

- Integrated high resolution gas chromatograph/Fourier transform infrared detector/mass spectrometer detector (Hewlett-Packard 5890 GC, 5965 IRD and 5970B MSD), equipped with Chrompack CP4020 Thermal Desorption Cold Trap Injector (TCT) unit (Chrompack International BV) used for desorption of samples collected on solid adsorbent cartridges, cold trapping, and injection onto a capillary column. This unit can operate either with GC/FID or GC/IRD/MSD systems.   This instrument can be used as a GC/MSD or as an integrated GC/IRD/MSD unit. The HP GC/IRD/MSD system includes both the MS/IR ChemStation, each with its own software. The IRD ChemStation can combine the GC/MSD data with GC/IRD data in a single report. The NIST Mass Spectral Library includes over 43,000 mass spectra and the EPA IR Library includes over 5000 IR spectra.   Both libraries can be quickly and easily searched and an integrated MS and IR search is also available. Palo Alto, CA

- Chrompack Thermal Desorption Cold Trap Injector (TCT) unit (Chrompack International BV) used for desorption of samples collected on solid adsorbent cartridges, cold trapping, and injection onto a capillary column. This unit can operate either with GC/FID or GC/IRD/MSD systems. Palo Alto, CA

Carbonyls Analysis

- Waters high performance liquid chromatograph (HPLC) equipped with Waters 2695 Alliance separation module, Waters 996 Photodiode Array Detector and Empower chromatography software. Milford, MA

SVOC Analysis

- Varian 1200 triple quadrupole gas chromatograph/mass spectrometer (GC/MS/MS) system with CP-8400 autosampler and Varian Workstation 6.20. Walnut Creek, CA

- Two Varian Saturn 2000 Ion Trap MS systems coupled to Varian CP-3800 GC, with MS/MS and chemical ionization capabilities. One system is equipped with 8200CX Automatic sampler

and the other with a CP-8400 autosampler for liquid injections. An Entech 7100 preconcentrator can be added for VOC analysis. Saturn Workstation 5.52 chromatography software. Walnut Creek, CA

- Waters high performance liquid chromatograph (HPLC), equipped with two Waters 501 high-precision pumps, Waters 484 variable wavelength UV detector, Waters system interface module (SIM), Waters busSAT/IN Module, Manual Waters Fraction Collector II Injector controlled by Empower chromatography software. Milford, MA

Extraction Equipment

- Dionex ASE 300 Accelerated Solvent Extractor automated system for extracting organic compounds from solid or semi-solid samples by using solvent at elevated temperatures and pressure to maintain solvent's liquid state during extraction. Salt Lake City, UT

- Set of Soxhlet apparatus of different capacities and dedicated glassware for sample and substrate preparations.

- CEM MSD 1000 microwave extraction system. Matthew, NC

- RE-111A Büchi Rotavapor rotary evaporation systems. Zurich, Switzerland

Other Equipment

- Alpha-Omega continuous formaldehyde analyzer (modified by DRI). Albuquerque, NM

- Shimadzu fluorescence detector for HPLC or stand-alone fluorimetry of liquid samples. Columbia, MD

- EG&G Model 384B Polarographic Analyzer system for voltammetric analysis of a variety of organic and inorganic species.

- Set of standards including NIST SRM and NIST-traceable materials. Gaithersburg, MD

Laboratory computers/data processing computers are linked using a TCP/IP ethernet computer network protected from the Internet by a secure firewall system. Data processing equipment includes pentium4 and other windows based computers as well as a Windows-NT based file server with RAID protected disk drives.

Standard operating procedures, quality control performance tests, and inter-laboratory comparisons have been established for laboratory analyses. All data are maintained in database format with applicable uncertainty for each value, and data tables are produced automatically using standard report formats that are designed for each project. The laboratory maintains and develops a broad range of sampling equipment for atmospheric collection of gaseous and particulate-phase organic species. The laboratory also functions in a research mode to develop new analytical methods and to evaluate existing methods.

The DRI Organic Analytical Laboratory (OAL) participated in the International Hydrocarbon Intercomparison Experiment, organized by National Center for Atmospheric Research (NCAR). The results of Tasks I, II, and III of this intercomparison have been published (Apel et al., 1994; 1999). The first task involved the circulation of a two-component hydrocarbon mixture of known composition and unknown concentration, prepared by NIST. The DRI values were within the acceptable range of 5% of the nominal values provided by

NIST. In task II the participating laboratories were asked to identify and quantify 16 components present, in the ppb range, in a mixture prepared by NIST. The agreement between the DRI values and the NCAR values, as well as with nominal values provided by NIST, were within acceptable ranges (15%). Task III was more complex - it involved the analysis of 60 commonly observed hydrocarbons in low ppbv concentrations in a mixture prepared and analyzed by Scott-Marrin, Inc., NCAR and U.S. EPA laboratory. The next tasks, IV and V, which were carried out in 1996 -1997, involved the analysis of ambient air samples in the ppbv and pptv concentration ranges, respectively. The DRI has successfully completed these tasks — the agreement between the DRI values and the NCAR values were within acceptable ranges (10%).

In the summers of 1995 and 1996 the DRI OAL participated in the NARSTO-Northeast hydrocarbon intercomparison study, involving the analysis of two ambient air samples by participating laboratories. Participants included Biospheric Research Corporation (BRC), State University of New York at Albany (SUNYA), EPA Region I, DRI, and 8 of the PAMS networks in the northeastern U.S. The DRI laboratory performed the best in comparison with all other participants (Fujita et al., 1997). In the summer of 1997, the DRI OAL participated in the SCOS97-NARSTO performance audit and laboratory comparisons involving speciated non-methane hydrocarbons (NMHC), carbonyl compounds, halogenated compounds and biogenic hydrocarbons (Fujita et al., 2003).

During the last six years, the DRI laboratory participated in non-methane hydrocarbon laboratory performance audits, organized by the Quality Assurance Section, Monitoring and Laboratory Division, CARB. The last intercomparison studies, organized in 1999-2002, involved the analysis of ambient air samples by California district laboratories and the DRI laboratory.

2.3.2 DRI, Division of Atmospheric Sciences, Environmental Analysis Laboratory (EAF)

This laboratory, established and directed by Dr. Judith C. Chow since 1985, is equipped with state-of-the-art instrumentation providing a full range of analytical capabilities for identifying and quantifying trace amounts of inorganic substances in addition to carbon fractions in gaseous, particulate, and liquid (wet deposition) air pollution samples collected in containers and on filters. EAF prepares and tests sampling substrates under low contamination conditions to minimize dynamic and field blank levels to obtain the best Lower Quantifiable Limits possible. Positive-pressure, filtered air by high-efficiency particle arresting (HEPA) filters in each laboratory area minimizes contamination, which is further controlled by sample handling in laminar flow hoods. Temperature and relative humidity are controlled for filter equilibration and gravimetric analysis. Standard operating procedures (SOPs), quality control (QC) performance tests, and inter-laboratory comparisons have been established for analyses of mass, carbon fractions, elements, and ions. Data processing and data validation procedures and software have been established that integrate field records, and conduct blank subtraction and error propagation. EAF is supported by eight professional research scientists, six laboratory technicians, two administrative assistants and six hourly staff who are usually students on one of the University of Nevada campuses.

The EAF Laboratory includes: 1) sample preparation, 2) gravimetric and light transmission analysis; 3) carbon measurements, 4) ionic measurements, and 5) elemental measurements. Relevant instrumentation for each laboratory is listed as follows:

Sample Preparation Laboratory

- Two Millipore distilled-deionized water systems capable of producing 100 gallons per day. (Billerica, MA)

- Lindberg 51894 Moldatherm box furnace. (Watertown, WI)

- Five Pure Air Corporation eight-foot laminar flow hoods. (Canoga Park, CA)

- Labconco Corp. Model 77500 4.5L benchtop freeze dryer, Lyph-Lock freeze dry system. (Kansas City, MO)

- Two Branson Model 5200 sonicators. (Danbury, CT)

- One Cole-Parmer Model 51401-00 sample shaker (Vernon Hills, IL)

- Dynac 0101 centrifuge. (Parsippany, NJ)

- CEM Mars 5 Laboratory microwave. (Matthews, NC)

- VWR Model 1410 vacuum oven. (Brisbane, CA)

- Environmental Express hot block digestor (Ventura, CA)

- Two 8' x 14' walk-in freezers, seven upright freezers and nine upright refrigerators.

Gravimetric and Light Transmission (b_{abs}) Laboratory

- Two Mettler MT-5 microbalances (Hightstown, NJ)

- Cahn 33 electrobalance. (Cerritos, CA)

- Sartorius R160D analytical balance. (Edgewood, NY)

- Two Mettler AE200 analytical balances. (Hightstown, NJ)

- Mettler PJ6000 electronic pan balance. (Hightstown, NJ)

- Two Tobias and Associates transmission densitometers adapted for the measurement of particle light transmission on filter media. (Ivyland, NJ)

Carbon Laboratory

- Five DRI/OGC thermal/optical carbon analyzers. (Reno, NV)

- Six DRI Model 2001 thermal/optical carbon analyzers (Atmoslytic Inc., Calabasas, CA) using both reflectance and transmittance analysis and pyrolysis correction.

- Model 6890N Gas Chromatography (GC)/5973 Mass Spectrometer (MS) Detector/NIST O2 MS library (Agilent Technology, Foster City, CA)

- Curie Point Pyrolyzer, Model JHP-3/3S (Japan Analytical Industry Co., Ltd, Tokyo, Japan)

Wet Chemistry Laboratory

- Two Dionex Model 500 Ion Chromatographs with AS 40 autosamplers. (Sunnyvale, CA)

- Astoria 302A Colorimetry System with a 301A autosampler. (Astoria, OR)

- Varian Spectro880 atomic absorption spectrophotometer with an SP5 autosampler. (Walnut Creek, CA)
- YSI Model 32 Conductivity Meter. (Yellow Springs, OH)
- Orion 720A pH meter. (Cole-Parmer, Vernon Hills, VA)
- Various specific ion electrodes.
- Brinkmann 702 SM Titrino Automated Titrator for pH and Karl Fischer analysis. (Burlingame, CA)
- Integrated Air System, Inc., 6-foot sterile bench. (Minneapolis, MN)
- Elemental Analysis Laboratory:
- Kevex 0700/8000 energy dispersive x-ray fluorescence spectrometer. (Santa Clara, CA)
- Panalytical Epsilon 5 energy dispersive XRF spectrometer. (Almedo, NL)
- Thermoelectron X Series ICP-MS with a New Wave Laser Ablation connection. (Madison, WI)
- Leitz Ortholux binocular microscope. (Munich, Germany)

3.   SCHEDULE AND DELIVERABLES

The following schedule assumes a contract initiation date of January 1, 2006 and receipt of comments on progress reports within two weeks following submittal and comments on the draft final report within six months following submittal. It further assumes that the field study will begin in August, 2006 and be completed within one year. The proposed schedule is summarized in Figure 1. The following list summarizes the key deliverables in chronological order for the saturation monitoring project and coordination for the Wilmington Study.

Saturation Monitoring

- Phase 1 interim report on results of laboratory evaluations of passive monitoring methods, including operational plan for the pilot study evaluation of methods at Long Beach. Plan will include protocols for evaluation of candidate monitoring methods and procedure and criteria for evaluating acceptability. (4/21/06).
- Phase 2 interim report on results of the field evaluations of candidate methods during the pilot study in Long Beach and an operational plan for the saturation monitoring study in Wilmington.
- Deliver saturation monitoring database. Final study database will be submitted in a format that is compatible with SES data modeling needs, which will be determined in consultation with the ARB and CEC. (December 2007)
- Submit quarterly progress report on study activities during the field study and subsequent data validation and analysis. Reports will be submitted on the first Monday of each quarter starting with 10/2/06 (total of six quarterly progress reports).
- Submit draft final report (1/30/08)
- Submit final report (9/30/06 or one month after receipt of comments on draft).

Wilmington Study Coordination
- Meeting with ARB staff in Sacramento (second week of January 2006).
- Submit draft conceptual study plan (2/28/06 or two months after contract initiation).
- Meeting with ARB staff in Sacramento (within three weeks of submitting the draft conceptual plan)
- Submit final conceptual study plan (4/31/05 or two weeks after receipt of comments on draft).
- Submit draft operational study plan (~ 6/15/06).
- Submit final operational study plan (~8/15/06 or two weeks after receipt of comments on draft).
- Pre-Study Workshop in the Los Angeles area (July 2006)
- Deliver final study database (December 2007)
- Submit quarterly progress report on study activities during the field study and subsequent data validation and analysis. Reports will be submitted on the first Monday of each quarter starting with 10/2/06 (total of six quarterly progress reports).
- Submit draft final report (3/30/08)
- Submit final report (11/30/06 or one month after receipt of comments on draft).

Figure 1. Proposed Schedule.

Activities	First Year 1	2	3	4	5	6	7	8	9	10	11	12	Second Year 1	2	3	4	5	6	7	8	9	10	11	12	Third Year 1	2	3	4	5	6	7	8	9	10	11	12
Phase 1: Laboratory Evaluations																																				
Setup and testing of chamber	█																																			
Exposure experiments		█																																		
Laboratory analysis		█	█																																	
Data compilation and analysis			█	█																																
Interim report - phase 1				▒																																
Phase 2: Pilot Study																																				
Preparation			█	█																																
Field sampling					█																															
Survey of potential sampling locations					█	█																														
Laboratory Analysis					█	█																														
Data compilation and analysis					█	█																														
Preparation of Operation Plan and QAPP				█	█	█	█																													
Interim report - phase 2							▒																													
Phase 3: Saturation Monitoring																																				
Preparation							█	█																												
Installation								█																												
Tier 1 sampling								█	█	█	█		█	█	█	█																				
Tier 2 sampling								█	█				█	█																						
Laboratory Analysis								█	█	█	█	█	█	█	█	█	█	█																		
Data compilation and validation									█	█	█	█	█	█	█	█	█	█	█	█																
Data analysis									█	█	█	█	█	█	█	█	█	█	█	█	█	█	█													
Quarterly reports									▒		▒		▒		▒		▒																			
Draft Final Report																									D											
Review and comments from ARB																										█	█	█	█	█						
Revision of Draft Final Report																																█	█			
Submission of Final Report																																	F			
Task5 Wilmington Study Coordination																																				
Meetings with ARB Staff	█		█																																	
Conceptual Plan		D		F																																
Operational Plan					D		F																													
Pre-Study Workshop in Los Angeles							█																													
Quarterly progress reports									▒		▒		▒		▒		▒		▒																	
Deliver final study database																								█												
Report																									D										F	

D – draft; F – final.

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4. PROJECT MANAGEMENT PLAN, EXPERIENCE AND FACILITIES

4.1 Key Personnel

Dr. Eric M. Fujita, Research Professor at the DRI, will be the Principal Investigator for this project. He will prepare the project study plan and QAPP, direct the field measurements and provide coordination between the field measurement program and analysis of the samples by DRI's Organic Analytical Laboratory and Environmental Analysis Facility, and lead the data analysis effort. Dr. Fujita has over 24 years of experience in managing and conducting air quality studies. He is the principal author of the field study plans for the 2000 Central California Ozone Study and 1997 Southern California Ozone Study (SCOS97-NARSTO). His research interests include chemical characterization of emission sources, reconciliation of emission inventory estimates for VOC and PM with ambient measurements, and measurement and characterization of exposure to toxic air contaminants. Dr. Fujita performed source apportionment analysis of fine particles in Colorado's Northern Front Range, California's South Coast Air Basin and San Francisco Bay Area, Phoenix, and Bangkok Thailand. Current research includes quantifying the relative contribution of gasoline and diesel exhaust to ambient PM and measuring on-road, near-road, and ambient exposures to air toxic from mobile vehicles. Dr. Fujita also performed volatile organic compound source apportionment studies for the 1987 Southern California Air Quality Study (SCAQS), 1990 San Joaquin Valley Air Quality Study (SJVAQS), 1993 Coastal Oxidant Assessment for Southeast Texas (COAST), 1995 Boston and Los Angeles Study, 1996 Phoenix Ozone Study, NARSTO-Northeast 1995 Summer Ozone Study, 1995/96 Washington Ozone Transport Study, 1996 El Paso/Juarez Ozone Study, and 1998 Central Texas On-Road Hydrocarbon Study. He has conducting similar studies in Houston and Mexicali, Mexico. Dr. Fujita also coordinated laboratory comparisons of VOC measurements during the SCOS97-NARTSO, COAST and NARSTO-Northeast ozone studies.

Dr. Barbara Zielinska, Research Professor at the DRI, will be the Co-Principal Investigator for this project. Dr. Zielinska will take the lead in conducting the laboratory evaluations and laboratory analysis of passive samples for organic species. She will be assisted by a graduate student who will devote much of the dissertation research to this project. Dr. Zielinska is the Director of the Organic Analytical Laboratory at DRI and has over twenty years of experience in the collection and analysis of trace atmospheric organic compounds, and in the instrumental analytical methods to be used in the proposed work. She will be responsible for the chemical analysis of all samples. Prior to coming to DRI she was an Associate Research Chemist for the Statewide Air Pollution Research Center, University of California, Riverside. Her current primary areas of interest include collection and analysis of trace atmospheric organic species present in both the gas and particle phases; development of analytical methods for identifying biologically active compounds in primary and secondary particulate organic matter; kinetics and products of gas-phase reactions of organics; measurement methods for volatile and semi-volatile compounds in ambient air; ozone precursors; particle-associated and volatile organic compound emissions from various sources, including diesel- and gasoline-powered vehicles, wood combustion and meat cooking.

Dr. John Sagebiel Assistant Research Professor at DRI, has extensive experience in sampling and analysis of trace organic gases and particulate matter and in collection of motor vehicle emission samples. He will make the GC/MS measurements for BTEX during the laboratory

evaluation. Prior to coming to DRI, Dr. Sagebiel conducted research at the Department of Environmental Toxicology, UC Davis. His work included sampling and analysis of trace organic species, primarily pesticides, in water, soil, air and fog. Since coming to DRI in 1992, Dr. Sagebiel has focused on issues related to mobile sources, and on analysis of ozone precursors and hazardous air pollutants in ambient air. Dr. Sagebiel has a Ph.D. in agricultural and environmental chemistry from the University of California, Davis.

David E. Campbell is an Assistant Research Scientist whose current research interests are the characterization and apportionment of gaseous and aerosol pollutants from mobile sources, and the influence of mobile source contributions on photochemical processes. He will have primary responsibility for field operations during the pilot study and during the saturation monitoring program. Research activities prior to joining DRI included monitoring and analysis of visibility reducing particles for the NPS/IMPROVE program. Mr. Campbell is experienced in the validation and analysis of large data sets using database, spreadsheet, and GIS. He is also familiar with all commonly used methods for collection and characterization of ambient aerosols. For 13 years Mr. Campbell worked for the primary contractor responsible for IMPROVE program sample collection and data analysis (Crocker Nuclear Lab, UC Davis). His duties included aerosol sampler design, testing, construction, installation, auditing and maintenance; gravimetric, elemental, and optical analysis of filter samples; development and application of quality control procedures; analysis of historical data for quality assurance. In addition, he participated in the evaluation of the Federal Reference Method PM2.5 samplers used by EPA's PM2.5 speciation network.

Full CVs are available at the DRI web site at http://www.dri.edu/.

4.2   Relevant Experience of Project Team

The proposed research team combines capability and expertise in chemical characterization of stationary and mobile source emissions, ambient and personal exposure monitoring and assessment and chemical analysis. Relevant current and recently completed studies by the project team include the following.

▪ Exposure to Air Toxics in Mobile Source Dominated Microenvironments sponsored by the Health Effects Institute (1/04 to 6/06). The study focuses on in-cabin exposure of commuters and residents living near major roadways in California's South Coast Air Basin. Desert Research Institute conducted the summer phase of the measurement program during September 2004 and fall-winter phase during November and December 2004. Measurements included acetaldehyde, acrolein, benzene, 1,3-butadiene, ethylbenzene, formaldehyde, n-hexane, MTBE, naphthalene, styrene, toluene and xylene and speciated particulate and semi-volatile organic aerosols. Continuous measurements of PM, black carbon, CO, CO_2, NOx, VOC, and particle size distributions were made in a mobile sampling van to characterize spatial gradients in air pollutant concentrations. The exposure measurements will be compared to the annual and seasonal average concentrations derived from the Multiple Air Toxics Exposure Study–III (MATES–III), which is being conducted by the South Coast Air Quality Management District (SCAQMD) from February 2004 to March 2005.

- Analysis of Samples Collected During MATES III for Organic Tracers. In 1986, the South Coast Air Quality Management District conducted the first basin-wide study to determine exposure levels and risks associated with toxics air contaminants. This initial study of ten toxic air contaminants was followed by a second study in 1998 of 40 toxic air contaminants. The third study in this series, Multiple Air Toxics Exposure Study–III (MATES-III), is currently underway and calls for a one-year sampling program for air toxics. The objective of MATES-III is to characterize the ambient air toxic concentrations and potential exposures in the South Coast Air Basin (SoCAB). In addition, the project will develop an updated toxics emission inventory and conduct air dispersion modeling to estimate ambient levels and potential health risks of air toxics. The results of MATES-III will determine the spatial concentration pattern of important hazardous air pollutants in the Basin, assess the effectiveness of current air toxic control measures, provide trend data of air toxic levels, and be used to update and develop appropriate control strategies for reducing exposures to toxics associated with significant public health risk. OAL will be conducting the analysis of organic compounds on the MATES-III PM2.5 filter samples to provide additional data that may be used to characterize certain sources contributing to ambient particulate matter.

- Section 211(b) Tier 2 High-End Exposure Screening Study of Baseline and Oxygenated Gasoline sponsored by the American Petroleum Institute (1/02 to 12/05). In this study, the Desert Research Institute and Southwest Research Institute are conducting a study of the upper-end distribution of inhalation exposures to evaporative and combustion emissions of baseline- and oxygenated gasoline. First, DRI and SwRI conducted exposure measurements under controlled conditions to establish quantitative relationships between tailpipe and evaporative emission rates to exposure levels in vehicle cabin and attached residential garage. In the main study, exposures levels are being measured in several high-end exposure microenvironments in Atlanta, Chicago, and Houston during winter and summer conditions. A number of key variables (including CO, BTEX, formaldehyde, 1,3-butadiene, MTBE, ethanol) are measured in ambient air within microenvironments, in subjects' personal breathing zones and breath.

- Atmospheric Transformations of Diesel Emissions (funded by the Health Effects Institute). The overall objective of this study is to investigate photochemical transformations of diesel emissions in the atmosphere. The specific aims are: (1) to characterize the gas- and particle-phase products of atmospheric transformations of diesel emissions under the influence of sunlight, ozone, hydroxyl radicals, and nitrate radicals (in the dark); and (2) to explore the changes in biological activity of diesel exhaust before and after the atmospheric transformations take place. The project is being executed with the aid of the EUPHORE simulation chamber in Valencia, Spain, which is currently the largest (~200 m3) and best-equipped outdoor simulation chamber in the world, allowing investigation of atmospheric transformation processes under realistic ambient conditions (dilution in the range of 1:300).

- Roseville Railyard Air Monitoring Project (RRAMP) sponsored by the Placer County Air Pollution Control District in cooperation with the Union Pacific Railroad (UPRR), Sacramento Metro AQMD, and USEPA Region IX. The purpose of the project is to monitor for diesel locomotive emissions at the UPRR's J.R. Davis Rail Yard, located in Roseville, CA. The main monitoring segment of the study is scheduled to occur in the summer months when persistent wind conditions favorable to upwind/downwind monitoring are most reliable. Using upwind/downwind monitoring, PCAPCD expects to detect differences

between upwind and downwind measurements that are attributable to the emissions at the railyard. However, for this approach to be successful, there needs to be a screening assessment of conditions primarily in the downwind area to assure that the downwind site location is not too close to the facility (such that the emissions plume stays aloft and does not impact the site) or too far from the facility (such that the dilution of the plume renders the plume signal undetectable). DRI conducted surveys of the spatial variations in pollutant concentrations around the Rail Yard. This information will be used by PCAPCD to select appropriate upwind and downwind monitoring locations for the RRAMP.

- The Gasoline/Diesel PM Split Study sponsored by U.S. Department of Energy (4/01 to 12/04). This study assesses the sources of uncertainties in quantifying the relative contributions of tailpipe emissions from gasoline-powered motor vehicles and diesel-powered motor vehicles to the ambient $PM_{2.5}$ in the urbanized region of Southern California using an organic compound-based chemical mass balance receptor model. As part of this collaborative study, Bevilacqua-Knight, Inc. with the U.S. EPA and West Virginia University conducted dynamometer tests of 59 light-duty vehicles (including 2 diesel vehicles) and 34 heavy-duty diesel trucks, respectively. Researchers from Desert Research Institute and University of Wisconsin Madison collected and chemically analyzed the source samples in parallel and worked independently on chemical analysis and data analysis. Chemical analysis of source samples consisted of gravimetric mass, elements, ions, organic and elemental carbon, polycyclic aromatic hydrocarbons, hopanes, steranes, alkanes, and polar organic compounds. Volatile air toxics were also determined for light-duty vehicles tests.

- Characterizing Exhaust Emissions From Light-Duty Gasoline Vehicles In The Kansas City Metropolitan Area sponsored by U.S. Environmental Protection Agency and consortium of other sponsors (6/04 to 6/06). A research team of Eastern Research Group, Bevilacqua Knight Inc, Desert Research Institute and NuStats Partners L.P. are conducting a program to evaluate exhaust emissions from light-duty gasoline vehicles. The program consists of measuring particulate matter (PM) and other toxic components in exhaust emissions of 480 randomly selected, light-duty vehicles in the Kansas City Metropolitan Area. Data obtained from this program will be used to evaluate and update existing and future mobile source emission models, evaluate existing emission inventories and assess the representativeness of previous PM emissions studies.

- Air Quality Monitoring Program for the Port of Los Angeles Port of Los Angeles Study – subcontract to SAIC. Deployment of mini-volume samplers in the port area to characterize the impact of particulate emission from port operations.

- Refinery Source Sampling (1998-2002). The characterization of volatile and particle-associated organic compounds emitted from stationary petroleum industry sources was carried out in collaboration with GE Energy and Environmental Research Corporation. Tests were performed on refinery combustion sources, including steam boilers, process heaters, and fluid catalytic cracking and catalytic reforming processes units, using both conventional source sampling methods and a dilution sampling approach (England et al., 2000).

5.   BUDGET

The total amount of the contact is $475,451 as detailed in the accompanying budget proposal. The budget for the saturation monitoring component of the study provides for following trips to Los Angeles.

Travel

Travel Expenses - See Note	Rate	Task 1- Pilot Study		Task 2 - Tier 1		Task 2 - Tier 2		Task 4		Total	
		No of units	Amount	Unita	Amount	Units	Amount	Units	Amount	Units	Amount
Destination: Los Angeles, CA											
Airfare	250	2	500	16	4000	4	$ 1,000			22	$ 5,500
Gasoline (rental) $/mi	0.12	1600	192	3000	$ 360	1500	$ 180		$ 250	1500	$ 982
Parking											
Misc											
Per Diem	$ 151.00	24	$ 3,624	64	$ 9,664	56	$ 8,456			0	$ 21,744
Car Rental	$ 40.00	16	$ 640	32	$ 1,280	32	$ 1,280			4	$ 3,200
Total Travel			$ 4,956		$ 15,304		$ 10,916		$ 250		$ 31,426

Note: Assume researchers will drive to Los Angeles, CA from Reno, NV using mobile lab.

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