Core C:
Engineering

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ABSTRACT – Engineering Core (Core C)

The Engineering Core will support the Center by supplying the technologies required to conduct the proposed studies. The objectives of the Engineering Core will be to support the five projects of the proposed Center by: i) providing sampling and monitoring devices required for characterizing the spatial and temporal variability of pollutants within the study Region; ii) providing technology for generating and delivering inhalation exposures to animals; and iii) conducting sampling and analysis of particulate and gaseous pollutants.

Project 1: The Core will generate the test atmospheres for the animal exposure studies by integrating our ambient fine particle concentrator with the photochemical chamber and parallel plate membrane denuder developed for the TERESA studies. The exposures generated will include components of the Boston, MA, air pollution mixture both separately and in combination. These components will include CAPs, secondary gases, photochemically aged CAPs and secondary PM formed from ambient gases. In addition, the Core will be responsible for characterization of the animal exposures including: (i) integrated measurements of PM_{2.5}, elemental carbon (EC) and organic carbon (OC), sulfate (SO_{4}^{2-}), water soluble OC, trace elements, formaldehyde, acetaldehyde and VOCs; and (ii) continuous monitoring for PM_{2.5}, black carbon (BC), particle size distribution, particle number (PN), O_3, CO, and NO_x.

Projects 2-5: The Core will conduct ambient monitoring, to characterize the spatial and temporal variability of particle and gaseous air pollutants within the study Region. To characterize the temporal variability of air pollution, the Core will operate the Boston HSPH Supersite. Measurements at the Supersite will include continuous and integrated PM_{10}, PM_{2.5}, PM_{2.5-10}, BC, EC/OC, SO_{4}^{2-} and NO_3^- . Additionally, continuous measurements will be conducted for PN, O_3, SO_2, NO_x, NO_2, and CO. To characterize the spatial variability of air pollutants within the study Region, the Core will operate a spatial network that will include a total of 40 outdoor monitoring sites. Monitoring will use one month durations, for each of four seasons, over a period of 4 years. At all of the spatial monitoring sites, the following pollutants will be measured: PM_{2.5}, BC, EC, OC, trace elements; PM_{10}, O_3, NO_2 and VOCs (benzene, toluene, ethylbenzene, and xylene). For all pollutants except VOCs, we will use the One Month Sampler, which is designed based on the multi-pollutant sampler (MPS) developed previously at HS.
1. OBJECTIVES

Each of the five proposed Projects and the Exposure Core rely upon technologies used to characterize particle and gas air pollution composition and concentrations. In addition, Project 1, the Inhalation Toxicology study, relies upon technologies necessary to generate test atmospheres/mixtures and administer exposures to laboratory animals. This Core will support the Center by supplying all of these technologies, required to for the proposed studies.

The specific objectives of this Core are:

- To provide sampling and monitoring devices required for characterizing the spatial and temporal variability of pollutants within the study Region;
- To conduct sampling and analysis of particle and gaseous air pollutants for all five proposed Projects and the Exposure Core. This includes collection and analysis of the Supersite and the spatial sites samples, and characterization of the animal exposures in Project 1;
- To provide technology for generating and delivering inhalation exposures to animals; and
- To develop, where necessary, technology for sampling and/or monitoring pollutants or generating and/or delivering inhalation exposures to animals.

Some of the methods and technologies to be used by this Core are established or routine, while others are more novel or specialized. Existing technologies will be tailored to the needs of the individual Center Projects and Exposure Core, and new technologies will be developed, as needed. This proposal describes the major initiatives to be accomplished within the Engineering Core.

2. BACKGROUND

Our group has many years of experience conducting studies of air pollution, including indoor, outdoor, and personal exposure sampling and analysis. Over the last three decades the Environmental Chemistry Laboratory of the Department of Environmental Health has been responsible for exposure assessment in support of our epidemiological, toxicological and exposure studies. These efforts have included supporting all particle and gas measurement needs of the current Center.

Some of our key achievements include the development of particle and gas sampling technologies. Our current and previous Harvard EPA Centers have supported and relied upon our development and/or evaluation of many of these systems. Several of our technologies have been licensed and are commercially available worldwide. These novel techniques encompass systems for personal and micro-environmental measurements, as well as systems for exposing humans and animals to source or ambient particles. These technologies have been widely used by our Center and by scientists worldwide, helping to advance our knowledge about the health effects of ambient air pollution. In the proposed Core we will continue such innovative developments while providing essential support for each of the Center's 5 Projects.
The methods to be used by the proposed Center are drawn from 4 broad categories: 1) continuous gas and particle monitoring; 2) integrated gas and particle monitoring; 3) long-term multi-pollutant sampling; and 4) exposure generation and delivery for inhalation toxicology studies in animals. In Section 3 (Approach), we describe these technologies as applied by the individual Center Projects and Cores.

The Engineering Core, through the Environmental Chemistry Laboratory, will support all particle and gas measurement needs of the proposed Center. More specifically, it will conduct: 1) ambient monitoring at the HSPH Boston supersite; 2) ambient monitoring at spatial network monitoring sites throughout the study Region, for the Exposure Core and Normative Aging Study (Project 2), Framingham Heart Study (Project 3), Viva Birth Cohort (Project 4) and the National Study (Project 5) within the study Region. This Core will also generate and deliver exposures for our inhalation toxicology study in animals (Project 1).

3. APPROACH

The Engineering Core will achieve its objectives using a combination of monitoring methods and exposure generation and characterization techniques detailed in the following sections.

3.1. Monitoring: Gaseous and particulate pollutants will be measured intensively at a central Supersite and throughout the study region, using a variety of sampling and analytical methods that will provide both spatial and temporal characterization, as described below.

3.1.1. Boston HSPH Supersite: In support of all five projects and the Exposure Core, we will continue ambient air pollution measurements at the Harvard School of Public Health Boston Supersite. This Supersite is located at the roof of the Countway Library, approximately one mile from downtown Boston. This site meets as best as possible the US EPA site selection criteria for PM sampling. This site is approximately five stories above ground level and at least 50 meters from the nearest street. Traffic on this street is composed primarily of automobiles and the street is not a significant truck route. In addition, the Supersite is not affected by any local point sources. Data from this site have been used for several major Harvard air pollution health effects studies, including those funded by our two previous EPA Centers. The Supersite has been in operation since 1997. [PM sampling was conducted at a previous HSPH site in South Boston during the period 1995-96.] Measurements at this site will include continuous and integrated measurements of ambient PM$_{2.5}$, PM$_{10}$, SO$_4^{2-}$, BC, EC, and OC. Particle Number concentration (PN) will be measured continuously. Concentration data of ambient O$_3$, SO$_2$, NO$_X$, NO$_2$, and CO will be obtained from local and state monitoring sites located in the Greater Boston. All particulate data will be reported in 30-minute intervals, with the exception of EC and OC, which will be reported in 1-hour intervals. The Environmental Chemistry Laboratory at HSPH has standard operating protocols documented for each method.

3.1.1.1 Continuous Monitoring Methods: Continuous PM$_{2.5}$ and PM$_{10}$ will be measured using two (Beta-Attenuation Mass Monitors (BAM 1020, Met One Instruments, Grants Pass, OR), and PM$_{2.5}$ will be measured using a Model 1400A Tapered Element Oscillating Microbalance (TEOM, Thermo-Scientific, Franklin MA) with a PM$_{2.5}$ cyclone placed upstream of the inlet. Because the TEOM sample filter is heated to 50°C, PM$_{2.5}$ concentrations will be corrected to compensate for the loss of semi-volatile mass that occurs at this temperature. Since the
magnitude of this loss is likely to vary by season, season-specific calibration factors will be used to compensate for such losses.\textsuperscript{21,22} The calibration factors will be obtained by regressing the continuous PM\textsubscript{2.5} and PM\textsubscript{10} mass concentrations averaged over 24-hour periods on the corresponding collocated integrated 24-hour PM\textsubscript{2.5} and PM\textsubscript{10} concentrations, measured as described below.

A condensation particle counter (CPC, Model 3022A, TSI Inc.) will be used to measure PN continuously, and reported as particle number per cubic centimeter. Ambient fine $\text{SO}_4^{2-}$ will be measured continuously using the Continuous Sulfate Analyzer recently developed by HSPH and Thermo-Environmental Instruments.\textsuperscript{23} Continuous BC will be measured using a model AE-14 Aethalometer (Magee Scientific Inc., Berkeley CA). Since EC is the predominant light-absorbing component of fine PM, BC is an optical measure comparable to EC measured chemically.\textsuperscript{24-28} Hourly average EC/OC concentrations will be measured using the Carbon Analyzer (Sunset Laboratory, Tigard, OR).

3.1.1.2 Integrated Sampling and Analysis: Daily integrated PM\textsubscript{10} and PM\textsubscript{2.5} samples will be collected on Teflon filters with Harvard Impactors\textsuperscript{29} using a custom-made sequential timing system. Gravimetric measurements will be made using an electronic microbalance (Mettler Model MT5). PM\textsubscript{2.5} filters will subsequently be analyzed for BC using an EEL smoke stain reflectometer (Model 43D by Diffusion Systems Ltd., London, UK) and for trace elements using X-Ray Fluorescence (XRF)\textsuperscript{30} at the Desert Research Institute (Reno, Nevada). Integrated 24-hour EC/OC concentrations will also be measured. Samples will be collected on pre-fired quartz fiber filters and analyzed using Thermal-Optical Reflectance (TOR)\textsuperscript{31} by Desert Research Institute.

3.1.1.3 Other Data: Meteorology data (daily mean temperature, relative humidity, and barometric pressure) will be obtained from the hourly surface observations of the National Weather Service First Order Station at Logan Airport (East Boston) (Earth-Info, Inc., Boulder, CO). Ozone, NO, NO\textsubscript{2}, NO\textsubscript{x}, CO and SO\textsubscript{2} concentrations, along with temperature and relative humidity measurements will be obtained from the Massachusetts Department of Environmental Protection local monitoring sites.

3.1.2 HSPH Multi-pollutant Spatial Monitoring Sites: The spatial network will include 40 outdoor monitoring sites. Site locations will be chosen to allow modeling of pollutant concentrations for the whole region used for Projects 2, 3, 4 and 5. Monitoring will use one-month durations, for each of four seasons, for a period of 4 years, for each site. Specifically, at each of the 40 sites four monthly samples will be collected per year in January, April, July and October. As described in the Exposure Core, spatial sites will be placed in communities within the Region where subjects of the three cohorts reside. Preference in locating spatial monitoring sites will be given to areas within which the greatest numbers of participants in the combined cohorts of Projects 2, 3, 4 and 5 reside.

At the spatial monitoring sites, the following pollutants will be measured: PM\textsubscript{2.5}, BC, EC, OC, trace elemental composition; PM\textsubscript{10}; O\textsubscript{3}, NO\textsubscript{2}, and BTEX (benzene, toluene, ethylbenzene, and xylene) VOCs. For all pollutants except VOCs, we will use the One Month Sampler (Figure 3.1.2), which is designed based on the multi-pollutant sampler (MPS) developed previously at
HSPH has just successfully completed a two-year study in New York City using the MPS with one week durations, and found very reliable performance by the monitoring systems. Teflon membrane filters will be used to collect both PM$_{10}$ and PM$_{2.5}$ at flows of 1.8 LPM; mass concentrations will be determined gravimetrically. Quartz fiber filters for EC-OC will sample at a flow of 0.8 LPM; filters will be analyzed using Thermal Optical Reflectance. Harvard/Ogawa passive samplers will be used to collect O$_3$ and NO$_2$, and samples will be analyzed using ion chromatography. PM$_{2.5}$ Teflon filters will be analyzed first for mass, then for reflectance, and finally by XRF. Carbopak tubes will be used to collect BTEX VOCs passively. These samples will be analyzed using thermal desorption-GC/MS.

**Figure 3.1.2: The One Month Sampler spatial monitor**

To minimize the possibility of exceeding the capacities of the different sampling devices, an electronic time-share unit will be used to cycle the sampling pump for one hour on/four hours off. For a total duration of one month, this will yield a sampling duration equivalent to six days. The five-hour cycle will assure that the one-hour sampling periods are distributed randomly during the entire one-month period. An elapsed-time meter will be used to indicate whether electric power was interrupted for any significant period of time. A simple data logger will be used to determine exactly if and when any power shut-offs occurred. The MPS is designed for continuous operation, so there is a constant flow of sample air through the elutriator (Figure 3.1.2) to provide a stable passive collection rate for gases in the side arms. However, for the One-Month Sampler, the flow is off for 4/5 of the sampling period. Without modification of the MPS design, there would be continuous passive sampling by diffusion of gases into the elutriator tube during the time the pump is off, albeit at a rate lower than that during active (pump-driven) sampling. This would nonetheless confound the results for the one-month passive measurements. Therefore, to restrict passive collection during the pump-off time intervals to a negligible rate, an inert diffusion tube (PFA Teflon) will be attached to the inlet of the elutriator (Figure 3.1.2). Its dimensions were determined based on the diffusion coefficients of the gases, such that the effective sampling rate for gases during pump-off intervals is only 0.06 cc/min, representing only 3% of the total effective passive collection rate (2 cc/min) during the pump-on intervals for the one month integrated sample.
3.2 Exposure Generation Technology: The Core will generate test atmospheres for the animal exposure studies in Project 1 using the technologies described below.

3.2.1 Harvard Fine Particle Concentrator (HFPC): Particle concentrator technology has been a critically important advance in inhalation toxicology studies of PM, because it allows inhalation exposures to real ambient particles at concentrations sufficient for toxicology assessment. No surrogate materials can adequately match ambient particles directly from urban air and inhaled directly by an experimental subject. This technology has been used in numerous studies relating Concentrated Air Particles (CAPs) composition with biological response of exposed subjects.\textsuperscript{40-49} The HFPC, shown schematically in Figure 3.2.1, was developed at Harvard School of Public Health, and has been described in detail in several publications.\textsuperscript{35-39} It consists of a size-selective inlet to remove particles larger than 2.5 µm aerodynamic diameter, followed by a series of three virtual impactors with cutpoint of 0.15 µm. This system enriches the ambient particle mass concentration by a factor of 30 or higher, without significantly distorting the size distribution.

3.2.2 TERESA: Exposures to primary and secondary pollutants from source emissions: The TERESA studies were presented in Project 1. The exposure technology developed for these studies, funded by the current and previous Centers, is a complex system designed to sample source emissions, simulate atmospheric photochemistry, generate an exposure, expose animals, characterize the exposure, and determine biological outcomes. The elements of this exposure system typically include: emissions sampling, dilution, and transport; photochemical reaction simulation to produce secondary particles and gases; parallel plate membrane denuder to eliminate excess gases; animal exposure system; and particle and gas characterization.

Each of the key components of the TERESA exposure system has been adapted for use in studies of different emissions sources. The components that will be required for exposure generation in Project 1 are described below in Sections 3.2.2.1-3. Results from previous TERESA studies of coal power plants and mobile source emissions are summarized in Section 4.1, TERESA Studies Preliminary Results.

3.2.2.1 Photochemical Reaction Simulation System: The purpose of the photochemical reaction system is to simulate transformation of the gases and particles from source emissions into realistic atmospheric mixtures of photochemically aged gases and particles for toxicological studies. For exposures to photochemically aged particles alone without primary and secondary gaseous co-pollutants, these gases are reduced to concentrations that have negligible toxicity using the non-selective diffusion denuder (Section 3.2.2.3). Realistic formation of secondary
particle mass is achieved using a photochemical reaction chamber that irradiates the ambient gases and CAPs with ultraviolet light that is a good representation of ground level solar radiation, in order to accurately simulate tropospheric conditions. In addition, concentrations and characteristics of the ambient gases and CAPs will be measured at both the inlet and outlet of the photochemical chamber, permitting us to determine the degree of photochemical oxidation achieved. We have successfully applied these techniques to the emissions of coal-fired power plants, and adapted them successfully to mobile source emissions in a laboratory pilot study (Preliminary Results, Section 4). Further, our exploratory studies with ambient air have shown that secondary particle matter is formed from typical urban ambient gases as well.

3.2.2.1 Photochemical Reaction Simulation: The presence of NOx and gas phase organics in the chamber will result in generation of the ·OH radical in the chamber through photochemical chain reactions. A simplified generalized mechanism for photochemical smog formation is shown below in Table 3.2. To initiate photochemical smog formation a source of radicals is required. The photolysis of aldehydes is a significant source of free radicals in the atmosphere. The photolysis of HCHO to form CO and 2 HO2· radicals occurs several times faster than the generic photolysis of RCHO to form CO, HO2·, and RO2·. HCHO and CH3CHO are relatively abundant in the atmosphere. The photochemical smog mechanism, whether in a chamber or the atmosphere, eventually results in accumulation of ozone, peroxyacetyl nitrate (PAN) and other PAN-like compounds, as well as secondary organic aerosol.

Table 3.2: Simplified chain reaction mechanism for the formation of photochemical smog

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant (ppm·min @298K)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO2 + hv → NO + O</td>
<td>0.533 min⁻¹</td>
</tr>
<tr>
<td>O + O + M → O3</td>
<td>2.183 E-5</td>
</tr>
<tr>
<td>NO + O3 → NO2 + O2</td>
<td>26.59</td>
</tr>
<tr>
<td>RH + · OH → RO2· + H2O</td>
<td>3.775 E+3</td>
</tr>
<tr>
<td>HCHO + hv → 2 HO2· + CO</td>
<td>1.61 E-3 min⁻¹</td>
</tr>
<tr>
<td>RCHO + · OH → RC(O)O2· + H2O</td>
<td>2.34 E+4</td>
</tr>
<tr>
<td>RCHO + hv → RO2· + HO2· + CO</td>
<td>1.91 E-4 min⁻¹</td>
</tr>
<tr>
<td>HO2· + NO → NO2 + OH·</td>
<td>1.214 E+4</td>
</tr>
<tr>
<td>RO2· + NO → NO2 + RCHO + HO2·</td>
<td>1.127 E+4</td>
</tr>
<tr>
<td>HO2· + HO2· → H2O2 + O2</td>
<td>8.232 E+3</td>
</tr>
<tr>
<td>H2O2 + hv → 2 · OH</td>
<td>5.394 E-4 min⁻¹</td>
</tr>
<tr>
<td>RC(O)O2· + NO → NO2 + RO2· + CO2</td>
<td>1.127 E+4</td>
</tr>
<tr>
<td>· OH + NO2 → HNO3</td>
<td>1.613 E+4</td>
</tr>
<tr>
<td>RC(O)O2· + NO2 → RC(O)O2NO2</td>
<td>6.893 E+3</td>
</tr>
<tr>
<td>RC(O)O2NO2 → RC(O)O2· + NO2</td>
<td>2.143 E-2 min⁻¹</td>
</tr>
<tr>
<td>NO + · OH → HONO</td>
<td>9.996 E+3</td>
</tr>
<tr>
<td>HONO + hv → NO + ·OH</td>
<td>0.096 min⁻¹</td>
</tr>
<tr>
<td>O3 + hv → O2 + O1D</td>
<td>2.74 E-3 min⁻¹</td>
</tr>
<tr>
<td>O1D + H2O → 2 · OH</td>
<td>3.23 E+5</td>
</tr>
<tr>
<td>CO + · OH → CO2 + HO2·</td>
<td>3.234 E+2</td>
</tr>
</tbody>
</table>

*Adapted from Seinfeld, 1986; Demerjian, 1980; Finlayson-Pitts and Pitts, 1986

3.2.2.1.2 Secondary Organic Aerosol (SOA) formation: Formation of SOA is a two-step process involving oxidation and partitioning. SOA can account for the majority of the organic aerosol mass in urban areas. Photochemical chamber studies of individual compounds indicate that the typical aerosol yields from aromatic compounds (e.g., toluene, xylene, trimethylbenzene) are low, on the order of 5-10% of reactive organic gases. However, atmospheric source
apportionment studies\textsuperscript{57-60} and chamber studies with actual source emissions\textsuperscript{53,61,62} indicate that the yields may be significantly larger, due to the combinations of semivolatile and intermediate-volatility organic compounds.

SOA is formed by photochemical oxidation of unsaturated hydrocarbons, mostly from parent compounds with at least 7 carbons (if cyclic). The cyclic aromatic compounds form SOA mostly via ring-fragmenting reactions with \textit{·}OH radicals. The photochemical oxidation of toluene\textsuperscript{63} is a good example of the ring-fragmenting mechanism:

As hydrocarbons become more oxidized and more polar, they tend to become less volatile and increasingly partition to the particle phase, both by condensation and nucleation. In addition, though the yield of SOA from ambient air may be relatively small, we also expect that the particle-phase organics may also be altered in the reaction chamber as in the atmosphere. This is especially true for the PAHs, which may form various oxy- and nitro-PAH derivatives.\textsuperscript{64}

3.2.2.2 Parallel Plate Membrane Denuder: We developed this novel non-selective diffusion denuder for use in the TERESA coal power plant study to reduce the concentrations of unreacted combustion gases to acceptable exposure levels, while allowing particles to pass virtually unchanged.\textsuperscript{65} When we adapted the TERESA approach to vehicular emissions in a highway tunnel, the denuder also served to reduce the concentrations of secondary gases formed in the chamber (such as O\textsubscript{3}, HCHO, PAN, etc.) permitting us to generate animal exposures to particles without interference from gaseous co-pollutants. The parallel plate membrane denuder consists of three channels, separated by two microporous PTFE Teflon membranes. Output from the photochemical chamber is passed through the inner channel, while clean air is passed in counter-flow fashion through the two outer channels. Gas molecules diffuse through the microporous membranes into the outer channels following the concentration gradient, while particles remain in the inner channel. The denuder can be used to provide removal efficiencies as high as 90-95%. A schematic of the denuder is shown below in Figure 3.2.2.2:
3.3 Generation of Exposure Mixtures for Project 1: The exposure generation plan for this project is presented schematically in Figure 4 below. The schematic shows all the elements described in the previous sections of the Core. The following is a brief summary of the exposure mixtures and how they will be generated (described in detail in Project 1, Sections 2.2-2.4).

In Project 1 we will expose animals to controlled mixtures of several basic components: CAPs, photochemically aged CAPs, secondary PM, ambient gases, secondary gases, and O₃. The following mixtures will be generated:

- **CAPs.** This mixture contains both CAPs and ambient air, and will be generated using the Harvard Fine Particle Concentrator (HFPC).

- **Photochemically aged CAPs with secondary gases.** The output of the HFPC will flow into the photochemical chamber where it will be photochemically aged and secondary PM and gases formed.

- **Photochemically aged CAPs and secondary PM without secondary gases.** The output of the HFPC will flow into the photochemical chamber where it will be photochemically aged and secondary PM and gases formed. The output of the photochemical chamber will then pass through the denuder to remove the secondary gases.

- **Photochemically aged CAPs with O₃.** The output of the HFPC will flow into the photochemical chamber where it will be photochemically aged and secondary PM and gases formed. The output of the photochemical chamber will then pass through the denuder to remove the secondary gases. O₃ will be added to achieve concentrations observed in mixtures that contain the secondary gases.

- **Secondary gases.** The output of the HFPC will flow into the photochemical chamber where it will be photochemically aged and secondary PM and gases formed. The output of the photochemical chamber will be filtered to remove the photochemically aged CAPs and secondary PM, leaving the secondary gases.
3.4 Exposure Characterization: A variety of continuous and integrated methods will be used to characterize the exposures generated, and are listed briefly here. Many of these methods are described in more detail in Section 3.1 above. Particle and gas exposures will be characterized using continuous measurements of particle mass (TEOM), size distribution (APS, SMPS), BC (Aethalometer), particle count (CPC), CO, NO, NOx and O₃, along with integrated measurement of particle mass (gravimetric), sulfate (Ion Chromatography), trace elements (X-Ray Fluorescence), EC/OC (Thermal/Optical Reflectance), water soluble OC, and formaldehyde and acetaldehyde (HPLC).

Sampling will be conducted at four locations, as shown in Figure 3.3, above: (1) concentrator inlet (ambient air); (2) concentrator outlet/photochemical chamber inlet; and (3) outlet of the photochemical chamber (aged emissions), and (4) at the point of exposure. Measurements at the first two locations will be used to assess the mass enrichment factor achieved by the HFPC. Monitoring of gas concentrations, particle mass and size distribution at the second and third locations will assess the performance of the photochemical chamber. Measurements at the fourth sampling location will be used to characterize exposure atmospheres.

4. PRELIMINARY RESULTS

4.1 TERESA Studies: To date, we have used the Toxicological Evaluation of Realistic Emission Source Aerosols methods in studies of both coal-fired power plants and mobile source emissions. These two applications of this approach have required different configurations and presented different technical challenges, reflecting the adaptability of the methodology and flexibility of our research team, which we anticipate will continue to provide innovative solutions in the proposed studies. These are described in the following sections:
4.1.1 Coal Power Plant TERESA: The TERESA technologies and approach were used successfully in field studies at three coal fired power plants with distinctly different emission controls, resulting in distinctly different pollutant concentrations. During these studies, we accomplished the following: 1) optimization of stack sampling methods to prevent condensation and particle loss from the hot, humid primary emissions; 2) development of a photochemical chamber that produced sufficient aged aerosol (secondary sulfate) for animal exposures and characterization, yet compact enough to fit within a small mobile laboratory;\textsuperscript{20,66} 3) development and validation of denuder technology to remove excess gaseous components from the exposure atmosphere;\textsuperscript{20,66} and 4) development of a state-of-the-art mobile toxicology laboratory.

The results from two scenarios, the primary and photochemically oxidized primary emissions (primary particles plus secondary sulfate), for all three power plants are presented below in Table 4.1.1. The primary emissions at each plant had very different concentrations of sulfur dioxide, nitric oxide, ratios of sulfur dioxide to nitric oxide, and primary particle mass and number concentrations. Even though each plant had different emission controls, our systems produced secondary particle mass concentrations suitable for inhalation toxicology studies.

<table>
<thead>
<tr>
<th>Species</th>
<th>Upper Midwest Plant</th>
<th>Southeast Plant</th>
<th>Midwest Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary particles\textsuperscript{a}</td>
<td>2.3 (2.6)</td>
<td>69.5 (10.4)</td>
<td>1.9 (1.3)</td>
</tr>
<tr>
<td>Primary particles plus secondary sulfate</td>
<td>69.5 (10.4)</td>
<td>1.9 (1.3)</td>
<td>224.3 (53.3)</td>
</tr>
<tr>
<td>Particle Count (#/cm\textsuperscript{3})</td>
<td>1,726 (1,277)</td>
<td>6,723 (3,550)</td>
<td>910 (964)</td>
</tr>
<tr>
<td>Total Sulfate (\mu g/m\textsuperscript{3})</td>
<td>0.2 (0.3)</td>
<td>36.1 (7.7)</td>
<td>0 (0)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} N=3; for all others, N=4

Preliminary biological outcome results for all exposure scenarios from the inhalation toxicology studies performed at all three power plants are summarized in Section 1.3.1.1 of Project 1.

4.2.2 Mobile Source TERESA Study: We have successfully adapted the TERESA approach for use in investigating vehicular emission sources, in a laboratory pilot study using diluted car exhaust, and are starting a field study using diluted fleet vehicular emissions from the ventilation stack of a northeastern highway tunnel. Because automobile exhaust is significantly different in chemical composition and physical characteristics compared to coal power plant emissions, and the reactions involved in its photochemical oxidation are also different, significant adaptations were needed. First, since the power plant emissions were essentially devoid of hydrocarbons, it was necessary to generate the hydroxyl radical for oxidizing the SO\textsubscript{2} to sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) using the photolysis of O\textsubscript{3} at 295nm.\textsuperscript{20,66} In contrast, because automobile exhaust is rich in volatile organic compounds, the ·OH radical, once generated, can be regenerated in
photochemical chain reactions. Second, carbonyl compounds are both contained in primary vehicular emissions and produced by photochemical oxidation of the volatile organics in the exhaust. Therefore, a more accurate spectral recreation of ground level solar radiation is needed, because the carbonyl group can be photolyzed at the short wavelength UV used for oxidation of the coal plant emissions, resulting in reactions that do not take place in the atmosphere.

In addition, for the oxidation of SO2 to H2SO4 in the coal plant emissions, it was necessary to first react most of the NO2 to nitric acid (HNO3), because the NO2 competes with SO2, and the reaction of NO2 with ·OH is many times faster than that of SO2. In contrast, photochemical oxidation of the organic compounds present in vehicular emissions is enhanced by the presence of NO2, which is photolyzed to form NO and ·O, and is a critical component of the reaction mechanism for the generation of photochemical smog (Section 3.2.2).

Also, the concentrations of pollutants in the ventilation stack of the highway tunnel are much lower than those in the coal power plant stack emissions. This means that it is not possible to dilute the output of the photochemical chamber in order to provide sufficient flow for exposure of animals; hence the chamber must be larger.

In order to adapt the TERESA approach to mobile source emissions, we first conducted pilot laboratory studies with diluted automobile exhaust. Tailpipe emissions from a single vehicle running outside the lab with the throttle slightly open were collected and diluted with ambient air to achieve a range of CO concentrations spanning the concentrations measured in the ventilation stack of the selected traffic tunnel. Simulations of photochemical oxidation were conducted using the photochemical chamber developed for the coal plant TERESA study, after replacing the lights with UV-340 fluorescent lamps that better represent the ground-level solar spectrum. The photochemical oxidation of the diluted exhaust followed a fairly typical pattern of conversion of NO to NO2, accumulation of O3, and an initial burst of ultrafine particles, shown in Figure 4.1.2.1 below.
The residence time in the chamber was optimized for the production of secondary PM from the exhaust, as determined by the evolution of the particle size distribution measured using an SMPS, Figure 4.1.2.2:

![Figure 4.1.2.2: The effect of residence time](image)

We also verified that the production of secondary particle mass was consistent. Figure 4.1.2.3 below shows secondary particle mass generated on across days with exhaust diluted to achieve consistent concentration of CO (as a surrogate for organics).

![Figure 4.1.2.3: Consistent SOA formation during 5 repeated experiments](image)
We found that the yield of secondary particle mass was improved when an inert seed aerosol was added (Table 4.1.2), and the stable concentration of secondary PM was achieved more quickly. The seed aerosol was added for three reasons: 1) to approximate the PM concentration expected in the tunnel; 2) to provide sufficient particle surface area to allow rapid aggregation of the freshly generated ultrafine particles, resulting in a stable accumulation mode size distribution; and 3) to make it possible to conduct pilot exposures using Primary and Secondary PM at similar concentrations, in contrast to the coal power plant TERESA studies.

<table>
<thead>
<tr>
<th>Baseline Seed Aerosol Concentration (μg/m³)</th>
<th>CO Concentration (ppm)</th>
<th>Residence Time (min)</th>
<th>Secondary Particle Mass Generated (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>5</td>
<td>50</td>
<td>54.5</td>
</tr>
<tr>
<td>26.0</td>
<td>20</td>
<td>50</td>
<td>108.8</td>
</tr>
<tr>
<td>9.5</td>
<td>5</td>
<td>100</td>
<td>51.5</td>
</tr>
<tr>
<td>12.5</td>
<td>20</td>
<td>100</td>
<td>99.1</td>
</tr>
</tbody>
</table>

After we optimized our technique for the formation of secondary particle mass from the dilute tailpipe emissions of a single car using inert seed aerosol, we conducted pilot exposures using normal male Sprague-Dawley rats. For these exposures, we used Mount St Helen’s Ash (Bates Ridge) as the seed aerosol, because it is chemically and toxicologically inert. Results from these pilot exposures are included in the proposed Project 1, Section 1.3.1.2.

5. GENERAL INFORMATION:

5.1 Expected Results: The Core will provide measurements of concentration and composition for particle and gaseous air pollutants throughout the study Region, in support of all five proposed Projects and the Exposure Core. This includes data required by the Exposure Core to generate the Exposure metrics used in determining the short- and long-term exposures to individual pollutants, sources and pollutant mixtures. The data provided by this Core will be indispensable for enabling the Center to achieve its mission, which is to determine the health effects of individual pollutants, sources, and mixtures across life stages. In addition, the Engineering Core will generate and characterize test atmospheres for the animal exposures in Project 1, further supporting efforts to understand not only the effects of these agents, but also the mechanisms of the biological responses they elicit.

5.2 Facilities: The Supersite funded by the current PM Center is equipped with state-of-the-art instrumentation for continuous measurement of a wide variety of particle and gas air pollutants, as detailed in this proposal. In addition, the Supersite will continue the integrated sampling and analytical methods already in use. The Environmental Chemistry Laboratory at HSPH will perform the ion chromatographic, gravimetric, and reflectometry measurements. The exposure generation technologies to be employed by the Core have been used in projects funded by the current EPA Center, including the Harvard Fine Particle Concentrator, the photochemical chamber and denuder technology.
5.3 Investigators: Dr. Petros Koutrakis will be the PI of the Engineering Core. Dr. Koutrakis has more than 25 years of experience conducting comprehensive air pollution studies in the United States and other countries to investigate the extent of human exposures to gaseous and particulate air pollutants. He has developed novel sampling devices and instruments for measurement and toxicological studies of ambient particles and gases, resulting in 10 patents. He also has extensive experience in administrative oversight of a large team of researchers, and will have prime responsibility for all scientific issues regarding air monitoring for exposure assessment. The Core will be co-directed by Dr. J Mikhail Wolfson. Dr. Wolfson is the manager of the Environmental Chemistry Laboratory and has 34 years of experience in chemical analysis and monitoring technology design and development. He will be directly responsible for overseeing the engineering aspects for the spatial site monitoring, and will assist Dr. Koutrakis in the administration, execution, and oversight of this Core. Dr. Joy Lawrence, a Research Associate in Environmental Health, will be directly responsible for all Core activities in support of Project 1. Dr. Lawrence has over 25 years research experience in air pollution/health studies. She has extensive experience in both technology associated with concentrated air particles (CAPs), and with technology and methods of simulating formation of secondary particles and gases from primary air pollution sources. Dr. Choong-Min Kang, a Research Associate in Environmental Health, will be responsible for continued operation of the HSPH central monitoring site. Dr. Kang has over 20 years experience in air pollution monitoring, including both gases and particles. His responsibilities include systematic oversight of performance of all measuring instruments, continuous and integrated, and inter-instrumental comparisons for further validation and calibration.

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