

ABSTRACT

The objectives of the Particle Technology and Monitoring Core will be to support the five projects of the proposed Center by: i) providing exposure and monitoring technologies, and; ii) conducting sampling and analysis of particulate and gaseous co-pollutants.

Project 1: The Core will conduct ambient and indoor monitoring. Ambient monitoring, to be conducted at the Boston HSPH Supersite will include measurements of particle mass (PM₁₀, PM_{2.5}, PM_{2.5-10}), black carbon (BC), elemental carbon (EC), organic carbon (OC), sulfate, nitrate, and particle count (PC). Indoor air measurements will be conducted at the home of each Project 1 participant. A micro-environmental automated particle sampler will be used to collect one-week integrated indoor samples for PM_{2.5} mass, elements, inorganic ions, and BC.

Project 2: The Core will use two modified passenger buses to expose human subjects to traffic-related emissions. One bus will be used for exposure to gases plus particles, and the other for exposure to filtered ambient air (gases only). The Core will also employ two portable carts for “in bus” monitoring, with instruments for both continuous and integrated measurements of PM₁₀, PM_{2.5}, PM_{2.5-10} mass, total particle counts, BC, O₃, NO₂, SO₂, CO, NMHC, temperature, and relative humidity.

Project 3: Human exposures to CAPs will be conducted using concentrators for coarse, fine, and ultrafine ambient particles. In addition to exposure generation and characterization (described below), the Core will provide both multi-pollutant personal exposure monitoring (PM_{2.5}, OC, EC, SO₄²⁻, NO₂) and exposure characterization.

Project 4: The Core will generate CAPs exposures for the animal PM toxicology study. A high-volume pre-collected ambient particle sampling system will be used, in parallel with the animal exposures, to collect ambient particles for *in vitro* toxicological tests. Characterization of animal exposures (described below) will also be the responsibility of the Core.

Project 5: The technologies to produce exposures of both primary and secondary particles and gases originating from mobile sources, using emissions from a traffic tunnel ventilation shaft, will be provided by the Core. In addition to the exposure generation, the Core will characterize exposures (as described below) and provide ambient, emissions, and reaction monitoring. This will include: SO₄²⁻, NO₃⁻, NH₄⁺, size distribution, O₃, SO₂, CO, NO_x, methane, and non-methane hydrocarbons (NMHC).

Exposure characterization for Projects 3, 4, and 5 will include: i) integrated sampling for PM_{2.5}, OC, EC, SO₄²⁻, NO₃⁻, NH₄⁺, organic speciation (PAH, aliphatic aldehydes), trace elements, NH₃ and gas phase aldehydes; and ii) continuous monitoring for PM_{2.5}, BC, particle size distribution, total particle count, O₃, SO₂, CO, NO_x, methane, and NMHC.

1. OBJECTIVES

The objectives of the Particle Technology and Monitoring Core will be to support all five projects of the proposed Center, by:

- Providing the large array of particle sampling and exposure technologies necessary to conduct each of the PM health effects studies. This will include:
 - a. Tailoring existing technologies to the needs of the individual Center Projects
 - b. Developing new technologies, as necessary, and;
- Conducting all pollutant monitoring and analysis of particulate and gaseous pollutants for each proposed Project. This will include:
 - a. Ambient monitoring at a supersite
 - b. Exposure characterization for human and animal inhalation studies
 - c. Personal and micro-environmental monitoring for study participants.

2. INTRODUCTION

Our group has a long history of success in the development of particle exposure and monitoring technologies. The existing EPA Center has supported the development and/or evaluation of many of these systems, several of which have been licensed and are currently commercially available worldwide. These novel techniques encompass systems for personal and micro- environmental measurements, as well as systems for exposing humans and animals to ambient or source-specific particles. These technologies, widely used by our Center and by scientists around the world, have undoubtedly helped to advance the field of particle health effects. The monitoring and exposure methods to be used by the proposed Center can be categorized into five broad groups, as summarized in Table 1. In Section 3, we provide a brief discussion about these technologies and their employment by the individual Center Projects in the generation and/or characterization of particle exposures.

Table 1: Exposure and Monitoring Systems for the PTM Core

Category	System Acronym	Description of System and Applications	Projects Supported	Core Section
Exposure	CAPS	Concentrated Ambient Particle Systems, for human and animal exposures	Animal (4), Human (3)	3.1
	SEES	Source-Specific Emissions Exposure Systems, for animal exposures to specific source emissions	TERESA (5)	3.2
	MPES	Mobile Particle Exposure Systems, for conducting human exposures inside motor vehicles during transit	Bus (2)	3.3
Monitoring	PAPS	Pre-collected Ambient Particle Samplers, for either toxicological or chemical analysis	Animal (4), TERESA (5)	3.4
	MAPSS	Micro-environmental Automated Particle Sampling Systems, for indoor and outdoor particle monitoring.	NAS (1), Bus (2)	3.5

In addition to its role in exposure generation, the Particle Technology and Monitoring (PTM) Core, through the Environmental Chemistry Laboratory (ECL) of the Department of Environmental Health, will support most of the particle and gas measurement needs of the Center. Over the last three decades the ECL has been responsible for numerous ambient particle and gas monitoring studies in support of our epidemiological, toxicological and exposure projects. Specific monitoring responsibilities of the PTM Core in each of the proposed PM Center Projects are presented in Section 4 and will include:

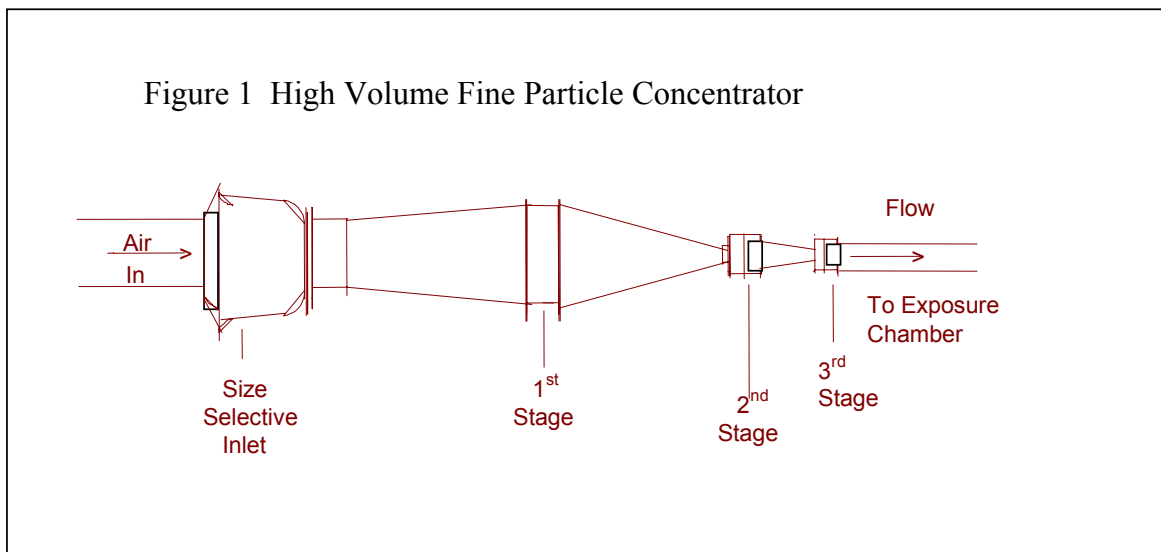
- Project 1:* Ambient gas and particle monitoring at the HSPH Boston Stationary Ambient Monitoring supersite (Section 4.1.1) and indoor monitoring (Section 4.1.2) for the NAS study participants;
- Project 2:* Exposure monitoring for the bus study participants (Section 4.2);
- Project 3:* Exposure monitoring for the human CAPs studies and personal monitoring for study participants (Sections 4.3.1), and;
- Project 4:* Exposure monitoring for animal CAPs (Sections 4.4), and;
- Project 5:* Source and exposure monitoring for the TERESA study (Section 4.4).

3. PARTICLE EXPOSURE AND MONITORING TECHNOLOGIES

3.1. Concentrated Ambient Particle Systems (CAPS): The development of the fine particle concentrator has made it possible to expose animal or human subjects to real ambient particles^{1,2,3}. The concentrator techniques use virtual impaction technology to separate particles by size and concentrate them in a small fraction of the incoming sample air. During the separation and concentration, particles remain airborne and can be transferred to the exposure chamber for inhalation studies. There are clear advantages of this method over techniques based on the suspension of artificial particles or ambient particles extracted from filter samples. Our group has developed fine, ultrafine, and coarse particle concentrators for inhalation toxicological studies. Concentrators built by our group are currently used for human and animal inhalation studies by our current Center as well as by other research groups in the US, Canada, The Netherlands, Japan, and Brazil.

3.1.1. High Volume Fine Particle Concentrator (HVFPC): The design and evaluation of the HVFPC has been described in detail in previous publications^{4,5,6}. The HVFPC, shown schematically in Figure 1, consists of the following components: i) a size-selective inlet which is a high volume conventional impactor with a 2.5 μm cutpoint and; ii) a series of three virtual impactors (stages I, II, and III) with 0.15 μm cutpoints. The resulting system enriches the mass concentration of fine ambient particles by a factor of about 30 or higher. The fine particle concentrator has been used routinely for exposure studies for over seven years in our laboratory, and its performance has been extensively investigated as a function of local meteorological conditions, ambient particle concentrations, composition, and size distribution⁷. The concentrator performance was characterized using the concentration enrichment factor (CEF), a ratio of

concentrated particle mass (or sulfate) concentration to the ambient concentration. The average CEF values for fine mass and sulfate were 28.7 (\pm 11.0) and 28.7 (\pm 11.5), respectively. In addition, the concentrator and ambient fine mass and sulfate concentrations were highly correlated



($R^2 = 0.84$ and 0.89 , respectively). A new HVFPC will be built before the summer of 2005, funded by the Canadian Foundation for Innovation (CFI), for the Toronto group and will be used for the proposed human inhalation CAPs studies, Project 3. The two existing HVFPCs at HSPH will be used for the animal inhalation CAPs studies, Project 4.

3.1.2. High volume ultrafine particle concentrator (HVUPC): The health effects of ambient ultrafine particles have not yet been fully investigated. This is in part due to the lack of particle generation methods that can be used to expose human and animal models to “real world” ambient ultrafine particles. We have recently developed an ultrafine particle concentrator that can be used to increase the concentration of particles with an aerodynamic diameter smaller than $0.1 \mu\text{m}$ ^{8,9,10}. The system operates with a 5,000 LPM input flow and delivers 58 LPM of concentrated aerosol. The HVUPC concentrates ambient ultrafine particles by a factor of 40-50, with insignificant size distortion. It consists of the following basic components: a) size-selective inlet; b) condensational growth unit; c) series of two virtual impactors; and d) thermal dilution-dryer section.

The size selective inlet is a two-stage conventional impactor that removes particles larger than $2.5 \mu\text{m}$. The condensational growth unit first mixes the sample air with steam to saturate it with water vapor. Then saturated air passes through a cooling system that causes supersaturation of the water vapor, which then condenses on the surfaces of the particles and causes them to grow to super-micron sizes. Next, the condensationally grown particles are drawn through a series of two virtual impactors with cutpoints of $1.0 \mu\text{m}$. Finally, a thermal drying system is used to restore the original size distribution of the concentrated aerosol by removing the excess water from the particle droplets. The concentrated aerosol (at a flow of 50 LPM) is first diluted with a small volume (8 LPM) of particle free air and then is heated up to 90 F, yielding an aerosol output flow of 58 LPM. The concentrated stream of dried aerosol passes through a size-selective outlet with a cut point of $0.15 \mu\text{m}$.

The US EPA has recently acquired two HUVPC systems for human and animal inhalation studies. Also, as part of our collaboration with the University of Rochester School of Medicine and Dentistry - EPA Particulate Matter Center, we are currently building another HUVPC for their use. A new HUVPC will also be built before the summer of 2005, funded by the Canadian Foundation for Innovation, for the Toronto group and will be used for the proposed human inhalation CAPs studies (Project 3).

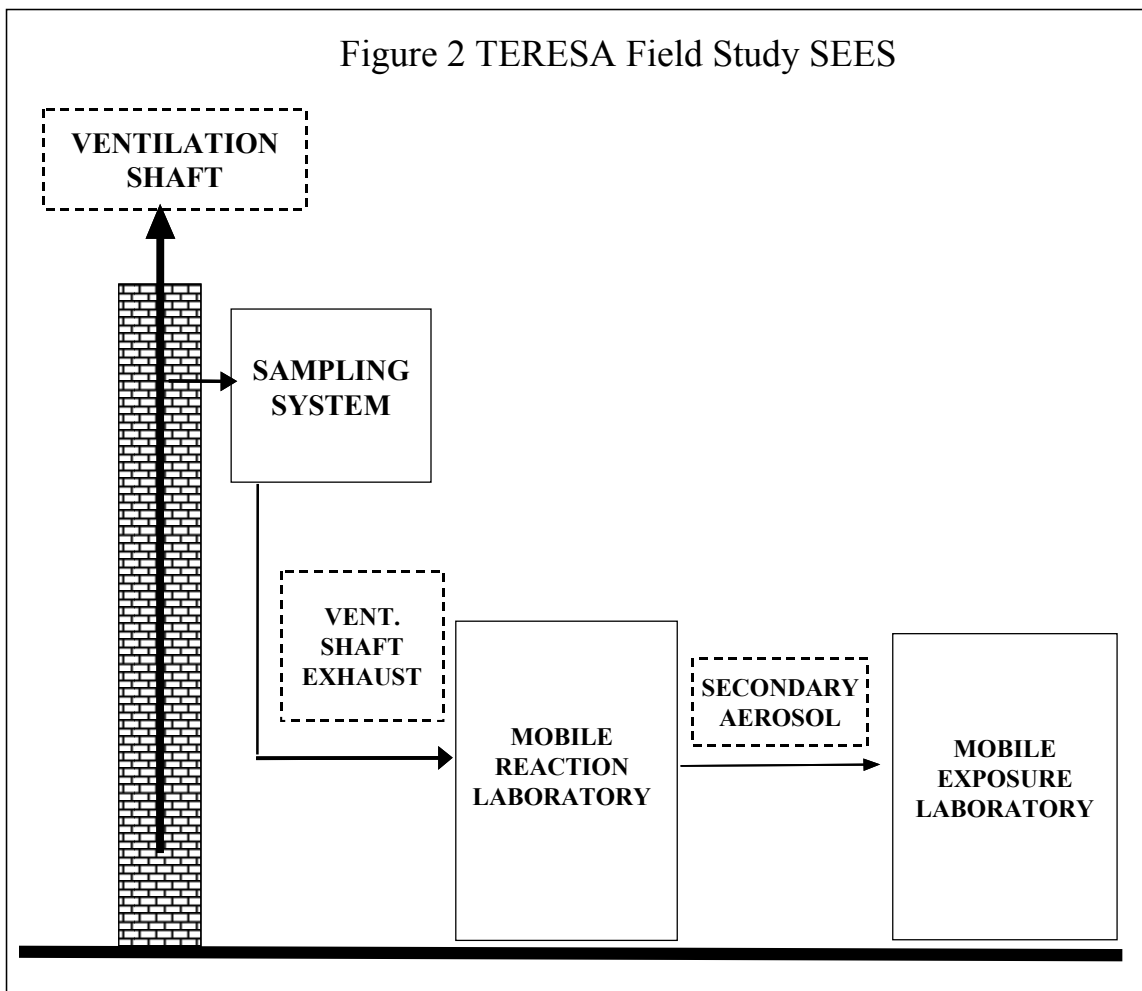
3.1.3. High volume coarse particle concentrator (HVCPC): This system, which was developed by the current PM Center, can be used to concentrate ambient coarse particles (aerodynamic diameter between 2.5 and 10 μm)^{11,12}. The HVCPC uses a size-selective inlet with a cutpoint of 10 μm , and a two-stage slit nozzle virtual impactor with a cutpoint of 2.5 μm . The system was designed to minimize particle losses and increases ambient coarse particle concentrations by a factor of about 70. In addition, the concentration process results in negligible distortion of the ambient coarse particle size distribution, which makes it particularly suitable for inhalation toxicological studies.

The size selective inlet is a 5,000 LPM single-stage conventional impactor with three parallel slit nozzle impactors using a polyurethane foam (PUF) substrate with a cutpoint of 10 μm . The PUF substrate has a high capacity for particle loading, with negligible changes in particle collection efficiency as a function of loading. The first stage of the virtual impactor has a total flow of 5,000 LPM, using eight parallel slit nozzles. The minor and major flows are 500 and 4,500 LPM, respectively. The second stage has a total flow of 500 LPM, with minor and major flows of 50 and 450 LPM, respectively. The total nominal concentration factor is the product of the two ratios of minor/total flow for the two stages, with a value of 100. The actual concentration factor is about 70, reflecting relatively small losses on the jets and other impactor surfaces. Because the total pressure drop is only about 100Pa, negligible volatilization of semi-volatile particle components is expected with this system.

A HVCPC system has been recently installed at the US EPA for human inhalation studies. The Canadian Foundation for Innovation also provided funding for the coarse particle concentrator to be used for human exposures to coarse particles to be conducted by in Toronto (Project 3). This HVCPC will be built by Harvard and installed prior to the commencement of the proposed Center.

3.2. Source-specific Emissions Exposure Systems (SEES): Historically, statistical source apportionment techniques have been used to identify different types of ambient particles sources and to estimate their relative contributions to human exposures. In the past we have employed source apportionment methods in our epidemiological and toxicological studies in an effort to link biological outcomes to specific source classes such as oil and coal combustion, traffic or road dust^{13,14}. More recently, our research team has engaged in studies to investigate the toxicity of primary and secondary particles from specific combustion sources. This is the Toxicological Evaluation of Realistic Emissions of Source Aerosols (TERESA) study that is co-funded by the Electric Power Research Institute (EPRI) and the existing EPA Center. TERESA is a comprehensive effort to evaluate both the formation and toxicity of secondary particles from coal combustion. The study involves on-site sampling and dilution of emissions at multiple coal-fired power plants across the U.S. The diluted stack gas is introduced into a reaction chamber where

atmospheric chemistry is simulated, and the secondary particles are extensively characterized. While still suspended in air, both primary and secondary particles (with excess concentrations of pollutant gases removed by diffusion denuders) are evaluated on-site for toxicity using normal and compromised laboratory rats. For the Source-specific Emissions Exposure Systems (SEES), we will adapt the technology developed for the power plant emissions to perform similar tests with the mobile source emissions from a traffic tunnel ventilation shaft in downtown Boston (Project 5). Figure 2 is a diagram of the field system for conducting the tunnel study. The component systems, modified for the proposed project, are presented in detail in Section 4.2 of the description of Project 5.



3.3. Mobile Particle Exposure Systems: Two Mobile Particle Exposure Systems (MPES) will be used for the Bus study, Project 2, which are described below:

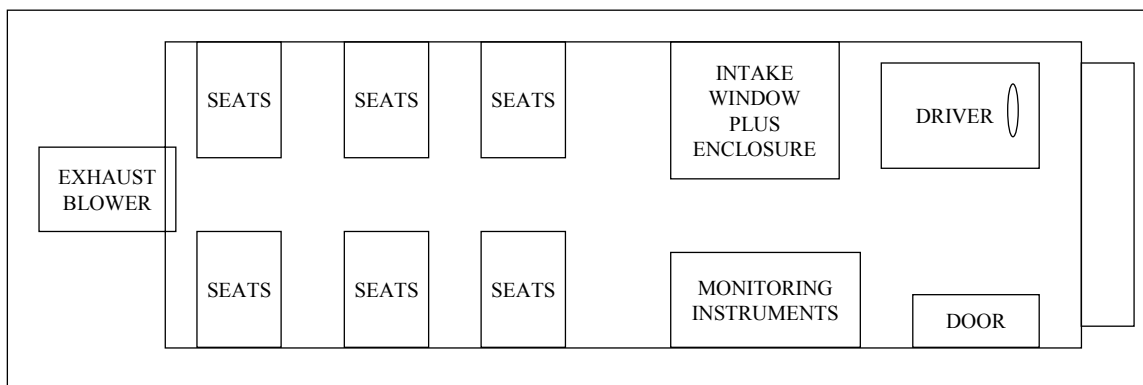
3.3.1. MPES #1 for Exposure to Unfiltered Ambient air: We will lease a bus similar to the one that was used for our previous study in St. Louis. This bus is large enough that, when some seats are taken out from the front of the bus for the monitoring equipment, there is still enough room for at least 12 passengers. Passenger seats from right side of the front of the bus will be removed to provide space for the monitoring equipment. A replaceable rear door will be modified to hold an

exhaust blower that will bring unfiltered outside air containing both particles and pollutant gases through open windows on both sides of the front of the bus. The interior space of the bus is about 15 x 8 x 7 ft (LWH), or 840 ft³. For a reasonable air exchange of 10/hr, the blower will provide a ventilation flow of about 230 ft³/min. With this rate, the residence time in the bus is only 6 minutes, so there is a relatively short lag time for composition changes in the outside air to result in changes inside the bus.

3.3.2. MPES #2 for Exposure to Filtered Air: This will be the original bus that was used in our St. Louis study to expose human subjects to traffic emissions. This bus is large enough that when some seats are taken out from the front of the bus to fit the HEPA (high efficiency particle air) filter system and the monitoring equipment, there is still enough room for at least 12 passengers (see Figure 3). An intake air blower will be connected to the window behind the driver's seat to push outside air through the HEPA filter. The filter will remove all particles, while allowing ambient air gases to pass through. As with MEPS #1, there will be an exhaust blower in the rear door, and the intake and exhaust blowers will be adjusted to have a flow of about 230 ft³/min, with a negligibly low positive pressure inside the bus to prevent unfiltered outside air from entering anywhere except through the HEPA filter.

3.4. Pre-collected ambient particle systems (PAPS): To adequately conduct toxicological studies, it is necessary to pre-collect relatively large amounts of size-fractionated ambient particles (several hundred milligrams to grams). Previously used particle sampling systems can not be used to collect large particle amounts because they have a limited collection capacity of the impaction substrate and, they exhibit extensive particle bounce-off and re-entrainment^{15,16,17,18}. In order to minimize particle bounce-off and re-entrainment, impaction substrates are usually coated with adhesives such as mineral oil or grease. However, these substances may interfere with toxicity measurements of the collected particles. Recently, we developed a new impaction substrate that does not require the use of adhesives such as grease or mineral oil to minimize particle bounce-off and re-entrainment losses^{19,20}. The impaction substrate consists of micro-porous polyurethane foam and can be used to collect large particle quantities (up to grams amounts), while maintaining unchanged its impaction characteristics such as cutpoint and collection efficiency curve sharpness. In addition, polyurethane foam, which is a porous polymeric material with stable physical characteristics and low chemical background (when cleaned properly), is toxicologically inert²¹. The use of polyurethane foam substrates improves the performance of inertial impactors, as

Figure 3: Mobile Exposure Particle System (MEPS) #2



compared to both coated and uncoated flat plate substrates^{19,20}. As a result, this method was used to develop an array of sampling systems that can be used to fractionate and collect large quantities of particles on inert PUF substrates that can be used for both the physicochemical and toxicological characterization of atmospheric aerosols. Systems include the development of a high volume cascade impactor²² (HVCI), the high volume low cutpoint impactor²³, a personal cascade impactor²⁴, and a compact cascade impactor system²⁵. These systems have been used extensively in the US and Europe to characterize the physicochemical and toxicological properties of atmospheric aerosols. The HVCI (flow 1,000 LPM) will be used to collect particle samples for the animal exposure studies in Project 4 and for the primary and secondary exposures to mobile source particles in Project 5.

3.5. Micro-environmental Automated Particle Sampling System (MAPSS): We have developed a personal and micro-environmental multi-pollutant sampler whose design and evaluation were supported by the existing EPA PM Center²⁶. Based on this sampler we have recently designed a Micro-environmental Automated Particle Sampling System (MAPSS) to collect one-week samples in the homes of the study participants for Project 1. The essential features of the MAPSS are the following: i) it weighs only a few pounds and it can be shipped by mail directly to the participant's homes and; ii) it can be easily employed by the participants. As soon as the MAPSS arrives, the participant will connect it to an electrical outlet and will place it on a table in the living room. A battery-operated clock will allow a programmed timer to both start and stop the sample collection for the one-week day period immediately preceding the participant's visit for medical examination and testing. At the end of the sampling period the participant will bring the MAPSS on the day she/he comes in for medical examination and testing. Consequently, there is a high likelihood that the vast majority of the samples will be collected successfully.

The design of the MAPSS includes the personal environmental monitoring system (PEMS) for PM_{2.5} sampling. PEMS collects particles onto a 37 mm Teflon membrane filter and operates at 1.8 LPM. This system will use a small, quiet vacuum pump (MEDO model VP0140) that we have used successfully for many other sampling systems²⁶. To provide adequate validation for each sample, the flow will be continuously monitored and logged. This will make it possible to obtain information about potential power interruptions and to determine whether a representative sample has been collected.

4. MONITORING

In addition to providing the necessary particle technologies for exposure generation and sampling, the PTM Core will be responsible for characterizing exposures for all five proposed projects. In the subsections below, we present the Core monitoring activities as they relate to the individual projects. Since many of the projects utilize the same integrated sampling and analysis techniques, they are summarized in Table 2.

4.1. The NAS Study (Project 1): For this Project, both stationary ambient and indoor particle measurements will be conducted.

Table 2 Summary of Sampling and Analysis Methods used by PTM Core								
Location / Pollutant	Measurement Method	Averaging Time	PM Center Proposed Project					
			1	2	3	4	5	
Stationary Ambient Monitoring (SAM) Supersite Measurements:								
PM _{2.5}	TEOM	Continuous	✓	✓		✓	✓	
PM _{2.5}	Partisol 2300/Gravimetric	24-hour	✓	✓		✓	✓	
PM ₁₀	TEOM	Continuous	✓	✓		✓	✓	
PM ₁₀	Partisol 2300/Gravimetric	24-hour	✓	✓		✓	✓	
Total particle counts	CPC	Continuous	✓	✓		✓	✓	
Size-specific particle counts	Climet	Continuous	✓	✓		✓	✓	
Elements	Partisol 2300/XRF	24-hour	✓	✓		✓	✓	
Black carbon	Aethalometer	Continuous	✓	✓		✓	✓	
Black carbon	HI/Reflectance	24-hour	✓	✓		✓	✓	
Elemental and organic carbon	Carbon Aerosol Instrument	1-hour	✓	✓		✓	✓	
Sulfate	CASM	Continuous	✓	✓		✓	✓	
Sulfate	HI/IC	every 6 th day	✓	✓		✓	✓	
Nitrate	Continuous NO ₃ ⁻ Monitor	Continuous	✓	✓		✓	✓	
Nitrate	HI/IC	every 6 th day	✓	✓		✓	✓	
CO	NDIR	Continuous	✓	✓		✓	✓	
Relative humidity, temperature	RH, temperature probe	Continuous	✓	✓		✓	✓	
Indoor Measurements:								
PM _{2.5}	PEM/Gravimetric	7-days	✓					
Elements	PEM/XRF	7-days	✓					
Sulfate	PEM/IC	7-days	✓					
Black carbon	PEM/Reflectance	7-days	✓					
Personal Measurements:								
PM _{2.5}	PEM/Gravimetric	24-hour			✓			
PM ₁₀	PEM/Gravimetric	24-hour			✓			
Elements	PEM/XRF	24-hour			✓			
Sulfate	PEM/IC	24-hour			✓			
BC	PEM/Reflectance	24-hour			✓			
NO ₂	Passive/Colorimetric	24-hour			✓			
Bus and Chamber Exposure Measurements:								
PM _{2.5}	DustTrak	Continuous		✓				
PM _{2.5}	TEOM	Continuous			✓	✓	✓	✓
PM _{2.5}	Teflon filter/Gravimetric	Exposure		✓	✓	✓	✓	✓
PM ₁₀	Teflon filter/Gravimetric	Exposure		✓				
Black carbon	Aethalometer	Continuous		✓	✓	✓	✓	✓
Elements	Teflon Filter/XRF	Exposure		✓	✓	✓	✓	✓
Elements	Teflon Filter/ICPMS	Exposure			✓			
Sulfate, Nitrate, Ammonium	Teflon Filter/IC	Exposure			✓	✓	✓	✓
EC/OC	Quartz Filter/TOR	Exposure			✓	✓	✓	✓
Organic Speciation (ie, PAH)	GC/MS	Exposure			✓	✓	✓	✓
Particle counts by size	Climet	Continuous		✓				
Total particle number	CPC	Continuous		✓				
Particle Size Distribution	SMPS, APS	Continuous			✓	✓	✓	✓
Endotoxin/Glucon	LAL	Exposure			✓	✓		
CO	Electrochemical or NDIR	Continuous		✓	✓	✓	✓	✓
NMHC	Portable GC	Continuous		✓			✓	✓
O ₃	UV photometric monitor	Continuous		✓	✓	✓	✓	✓
NO ₂	Electrochemical monitor	Continuous		✓				
NO _x	Chemiluminescence	Continuous		✓				
SO ₂	Diffusion denuder/IC	Exposure		✓		✓	✓	✓
SO ₂	Pulsed fluorescence	Continuous			✓	✓	✓	✓
Ammonia	Diffusion denuder/IC	Exposure						✓
Aldehydes	DNPH cartridge/HPLC	Exposure						✓
Relative humidity, temperature	RH, temperature probe	Continuous		✓	✓	✓	✓	✓

4.1.1. Stationary Ambient Monitoring (SAM) supersite: Ambient air pollution measurements will be conducted at the EPA PM Center supersite, located at 10 Shattuck Street near downtown Boston. Monitoring will include a broad array of continuous and integrated sampling and measurement techniques for gases and particles. As reported in the Quality Monitoring Plan (QMP), the Environmental Chemistry Laboratory at HSPH has available standard operating protocols for all methods to be employed, most of which are already in operation at the supersite. Continuous and integrated methods to be employed at the SAM supersite are specified in subsections 4.1.1.1 through 4.1.1.3 below.

4.1.1.1. SAM Integrated Particle Measurements: Particle measurements are described in Table 2 and will include PM_{2.5} mass, trace elements, SO₄²⁻, NO₃⁻, BC, EC and OC, and PM₁₀ mass and size. The Partisol Model 2300 Sequential Sampler (Rupprecht & Patashnick, Albany, NY) will be used to collect 24-h integrated (16.7 LPM) PM₁₀ and PM_{2.5} samples at the SAM site. PM_{2.5} and PM₁₀ samples will be analyzed for mass using gravimetric analysis. PM_{2.5} samples will be analyzed for BC using an EEL smoke stain reflectometer. Finally, one out of six PM_{2.5} samples will be analyzed for SO₄²⁻ and NO₃⁻ using ion chromatography for QA purposes, to calibrate the continuous SO₄²⁻ and NO₃⁻ monitors.

4.1.1.2. SAM Continuous Particle Measurements: Continuous PM_{2.5} and PM₁₀ mass concentrations will be measured using two Tapered Element Oscillating Microbalances (TEOMs) equipped with PM_{2.5} and PM₁₀ size selective inlets, respectively (Model 1400A, Rupprecht and Patashnick, Albany, NY). Since the TEOM 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. The magnitude of this loss is likely to vary by season, thus season-specific calibration factors will be used to compensate for these losses^{27,28}. The calibration factors will be obtained by regressing the continuous PM_{2.5} and PM₁₀ mass concentrations, averaged over 24-h periods, on the corresponding collocated integrated 24-h gravimetric measurements.

A condensation particle counter (CPC) (Model 3022A, TSI, Inc.) will be used to measure total particle counts (PC) continuously. In addition, size-resolved particle count concentrations will be measured using a particle sizer (Model CI500, ClimeT Instruments Company, Redlands, CA). Particles will be sized and counted into five channels (0.3-0.5, 0.5-1, 1-5, 5-10, 10-25 microns).

A model AE-14 Aethalometer (Magee Scientific Inc., Berkeley CA) will be used to measure continuous BC concentrations (every five minutes). Since EC is the predominant light-absorbing component of fine particle mass, the BC optical measure is comparable to that of EC, which is a chemical measure^{29,30,31,32,33}. In addition, a carbon aerosol analysis instrument (Sunset Laboratory) will also measure 1-hour EC and OC concentrations³⁴.

Fine particle SO₄²⁻ concentrations will be measured every 5 minutes using the Harvard/TECO Continuous Sulfate monitor³⁵. The monitor is based on the thermal conversion of SO₄²⁻ to SO₂, which is subsequently measured using a pulse fluorescence monitor. For QA purposes, continuous measurements will be compared to those obtained from the collocated 24-h SO₄²⁻ integrated measurements (see previous section), once every sixth day. Finally, fine particle NO₃⁻ concentrations will be measured at the central SAM site using an automated NO₃⁻ monitor with a time resolution of ten minutes³⁶. For QA purposes NO₃⁻ continuous measurements will be

compared to those obtained from the collocated 24-h NO_3^- concentrations, (see previous section), once every sixth day.

4.1.1.3. SAM Gaseous Co-Pollutants and Meteorological Parameters: Carbon monoxide will be measured at the Harvard supersite using a US EPA reference method (Model 48 gas analyzer, Thermo Environmental Instruments, Franklin, MA). Continuous data will be averaged into hourly means. O_3 , NO_2 , SO_2 , temperature and relative humidity hourly measurements conducted at several Boston sites will be obtained from the Massachusetts Department of Environmental Protection. Also meteorological data including 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).

4.1.2. Indoor Particle Measurements for the NAS study (Project 1): Weekly indoor particle sampling will be performed for the NAS study, Project 1, using the Micro-environmental Automated Particle Sampler (MAPSS), described in section 3.5 (above). Briefly, it includes a 1.8 LPM PEMS for $\text{PM}_{2.5}$ sampling with a 37-mm Teflon membrane filter, using a small vacuum pump. The flow will be continuously monitored and logged. The Teflon membrane filters will be analyzed for $\text{PM}_{2.5}$ mass by gravimetric determination, and also for elemental concentrations, sulfate, and BC as described in Table 2. Using multi-day sampling, the PEMS will collect sufficient quantities of particles for mass and speciation measurements and thus it is expected that the detection limits will be similar to those for the supersite integrated samples.

4.2. Exposure Monitoring for the Bus Study (Project 2): Both continuous and integrated measurements of particle and gases, temperature, and relative humidity will be performed using two portable carts, as follows:

4.2.1. Bus Study Continuous Particle Measurements: Continuous measurements of $\text{PM}_{2.5}$ concentrations will be measured using the Dust Trak aerosol monitor (Model 8520, TSI Inc, St Paul, MN). A Nafion diffusion dryer will be added upstream of the Dust-Trak in order to control for changes in relative humidity. A portable instrument will be used to measure size-resolved particle counts (Model CI500, Climet Instruments Company, Redlands, CA). Also a portable instrument (CPC Model 3007, TSI Inc, St Paul, MN) will be used to measure total particle number concentrations, as a surrogate for ultrafine particles. BC will be measured continuously using a portable Aethalometer (Model AE-42, Magee Scientific Inc., Berkeley, CA).

4.2.2. Bus Study Integrated Particle Measurements: Integrated $\text{PM}_{2.5}$ mass measurements will be made using a Personal Exposure Monitor (PEM) and subsequent gravimetric analysis. These measurements will be used to calibrate the Dust Trak measurements^{37,38,39}. Integrated PM_{10} mass measurements and trace elements will be made with a second PEM.

4.2.3. Bus Study Gaseous Co-pollutants: Continuous measurements of CO will be made using a portable high resolution monitor⁴⁰. This new instrument gives good resolution for CO at the 1 ppm range. Semi-continuous measurements of non-methane hydrocarbons (NMHC) will be made using a portable gas chromatograph (Model OVA 128, On-Site Instruments, LLC, Lewis Center, OH). Continuous measurements of O_3 will be made using a portable UV photometric monitor (Model 202, 2B Technologies). Continuous measurements of NO_2 will be made using a portable

electrochemical monitor⁴¹. Integrated measurements of SO₂ will be made using a 7.5cm glass annular denuder system⁴² (Model 2000-15D1, URG, Chapel Hill, NC), as described in Table 2. Continuous measurements of temperature and relative humidity will also be made (Model 7001, Telaire, Goleta, CA).

4.3. Human CAPs Exposure Study (Project 3): For this Project personal monitoring and physiochemical characterization of exposures will be conducted.

4.3.1. Personal Monitoring for the Human CAPs Study: All subjects will be equipped with personal exposure monitors both the day before and the day after they are exposed. Harvard multi-pollutant samplers for PM_{2.5} mass, trace elements, BC, SO₄²⁻, and NO₂ will be used⁴³. Personal filter samples will be sent to Harvard School of Public Health for analysis, as described in Table 2.

4.3.2. Chemical and Physical Characterization for the Human CAPs Study: Sample air for measuring particle concentrations and co-pollutant concentrations will be from the CAPs airstream. Continuous measurements (described below) will be performed for every human exposure experiment, and integrated PM samples (described below) for only CAPs exposures. Integrated PM samples will not be collected for the particle-free (HEPA filtered) air exposures.

4.3.2.1. Continuous (1-15 min time resolution) measurements: Continuous measurements will be made for gaseous co-pollutants, NO, NO₂, SO₂, CO, CO₂, and O₃, and for temperature/relative humidity. Particle measurements will include: number and size-distributions (Scanning mobility particle sizer, SMPS, 7-300 nm – GRIMM model 5403, and Aerodynamic Particle Sizer, 370 nm – 20 µm - TSI model 3321), mass concentration (TEOM model 1400a, Rupprecht & Patashnick Co. Ltd), aerosol diameter concentration (TSI-Electrical Aerosol detector), and black carbon (aethelometer model AE-1, Magee Scientific). All continuous measurements will be conducted by the University of Toronto group.

4.3.2.2. Integrated PM samples (for 2 hour exposure duration): i) Low-volume particle sampling (16 LPM): a) Teflon filters will collect PM for gravimetric mass determination, and for SO₄²⁻, NO₃⁻, NH₄⁺ and Cl⁻ ions using ion chromatography; b) Pre-fired Quartz filters will be collected for EC/OC analysis using a Thermal-Optical Transmission Instrument, and; c) a Nuclepore filter will collect PM for the LAL test for endotoxin and glucan. ii) Medium-volume particle sampling (60 LPM): a) Teflon filters will collect PM for elemental analysis (e.g., Fe, Zn, Al, Si, V, Se, Cd, Cr, As, Cu, Pb, Mn, Ca, Mg) using X-ray fluorescence (XRF), and; b) a separate Teflon filter will collect PM for organic analysis (PAHs, n-Alkanes, petroleum biomarkers (hopanes and steranes) using thermal desorption-gas chromatography mass spectrometry (TD-GCMS) and/or solvent extraction GCMS.

4.4. Animal Exposure Studies (Projects 4 and 5): Chemical and physical characterizations of exposures will be conducted for Projects 4 and 5. Exposure atmospheres will be comprehensively monitored for particle mass, number and size as well as inorganic and organic components using an array of continuous and integrated methods. Also gaseous co-pollutant exposures, temperature, and relative humidity will be measured. For Project 4, measurements will be made for the exposure atmosphere only. For Project 5, sampling will be conducted at three locations: i)

photochemical reaction chamber inlet (primary emissions); ii) outlet of the photochemical reaction chamber (aged emissions); and iii) downstream of the exposure empty animal chamber (exposure), as described in section 4.8 of Project 5.

4.4.1. Integrated Particle Measurements: Separate particle Teflon samples will be collected for gravimetric determination of mass, elemental, ionic and OC speciation analysis. Samples will be analyzed for elements, SO_4^{2-} and NO_3^- and ammonium (NH_4^+) ions, and particle strong acidity (H^+), as described in Table 2. Organic speciation, emphasizing known toxic species of combustion origin (e.g. PAHs), will be conducted at the University of Crete⁴⁴, using gas chromatography/mass spectrometry. Samples for EC/OC analysis will be collected on pre-fired quartz fiber filters analyzed by DRI using the thermal optical reflectance method.

4.4.2. Continuous Particle Measurements: Continuous particle mass measurements ($\text{PM}_{2.5}$), will be made using a tapered element oscillating microbalance (TEOM, see section 4.3.2.1, above). Particle size distribution will be monitored continuously using a Scanning Mobility Particle Sizer (SMPS, TSI model 3080, St. Paul, MN) and an Aerodynamic Particle Sizer (APS, TSI Model 3310, St. Paul, MN) to determine particle number concentrations for sizes between 0.01 and 1.0 μm and from 0.5 to 20 μm , respectively. Total particle count will be measured with a CPC. BC will be measured continuously using an Aethalometer (see section 4.3.2.1, above).

4.4.3. Gaseous Co-pollutant Measurements: In addition, gaseous co-pollutants will also be measured using continuous and integrated monitoring methods. Continuous measurements include: O_3 (UV absorbance), SO_2 (pulsed fluorescence), NO_x (chemiluminescence), and CO (non dispersive infrared spectroscopy). Non-methane hydrocarbons (NMHC) will be measured semi-continuously using a compact gas chromatograph system (Model 25, Quadrex Corp., Woodbridge, CT). Integrated concentrations of ammonia (NH_3) and aldehydes will be measured as described in Table 2.

4.4.4. Pre-collected Ambient Particle Systems (PAPS): PAPS samplers (described above in section 3. 4) will be used to collect large amounts of ambient particles to be available for future chemical and toxicological tests, in parallel with the animal exposures to CAPs for Projects 4, and to source-specific particles for Project 5. Specifically, the High Volume Cascade Impactor (HVCI) will be used to collect both coarse and fine fractions of ambient PM at a flow of 1100 LPM²².

5. EXPECTED BENEFITS

All five proposed projects rely upon state-of-the-art particle sampling or exposure devices. These technologies have been already developed, or will be developed, by the Particle Technology and Monitoring Core and will become available to the different projects. Besides supporting the individual Projects this Core will also be critical in our efforts to integrate the Center research. The engineering team of this Core will assist the Project Investigators in the design, conduct and data interpretation of the different studies. Finally, this Core is critical to the Center's success because it will be responsible for generating and characterizing the exposures for all five proposed projects. Towards this end the Core will utilize similar sampling and analytical protocols for measuring a large spectrum of exposures across the projects. This will ensure that high quality exposure data will be generated for all projects, which will be used to investigate associations between health

outcomes and toxic components.

Technologies developed by our group (with extensive support from the current EPA PM Center) have been already employed by many research groups and have contributed in advancing the particle health effects field. One of the main objectives of this proposed Core is to continue making available the developed technologies to researchers in both the United States and around the world. Besides transferring technology, Core investigators will collaborate and assist outside groups, as needed.

6. GENERAL INFORMATION

6.1. Research Personnel: This Core will be led by Dr. Philip Demokritou who is an Assistant Professor of Aerosol Technology and Indoor Air Quality, at the Harvard School of Public Health. Drs. Petros Koutrakis, Professor of Environmental Sciences, and Jack M. Wolfson, Research Associate, will be co-leaders for this Core. The Core leaders have been the developers of many particle sampling and exposures devices and have been awarded several US patents. Mr. Mark Davey, field project manager and supervising engineer, will be responsible for exposure monitoring equipment and operator training. Steve Ferguson, engineering supervisor, will be responsible for design and construction of custom-made exposure generation and monitoring equipment. Jim Sullivan, data manager, will be responsible for management of all exposure monitoring data for the research projects.

6.2. Facilities: The Aerosol Laboratory at the Harvard School of Public Health will be available for the development, construction and maintenance of all the different particle devices. The Environmental Chemistry Laboratory at HSPH will perform the ion chromatographic, gravimetric, and reflectometry measurements. Elemental analysis and elemental and organic carbon measurements will be conducted at either the Desert Research Laboratory (DRI), under the Direction of Dr. Judith Chow) or at Sunset Labs (as needed). Organic speciation analysis will be conducted at the University of Crete, under the direction of Professor Euripides Stephanou. Facilities at the University of Toronto will be responsible for the continuous particle and gaseous co-pollutant measurements, under the direction of Drs. Jeff Brook and Bruce Urch. Most of the instruments and equipment needed for the proposed research projects are currently available (or have already been funded independently) at our facilities. The most important items at HSPH include: 1) a fully equipped exposure laboratory with two fine particle concentrators and animal exposure chambers; 2) two ion chromatographs; 3) a temperature/relative humidity-controlled balance room with an electronic microbalance; 4) several particle sizing instruments for both fine and coarse particles; 5) a mobile photochemistry reaction chamber laboratory; 6) a mobile animal exposure and toxicology laboratory, and; 6) a mobile human exposure facility (diesel bus). The Toronto facility will have concentrators for ultrafine, fine, and coarse ambient particles, and has a fully equipped laboratory for conducting human exposures to concentrated ambient particles.

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