

# **ASSESSMENT OF AGED COAL-FIRED POWER PLANT EMISSIONS: THE TERESA STUDY**

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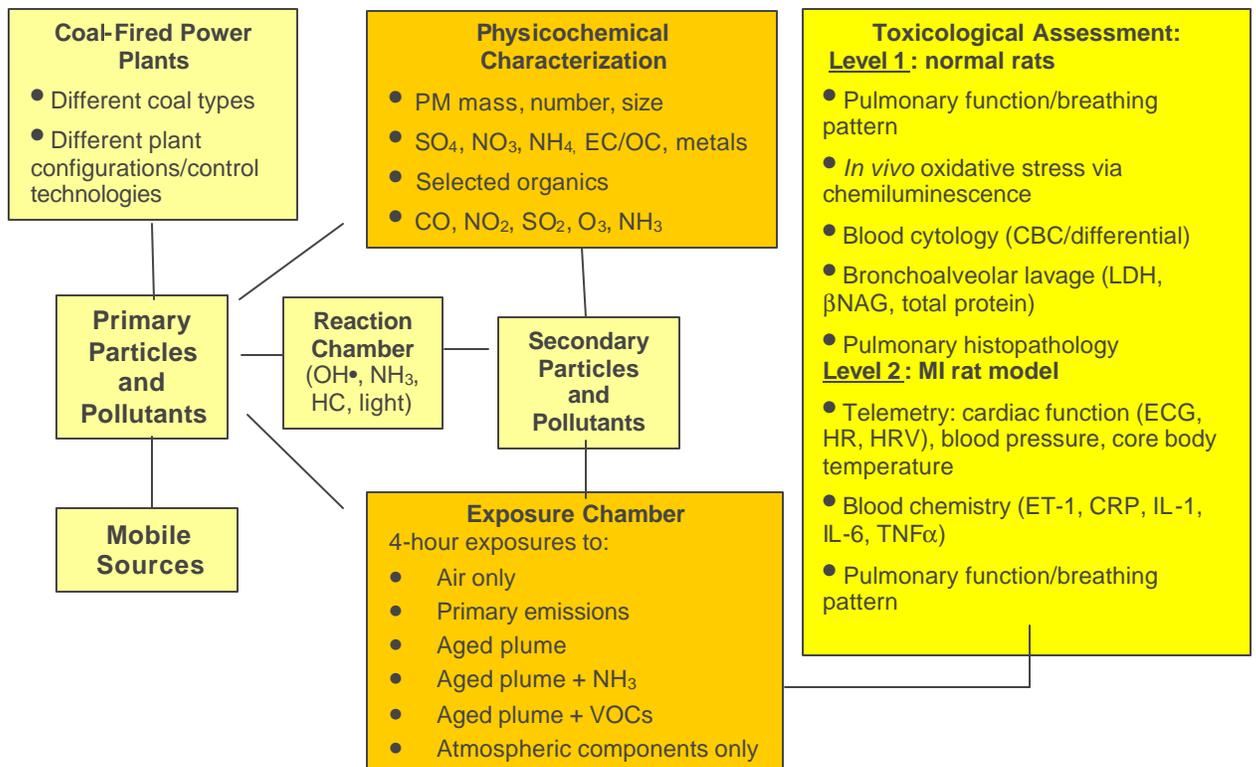
## **ABSTRACT**

The Toxicological Evaluation of Realistic Emissions of Source Aerosols (TERESA) study is a comprehensive effort to evaluate the formation and toxicity of secondary particles from coal combustion. To date, the toxicity of coal combustion emissions has been examined only in terms of primary particles, but these emissions are not likely to reflect population exposures because of atmospheric chemistry. TERESA involves on-site sampling of emissions at multiple coal-fired power plants across the U.S., followed by simulation of atmospheric chemistry in a reaction chamber and exposure of normal and compromised rats in order to understand the toxicity of secondary emissions. In preparation for fieldwork at the first TERESA study plant in the Upper Midwest, the sampling apparatus and reaction chamber are currently being developed and tested. Stack samples will be diluted with dry air and introduced into the chamber, where hydroxyl radicals are added to convert SO<sub>2</sub> to sulfate. Light, NH<sub>3</sub> (gas), VOCs, and inert particles are also added. Target mass concentration output from the chamber will be in the range of 200-300 µg/m<sup>3</sup>. Extensive characterization of emissions will be carried out, including gases (CO, CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, O<sub>3</sub>, NH<sub>3</sub>, hydrocarbons), particle number, size distribution, mass, and composition (including SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, strong acidity, metals, EC, OC, and organics). Aged emissions will enter an exposure chamber in a mobile toxicological laboratory, where rats will be exposed and multiple toxicological endpoints will be evaluated. Particle formation, composition, and toxicity will be compared for different atmospheric conditions and dilution scenarios. The ultimate goal of TERESA is to compare the toxicity of secondary coal combustion emissions, mobile source emissions, and concentrated ambient particles (CAPs) to better understand the components of PM responsible for adverse health effects. The TERESA study is the first to investigate the toxicity of actual power plant emissions using mobile laboratories, and the first to incorporate secondary atmospheric chemistry. This paper describes the study design and outlines preliminary results of the atmospheric simulation work.

# INTRODUCTION

The complex nature of ambient PM makes it a major challenge to study in epidemiological and toxicological settings. The promulgated National Ambient Air Quality Standard (NAAQS) for PM<sub>2.5</sub> is mass-based, which assumes that all PM is toxicologically equal. However, since PM is derived from multiple sources and varies widely in composition, this assumption is likely to be invalid. Indeed, recent findings from a large epidemiological study in Atlanta (Aerosol Research and Inhalation Epidemiology Study; ARIES) suggest that adverse health outcomes are associated with the carbon-containing fraction of PM, which may be derived from mobile and other sources, rather than the sulfate fraction derived primarily from coal combustion. To better understand these findings and verify if they hold true in a toxicological (controlled) setting, the TERESA (Toxicological Evaluation of Realistic Emissions of Source Aerosols) study was initiated. This study will investigate the formation and relative toxicities of secondary products from coal combustion and mobile source emissions through on-site sampling of emissions at multiple coal-fired power plants across the U.S. Emissions will be “aged” in a reaction chamber and converted to reaction products in a manner that simulates the conversion experienced by coal power plant plumes in the atmosphere en route to ambient receptor sites. Normal and compromised laboratory rats will be exposed to these emissions and a number of toxicological endpoints will be evaluated. The overall study design is shown in Figure 1.

Figure 1. TERESA study design.



TERESA is a significant improvement over previous studies to investigate the toxicity of coal combustion-derived particulate matter by virtue of several highly innovative and unique design features. First, all toxicological studies of coal combustion emissions to date (some of which have shown biological effects) have used primary emissions, ie. coal fly ash (e.g. MacFarland et al., 1971; Alarie et al., 1975; Raabe et al., 1982; Schreider et al., 1985; Dormans et al., 1999). The relevance of primary emissions to human population exposures is unclear, since primary PM emissions are now very low with the widespread introduction of particulate controls on power plants. It is the secondary particulate matter formed from SO<sub>2</sub> and NO<sub>x</sub> in stack emissions as well as any residual primary PM that is of interest with respect to evaluating the health impacts of power plant emissions. No efforts to consider and account for secondary atmospheric chemistry have been made to date. By examining aged, atmospherically transformed aerosol derived from stack emissions, TERESA will enable the investigation of the toxicity of emissions sources in a manner that more accurately reflects the exposure of concern. In addition, the project will allow investigation of the effect of different atmospheric conditions on the formation of secondary PM. This project is the first to develop and demonstrate reactive chemistry processes for coal combustion emissions in a toxicological setting. Reactive chemistry in the context of health effects assessment has been considered in other settings, however. For example, a body of literature is accumulating which evaluates the pulmonary effects of the reaction products of terpenes with ozone (Rohr et al., 2002; Rohr et al., 2003; Wilkins et al., 2003) and ozone/nitrogen dioxide (Wilkins et al., 2001).

Another advantage over previous studies is that the primary PM used in those studies has typically been generated through the use of pilot combustors in a laboratory setting. There is concern that pilot combustors may not accurately mimic stack emissions due to differences in surface to volume ratios and thus time-temperature histories. The fact that TERESA involves assessment of actual plant emissions in a field setting is a critical strength of the study, since it eliminates any question of representativeness of emissions. Some studies have also collected coal fly ash (CFA) from power plant electrostatic precipitators (ESPs) and used this material in intratracheal instillation or *in vitro* studies (e.g. Broeckaert et al., 1997; Costa and Dreher, 1997). Neither of these modes of delivery of PM is optimal due to the likelihood of extremely high tissue doses and overload. Concerns also exist regarding differences between the collected particles and those that penetrate the ESPs into the ambient environment, as well as possible alterations in the physicochemical properties of the collected particles while in storage.

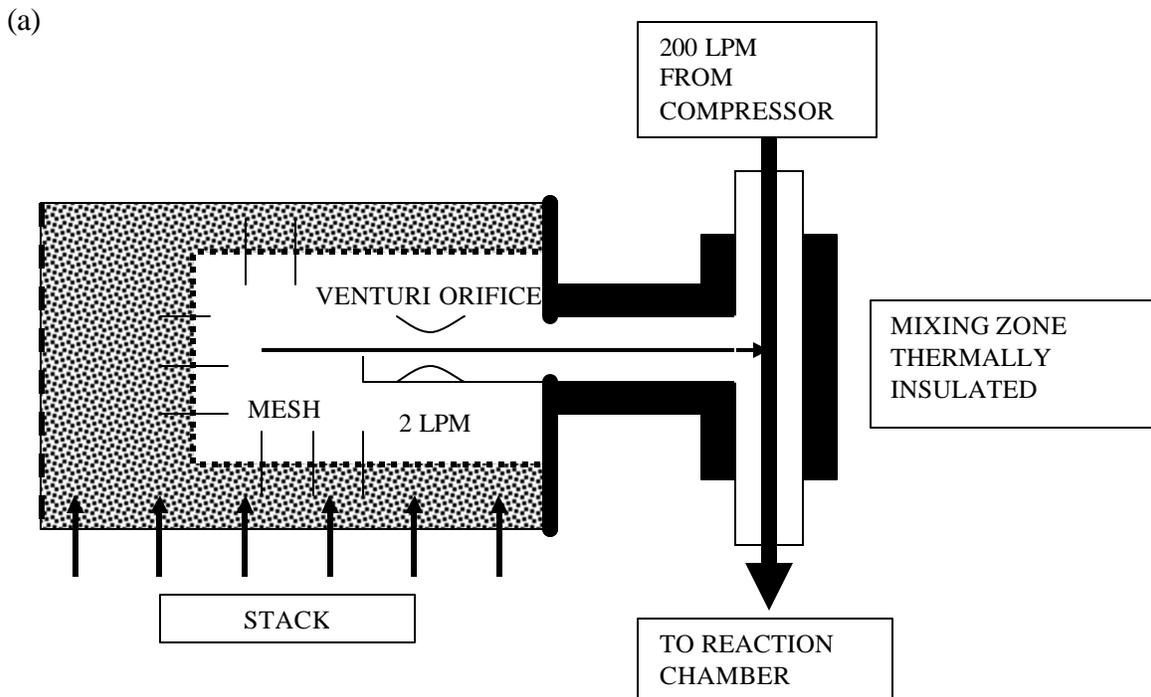
The overall goal of the TERESA study is to investigate and clarify the impact of the sources and components of fine particulate matter (PM<sub>2.5</sub>) on human health via a set of realistic animal exposure experiments. Specific objectives of the study are to: (1) evaluate the relative toxicity of coal combustion emissions and mobile source emissions, their secondary products, and ambient particles; (2) provide insight into the effects of atmospheric conditions on the formation and toxicity of secondary particles from coal combustion and mobile source emissions through the simulation of multiple atmospheric conditions; (3) provide information on the impact of coal type and pollution control technologies on emissions toxicity; and (4) provide insight into toxicological mechanisms of PM-induced effects, particularly as they relate to susceptible subpopulations.

## EXPERIMENTAL

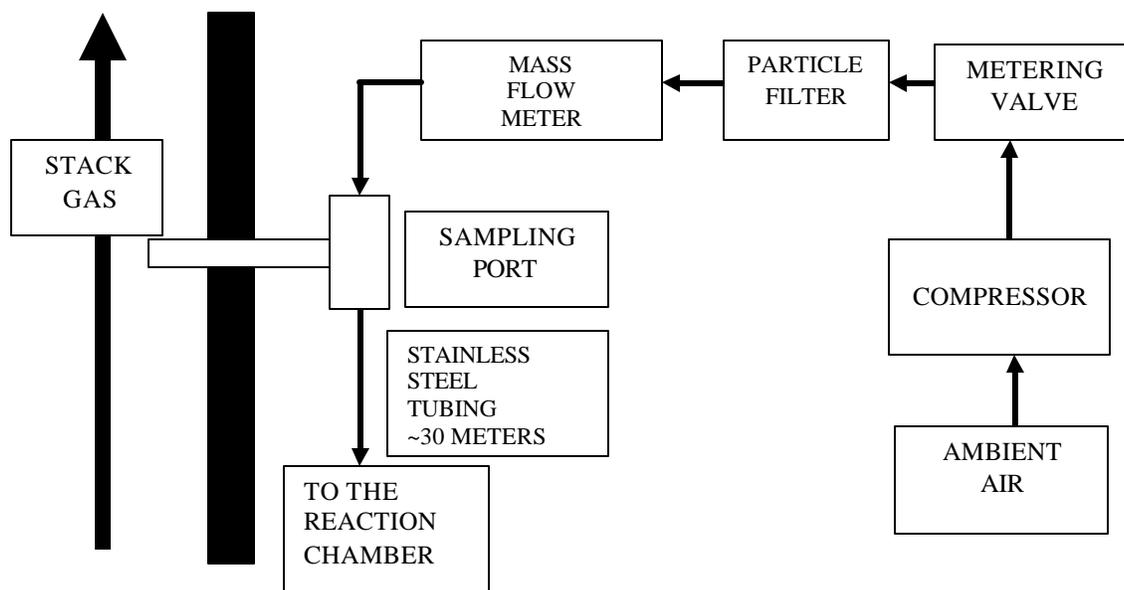
**Plant selection.** Currently, the TERESA program includes three coal-fired power plants, with additional plants planned. The first plant is located in the Upper Midwest and utilizes Powder River Basin (Wyoming) coal, with very low sulfur and low ash. One of the remaining two plants will use low sulfur (<1%) eastern bituminous coal, and the other will use medium-to-high sulfur (>2-3%) eastern bituminous coal. At least one of the plants will have a selective catalytic reduction (SCR) unit for NO<sub>x</sub> removal, and the medium-to-high sulfur unit will utilize a wet or dry scrubber for post-combustion SO<sub>2</sub> removal.

**Stack sampling/dilution system.** A system will be installed to collect and dilute emissions from the power plant stack (Figure 2). A stainless steel fine mesh screen will be used to remove particles larger than 10 $\mu$ m in order to prevent clogging in the sample flow control and dilution components. A novel design consisting of a novel Venturi critical orifice and a Venturi aspirator will be used to control the flow of dilution air. The Venturi aspirator accelerates a flow of 200 LPM of compressed, particle-free ambient air through a narrow constriction; thus, by the Bernoulli principle, a vacuum is created in a side arm perpendicular to the constriction, which draws the stack gas through the Venturi orifice and simultaneously dilutes it with ambient air. Because the Venturi orifice requires a minimum 10 kPa pressure drop to achieve a sample flow of 2 LPM, a wide range of dilution ratios can be achieved by varying the dilution flow. The dilution air will cool the stack gas to ambient temperature and prevent condensation of water in the sampling line. The diluted stack gas will be transported to the reaction chamber through a 30-meter long stainless steel tube; the relatively high flow of 200 LPM will allow for a very short residence time in the tube, minimizing the losses of ultrafine particles and reactive gases.

Figure 2. Sampling and dilution system. (a) sampling port; (b) dilution system.



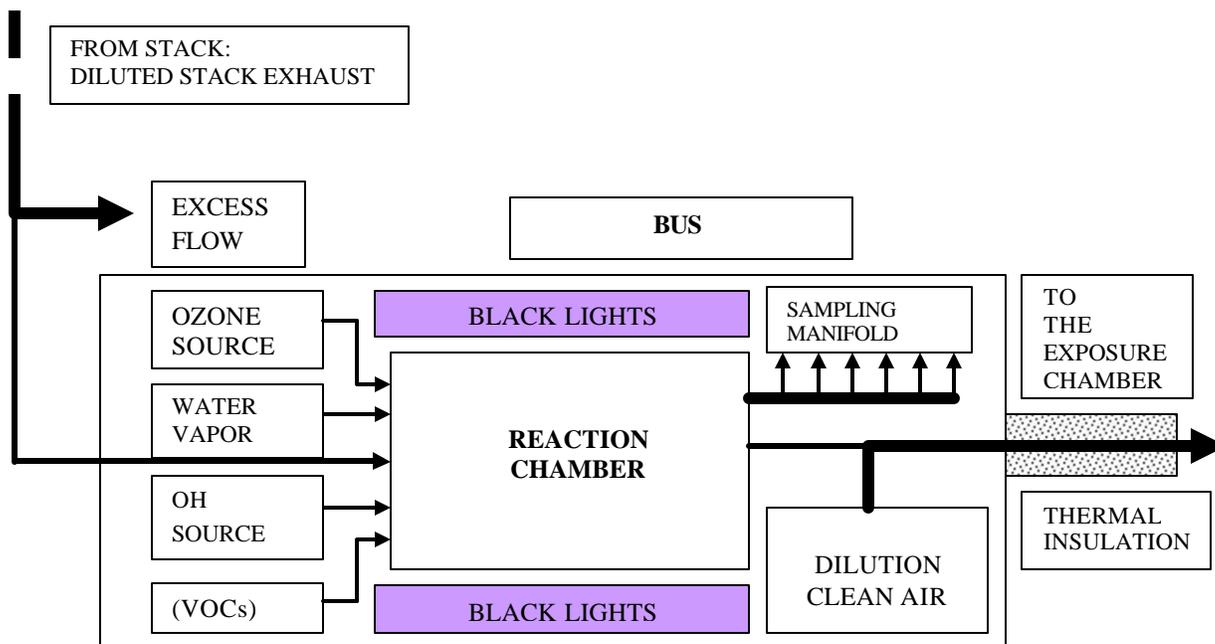
(b)



**Atmospheric reaction simulation system.** The atmospheric reaction simulation system is a critical component of the TERESA study design, since the basis for the toxicity assessment lies in the generation of realistic exposure atmospheres. The formation, composition, and toxicity of particles will be related to different atmospheric conditions and plume dilution scenarios through variations in reaction conditions.

The atmospheric reaction simulation system (Figure 3) will be placed in a mobile chemical laboratory. In the coal power plant setting, diluted stack emissions will flow under positive pressure into a reaction chamber inside the mobile chemical laboratory. In the reaction chamber, diluted stack exhaust is exposed to atmospheric oxidants (i.e., hydroxyl radicals, •OH) to convert SO<sub>2</sub> and NO<sub>x</sub> in the stack exhaust to sulfuric acid and nitric acid. The chamber has been designed to oxidize approximately 30% of SO<sub>2</sub> to sulfuric acid within an approximately 60-minute residence time. Although a larger fraction of the SO<sub>2</sub> could be oxidized during a longer residence time, it is necessary to minimize residence time in order to (1) keep the chamber small enough for a mobile reaction chamber facility; (2) keep equilibration times sufficiently short to prepare for animal exposures; and (3) reduce losses of ultrafine particles within the chamber. A key reason for maintaining approximately 30% SO<sub>2</sub> conversion is that it represents a reasonable atmospheric scenario, taking into account transport, deposition, and typical rates of oxidation. By converting a similar fraction in the chamber, an environmentally relevant ratio of metals to sulfate will be maintained in the exposure chamber, representative of atmospheres downwind of power plants. Under typical ambient conditions during warm seasons, SO<sub>2</sub> conversion occurs at a rate of ~3% per hour; to allow reasonable residence times within the reaction chamber, oxidant concentrations will be increased to accelerate aging.

Figure 3. Reaction chamber.



The reaction chamber is constructed using 2 mil Teflon film to allow passage of UV light, and measures 12 in x 4 ft x 5 ft (approx 300 L). The chamber configuration was designed to maximize the number of lights while also minimizing the surface-to-volume ratio. The Teflon film has essentially no absorbance in the region of the spectrum of interest (320-500 nm). In addition, Teflon is non-reactive, which minimizes both the potential loss of SO<sub>2</sub> and O<sub>3</sub> on the chamber walls and the formation of secondary products through heterogeneous chemistry (Cocker et al., 2001). Photolysis within the reaction chamber is induced using Q-Panel UV 313. The UV 313 lights provide greater light intensity in the lower end of the light spectrum. A filter of cellulose acetate is used to absorb light = 290 nm. The OH radical generation system has been already optimized using two prototype photochemical chambers. The most successful system utilizes the photolysis of O<sub>3</sub> induced by the short wavelength light emissions described above. Similar approaches have been used in photobiology for testing biological effects of solar light. The increased energy in the lower end of the solar spectrum should also allow photolysis of carbonyls and dicarbonyls, thereby benefiting the (subsequent) mobile source emissions portion of the study, as well as the scenario utilizing VOCs. Since stack effluent is diluted with ambient air, when necessary, water vapor will be added to the chamber to maintain sufficient humidity (about 60%) to enhance formation of sulfuric acid and particle growth. RH will be monitored continuously and adjusted using a feedback system.

In addition to the diluted stack exhaust and oxidants, other reactants will be added to the reaction chamber. Some of the exposure scenarios include the addition of ammonia gas (NH<sub>3</sub>) as a partially neutralizing medium for the acidic sulfate aerosol prior to exposure. VOCs (*d*-limonene, *a*-pinene or another terpene) will also be added for some of the exposure scenarios to simulate the conversion of VOCs to organic PM from the power plant plume

mixing with biogenic emissions. Particulate formation and toxicity from oxidation of these compounds in the presence of ozone has been characterized (Rohr *et al.*, 2002).

To provide the flexibility to proceed with a conversion rate for SO<sub>2</sub> of 30%, a “gas cleaning system” has been designed and evaluated; the system uses a gas-permeable membrane to allow removal of excess SO<sub>2</sub>, NO<sub>x</sub>, ozone, and other pollutant gases, while keeping the secondary particles suspended in air. This system will allow achievement of final exposure atmospheres that have gaseous pollutant levels below concentrations expected to cause health effects, while maintaining particle levels at concentrations at target levels.

**Exposure scenarios.** The first five of the six different exposures reflect a variety of typical atmospheric conditions as shown in Table 1 below. A sixth control exposure will be conducted using only the atmospheric components (no emissions) of the scenario shown to induce the largest effects of 3, 4, and 5. In addition, laboratory work will be conducted to investigate the contribution of gases versus particles to any biological effects observed by filtering out only particles (not gas phase components) from the atmosphere of the scenario (3, 4, or 5) shown to induce the largest effects.

Table 1. Exposure scenarios and corresponding atmospheric conditions.

Scenario	Composition	Simulated Atmospheric Condition
1	Gas- and particle-free air	Sham exposure
2	Primary (un-aged) emissions diluted to the range of 50 µg/m <sup>3</sup> SO <sub>2</sub> using clean air (same dilution as for 3, 4, and 5 below)	Primary stack emissions
3	Primary emissions + hydroxyl radicals	Aged plume, oxidized stack emissions, sulfate aerosol formation from nucleation
4	Primary emissions + hydroxyl radicals + ammonia	Aged plume, sulfate aerosol partially neutralized by ammonia
5	Primary emissions + hydroxyl radicals + ammonia + VOCs	Aged plume, mixture of neutralized sulfate and secondary organic aerosol derived from biogenic emissions

**Exposure characterization.** Exposure atmospheres will be comprehensively monitored for pollutant gases, particle number and size distribution, and inorganic and organic particle composition using an array of continuous and integrated methods. Following transfer from the reaction chamber, the diluted photochemically aged air will be drawn through a manifold that provides sampling ports for characterization, and into an exposure manifold. Sampling will be conducted at four locations: (1) input into the photochemical reaction chamber (i.e. diluted primary emissions); (2) continuous measurements alternating upstream and downstream of the photochemical chamber; (3) output of the photochemical reaction chamber upstream of the gas cleaning device (i.e. aged emissions); and (4) input into the animal exposure chamber (diluted aged emissions). The locations of the sampling ports are indicated schematically in Figure 4. The specific sampling parameters for each of these locations are described in Table 2 below.

Figure 4. Location of sampling ports.

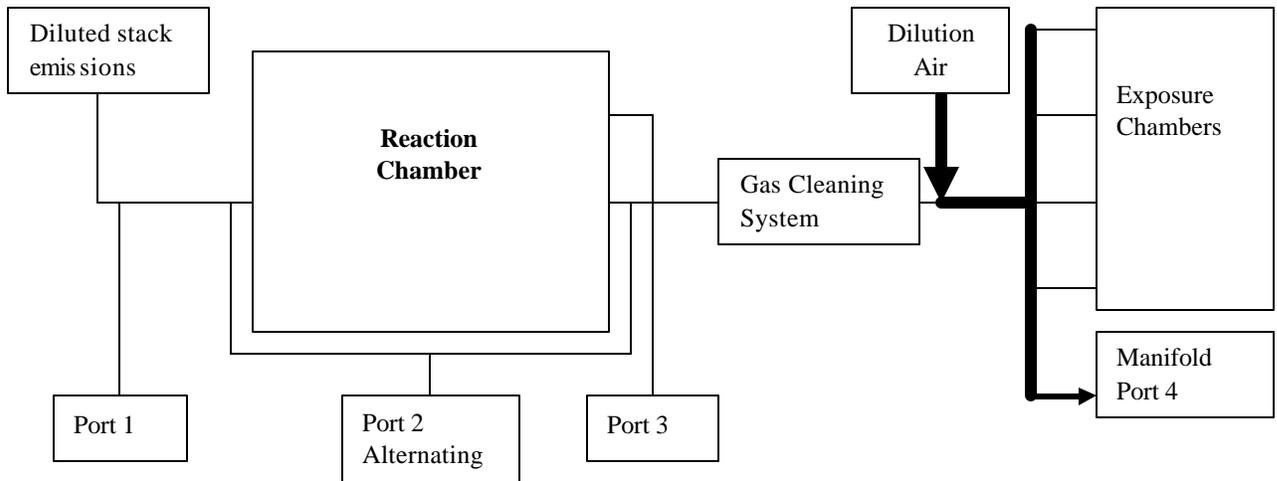


Table 2. Summary of sampling locations and analytical methods.

Site	Process for Measurement	Particles	Gases	Other
1	Chamber Input (Diluted Primary Emissions)	<i>Integrated (TSP)</i> : Mass, $\text{SO}_4^{2-}$ , $\text{H}^+$ , $\text{NO}_3^-$ , EC/OC, $\text{NH}_4^+$ , Specific Organics* <i>Semi Continuous (PIXE Streaker)</i> : elemental analysis		---
2	Chamber Performance (Alternating up and downstream)	<i>Continuous</i> : APS and SMPS (size distribution)	<i>Continuous</i> : $\text{SO}_2$ , CO, NOx, $\text{O}_3$	---
3	Chamber Output (Aged Emissions)	<i>Integrated (TSP)</i> : Mass, $\text{SO}_4^{2-}$ , $\text{H}^+$ , $\text{NO}_3^-$ , EC/OC, $\text{NH}_4^+$ <i>Semi Continuous (PIXE Streaker)</i> : elemental analysis	<i>Integrated (HEADS)</i> : $\text{SO}_2$ , $\text{HNO}_3$ , $\text{HNO}_2$ , $\text{NH}_3$ ; HCHO	<i>Continuous</i> : Temperature, RH
4	Exposure Chamber (Diluted Aged Emissions)	<i>Continuous</i> : TEOM (Mass), CPC (total count), Aethalometer (BC) <i>Integrated</i> : Mass, $\text{SO}_4^{2-}$ , $\text{H}^+$ , $\text{NO}_3^-$ , $\text{NH}_4^+$ , EC/OC,	<i>Continuous</i> : $\text{SO}_2$ , CO, NOx, $\text{O}_3$ <i>Integrated</i> : $\text{NH}_3$ , HCHO	<i>Continuous</i> : Temperature, RH

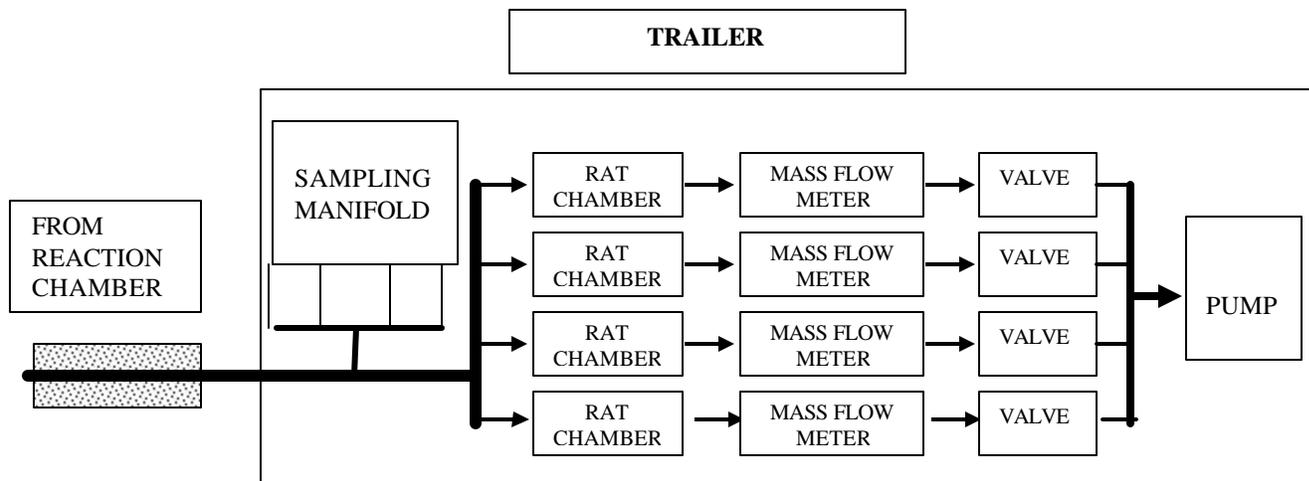
Specific Organics: target combustion derived particulate organics (e.g., PAHs)

Integrated particulate samples for mass, sulfate, nitrate, particle strong acidity, ammonium, and specified organic species will be collected on Teflon membrane filters with no size selective inlets. Since the contribution of the secondary aged aerosol is expected to be much,

much greater than the contribution of the primary emission coarse and fine particles (as discussed above), there is no need to separate the coarse or fine particles from the collected particulate samples. Integrated particulate samples for EC/OC analysis will be collected on pre-fired quartz fiber filters, again with no size selective inlet. Sulfate, nitrate, and ammonium ions will be measured by ion chromatography, and particle strong acidity will be measured by pH analysis. For plants using SCR, if a significant amount of ammonia is generated, this ammonia will either partially or completely neutralize the strong acidity (H<sup>+</sup>). It is not feasible to accurately measure the gas phase ammonia concentration. However, measurements of sulfate, ammonium ion, and H<sup>+</sup> will allow the determination of the relative contribution of this ammonia to the composition of the primary emission particles. If there is an excess of ammonia compared to primary emission of acid sulfate particles, then there will be enough to subsequently neutralize part of the secondary acidic sulfate particles produced in the reaction chamber. Thus, measurements of both primary and secondary particles will reveal the magnitude of the ammonia effects. Organic and elemental carbon will be measured by the thermal optical reflectance (TOR) method. Organic speciation of PM<sub>2.5</sub> will be conducted by gas chromatography, emphasizing known toxic species of combustion origin (e.g. PAHs). A commercially available circular Streaker sampler will be used to automatically collect sequential particle samples for measurement of both trace metals and black carbon. We expect adequate sensitivity for both measurements using sample durations of about one hour. The collected samples will be analyzed for elements using proton induced x ray emission (PIXE). The filters obtained by the Streaker sampler will also be analyzed by light transmittance, using a custom-built photometer, to determine black carbon. Size distribution of primary and aged emissions will be evaluated continuously using an aerodynamic particle sizer (APS) and scanning mobility particle sizer (SMPS). Continuous particle count will be measured at the exposure chamber using a condensation particle counter (CPC), and continuous mass concentration will be monitored using a TEOM (Tapered Element Oscillating Microbalance). In addition, continuous black carbon will be measured using an aethalometer. Continuous measurements of CO, CO<sub>2</sub>, ozone, SO<sub>2</sub>, and NO<sub>x</sub> will be conducted. Gaseous ammonia will be measured by the diffusion denuder technique with ion chromatographic analysis. Formaldehyde will be sampled using DNPH or DNSH coated cartridges and analyzed by HPLC.

**Animal exposure laboratory.** Animal exposures will be performed using both normal and compromised laboratory rats in a temperature- and RH-controlled exposure chamber located in a separate mobile toxicological laboratory (Figure 5). Photochemically-aged air will be drawn from the atmospheric reaction chamber into a sampling manifold, and diluted with humidity-controlled clean air (ambient air with pollutant gases and particles removed) to maintain the target particle mass levels and to achieve a sulfate particle concentration of approximately 250 µg/m<sup>3</sup>. Air will be drawn through individual exposure chambers in parallel. Exposures will be 4 hours in duration and will be immediately preceded and followed by a 1-hour exposure to humidity adjusted zero air (baseline and recovery periods, respectively). Animals will be maintained and studied in accordance with the National Institutes of Health guidelines for the care and use of animals in research. All protocols will also be approved by the Harvard Medical Area Standing Committee on Animals.

Figure 5. Animal exposure facility.



**Toxicological assessments.** Normal rats will be exposed to all scenarios and a Stage I toxicological assessment will be performed. The scenario inducing the greatest effects will then be utilized in the Stage II toxicological assessment using a rat model of myocardial infarction (MI), which is a model of a “heart attack” in humans. Susceptible animal models mimic human diseases or conditions that may make humans more sensitive to the effects of air pollution. These models can help determine which population subgroups are at highest risk as well as provide additional insight into the mechanism(s) of PM effects.

In the Stage I toxicological assessment, pulmonary, cardiac, and systemic effects in normal female Sprague-Dawley rats will be evaluated via bronchoalveolar lavage (BAL), histopathology, pulmonary function, *in vivo* oxidative stress, and blood cytology. Pulmonary function will be evaluated using the BUXCO system (Buxco Biosystem 1.5.3A). Markers of pulmonary function include peak expiratory flow (PEF), tidal volume (TV), respiratory frequency (F), and minute ventilation (MV) (Clarke et al., 1999). Bronchoalveolar lavage (BAL) will be performed, and BAL fluid will be analyzed for cellular content (cell viability, total cell counts, cell type) and biochemical markers of pulmonary injury (lactate dehydrogenase (LDH),  $\beta$ -n-acetyl glucosaminidase ( $\beta$ NAG), and total BAL protein) using standard methodologies. Pulmonary histopathology will be assessed by fixing lungs and randomly selecting three slices for processing by paraffin histology techniques. *In vivo* oxidative stress of heart and lung tissue will be conducted via organ chemiluminescence (CL), a novel method that refers to the ultra-weak light emission produced by biological systems due to the de-excitation of high-energy byproducts of the chain reaction of lipid peroxidation (Boveris and Cadenas, 2000; Boveris et al., 1980). This method has been successfully used in models of oxidative injury in the lung (Gurgueira et al., 2002; Evelson et al., 2000; Turrens et al., 1988; Barnard et al., 1993). Blood cytology (total white blood cell

counts and differential profiles) will be evaluated 24 hours following the last day of exposure.

The scenario producing the greatest effects in normal rats (Stage I toxicological assessment) will be repeated using a myocardial infarction (MI) rat model (Wellenius et al, 2002). To produce the MI model, the fine tip electrode of a portable high-temperature thermocautery unit is briefly and repeatedly applied to one or more branches of the left coronary artery. Visible discoloration of the affected region indicates that blood flow has been successfully interrupted. Telemeters for electrocardiogram monitoring will be surgically implanted in Male Sprague-Dawley rats, and monitoring of heart rhythm will be monitored throughout exposure. Blood chemistry and pulmonary function will also be evaluated. For the MI exposures, three exposure scenarios will be assessed: (1) sham (room air); (2) one aged power plant emission scenario; and (3) one aged mobile source emission scenario.

Cardiac function will be assessed by electrocardiography (ECG), with endpoints of interest including heart rate, heart rate variability (standard deviation of the normal beat-to-beat intervals; SDNN), and arrhythmias. Blood chemistry will be evaluated by measuring complete blood count, circulating cytokines (interleukins-1 and -6), C-reactive protein (CRP), tumor necrosis factor alpha (TNF- $\alpha$ ), and the vasoactive mediator endothelin-1. All biochemical markers will be determined using standard immunoassay techniques. Pulmonary function will be assessed using the BUXCO method as described earlier.

**Data analysis.** The biological effects observed during the six exposure scenarios performed at each plant (sham, primary emissions, oxidized emissions, neutralized emissions, emissions plus volatile organic compounds, and atmospheric components only for the aged emission scenario which shows the highest health effects) will be conducted. For each biological endpoint, two-way analysis of variance (ANOVA) tests will be employed to assess differences. To determine the effect of PM composition on biological response, mixed effects models containing exposure metrics as fixed effects will be fitted to each response outcome measure. Multivariate analyses will be carried out in relationship to various component concentrations. Statistical significance for all analyses will be based on  $\alpha = 0.05$ .

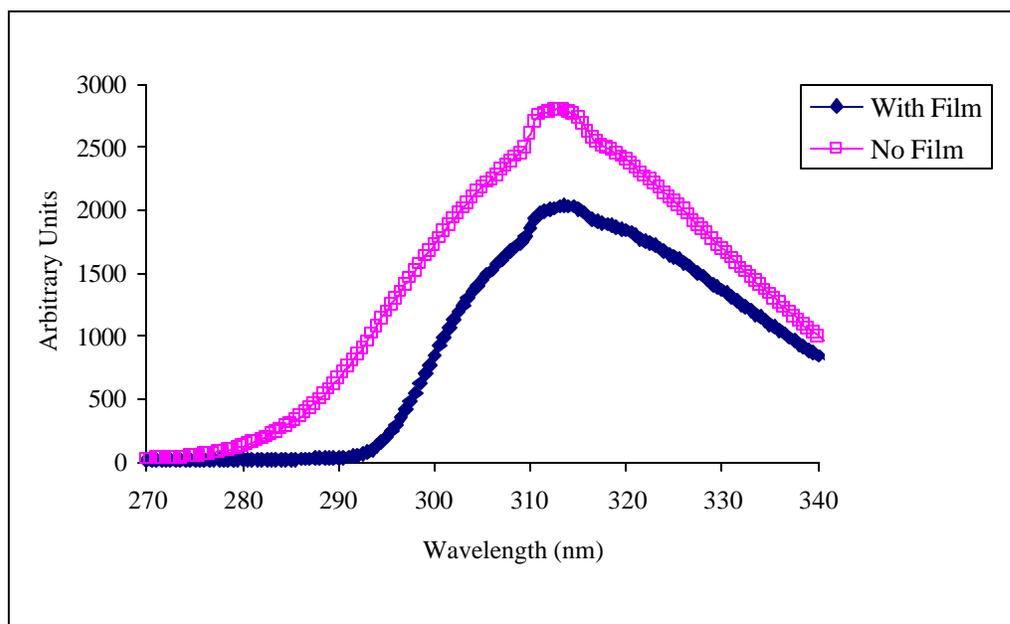
**Mobile source and CAPs assessment.** The mobile source assessment will involve the sampling of diesel and/or gasoline engine emissions directly from a vehicle. The specific type and age of vehicle will be determined through a consultative process with individuals with appropriate expertise. The methodologies for atmospheric simulation, animal exposure, and toxicological assessment will be completely analogous to the methods used for coal combustion emissions, and the same mobile atmospheric reaction simulation and animal exposure laboratories will be used to ensure similarity of exposure methods and conditions. For the CAPs comparative toxicity assessment, existing CAPs data from the HSPH laboratory will be used. HSPH has conducted a number of investigations in rats and canines using CAPs (Clarke et al., 1999, 2000; Godleski et al., 2000; Saldiva et al., 2002; Gurgueira et al., 2002; Wellenius et al., 2002).

## RESULTS AND DISCUSSION

Currently, methods development and validation work is underway to prepare for fieldwork at the first TERESA plant. The following sections describe preliminary results of these efforts.

*Light Source.* The spectral quality of the light irradiated to the reaction chamber was investigated using spectroradiometry. The objective of the light sources in the reaction chamber is to provide as much light in the lower end of the solar spectrum as possible in order to photolyze  $O_3$  to produce  $O^1D$ . At the same time, the light sources should not produce light of shorter wavelength than the solar spectra, that is, lamps should not emit light of wavelength below 290 nm. Figure 8 shows that UVB-313 lamps are effective at emitting low wavelength radiation, but they produce emissions below 290 nm not present in solar spectra at ground level. In order to avoid this, the lamps were covered with cellulose acetate film (13 mil), which effectively removes radiation below 295 nm while being almost fully transparent for longer wavelength emissions. The emission spectra of UVB-313 lamps covered by this film are shown in Figure 6, where it can be seen that all the radiation below 290 nm has been removed.

Figure 6. Emission spectra from UVB-313 lamps.



*Reaction chamber performance.* The ability of the reaction chamber to oxidize diluted power plant emissions was assessed using simulated emissions. Emissions consisted of a mixture of  $SO_2$  and  $NO$  in the same concentration ratio as expected at the first field power plant in the Upper Midwest ( $ppbNO/ppbSO_2 = 0.6$ ). Also, the simulated emissions represent a stack

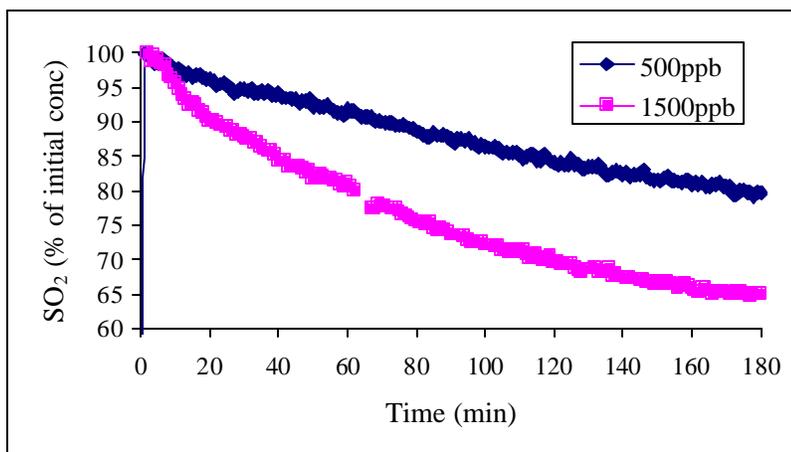
dilution of 1:200. Given these constrictions, the actual concentration of SO<sub>2</sub> and NO through the chamber were 1000 ppb and 600 ppb, respectively.

The primary force to oxidize SO<sub>2</sub> is the photolysis of O<sub>3</sub>. In order to produce an environment rich in O<sub>3</sub>, diluted simulated emissions were mixed with O<sub>3</sub> produced by Pen-Ray lamps. The added O<sub>3</sub> was sufficient to completely oxidize NO to NO<sub>2</sub> and produce excess O<sub>3</sub> inside the chamber. Relative humidity in the chamber was 50%, and temperature was 30 C. Residence time was 60 minutes and total flow through the chamber was 5 LPM.

A run typically consisted of an equilibration stage and a reaction stage. In the equilibration stage, the mixture of gases was equilibrated inside the chamber for enough time to achieve steady concentrations of NO, NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>. This stage was performed in the absence of light and typically lasted several hours. The reaction stage was initiated when UVB-313 lamps were turned on. The performance of the chamber was measured as the rate of SO<sub>2</sub> conversion and production of particles.

Figure 7 shows the conversion of SO<sub>2</sub> over time for two runs performed at two O<sub>3</sub> concentrations (500 ppb and 1500 ppb). As expected, the conversion rate was higher for the mixture with higher O<sub>3</sub> concentrations. Using this method, the total conversion rate of SO<sub>2</sub> after equilibration was estimated as 25% (250 ppb of SO<sub>2</sub>) for the 500 ppb O<sub>3</sub> mixture and 40% (400 ppb) for the 1500 ppb O<sub>3</sub> mixture.

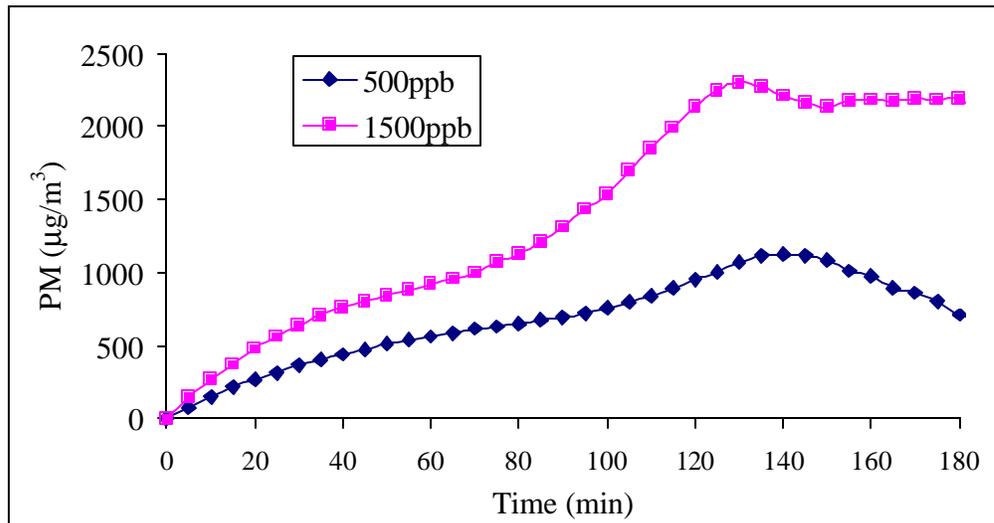
Figure 7. Conversion of SO<sub>2</sub>: effect of O<sub>3</sub> concentration.



The aerosol mass produced inside the reaction chamber can be estimated using the reported volume concentration of aerosol by the APS and SMPS. These estimations were conducted assuming an aerosol density of 1g/cm<sup>3</sup>. The total aerosol concentration is the sum of the concentrations reported by the SMPS in the range of 13 to 600 nm, and by the APS in the range of 600 to 20,000 nm. As shown in Figure 8, mass increased rapidly after lights were turned on, with a much higher production rate for the mixture tested at a higher O<sub>3</sub> concentration. The observed aerosol mass concentration was approximately 1000 μg/m<sup>3</sup> for the reaction at low O<sub>3</sub>, and 2000 μg/m<sup>3</sup> for the reaction at high O<sub>3</sub>. The expected H<sub>2</sub>SO<sub>4</sub> mass

given the SO<sub>2</sub> conversion of 250 ppb (at low ozone) and 400 ppb (at high ozone) is 1000 and 1600 µg/m<sup>3</sup>, respectively. Therefore, the observed and expected mass measurements are roughly in good agreement. Sources of uncertainty in the mass measurements include particle density, amount of aerosol-bound water, and particle losses inside the chamber.

Figure 8. Aerosol formation in reaction chamber: effect of O<sub>3</sub> concentration.



The above results document the validity of the reaction chamber in oxidizing simulated emissions to form particles. During fieldwork, it is expected that the ozone concentration will be approximately 1000 ppb; however, the gas-permeable membrane (analogous to a nonspecific denuder) will allow removal of excess ozone (and other gases), while maintaining sufficient secondary aerosol for exposure. Target PM exposure concentrations are in the order of 200 – 300 µg/m<sup>3</sup>.

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