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Title: BALTIMORE SUPERSITE: HIGHLY TIME AND SIZE RESOLVED CONCENTRATIONS OF URBAN PM2.5 AND ITS CONSTITUENTS FOR RESOLUTION OF SOURCES AND IMMUNE RESPONSES

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Project Period: January 1, 2000 to December 31, 2003
Project Cost: $3,400,000

PROJECT SUMMARY
We propose to conduct a Supersite project in Baltimore to provide an extended, highly time, size, and compositionally resolved data set, including an indicator of cardiopulmonary response in support of testing hypotheses relating to source attribution and health effects of PM. Such information is needed to support development of State Implementation Plans and the setting of National Ambient Air Quality Standards. Specific hypotheses involve investigations of the toxicity of aerosol components as affected by age, industrial vs urban character, and seasonal differences in source terms and atmospheric chemistry. The toxicological metrics chosen, i.e., cytokine and reactive oxygen species (ROS) assays, will be used in correlations with PM metrics, in much the same manner as EPA's Integrated Air Cancer Program used mutagenicity assays to apportion ambient PM mutagenicity among air pollution sources. The project will encompass hourly resolved cytokine/ROS assays of PM2.5 as a metric of toxic response; along with similarly time-resolved measurements of PM mass, number vs size distribution, light-scattering coefficient; PM sulfate, nitrate, organic carbon, and elemental carbon using commercial continuous and semi-continuous monitors. In addition, three important new instruments will be fielded: UMCP's semi-continuous monitor for quantitatively determining aerosol metals and trace elements; UDE's third generation single particle mass-spectrometric analysis system (RSMS III) for continuous size and semi-quantitative determination of individual aerosol particle constituents, from 10 nm to 2.5 μm; and JHU's advanced 3 wavelength LIDAR for three dimensional mapping of Baltimore's wind fields and aerosol concentrations, including plumes from discrete sources. Traditional 24-hr collections for FRM mass and selected aerosol constituents will provide the link with PM network data. Extensive exploratory organic compound analyses will be performed to reveal the presence of potentially useful

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tracer species for receptor modeling, and identities and concentrations of potentially toxic PM organic constituents, especially, water soluble polar organic compounds which might contribute to cardiopulmonary-related responses.   Gram quantities of PM2.5 will be collected weekly and archived for subsequent use by the research community

     The Highly-time (hourly and subhourly) size, and species resolved composition metrics will permit resolution of their contributions by sources, thus, providing the link between the health effects metric and sources. Source allocations will be reinforced by inclusion of the standard meteorological data in the multivariate analyses and 3-dimensional wind field and particle concentration maps. Plume width and, thus, time of influence on a fixed site increases with increasing distance from the source. Thus, with highly time-resolved pollutant metrics local (even individual), more distant, and regional source contributions will likely be readily resolved into different factors by multilinear regression and advanced factor analysis techniques. The 3-D maps will powerfully and visually document the movement of particles from the sources to the receptor, and ultimately improve our understanding of atmospheric stability and seasonal-mesoscale flow patterns in driving aerosol fields over Baltimore city. Note that Baltimore, like most of the large northeastern deepwater port cities, experiences highly complicated local flow patterns which make source-based modeling extremely difficult.

   Time-resolved rotating drum impactors (RDI) will be used to separate fresh accumulation aerosol from nearby sources from aged and cloud processed aerosol, and from tailing coarse particle fractions. The spectra determined from RDI measurements will be used to confirm plume "hits" and as a calibration reference for single particle measurements. Cytokine and ROS assays on selected RDI samples will be performed to investigate differences in aerosol age. Mulitvariate calibration models will be used to statistically interpret and interrelate data developed by the variety of new and established techniques. Professor Hopke will utilize his considerable experience in both aerosol measurements and advanced data analysis methods (MLR, PLS, and back propagation neural networks), to provide these critical data analyses.

     The equipment will be installed in trailers and deployed to a primary urban site, an industrially influenced urban residential site, and community sites, in support of hypotheses suggested above. Measurements will be made continuously over a 12 month period and will encompass 45-day intensive campaigns to be conducted in summer and winter in South Baltimore to test hypotheses regarding effects of industrial influence and source resolving power of our measurement strategy.

          The influence of emissions from source regions at various distances, the variety and severity of local sources, the rich regional and interpretive contexts provided by the IMPROVE site at the Shenandoah National Park, the NARSTO upper air station at Ft. Meade, and abundance of prior regional   source attribution studies make Baltimore an excellent location for the proposed measurements and hypothesis testing. Given the severity of diverse sources in close proximity to densely populated areas combined with the complex wind fields, the Baltimore community of scientists and regulators desperately needs the extensive, array of high-quality data which we propose to develop.

Supplemental Keywords: Receptor modeling, aerosol particles, trace elements

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PROJECT DESCRIPTION

THE BALTIMORE SUPERSITE TEAM

The University of Maryland proposes to lead the following select group of internationally-recognized urban aerosol scientists most of whom have worked with one or more members of the team in workshops, pier review panels, proposals, and/or publications:

- University of Maryland at College Park (UMCP), led by Dr. John. M. Ondov, will be responsible for overall project management, deployment of a semi-continuous monitor for accurate determination of aerosol metals, a high-frequency aerosol slurry sampler for biologic testing, and a bulk PM2.5 collector, and retrospective quantitative elemental analyses.
- University of Delaware (UDE), led by Drs. Anthony S. Wexler and Murray V. Johnston, will deploy, and operate a 3nd generation automated single-particle mass spectrometer system for near-real time constituent analysis.
- Clarkson University (CU), led by Dr. P. K. Hopke, will be responsible for multivariate data reduction, hypothesis testing, data base development and management, and project quality assurance.
- University of Maryland at Baltimore (UMAB), led by Dr. Katherine Squibb, will be responsible for retrospective cytokine assays.
- Johns-Hopkins University (JHU). Dr. Timothy J. Buckley, will be responsible for measurements at urban community sites, integration with a series of health effects and exposure studies to be conducted during the project period, and local implementation of the QAQC plan; Dr. Marc B. Parlange for measurements with an advanced 3-color scanning LIDAR system for 3- dimensional mapping of urban wind fields and PM concentrations.
- Florida International University (FIU), led by Dr. Wolfgang Rogge, will be responsible for organic compound analysis for source identification.

GOALS OF THE BALTIMORE SUPERSITE PROGRAM

The goal of the Baltimore Supersite is to conduct special, detailed, and extensive high-quality, chemical and physical characterizations of urban aerosol particles in a relevant airshed in support of the following three **priority** objectives: i) development of State Implementation Plans (SIPS), ii) setting of National Ambient Air Quality Standards (for PM2.5, and possibly its constituents); and iii) evaluation and field testing of advanced measurement technology and methods to facilitate their transition to the monitoring arena. As specifically stated by EPA, priority objective i encompasses the development of data needed to substantially improve knowledge of source receptor relationships. Priority ii encompasses development of monitoring data **and samples** to support health and exposure studies, and health risk assessments. Implicit in this objective is the improvement of knowledge of relationships between PM and its toxic and epidemiologic effects on humans. As discussed below, we believe that the key to achieving such improvements lies in the application of advanced

technologies to provide far higher temporal resolution and far richer speciation of PM constituents than can be achieved by either EPA's traditional monitoring networks or even its soon-to-be-implemented Speciation Program. In addition, a key component of our proposal is the application of biological assays as a metric of human cardiopulmonary response.

BACKGROUND AND RATIONALE
Metrics of Cardiopulmonary Response
In our supersite we will measure metals and cytokine and reactive oxygen species induced in cell cultures by exposure to PM. Here we provide the rationale for these measurements. Recent epidemiologic studies have recently shown that short-term increases in urban particulate air pollution are associated with increased mortality and morbidity from respiratory and cardiovascular diseases (1-10). The studies suggest that non-accidental death rates in cities correlate with daily levels of respirable aerosol particles, even at particulate concentrations below the current National Ambient Air Quality Standard. Mortality victims tend to be elderly, with pre-existing respiratory disease, however Costa and Dreher (11) have reported that individuals with asthma appear to be at higher risk. Other studies have established a link between levels of airborne particles and respiratory symptoms in children and hospital admissions for bronchitis, asthma and pneumonia (12-17).

The precise mechanism by which air particles exert their toxic effects is not known. However, recent evidence suggests strongly that particles sufficiently small to reach the alveoli of the lung may directly initiate (or exacerbate) irritation of respiratory tissues by stimulating local cells to release reactive oxygen species (ROS; e.g., hydrogen peroxide and superoxide free radicals) and inflammatory mediators, such as cytokines like TNFα and IL-6 (18,19). Cytokines are messenger chemicals which help to regulate the immune response. Certain cytokines summon and activate additional immune cells such as polymorphonuclear phagocytes (PMN). These cells attack bacteria and foreign particles, delivering a burst of ROS which is accompanied by collateral damage to surrounding cells. Tissue damage can lead to changes in fluid balance which in turn can affect cadiopulmonary function. Recent animal studies have demonstrated that inhalation of particles induces inflammatory responses in the lungs (20). Numerous studies *in vitro* (21-23) further support the conclusion that the respiratory toxicity of respired particles lies in their ability to stimulate immune responses through an enhanced production of cytokines and reactive oxygen species (ROS). Thus, experimental evidence strongly suggests that a release of inflammatory mediators contributes to the toxic effects of particulate air pollutants.

There are many specific components of air particles could play a role in stimulating respiratory cells to produce cytokines and ROS. Possible candidates include endotoxin and inorganic compounds (11,20-22,24), mineral oxides (25,26), water-soluble metals (11, 20); diesel soot and/or its components (27), polar organic compounds (OC, e.g., produced by atmospheric oxidation of volatile OC), and the ultrafine aerosol particles. Recent studies indicate that, of these, water-soluble inorganic compounds seem to exert the most profound effects (11,20,22,24, 27,29,30-32). Adamson and coworkers (20) showed in animals that the pulmonary response and cell injury resulting from exposure to urban air particles was much greater for the water-soluble fractions compared to the insoluble material. Similarly, animal studies by Costa and Dreher (11) suggest that the dose of soluble metals, not particulate mass, relates most closely with associated cardio-pulmonary effects in both healthy and compromised hosts. In *in vitro* studies, Veronesi et al. (23) found that acidic,

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water soluble components of residual oil fly ash (ROFA) were responsible for the stimulation of cytokine release by respiratory epithelial cells. These studies argue against the importance of polar organics in the respiratory response to particulate matter.

Studies by Carter and coworkers (22) also suggest that specific metals might be more active than others in stimulating airway cells. Carter's results indicate that exposure to V increases cytokine production in airway epithelial cells and that vanadium compounds, but not those of Fe or Ni, mimic the cytokine response of airway epithelial cells to residual oil fly ash. Results reported by Becker et al. (21) also indicated that the Fe component of aerosol particles was not an important mediator of the cytokine response of alveolar macrophage, again suggesting that the inflammatory response is metal specific. Taken together, these studies provide strong evidence that water soluble components of urban PM are key determinants of the respiratory effects observed during air pollution episodes, due to their ability to stimulate the production of cytokines and ROS within the lung. The *in vitro* studies with airway cells strongly support and provide a mechanism for the inflammatory responses observed in whole animal studies. These results also demonstrate that cytokine and ROS responses by respiratory cells in culture are good indicators of *in vivo* responses to particles. These assays, then, provide us with a means of predicting key toxic response one would expect to see in an inhalation study and in humans exposed to these particles. By determining the immuno-reactivity of particles in ambient air, we can begin to identify key sources that will allow us to regulate and minimize human health effects of air pollutants.

These observations are especially important in view of the fact that the masses of various inorganic constituents, including first-series transition metals capable of producing ROS, heavy metals, and toxic metalloids, are predominately associated with primary aerosol emissions from high-temperature combustion sources (HTCS), such as coal- and oil-fired power plants (CFPP and OFPP), municipal and medical incinerators, diesel powered vehicles, and residential furnaces.

In addition to metals, secondary organic compounds are of interest as they are polar and, therefore, could in-part be responsible for cytokine and ROS production observed for soluble PM extracts (27). Little is know about the ambient concentrations of such compounds, so they need to be determined.

Nature of Urban Aerosols. In HTCSs, both particle composition and size are primarily governed by fuel composition , time-temperature history, and the type and efficiency of emission control devices (33). Most HTCSs are controlled, and virtually all of them emit large fractions of their mass in particles of respirable size. Their unique compositions provide the basis for receptor modeling and, thus, for tracing their movement in the atmosphere. Vanadium, for example, is highly enriched relative to the other elements in fuel oil due to the presence of V porphyrins and, for this reason, is extensively used as an inherent tracer of emissions from fuel-oil combustion (34). Likewise, Zn and Cd, Se, As, Ti, C, and sulfate are inherent tracers (i.e., marker elements) of particles from municipal incinerators; local coal combustion, steel production, paint manufacture and spray painting, diesel motor vehicles, and regionally-distributed secondary aerosol (31).

Theory and more than a decade of experimental evidence show that the discrete aerosol particle populations emitted from these sources largely remain discrete over the urban scale (33,36). Masked by the overwhelming presence of the secondary aerosol, these primary aerosol populations are not readily detected in aerosol mass or sulfate size distributions but are, instead, revealed through

measurement of key marker species (33). The result is that urban atmospheres are comprised of complex mixtures of physically-discrete aerosol populations rather than complex aggregates of particles from many sources. As a consequence, cardiopulmonary responses associated with specific atmospheric particle populations should be resolvable and attributable to specific types of sources which would, therefore, be subject to targeted control.

As discussed by Ondov and Wexler (36 and references therein), primary particulate mass emissions from HTCSs are emitted in narrow accumulation aerosol peaks with geometric mean diameters between 0.1 and 0.3 μm, and are observed in this size range in ambient size spectra of the their marker elements. Once in the atmosphere, these particles grow by capturing water vapor, sulfur dioxide (which becomes converted to secondary sulfate) and various other materials of secondary origin, including polar organic compounds. Thus, older or more highly-processed aerosol particles are substantially larger, i.e., with geometric mean sizes typically between 0.4 and 1 μm. (This includes "droplet" modes observed in size spectra for particles collected near the Chesapeake Bay (37) and over Lake Michigan (38). Thus, size selective sampling can be used to resolving local and distant sources. This has been well demonstrated (33)

It is important to realize that most toxic particulate air pollutants, including metals, metalloids, soot and its associated organic matter, are emitted in the primary particles, i.e., those emitted directly from the sources. Nearly all of the Secondary aerosol mass (e.g. sulfate, nitrate, ammonium, polar organic compounds) becomes associated with the primary particles. The role of secondary aerosol materials is, then, often to mediate primary particle size and chemistry, e.g., solubility of metals and their valence state. The role of polar secondary organic compounds and their immune responses is not well known, however, being water soluble, these may contribute to the toxicity attributed to soluble PM fractions.

Receptor Modeling. The data will be collected with very high time, size, and composition resolution and on a single particle basis. This advanced approach will facilitate receptor modeling, which is now discussed. As discussed by Gordon (35) the contributions of sources to ambient concentrations of PM2.5 mass and its various elemental constituents are frequently well-determined by receptor modeling techniques, i.e., models which assess source contributions based on observations of pollutants at sampling, i.e., receptor, sites. These typically involve chemical mass balance (CMB), multiple linear regression (MLR), factor analysis (FA), or some combination or modification of these basic model types. Note that despite efforts to improve emisison inventories for criteria and toxic air pollutants, the lack of accurate inventories generally precludes accurate source attribution by the emission/dispersion modeling approach. Instead, the agency relies heavily on receptor-based modeling for source attribution and for evaluation and development of source-based models. Receptor models have been approved for use in the development of SIPs and are EPA's most reliable tools for developing source-receptor relationships, especially in with complex air flow regimes.

Chemical mass balance(CMB) models permit quantitative estimation of the concentrations of PM and PM constituents attributable to the various generic sources provided that the relative abundances of various constituents of their emissions (i.e., "source profiles") are known. In the CMB approach, one assumes that the aerosol mass concentration (M) measured at the receptor is the linear sum of the contributions of its various sources. Generally, M_j is expressed in μg/m^3.

Provided that the "source profiles" (i.e., relative abundances of the pollutant species, X, for each of the sources) are known, coefficients representing the fractional contributions to these sources may be determined either by matrix inversion or by a least-squares fitting method. Once M_js are found, the contributions of toxic components and source-marker species are determined as the products of the Ms and Xs. Two great advantages of CMB are that quantitative apportionments are obtained directly and that the magnitude of the results are constrained by the ambient concentration data. However, it is necessary that all sources (or at least generic source types) influencing the receptor be identified and that accurate source profiles be available. Ambient PM concentrations and its various elemental constituents in Washington, DC, and rural areas around the Chesapeake Bay are well fit using available profiles (39). For example, 90% of aerosol PM is typically accounted for and differences between observed and apportioned concentrations of key source marker species are often <15% (35). A CMB can be determined on individual aerosol samples and the results correlated with cytokine and ROS responses. This approach would be most useful when applied to samples strongly influenced by a source whose PM elicits a strong response. This favors short sample collections and conditional sampling (i.e., winds from a narrow range of directions) to isolate aerosol from sources lying in certain directions.

As recognized by Lewis et al. (40), virtually any property of or "response" to aerosol particles emitted from a source (or sources) may be determined by MLR, by regressing the "response" variable (e.g., in units of response/cubic meter of air) against a series of tracer variables (e.g., concentrations of intrinsic tracer species specific to each of the sources). The responses and concentrations of the marker species must be determined in each of N samples and the coefficients are determined by regression, and is therefore, especially suitable for large data sets. Lewis et al. (35)used MLR to apportion the mutagenic activity associated with ambient urban aerosol particles among sources emitting soot.

Recently, new approaches to factor analysis have been developed. One method, Positive Matrix Factorization (PMF), utilizes a least-squares formalism that permits the weighting of individual data points within the analysis. Note that such a weighting scheme permits these methods to incorporate "missing" values into the analysis by giving such data points appropriately low weights, thereby, removing a heretofore, annoying and confounding problem. The method has been successfully applied to precipitation (41-42) and more recently, to data from Alert, N.W.T. (43), to National Park Service data (44,45), and to NOAA data from Barrow, Alaska (46).

Chemical mass balance calculations have most often performed using elemental constituents of fine particles because the reactivity of obvious organic tracer candidates (e.g., PAH) made them largely unsuitable (47-51). However, Rogge *et al.* (51) recently determined that *n*-alkanes, isoalkanes, anteisoalkanes, higher molecular weight *n*-alkanoic acids, hopanes, steranes, indeno[*1,2,3-cd*]pyrene, indenofluoranthene, benzo[*g,h,i*]perylene, coronene and elemental carbon were sufficiently stable to be used as tracers in urban atmospheres. Their utility in apportioning sources of atmospheric fine organic carbon has been demonstrated in Los Angeles where 85% of the fine organic carbon aerosol PM was successfully apportioned (51,52). However, the spectrum of possibly-important organic marker species has not been extensively investigated in Northeastern air sheds, including Baltimore. For example, many past studies quantified only a few compound classes found in airborne particulate matter. Recent studies by Rogge et al. (53-67) and other researchers (68-73) identified and quantified far more than 100 organic compounds in ambient and

source samples. But these studies have almost exclusively been in California and virtually no comparable data are available for Baltimore or much of the North East. Profiles for road dust, wood burning, and plant debris (a substantial road dust constituent) developed in California will not be highly applicable to Baltimore where vegetation is characterized by more hardwood species and street dust is contaminated with fugitive industrial emissions. Furthermore, California automobiles use more efficient catalytic convertors than do those sold in the eastern states. In addition, the organic source profiles may have changed in both absolute and relative magnitudes. For example, the regional vehicle fleet now contains a much higher proportion of catalytic converter-equipped vehicles, altering the emission signature (74). Clearly, detailed surveys of the kinds of compounds that might be suitable for source attribution need to be performed in Northeaster cities, wherein lie most of the US population.

Need for Highly-Time and Size Resolved Data
Currently, most of the data obtained for receptor modeling is derived from samples collected over 12 or 24 hour periods. This is far longer than time scales for changes in source strengths and important meteorological parameters, e.g., wind direction, mixing height, temperature, and relative humidity (RH). The accompanying homogenization of source signals by this practice severely reduces the resolving power of correlation techniques (e.g., multilinear regression and factor analysis), such that little information is often gained. Some years ago, Lioy et al. (75) showed that one could resolve more sources with principal components analysis if one had more (i.e., 6 hr resolution) highly time resolved data. Since more highly time resolved data will involve fewer sources contributing to the sample, it should be possible to improve the precision with which source contributions to the sample are estimated. Likewise improved size resolution will facilitate receptor modeling. The ultimate in resolution is size-resolved single particle analysis.

Baltimore's Suitability for the Proposed Investigation
   Baltimore is a populous and important, midAtlantic, industrial deepwater port city, located 50 km north of Washington, DC, and 150 km east of the Appalachian mountains. A mere two hour drive to Philadelphia and four hours to New York, Baltimore is a major transportation thoroughfare between populous southern and norther cities. Its location makes it an excellent end member of the great northeastern "megalopolis" extending from the Baltimore/Washington region to Boston. This corridor is highly important as it contains most of the major Northeastern US cities and the single largest concentration of the US population. Baltimore is an excellent choice to study the properties of local, regional, and interregionally transported aerosol emissions affecting urban air quality and investigating our hypothesis regarding aerosol age, time-resolved sampling, and toxicological response. Like much of the Northeast, PM air quality in Baltimore is heavily influenced by secondary sulfate formed during transport of sulfur emissions from the heavily industrial Ohio Valley (35) which lies >300 kilometers to the west. Air traveling from the Ohio Valley is orographically projected by the Appalachians which facilitates cloud processing and concomitant heterogeneous conversion of sulfur dioxide to sulfate, providing a more aged/processed aerosol which can be differentiated from local emissions by particle size (33,36), by chemical composition (e.g., S:Se ratio,35; and presence of Hydroxy methane sulfonic acid 76),

and thus by advanced FA of time- and size-resolved chemical data. Few sources (most notably one oil- and one major coal-fired power plant which lie 60 and 200 km due west, respectively) lie to the west, allowing for observation of mainly aged/processed inter-regionally transported aerosol during west winds which dominate the region's climatology.

The city is also influenced by urban emissions in Washington, DC, and a cluster of coal-fired power plants, and municipal and sludge incinerators along the Potomac River extending 50 to 90 km southwest of Baltimore. Locally, most of the Baltimore's industry is concentrated in the 125 km^2 area comprising South Baltimore and Dundalk (Figure 1), just a few kilometers from the center of the City, and immediately adjacent to populous neighborhoods.

Figure 1. Map of Baltimore showing many of the sources clustered around Curtis Creek and west of the Middle River. Green dots are chemical plants; red, medical waste or sludge incinerators; yellow are land fills; and brown, a rendering plant.

In all, the South Baltimore/Dundalk area contains >40 industrial facilities, including 16 chemical manufacturing plants; 5 bulk materials shipping terminals; 2 medical waste, 1 municipal, and 1 sludge incinerator, 6 land fills for storage of domestic and industrial, including hazardous, waste; the nation's largest Yeast Plant, a rendering pant, an automotive painting plant, and a major Steel plant. In addition to industrial sources, emissions from some 30,000 heavy diesel vehicles using the City's three major toll facilities (Ft. McHenry, Harbor Tunnel, and Key Bridge) each day adds to the areas air pollution problems.

Mean and max PM10 concentrations in south Baltimore (Fairfield) substantially exceed those observed in rural and suburban areas of Maryland by as much as 50% (In 1997, means were31 μg/m^3 at Fairfield vs. 17 to 20 μg/m^3; maximum at Fair field were 86 μg/m^3, respectively, versus 50 to 70 μg/m^3 at rural and suburban sites (77). Total aerosol carbon concentrations in summer range from to 2 to 10 μg/m^3 (78), about 20% of this is elemental carbon, the remainder is characterized as
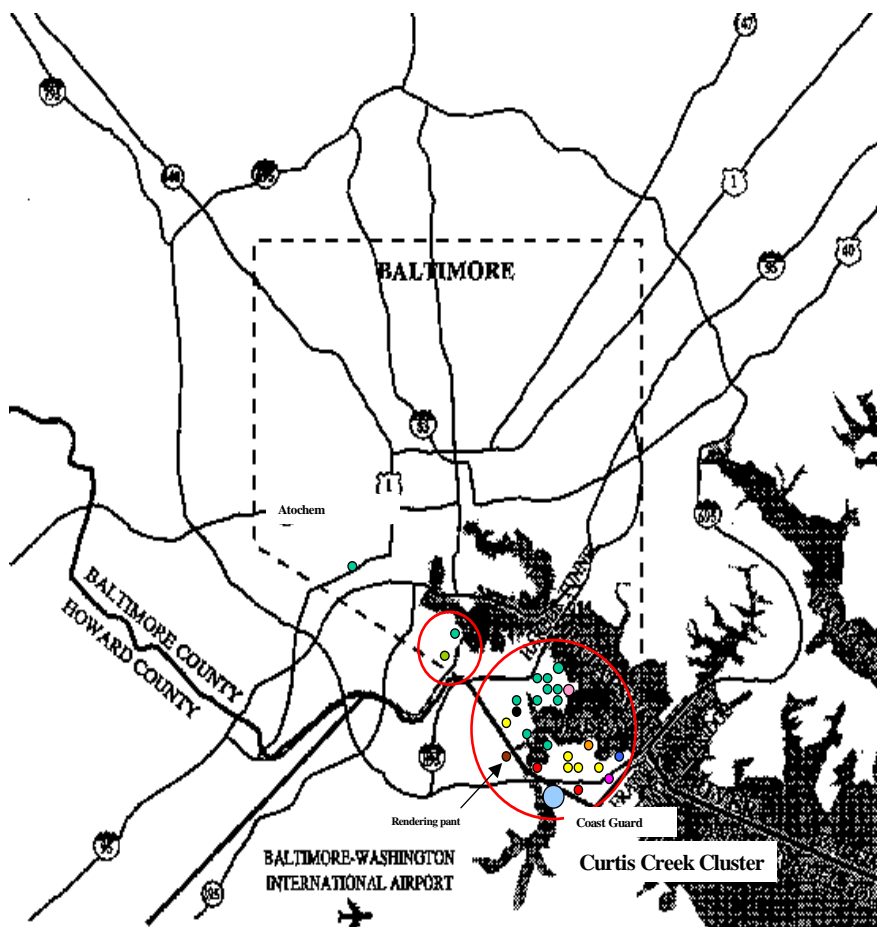
organic carbon by thermal-optical analysis (79). During the AEOLOS intensive of August, 1995, concentrations of Ca, Cr, Hg, Ti, Cl, Mn, Mo, Sb, and Zn measured in east Baltimore during winds from the direction of the BRESCO municipal incinerator, exceeded those measured upwind of the City by from 10 to >20-fold. Note that Sb, Zn, Hg, Cr, and Cl are highly enriched in incinerator emissions and that CMB modeling attributes major fractions of the aerosol burden of these elements to incinerators in Maryland (35,36). In samples influenced by winds from the Bethlehem Steel plant and sources in Hawkins Point, Cr, Fe, Mn, Sb, V, and Zn concentrations exceeded those outside the city by from 4- to 10-fold. Lastly, Baker (80) has observed 10-fold enrichments in PAH concentrations in the Curtis Creek area, presumably due to the high density of motor vehicles in the area. While there may be other factors, it is, perhaps, poignantly relevant that the percentage of obstructive pulmonary disease deaths in the south Baltimore region is nearly 1.7-fold greater than for the whole of the city (81).

Thus, Baltimore clearly offers a rich "laboratory" for studies of air pollution and health. Its industrial character, now-aged inner-city housing, and heavy traffic pose diverse environmental exposures for the city's population. The intensity and magnitude of its diverse sources in proximity to densely populated areas leads to a complex matrix of chemical exposures. These conditions have lead to heightened community concerns over their environment and its impact on health. Several prominent epidemiologist, toxicologist, and community health scientists have attested to the need for supersite-quality data and information for Baltimore (Appendix I). Likewise, the Maryland Department of Environment attests to the need for the supersite project to support the development of their SIP. Note that because air pollutant transport vectors are so affected by complicated interactions of sea breeze, drainage flows, heat island, mesoscale circulations, and prevailing westerly winds, source-based modeling is extremely difficult. This further accentuates the need for detailed receptor modeling data and improved methodology in support of SIP development.

Lastly, UMCP was an early pioneer in the development of receptor modeling. Over the last 25 years the Maryland group has conducted numerous source attribution studies in the Washington, DC, area (35), rural Chesapeake Bay areas (39), and more recently in Baltimore (82), using standard PM monitoring techniques and highly-size resolved sampling methods (i.e., with Micro-orifice impactors, 33,34,36). The rich understanding of PM issues and the nature of sources in the region provides a rich context for planning the measurements and interpreting the data to be developed in the proposed supersite project. UMCP has an extensive library of source profiles for CMB modeling and is actively seeking to improve it. Several studies have been completed in the areas traffic tunnels to develop the motor vehicle profile, including an ongoing study by UMCP. Moreover, UMCP has developed hundreds of size spectra for toxic elements and those which are useful markers of HTCSs, in and around Washington, DC (34), rural Chesapeake Bay sites (83) and more recently Baltimore (82). The recent EPA study at Lake Clifton provides a basis for year-to-year trends. The upper-air station operated by NARSTO 20 km south of Baltimore at Ft. Meade, and the IMPROVE site at the Shenandoah National Park help provide the regional context for our study.

OBJECTIVES AND HYPOTHESES
Our primary objectives will be to i) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques; ii) provide important

information on the potential for health effects of particles from specific sources and generic types of sources, iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, v) provide support to existing exposure and epidemiologic studies to achieve enhanced evaluation of health outcome-pollutant and -source relationships, and vi) test the specific hypothesis listed below.

> 1. Reduced (i.e., hourly and sub-hourly; two-hourly for organic compounds) sampling/analysis times will immensely improve source attribution.

> 2. Various health effects of PM are associated with its specific chemical and physical (but mostly chemical) components that, owing to the vast number of these, a source based allocation of air toxins will provide the most useful information for PM standards and control.

> 3. Different aerosol constituents and properties will have different abilities to elicit cytokine responses and that these difference might reflect differences in the extent and mode of action in producing adverse health effects. For example, residual oil fly ash elicits a response (largely attributed to V), whereas coal-fly ash elicits a lesser response.

> 4. Aerosol age affects the size, chemistry, and health effects of PM. Thus spatially distant upwind, industrial area, and center-city aerosols differ significantly in temporal variability and biologically relevant composition.

> 5. Taken together, detailed sub-hourly information of major, minor, and trace inorganic and organic aerosol constituents, size-resolved aerosol particle concentrations, and cytokine responses will permit unprecedented resolution of sources of toxic PM components and their toxic effects.

> 6. 24-hour and short-term concentrations, cytokine and ROS responses, and health effects of potentially toxic aerosol components in areas of Baltimore that are strongly influenced by heavy industry measurably exceed those observed in an urban downtown site that is weakly influenced by industrial sources.

> 7. Some acute health responses are more closely associated with highly elevated short-term exposures than they are with 24h averages.

> 8. Spatial distribution of various fine aerosol particle constituents are highly inhomogeneous due to both variations in sources and regional circulations.

Ancillary objectives include i) partnering with Maryland's Department of Environment to share resources, data, and expertise to reduce project costs and ensure assimilation of results into Maryland's SIP development process, and to ii) augment the body of data collected by EPA's

National Exposure Research Laboratory (NERL) Laboratory during their 1997-1998 year-long advanced monitoring study. This will be a cooperative agreement. We look forward to working closely with EPA colleagues.

PROPOSED PROJECT DESIGN

To meet these objectives, we propose to implement an advanced monitoring program highly-focused on the development of improved source-receptor relationships and which features highly-time resolved measurements of PM constituents and encompasses an innovative yet precedented, surrogate health-effects concept, to extend the source-receptor paradigm to encompass correlation of the surrogate to PM sources and component species. Specifically, we plan to apply assays for cytokines and reactive oxygen species (ROS) to PM samples in a manner analogous to EPA Integrated Air Cancer Study's use of mutagenicity assays to apportion mutagenic contributions from sources which ultimately lead to improved estimates of cancer risks from air pollution sources (84,85).

The project will further encompass detailed i) organic compound identification and analysis ii) collection of multiple gram quantities of PM2.5 for archival storage, more detailed chemical and physical characterizations, and animal exposure studies (to be done by others not in this study); iii) three dimensional mapping of Baltimore's wind fields and aerosol concentrations, including plumes from discrete sources, iv) state-of-the art neural network and advanced factor analysis (FA) algorithms developed by Professor Hopke for on-the-fly data reduction, hypothesis testing, and data quality analysis and method intercomparisons, v) continuous/semicontinuous monitoring of mass, sulfate, nitrate, elemental and organic aerosol carbon (EC and OC, respectively), aerosol number concentration distribution, and light scattering using commercially-available instruments, vi) rotating Drum impactor (RDI) measurements for quantitative determinations of size spectra of elemental PM constituents; vii) measurements of FRM mass, EC, OC, and elemental composition via standard 24-hour monitors, and viii) criteria and PAMS gases (VOC, aldehydes, SO_2, NO_X, O_3, CO, ix) integration with toxicological and epidemiological field studies planned and proposed by JHU and the University of Maryland School of Nursing (UMSON), and x) integration and collaboration with Maryland's Department of Environment.

Important new instruments to be field tested are

- ! UMCP's new semi-continuous monitor for quantitatively determining aerosol metals and trace elements,
- ! UDE's third generation single particle mass-spectrometric analysis system (RSMS III) for continuous size and semi-quantitative determination of individual aerosol particle constituents, from 10 nm to 2.5 μm.
- ! JHU's state-of-the art 3 wavelength LIDAR for three dimensional mapping of Baltimore's wind fields and aerosol concentrations, including plumes from discrete sources.

STRATEGIC APPROACH

Our overall strategic approach is to combine highly time, size, and composition resolved PM data

with cytokine/ROS assays to maximally develop relationships between sources, PM constituents, and indicators of human health effects. Hourly resolved cytokine assays will be employed for determining the potential for respiratory oxidant production and related respiratory irritation and stress, thus, providing a useful measure of toxic response. From this vantage point, we can examine the kinds of particles, and kinds of organic and inorganic species responsible for this important health-effects metric. The Highly-time (hourly and subhourly) size, and species resolved composition metrics will permit resolution of their contributions by sources, thus, providing the link between the health effects metric and sources, i.e., quantitative estimates of the potential for PM emissions from sources to elicit adverse cardiopulmonary effects. Hourly resolution would also permit more optimal correlations with Asthma data to be provided by the Johns Hopkins University. Source allocations will be reinforced by inclusion of the meteorological data in the Multivariate analyses and with 3-dimensional wind field and particle concentration maps. Plume width and, thus, time of influence on a fixed site increases with increasing distance from the source. Thus, with highly time-resolved pollutant metrics local (quite likely even individual), more distant, and regional source contributions will likely be readily resolved into different factors by the advanced FA technique (PMF) developed by Professor Hopke. As discussed above, PMF utilizes a least-squares formalism that permits the weighting of individual data points within the analysis. Such a weighting scheme permits these methods to incorporate "missing" values into the analysis by giving such data points appropriately low weights, thereby eliminating an annoying and complicating problem. With improved time resolution and accompanying improved source resolution, FA can often provide information on source profiles that can then be employed in a CMB analysis. These can be used to augment the UMCP library of source profiles that have been developed for the Baltimore area (82). Thus, we can explore the quality of the CMB analysis of the highly time resolved samples as compared with the 24 hour samples obtained in the chemical speciation samplers. In combination with improved FA methods, there should be a substantial improvement in the ability to identify and resolve sources potentially to the level of specific locally important sources. Although we are not trying to solve the local air quality problems in Baltimore, this local environment can be used effectively to test our hypothesis regarding highly-time-resolved sampling.

The 3-D maps will powerfully and visually document the movement of particles from the sources to the receptor, and ultimately improve our understanding of atmospheric stability and seasonal-mesoscale flow patterns in driving aerosol fields over Baltimore city. Note that Baltimore, like most of the large northeastern cities, wherein lie the bulk of the US population, is a deepwater port city situated around a complex array of rivers and inlets. This induces complicated local flow patterns due to various phenomena such as sea breeze and drainage flows which interact with local heating patterns due to the urbanization mixed with various mesoscale circulations and prevailing westerly winds. These interactions make source-based modeling extremely difficult. The LIDAR measurements will be especially useful in this regard.

Time-resolved rotating drum impactors (RDI) will be used to separate fresh accumulation aerosol from nearby sources from aged and cloud processed aerosol and from tailing coarse particle fractions. The spectra determined from RDI measurements will be used to confirm plume "hits" and as a calibration reference for single particle measurements. Cytokine and ROS assays on selected RDI samples will be performed to investigae differences in aerosol age (i.e., hypothesis 4).

Traditional 24-hr collections for FRM mass and selected aerosol constituents are proposed to provide the link with PM network data and will be useful in testing hypothesis (1 above).

Collection of gram quantities of PM2.5 will permit more extensive elemental and organic compound analyses. Primarily the bulk material will be useful in developing a list of target analytes for the organic analysis work and provide extra material for testing cytokine and ROS assays. Moreover, we expect to be able to make available a year's worth of weakly PM2.5 collections, of in excess of 1 g, each, to our colleagues in the toxicological research community, including JHU and EPA (Appendix II).

The single particle mass spectrometer system will produce an enormous amount of data (almost 200 species in 10 size ranges, will be generated each hour. We will apply neural network technology for "on-the-fly" classification of particles based on their mass spectra. This will ensure timely inclusion of the data into our database so it can be used to guide retrospective analyses/assays of samples to be collected during the project.

A major task to be completed is to statistically interpret and interrelate data developed by the variety of new and established techniques used to characterize the suspended particulate matter. The purpose will be to to develop a deeper understanding of what the various measurement methods truly measure and how these measurements can be related back to the objectives of the program. Therefore, Professor Hopke will utilize his considerable experience in both aerosol measurements and advanced data analysis methods (MLR, PLS, and back propagation neural networks), to provide these critical data analyses. We plan to develop a complete description of the useful range, limitations and accuracy of each of the techniques that can be used to describe the physical characteristics of the particles.

All of the project information will be incorporated into a professionally constructed, web-ported, data base built on UMCP's existing air sampling and measurement system, and will be designed to let users view time series of any of the sampling or analysis parameters. Data from the various semi-continuous and continuous monitors will be reprocessed to produce hourly averages for entry into the data base. All of the information developed, including access to the project data base will be provided to the State of Maryland for use in SIPs development, and to JHU and UMSN for correlation with CLINICAL health metrics determined in their studies.

Integration with Health Effects Studies

The supersite developed in collaboration with the Johns Hopkins University School of Public Health will exist in an environment that is fertile and productive with public health research including programs in toxicology, epidemiology, and exposure assessment (Appendix II). Under the direction of investigators at the Johns Hopkins University Schools of Public Health and Medicine, a number of exposure and health effects studies are funded and will occur during the period of ambient monitoring under this proposed Supersite. Intensive ambient monitoring coincidental with these health and exposure studies (Figure 2) will allow expanded interpretation of the ambient concentration measurements and source characterization with respect to health and exposure. Similarly, the exposure and health studies will benefit tremendously through the access to data which will allow greater assessment of ambient and source contribution to exposure and effects. In addition to the funded and pending studies shown below, it is anticipated that nearly as many studies will be proposed over the next two years during the time of this proposal's review and the projected one year

set-up period. Although not all studies will be coincidental with the proposed Supersite, these studies demonstrate a pattern of successful research funding that is likely to continue during the proposed monitoring period.

Figure 2. Coincidence of Supersite Ambient Monitoring with Health/Exposure Study Monitoring
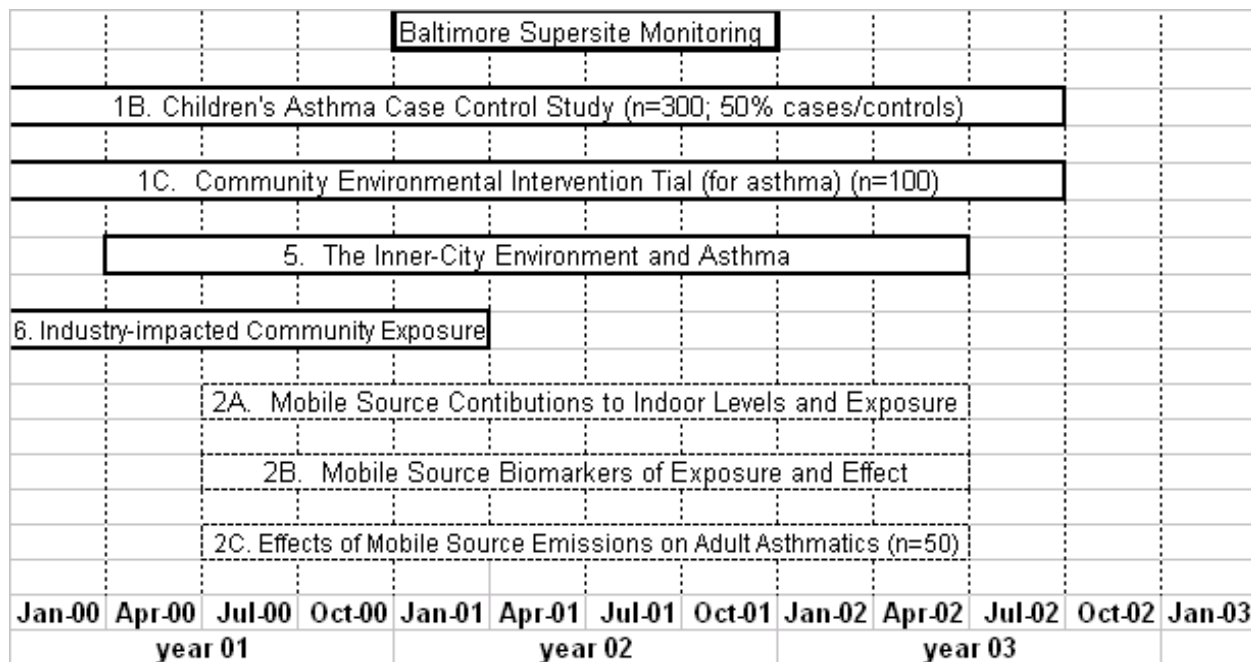
Monitoring of PM and related pollutants (NO_2, and O_3) is a component of all of the health studies shown above (except 5). In studies 1B, 1C, 2A, 2B, 2C and 6, monitoring is conducted at the level of the individual (personal monitoring) and the residence. In study 2C, daily peak expiratory flow (PEF) and FEV_1 will be coupled with daily measurements of exposure over 14 days for 50 asthmatics. Intensive supersite monitoring under the current proposal will expand the analysis of the health outcome assessment to include time and space (e.g., LIDAR) resolved ambient particle mass, chemistry, and sources. Projects 1B, 1C, 1D, 2A, 2B and 2C are well suited in design and timing for coordination and linkage with intensive ambient monitoring under the current proposal. Coincidental exposure and central site (Clifton Park) monitoring will allow us to examine the adequacy of the ambient measurement as an exposure surrogate. Therefore, the proposed study in combination with existing health and exposure studies will allow the investigation of linkages between ambient PM concentrations, exposure, and health outcome among asthmatics, a population subgroup thought to be susceptible to PM's effects. Such investigations have been identified as a priority by the National Academy of Science in their recent report on "Research Priorities for Airborne Particulate Matter".

Furthermore, during the periods of community-based intensive monitoring (described below), we will be able to investigate time resolved spatial associations between ambient PM at the central site and the community location. We expect greater variability between sites than has been previously

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reported (86) and as suggested by Dubowsky et al. (87) due to our siting of the platform within the community, e.g., within an urban corridor. We will be able to test whether such siting provides a better representation of the communities ambient exposure.

DETAILED SAMPLING AND ANALYSIS PLAN
Deployment of Instruments

We propose to equip two measurement platforms. The first is a primary platform comprising the full set of traditional and advanced monitoring instruments. The second is a secondary platform consisting of a selected subset of measurements. Instruments to be installed in each platform are listed in Attachment I and described below. These will be housed in towable trailers (2 for the supersite platform, 1 for the secondary platform). The platforms will be allocated among three kinds of sites in support of specific objectives and hypotheses described above. These are as follows.

1.   Urban Supersite
2.   Industrially-influenced urban residential site
3.   Community sites in support of health effects and exposure studies

Experience has shown that little is gained by multi-site multivariate data collections, except in support of well defined hypotheses. Therefore, detailed measurements will be concentrated at the downtown site. The main platform will be deployed for in excess of 10.5 months at an urban supersite location to collect a large body of data at a single location for resolution of temporal trends and to support hypotheses 1 -5 and 7. The urban Super Site will be centrally-located northwest of the downtown area and well outside the south-Baltimore industrial area. This is, therefore, in an area, that tends to be well isolated from much (but not all) of the industrial emissions in south Baltimore, owing to the generally southwesterly and westerly winds and complex land/Bay interactions. Thus, to provide a different, yet, important atmosphere, to better test hypotheses 1, 6, and 7, and to characterize, as fully as possible, important spatial differences, the main platform will be moved to the Industrially-influenced urban residential site for two 45-day intensive periods (Intensives); one in summer, and one in winter. The secondary platform is to be allocated to the two community locations for approximately two (20 21-day periods at each of two locations, i.e., East Baltimore and Mid-twon (i.e., 42 days at each location for a total of 84 days of sampling) to serve as community-wide air stations in support of health effects and exposure studies, and to provide yet additional spatial information. In support of the latter, our intention is to deploy the platforms such that the primary platform is deployed at the urban Supersite when the secondary platform is deployed at Community sites.

Sampling Sites
Urban Super Site. Lake Clifton Park is our primary choice for this site, because it is a largely grassy area surrounded by residential neighborhoods and only lightly influenced by heavy industry; and because extensive speciation-site type measurements were conducted there for a one-year period (1997-1998) by EPA. The existence of this high-quality data set will permit observation of year-to-year differences with our proposed single-year study. Furthermore, UMCP performed bulk PM2.5 collections at Lake Clifton for use in a NIST Standard Reference Material and for pilot toxicological

studies by EPA's Pulmonary Toxicology Branch at (NHEERL) at RTP; and used this site for tracer studies of the fate of diesel soot. In addition, Lake Clifton was formerly the site of MDE's PAMSII site and MDE is currently negotiating with EPA Region III to return the site to this location. A secure fence is already installed at Lake Clifton as is a power transformer and feeder cables. The compound, located on North Rose Avenue, is now vacant and can readily accommodate the two trailers comprising our Super Site platform. It lies about 4 km from the JHU Homewood Campus, i.e., nicely within the range of the JHU LIDAR.

Non-Urban Background Site. To accommodate a reduction in the funds requested we have eliminated this site. However, we hope to relocate a Maryland SLAMS site to this location. Should this be possible, our choice for the non-urban site is the UMBC campus to the west-south-west of the city (Figure 1). The site lies upwind (or at least outside) of Baltimore during all but relatively infrequent, easterly winds, and is elevated relative to the surrounding areas. The site would permit definitive classification of City vs more regionally-dispersed and transported pollutants from the Washington, DC, area, 100 km south-south west of Baltimore, the Ohio Valley, >300 km to the west, and source regions in Pennsylvania, in support of testing hypothesis 1, that we can resolve regionally distributed sources using highly-time-resolved measurements made a the primary site.

Industrially-Influenced Urban Site. The Fairfield monitoring site (1900 Patapsco Ave.) in South Baltimore is and excellent choice for our industrially-influenced urban site. The site is a SLAMS (State and Local Air Monitoring Station)/NAMS (Neighborhood Air Monitoring Station) outfitted with High-volume PM10 and Andersen Sequential PM2.5 monitors operated (every 6th day and, periodically, every 3rd day, respectively) by MDE The site lies between the working-class neighborhoods of Brooklyn and Fairfield. More than 18 substantial point industrial and municipal sources are located along a, roughly, 225° arc extending west from the Fairfield/East Brooklyn communities on the Patapsco River/Curtis Bay inlet, south through Brooklyn along Curtis Bay/Curtis Creek, and east through Hawkins Point (Figure 1). These sources are superbly positioned to allow us to test the ability of highly-time resolved monitoring to permit resolution of sources and evaluate toxic potential in support of hypotheses 1-6, and achieve spatial characterization objectives for this highly-polluted neighborhood; one that is typical of many Northeastern cities.

Community Sites. Community sites will chosen to augment the existing health and exposure field studies planned by JHU. The six projects of opportunity previously identified in Figure 2 will occur at two locations. Projects in Center no. 1 are focused on the community in East Baltimore near the Johns Hopkins School of Hygiene and Publich Health while the projects in Center no. 2 are focused on the community in the Mid-Town District of the City. Both studies are anticipated to be coincidental with our proposed Supersite monitoring. We anticipate that two 21-day community-based intensive monitoring campagns will be interfaced with 2-3 exposure/health studies. The LIDAR support during these campaigns, combined with simultaneous Super- and Community -site measurements proposed will provide a highly-complete picture of the spatial distributions of PM and its components between them.

Measurements and Analyses Methods
The majority of the measurements were selected for the express purpose of determining source receptor relationships for a variety of pollutant metrics, including cytokine responses (see description, below section, page). In so far as our primary hypothesis postulates that reducing measurement times will permit improved source resolution, we have elected to field a new-generation highly-time resolved instruments and to deploy them as long as possible. Other measurements were chosen by the need to maintain links with traditional technology and foster a measure of commonality among the various Supersites. Measurements will be of two types, continuous or semicontinuous collections/measurements to be performed throughout the 12 month study period and off-line retrospective analyses of collected samples.

As indicated in Attachment I the various instruments and measurements to be deployed at each site are conveniently grouped into three categories: i) commercial continuous and semi-continuous monitors, ii) special instruments, and iii) collections for off-line analyses. The first category includes basic meteorological measurements; monitors for physical aerosol properties (i.e., number vs size distribution and light scattering), aerosol mass, sulfate, nitrate, and EC/OC; VOC; NOx, SO_2, and O_3.

Commercial Continous/Semi-Continuous Monitors
Meteorological Measurements. Meteorological measurements to be fielded comprise wind speed and direction, barometric pressure, Temperature and RH (measured at two heights to estimate atmospheric stability) and solar insolation; all of which will be installed on both the primary and secondary platforms. In addition, JHU will deploy a 3-D sonic anemometer and Krypton hygrometer on the primary platform to obtain sensible momentum and heat fluxes to better determine atmospheric stability and mixing, and combined with LIDAR to characterize the vertical structure of the boundary layer. Such information should be extremely useful to MDE and EPA for model development and will facilitate interpretation of LIDAR time-series measurements described below. Data from these sensors will be recorded continuously (5 minute averages of data recorded at intervals of 1 to 10 s) throughout the 12-plus month measurement period. Sensors to be used are high-quality research grade units or in the case of solar insolation are deemed adequate for our study.

Physical Aerosol Properties. Number vs size distribution and light scattering instruments will be installed on both platforms. The latter will serve to give an indication of suspended particle surface area, permit calculation light extinction coefficient and visual range. Furthermore, the integral light-scattering moment of the distribution can be a useful descriptor metric of the accumulation aerosol. We propose to use relatively a simple and inexpensive (Radiance Research M903) single-band integrating nephelometer. More sophisticated nephelometers can provide crude size distribution information, but at highly-elevated cost. Such instruments are not needed here, because we will obtain far superior size distribution data at appropriate time intervals with high-quality aerosol spectormeters. Specifically, a Scanning Mobility Particle Spectrometers (SMPS) will be deployed at the supersite platform and community site platform to measure aerosol number distribution in the ultrafine/near accumulation region (0.020 to 0.5 μm). One will be supplied by Clarkson Unviersity and the second unit will be obtained by factory upgrade of UMCPs older differential mobility analyzer. (Note that the latter is inappropriate for ambient aerosol monitoring as it requires >30

minutes to sequentially scan its size domain.)   Clarkson University and UMCP will each provide optical single-particle spectrometers (Climet 208 C with high-resolution pulse height analyzer and a Particle Measurement Systems high-volume forward scattering LASER spectrometer, respectively) for measuring the size distribution of particles with diameters in the 0.5 to >10 μm range. These will be assigned to the primary and secondary platforms, respectively, for the entire measurement period. During the Community-based intensives, JHU's Aerodynamic Particle Sizer (APS, Thermal Systems, Inc.) will be collocated on the secondary Platform to permit rigorous field comparison of these two fundamentally different instruments.   Aerosol particle scattering coefficients and concentrations in discrete size ranges will be used as metrics in the advanced FA investigations to investigate source-receptor and immunological response hypotheses.

Semi/Continuous Mass, Sulfate, Nitrate, and EC/OC Monitors. Various monitors for each of these parameters continue to be developed and tested.   For aerosol mass, the R&P (Rupprecht and Patashnick Co., Inc.) TEOM (Tapered Eement Oscillating Microbalance) is by far the most widely used instrument. It is extensively used in Europe and the U.S.A., and was used by EPA in their Lake Clifton study. The MDE currently has one TEOM deployed at Ft. Meade and has agreed to deploy another at our Super site. MDE finds FRM and TEOM PM2.5 mass measurements to be highly correlated (90) in Baltimore. Therefore, in the interest in continuity and comparability of data and uniformity for field technicians, we will probably purchase another TEOM for use on our secondary platform. R&P is also marketing sulfate and nitrate monitors designed by Herring.   To our knowledge, these are currently the closest to production (however pricing is not yet set on either) and appear to give reliable results.   Nevertheless, we will review results of instrument intercomparisons made over the next 18 months or so and will consider other choices (e.g., the Harvard CAMM and TBS instruments for aerosol mass and sulfate/nitrate, respectively) should this appear prudent. Note that we are aware of only two commercially available (or soon to be) field instruments for EC and OC measurements, i.e., R&P's (Series 5400) Ambient Particulate Monitor and an instrument being targeted for limited sales by Sunset Laboratory (SL). EC/OC measurements are, more or less, operationally defined. Aerosol is collected on a filter and subjected to various heating cycles to remove volatile carbon, followed oxidation of EC. Differences in aerosol collection temperatures and more importantly, filter face velocities, can substantially influence these measurements.   The SL instrument measures laser transmission through the filter to better account for OC to EC conversion (an unwanted artifact) and has a high-temperature cycle to determine carbon in the form of carbonate. However, their instrument is pricey (estimated $55k) in comparison with the R&P instrument ($26 k). Detection limits reported for the two instruments are comparable (0.1 and 0.25 μg carbon, absolute, for SL and R&P respectively) and either should be capable of measuring carbon in as short as 30 minutes in Baltimore. We would like to install an EC/OC instrument on both platforms and we believe it likely to be adequate for investigation of project hypotheses, however funds are available to install an EC/OC instrument only at the Lake Clifton supersite. Again, we will reevaluate this choice as new information becomes available. If need be, we can deploy a single Sunset Laboratory instrument on the primary platform.

NOx, O$_3$, SO$_2$, CO, and VOC measurements. Monitors for these gases will be supplied by MDE for insulation in our primary platform and will be made available on an hourly basis.   VOC

measurements for 56 ozone precursor hydrocarbon compounds will be determined on site by automated gas chromatography on 40-min samples collected each hour during 5 months (May - September) comprising the ozone season. Due to their reactivity, the VOC analyses may be of limited value, however, they will likely be useful in interpreting polar organic compound analyses of aerosol particles to be collected by FIU (see below). Professor Rogge will provide a model 300 gas filter correlation analyzer (Advanced Pollution Instrumentation Inc., San Diego, CA) with a 0 to 10 ppm scale for improved CO measurements. The Maryland Department of Environment will install a similar (0 to 50 ppm), but older instrument in the secondary platform.

Collections for Off-Line Analyses

FRM mass and Speciation Sampling. The MDE will provide Andersen FRM mass and Speciation samplers for use on the Secondary Platform. We will purchase an additional pair of these samplers for installation at Lake Clifton. These are will be operated daily to collect samples for gravimetric, XRF, and EC/OC analyses. Gravimetric analyses will be done by UMCP. XRF and EC/OC determinations will be done by contract reliable contract laboratories (EC/OC by Sunset Laboratory, using the method of Birch and Cary (79). We intend to rely on the nitrate monitor for nitrate an will only occasionally field denuders and nylon filters for off-line nitrate analyses by ion chromatography. We intend to analyze one-third of the daily speciation samples for elements determined by XRF. The data will be used in multivariate calibration analyses involving the UMCP SEAS and UDE's RSMSs III measurements described below and the hourly EC/OC measurements described above.

Size Segregated Aerosol Sampling. Size-segregated aerosol samples will be collected daily for 24 hours throughout the field study with a 3 stage rotating drum impactor (RDI, 88) to collect particles in the ranges <0.3, 0.3 to <1.0, and 1.0 to 10 μm. Four of the samples will be chosen each month for retrospective elemental analyses by PIXIE, without subdivision of the substrates into sub-daily intervals. During intensive studies at the industrially-influenced site in south Baltimore, 8-stage drum impactor samples will also be collected daily. Five sets will be chosen for retrospective PIXIE analysis after the substrates are divided into 24 (hourly) intervals. Alternately we will select 10 sets of 12 hourly divisions for analysis. These samples will be used to permit resolution of "hits" from discrete plumes from local sources (sub-0.3 μm fraction), aged intra and interregionally transported aerosol (0.3 to 1 μm fraction), and coarse particles (1 to 10 μm fraction) of road dust and fugitive emissions (e.g., from Baltimore's many bulk storage facilities) dispersed by traffic-induced turbulence and wind. Drum impactors/PIXIE analyses have been used successfully in remote areas (90) and should be effective when deployed at urban sites. The Drum impactors will be operated with high-precision flow controllers designed and built by UMCP. These will eliminate artifact broadening of narrow accumulation aerosol peaks which are caused by flow rate fluctuations during sampling.

Bulk PM2.5 collections. Bulk PM2.5 collections will be made weekly primary platform sites using the UMCP's ultra-high-volume sampler (UMUHVS). The device is comprises 1- and 3-meter cyclones (to allow PM2.5 to be collected at nearly 6000 and 9000 LPM), computer controlled 27 HP Roots Blower, and an enclosure holding 10 discrete 8"x10" filter holders (91). The system as sufficient power to collect PM on Teflon membrane filters (Gellmann, 3 μm pore). At modest

ambient PM2.5 loadings of 15 $\mu g/m^3$, we can collect 1.4 g/week. The filter face velocity is substantially lower than that of standard high-volume samplers used to collect samples for organic compound analyses. The system is already installed in a 24-ft trailer and has been operated at the Atlanta Supersite in August. In addition to submitting the material to elemental analyses and cytokine/ROS assays, we intend to use this material for exploratory organic compound analyses and will archive the remaining material (1 g/week) for eventual distribution to the toxicology community.

PM2.5 Collections for Cytokine/ROS Assays. Virtually all of the mass of the various elemental constituents of the urban atmospheric aerosol lies in particles with diameters >50 nm (33). This material is typically collected on filters or by impaction onto dry (often sticky) surfaces. However, as these methods promote particle agglomeration, it is often difficult to quantitatively remove the collected particles from the substrates so that they can be used in bioassays. In addition, these methods are not well suited to the collection of numerous 60-min samples. Therefore, we propose to collect samples for bioassay using a novel aerosol concentrator developed jointly by UMCP and the Harvard School of Public Health, in which aerosol particles are hygroscopically grown to form 4 μm droplets prior to collection by impaction into glass impactor. The sampler (UMHFAS) is a component of the semic-continuous elemental aerosol system (SEAS) described below for semi continuous sampling and on-line analysis of hourly aerosol slurry samples. In addition to providing the sample in an aqueous suspension, the method has been automated to provide for multiple sequential sample collection using an XY fraction collector. The sampler will provide a total PM2.5 sampling rate of 200 L min^{-1} to provide sequential hourly PM2.5 samples at the primary platform sites through out the project period. At average ambient PM2.5 concentrations >90 μg PM2.5 will be collected in hourly samples, even at levels as low as 8 μg m^{-3}. Approximately 1000 hourly samples will be retrospectively selected for cytokine/ROS assays described below.

Cytokine/ROS assays. The specific aims of the project are to test the ability of $PM_{2.5}$ samples to stimulate the secretion of four cytokines by cultured alveolar mouse macrophage (RAW 264.7). Both Th 1-type ((IL-6 and TNFα) and Th 2-type (IL-8 and GM-CSF) cytokines will be measured to detect the potential for particles to induce either an inflammatory response or to enhance an allergic asthmatic response (21,27). The cytokine TNFα plays a significant role in stimulating the inflammatory response by activating macrophage and neutrophils, thereby increasing ROS and NO production, while IL-6 plays a role in the induction of acute phase proteins and the regulation of B and T cell responses. Cytokines IL-8 and GM-CSF (granulocyte/macrophage colony stimulating factor) play an important role in upregulating the asthmatic response, as GM-CSF activates eosinophils while IL-8 acts as a chemoattractant for activated eosinophils. Alterations in IL-8 and GM-CSF secretion will be used as a measure of the potential for $PM_{2.5}$ particles to induce and/or increased the severity of asthmatic episodes.

Particle preparation: $PM_{2.5}$ samples will be lyophilized to concentrate the sample and weighed to obtain a dry weight measure. At the time of analysis, each sample will be resuspended in RPMI 1640 with penicillin (50 U/ml) and streptomycin (50 μg/ml) at a concentration of 1 mg/ml and sonicated for 20 minutes in an ultrasonic water bath. *Cell culture*: RAW 264.7 mouse macrophage cell line (American Type Tissue Culture Collection, Rockville, MD) will be maintained in RPMI

1640 (Mediatech, Fairfax, VA) supplemented with 50 U/ml penicillin, 50 μg/ml streptomycin, 2 mM L-glutamine, 1 mM sodium pyruvate, l0 mM N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid buffer (GIBCO BRL, Gaithersburg, MD), pH 7.3, and containing 10% defined newborn calf serum (NCS; Hyclone, Logan, UT) at 37^0 C in 5% CO_2-enriched air (29). All media and reagents will be tested for endotoxin to assure a concentration of <0.1 ng/ml. New cultures will be started monthly from frozen stocks. *Cytokine assay*:   For the cytokine assays, cells will be seeded in 96 well plates (1 x 10^5 cells per well) and allowed to attach for 2 hr. Fresh RPMI 1640 media supplemented with 50 U/ml penicillin, 50 μg/ml streptomycin, 2 mM L-glutamine, and 1 mM sodium pyruvate, will be placed in each well and an aliquot of a $PM_{2.5}$ sample will be added to give a particle concentration of 50 ug/ml. After 24 hr, media from each 96 well plate will be tested for IL-6, IL-8, TNFα, and GM-CSF using commercially available ELIZA kits (R&D Systems, Minneapolis, MN and Endogen, Cambridge, MA). Results from the cytokine assays will be expressed as ng cytokine released/ml. Viability of cells remaining in the wells will be determined by trypan blue exclusion. Samples showing significant toxicity to the cells (viability <90%) will be diluted and re-evaluated. To standardize assays run on different days, each run will include urban particulate matter SRM 1648 samples (NIST, Gaithersburg, MD).

The role of metals versus endotoxin in the induction of cytokines in this system will be determined in a subset of samples by running experiments with and without polymyxin B (an endotoxin inhibitor). Endotoxins are well established inducers of cytokines in macrophage cells, and are often components of $PM_{2.5}$ fractions due to the presence of gram-negative bacteria, molds and fungi in this fraction (30-32). $PM_{2.5}$ samples will be tested for endotoxin using the *Limulus polyphemus* amebocyte assay (Whittaker Bioproducts, Walkersville, MD). The standard assay will be run with and without polymyxin B on $PM_{2.5}$ samples with endotoxin concentrations greater than 0.1 ng/ml, so that the effects of metals in the samples can be separated from those produced by endotoxin.

Sampling and Analyses for Organic Compounds. Organic compounds will be sampled daily for 24 hours using modified high-volume air samplers by drawing air through a quartz fiber filter and a polyurethane foam (PUF) trap in series. In addition, volatile organic compounds will be sampled by MDE using stainless steel SUMMA canisters collected 24 hrs every 6th day all year. MDE analyzes these or 56 PAMS compounds and a complete list of toxic organic compounds (TO14, including benzene and many substituted benzenes). During the two 45-day intensives organic compounds will be sampled for consecutive 2-hour (possibly hourly) intervals in support of our primary hypotheses regarding source resolution. Immediately after each filter sample is removed from the sampling device, they will be stored in a freezer at -2°C and retrospectively analyzed within one month after collection. As discussed below, we are interested in total (gaseous + particulate) concentrations of the various species. Thus, we can operate the particle sampler at a higher flow rate (i.e., 0.5 m^3 min^{-1}) than would otherwise be advisable (due to "blow-off" losses from the filter) if accurate gas/particulate partitioning were desired. Two-hour sampling will correspond to   80 m^3. Total ambient concentrations (gaseous + particulate) of individual PAHs recently measured (92) at the Ft. McHenry National Monument (about 1 km from the proposed study site) ranged from 0.01 ng m^{-3} (methylanthracene) to 21 ng m^{-3} (phenanthrene). At these concentrations, target PAH analytes will be present in 2-hour samples from Baltimore at levels 5- to >130-fold

greater than our method detection limits. While we have not yet measured other hydrocarbons in Baltimore, based on PAH/hydrocarbon ratios for Los Angeles and measured PAH concentrations in Baltimore, we will have ample analytical sensitivity for these compounds, as well.

Filter/PUF-Analysis.
The objectives of the organic compound analyses are to support the primary hypotheses, elucidate atmospheric chemistry, provide important compositional information to the health effects community, and especially to identify marker species for source attribution. Because our primary hypotheses involve source attribution, gas/particle resolution is not essential. However, PUFF and filter samples will be extracted and analyzed separately. Professor Rogge will deploy a denuder system during collection of some of the samples in an effort to obtain better measurements of the true PM2.5 organic mass component. As there are relative few data on organic compound species in the Northeast and fewer in Baltimore, exploratory efforts will be made to identify the kinds of compounds present. At least the following compound classes will be searched for and when identified also quantified: n-alkanes, n-alkanoic acids, n-alkanols, n-alkanones, furans, furanones, resin acids, sterols, PAHs, compounds identified in smog chamber experiments as possible secondary organic atmospheric reaction products, and others. Compounds analyzed for will include species known to be useful markers of sources (Attachment II). Beyond the listed compounds, best efforts will be used to quantify all identifiable compounds in the sample extracts. Bulk PM2.5 samples collected early in the study (during testing to be conducted before the onset of our 12 month field study). Additional bulk PM2.5 samples will be analyzed periodically to identify seasonal differences in compounds and classes. Four daily Filter/PUF sample pairs will be selected for analysis each month. At least 90 of the samples collected during the intensives will also be analyzed retrospectively. The analyses will provide compositional information (monthly averaged) throughout the 12 months of sampling, highly-time resolved samples for testing hypotheses listed above, and a major contribution to our knowledge of the chemical composition of organic particulate matter. The analysis will be conducted via GC-MS, using well-established micro-methods (93-98) for these kinds of samples.

Special Measurements
SEAS. The new semi-continuous aerosol monitor for the determination of aerosol metal concentrations (99) recently developed by the University of Maryland (@College Park, UMCP) in collaboration with the Harvard School of Public Health under an EPA STAR Grant award. The semi-continuous system consist of a high-frequency aerosol sampler (HFAS) and state-of-the-art true simultaneous mutlielement Graphite Furnace Atomic absorption spectrometer. The HFAS consist of a state-of-the-art dynamic aerosol concentrator in which particles are grown by condensation of water vapor to facilitate separation from the air stream. PM 2.5 is sampled at 200 L min^{-1} and delivered to GFAA system or to a sample fraction collector for on or off-line analyses, respectively. In <10 (for urban air) to 20 (rural air) minutes we typically collect enough slurry to permit 4 suites of 4 or 5 elements to be determined, each in triplicate, however, virtually any sampling period up to a few hours may be selected. At the 200 L min^{-1} sampling rate, analyte masses delivered to the GFAA at the smallest concentrations observed by our group in rural Maryland air exceed instrumental sensitivities (rivaling far more expensive ICP-MS but with far less sample volume

requirement) achieved at UMCP our laboratory by factors of 2 to >400 for Al, As, Cd, Cu, Fe, Mn, Ni, Pb, Se, V, and Zn. These should be more than adequate for proposed 1-hr sampling periods. In addition to high temporal resolution, it is of paramount importance that analytical concentration measurements be accurate. Tests with NIST Standard Reference Material 1648 ("Urban Particulate Material") confirm these results for Cd, Pb, Zn, Se, As, Cr, Mn, Cu, and Ni. Tests for the remaining elements are in progress. Additional field tests of the instrument are being made in College Park, MD, and at the Atlanta Super Site in August, 1999.   A schematic of the collector is shown in Attachment III. Detection limits for achieved in aerosol slurry samples collected for 60 minutes are listed in Attachment IV.

   The SEAS will be deployed at primary platform sites.   The instrument will be configured to permit continuous collection of hour long samples with on-line analyses for As, Cu, Mn, Ni, and Cr throughout a 12 month sampling period. Twelve additional elements (Cd, Se, Ag, Pb, Al, Fe, Zn, Ca, V, Ti, Be, Ba, and Bi - Bi is used as an internal standard) will be analyzed retrospectively in up to 1000 of the samples (i.e., 40 days worth) on an identical Graphite Furnace (with Zeeman background correction) analytical platform. The elements selected include criteria pollutants (Pb and Be), hazardous air pollutants (known as air toxins; i.e., Cd, Cr, Cu, Ni, As, and Se), first series transition metals either known (V and Zn) or suspected to elicit respiratory inflamation (Ti, V, Cr, Mn, Fe, Ni, Cu, Zn; i.e., all but Sc and Co); essential nutrients (Fe, Zn, Se, Cr), and the aquatic toxin, Al. In addition, most are primary source marker species (i.e., As and Fe, steel; Zn, Cd, Cr, Pb, Ag, incinerators; Ni and V, residual fuel oil combustion; Se, coal combustion; Ti, paint manufacture and applications (fine particles) or crustal dust (coarse particles); Ca limestone/construction material; and Cu, Cd, Zn, respective smelter emissions and/or metals processing.

  The analytical platform permits truly-simultaneous determinations of up to 5 elements. Analyses are done in suites of 4 or 5 elements (i.e., suite 1: As, Cu, Mn, Ni, Cr to be done online; suite 2: Cd, Se, Ag, Pb; suite 3: Al, Fe, Zn, Ca, and Bi (Bi is an internal standard); and suite 4: V, Ti, Be, Ba). Until more experience is gained, 3 replicate analyses will be made for each element during both on- and off-line analytical protocols. Analysis of each suite about 5 minutes per replicate, so that the time to complete 3 replicates is 15 minutes per suite, allowing for more than enough time for online analyses of samples and analysis of 1 reagent blank and 2 multi element standard solutions each hour. However, we envision that reagent blanks will be analyzed in triplicate every 6 hours and 3 to 5 multielement standard solutions (i.e., of different concentrations) will be analyzed several times each day. The system will require maintenance every 3 days to replace the furnace tube and various reagents.   Series of samples will be selected for analyses for the remaining elements based on the online results and observations made with continuous aerosol and gas instruments described above and with those made with the RSMS III and LIDAR instruments described below.

Single Particle Mass Spectrometry (RSMS III)
We propose to use an on-line single particle analysis technique to measure the particle-by-particle size and composition over the size range from 10 nm to 2.5 microns. Particles of a narrow size range are focused aerodynamically to the source region of a mass spectrometer. The focused particle size is selected by adjusting the upstream pressure -- the Cunningham continuum correction factor is pressure dependent and the variation in upstream pressure determines the mean free path and therefore the particles size focused. For particles too small to be detected by light scattering, an

excimer laser oriented colinear with the particle beam is fired at a fixed rate and particles are randomly hit. For larger particles, light from a doubled YAG laser is detected from forward scattering by two PMTs to synchronize the laser with the particle arrival. In either case, if a particle is in the beam when the excimer fires, it is desorbed and ionized. The ions are analyzed in a time-of-flight mass spectrometer. Spectra from each particle are recorded and stored on a PC. The instrument has been tested in the laboratory and found to have a 0.1 mass percent sensitivity to metals in 50 nm particles. The instrument and these tests are described in more detail in Carson et al. (100) and Ge et al. (101). Figure 1 shows a schematic of the instrument.

RSMS-II can analyze for a wide range of compounds and compound classes including a) speciation of inorganics such as metals and metal oxides, refractory crustal materials such as silicon dioxide, and electrolytic compounds such as sulfates and nitrates, b) speciation of aromatic organic compounds, and c) distinguishing elemental from organic carbon (see Attachment 2). Since the compounds can usually be speciated, we can use composition information to determine source. For instance, we have shown that sulfur speciation is straightforward so that HMSA can be used as a marker for cloud processing while MSA can be used as a marker for sea spray particles. The analysis is surface selective for larger particles at low laser power but samples the bulk of smaller particles (101). The hit rate, measured in the laboratory and with ambient particles, ranges between 10 and 300 particles per minute under typical atmospheric concentrations, depending on the particle size sampled. RSMS III will be automated and capable of sizing particles as large as 2.5 μm.

LIDAR
Active remote sensing of particles in the atmospheric boundary layer will be accomplished by deploying the Johns Hopkins Elastic LIDAR. The LIDAR is undergoing modifications to become the world's first 3 - color system (1.064, 0.532, 0.355). The attenuation coefficient for each of the colors can be used to integrate particle concentrations up to 2.5 micron to determine PM 2.5 more accurately. The system will be used to measure the three-dimensional distribution and transport of aerosols throughout the south Baltimore study area during the intensive phase of this experiment and on a routine basis throughout the entire study project. The LIDAR will augment the point sensors used in this project by providing a noninvasive instrument capable of mapping the particulate concentrations in three dimensions at long ranges (to 10 km) with high (1.5 meter) spatial resolution. The LIDAR will be used to map wind velocities in the boundary layer, emissions from cars, power plants, various manufacturing facilities, and the general development of the boundary over the course of the day above the city and the surrounding area, including the Chesapeake Bay. The LIDAR provides a means for obtaining real-time horizontally and vertically resolved information such that emission fluxes can be determined from various sources through the city. With the LIDAR, full-scale field measurements of stack effluent as a function of down wind distance, vertical height and prevailing wind speed can be obtained. The ability to generate time sections of pollutant distributions above the city is crucial to resolving many of the issues related to air quality and ultimately to human health. Vertical layering of pollutants is well known, but detailed descriptions of the temporal evolution of these layers would not be available without the power of the scanning LIDAR system. The scanning capability allows regular detailed temporally and spatially distributed measurements of aerosols which can be used to analyze sources and dispersion in the turbulent atmosphere. In addition to characterizing the evolution of events above the south Baltimore site, and

the city more generally, the LIDAR will aid in both the identification of mesoscale transport of particulates from outside Baltimore city and their ultimate dispersal away from local sources. Finally, the LIDAR is the ideal supplement to the point sensors to be deployed in this project, which locally are very accurate, but do not provide information on the local spatial variability of the particles.

Over the 12-month field study period, the LIDAR scans will be made 4 times a day, every other day, to investigate seasonal aerosol patterns throughout Baltimore and to provide mixing layer height over the City, a highly useful parameter that cannot be otherwise reliably be obtained. The LIDAR will be located at the Wynman Park building near the Homewood campus of johns Hopkins. The location of the building is ideal so that the investigators will have easy and regular access to the instrument during the normal course of their work. The same measurements as the south Baltimore study will be employed.

During the intensive south Baltimore study, the LIDAR system which will be deployed from the roof a building overlooking the study area. At the start of each hour a full three-dimensional scan over the study site will be taken. (210 degrees at 10 degree slices). During the rest of the time period horizontal scans will be used to develop times series particulate motion and wind fields. In addition individual plumes will be followed, and street emissions followed along with the evolution of the atmospheric boundary layer inversion. Graphic presentations of the various scans will be entered into the project data base.

DATA REDUCTION, VALIDATION, INTERPRETATION, AND DISSEMINATION
On-the-fly data reduction of RSMS III Data

The development of the on-line system to characterize individual airborne particles has resulted in a practical instrument that yield a large quantity of data on the size dependent composition of the particles. The next step is to be able to relate the vast quantity of data efficiently for use in guiding retrospective analyses and hypothesis testing. Dr. Hopke has been actively examining the problem of single particle classification for almost 15 years. The previous efforts have been based on data produced by computer-controlled scanning electron microscopy, but the basic classification and quantification concepts will be the same. The idea is to sort the particles into homogeneous groups where we mean that all of the particles within the group have basically the same characteristics. Not all particles will fall into well defined groups, but we can typically classify more than 70% to 75% of the particles into classes. The mass of each particle is estimated based on its aerodynamic diameter and thus, the airborne particle mass for each class can be determined.

The critical task is the particle classification. Professor Hopke has used several approaches including hierarchical cluster analysis, rule-building expert systems, and more recently, artificial neural networks particularly Kohonen (102) and Adaptive Resonance Theory (ART) networks. The Kohonen approach has been tested with both simulated and real data (103). ART-2a has been applied to the particle-by-particle data provided by the CCSEM analysis (104,105) and more recently Hopke has demonstrated the utility of the ART-2a approach for ATOFMS data as well (106). The ART-2a is the more likely candidate for the problem of the classification of the particle by particle data since it can dynamically update the classification as it processes new particles. One of the major tasks will be to set up the system to handle the large data sets that are produced by the RSMS III system. Instead of thousands of particles that we have analyzed in the past, we must be prepared for

hundreds of thousands of particles. Professor Hopke will choose the most appropriate approach and adapt it to efficiently classify the particles, estimate the individual particle masses, and calculate the class mass fractions and their uncertainties, on-line.

Multivariate Calibrations and Data Quality Analyses
The proposed measurements will produce both traditional 24-hr measurements of aerosol mass and elemental constituents and more highly -time resolved measures of these species as well as particle types. The problem is to relate (i.e., calibrate) the measurement of components using the sophisticated measurements at the supersite to the measured component concentrations obtained from chemical Speciation monitors and to the FRM mass concentrations, and to identify deficiencies and differences, and ultimately identify their causes. This problem will be solved using one of several multivariate calibration methods including partial least squares and back propagation neural networks. Such tools are sorely needed if we are to understand the quality of our data. Partial least squares and artificial neural network modeling tools to be applied to this problem are described in Appendix III. By using these methods to examine the relationships among the methods, we will better understand the response of the speciation or FRM sampler to various composition aerosols. We can also use the same methodology to understand the response of one instrument like light scattering to other appropriately time resolved data or the relationships between the remote sensing measurements and the related monitoring data.   Finally these models can be used to help examine the sources of airborne particulate matter based on the detailed speciation results that will be obtained in these studies. One reference for the application of multivariate statistics to data quality is: Xie et al. (Xie, Y., Hopke, P. K., Paatero, P., *Anal. Chim. Acta, 384*:193-205, 1999; see also: Martens, H., Nales, T., *Multivariate Calibration*, John Wiley & Sons, Chicester, UK, 1989).

An example of how the techniques can be applied is as follows. If 24-hr FRM mass measurements made on 365 days were the Y block, and hourly averages of the semicontinuous mass data were used to construct a 24 element wide by 365 element long Y block, then the model could be run to produce a table of factor scores representing weights of the hourly values needed to give agreement with the predicted 24-hr values. If one or more large hourly scores are observed, for example, on a given day, or if they are consistently large at certain times of the day, then there would be reason to seek the cause. In this way, the multivariate method can be used to identify bad data , e.g., due to operator error, and reveal shortcomings in the method such as poor performance related to weather or seasonal conditions. Likewise, 24-hour and hourly composition data derived from speciation and time-resolved systems, respectively, could by used to identify problematic periods and trends. Thus, we advocate performing many such analyses.

Data Base and Dissemination of Results
To effectively manage the large volume of data that will be produced through this measurement program, it will be necessary to have an effective data basing system. The University of Maryland already has a relational data management system that has been developed primarily for their instrumental neutron activation analysis data, but was designed to accommodate data from other instruments. This system will serve as an excellent starting point for an expanded system that will also be interrelated with the meteorological data base. The data base be professionally constructed and will feature multi-level password protection, multi-level data quality flagging, and instantaneous

display of summary statistics and user-selected time series plots of any of the sampling or analysis parameters.   The data base will be made available on the web via password protected access by project participants including MDE and EPA personnel.   Data from the various semi-continuous and continuous monitors will be reprocessed to produce hourly averages for entry into the data base. Project data will be archived on CD ROM and on hard drives which, we believe, should preserve the data in retrievable form for 10 years or more. We plan to make at least two copies of the project data on CD ROM. Additionally, we plan to archive data on separate hard drives at UMCP and on an additionally redundant pair of hard drives at Clarkson Unviersity.

Data dissemination will include workshops, conference presentations, and peer-reviewed publications. We intend to hold three work shops: two to allow project participants to discuss and interpret data, and a third to disseminate the information to Baltimore City health professionals, community interest groups, individuals, and other stakeholders, e.g., the Concerned Citizens for a Better Brooklyn.   All of the information developed, including access to the project data base will be provided to the State of Maryland for use in SIPs development, and to JHU and UMSON for correlation with CLINICAL health metrics determined in their studies. Lastly we will make the data available NARSTO's Permanent Data Archive.

EXPECTED RESULTS OR BENEFITS
The proposed project should provide the State of Maryland and the Scientific community with an unprecedented quantity of high-quality highly time-, size-, and compostionally-resolved data, new organic compound data, and extensive characterizations of PM distributions, wind fields, boundary layer height; all of special utility to receptor-based source attribution for reconciling local emissions data and development of SIPs,   We expect to demonstrate that source resolution will substantially benefit from collection of highly- time-, size-, and composition-resolved data; how certain constituents of particles from certain sources account for important immumological responses; how concentrations of PM constituents and their immunological responses differ between industrial, urban, and non-urban environments, and further provide insights into the affects of aerosol age on these responses. Many high-quality manuscripts will be published in peer-reviewed journals, and several new Ph.D. urban aerosol scientist will be trained.

COLLABORATIONS
The Baltimore Supersite project will be conducted in collaboration with and benefit from a constellation of epidemiologist, toxicologist, health care professionals, and exposure assessment scientist. Their contribtuions are described in Appendix II. Individuals and their project titles are as follows: From JHU, **M. Wills-Karp**, Particulate Matter Induced Exacerbations of Allergic Asthma; **J. Jaakkola**, The Relationship of Air Pollutnats and Allergens to Asthma Morbidity; **P. A. Eggleston**, Community Environmental Intervention Trial; **T.J. Buckley**, Evaluation of Indirect PM10 Exposure Assessment in a Cross-Sectional Epidemiological Study of Asthma Exacerbation in Urban Children, and VOC Exposure in an Industry Impacted Community; **J. M. Samet**, Environmental Epidemiology and Human Exposure Assessment; **T. W. Kensler**, Biomarkers and Prevention; **J. A. Yager**, Molecular Toxicology; **W. Mitzner**, Environmental Lung Disease; **M.A. Trush**, Pilot Projdect Program; **S. P. M. Reddy**, Molecular Basis of PM-Induced Respiratory Toxicity; and **A. Togias**, The Inner-City Environment and Asthma;   Several additional projects are

pending. In addition UMCP has a long-standing collaboration with **B. Sattler**, Baltimore Environmental Justice Project. Lastly, we hope to continue past collaborations with various EPA colleagues.

GENERAL PROJECT INFORMATION
Project Schedule
The proposed project period is Jan 1, 2000 to Dec 31, 2003. The first 18 months will be dedicated to purchase, calibration, and construction, and installation of instruments, data base management program constructed, and coding the "on-the-fly" particle classification program for RSMS III. During the first 3 months, our external advisory panel members will be selected and first project planning meeting will be held. Support staff candidates will be interviewed and hiring decisions will also be made within the first 3 months. The UMUHVS and a HFASS are already installed in a trailer and will be deployed later in the first project year, when the former will be operated to collect exploratory samples for organic compound analyses and cytokine/ROS assays. Exploratory LIDAR measurements will also be made during this period. We anticipate initiating our 12-month field study in the 18th month, presumably in mid to late summer of 2001. Intensive campaigns in South Baltimore will be conducted in Jan. and June of 2002. Community campaigns will be conducted according to the schedule in Figure 2. A data analysis workshop will be held in the second part of the measurement period, and again early in the 4th year of the project. The last 16 months of the project will be dedicated to data interpretation, synthesis, and developing a final project report.

Personnel and Proposed Management
Dr John Ondov (UMCP), PI, will serve as be responsible for overall project management, integration of individual project components and coordination of the final synthesis of the results. Ondov will be assisted by an internal steering committee composed of the individual co-investigators, through frequent telephone conference and email communications. An external advisory committee, comprised of air pollution monitoring, epidemiology, toxicology, and policy/regulatory experts from the scientific community at large and EPA, to review the project plan early in the first year. Day-to-day operation of the project will be the responsibility of a Post-Doctoral aerosol scientist to be hired for the project in the capacity of Field Manager. Two field sampling technicians will be hired for the project to ensure uninterrupted maintenance of the sites. The technicians will further be supported by graduate research assistants from UMCP and JHU, especially, during intensive campaigns. These individuals will report directly to the Field Manager. The **Dr. Ondov** and will be responsible for the deployment the UMCP SEAS instrument, the high-frequency aerosol slurry sampler for biologic testing, bulk PM2.5 collections, and Dr. Susan s (UMCP) retrospective quantitative elemental analyses. **Drs. Anthony S. Wexler** and **Murray V. Johnston** (Univ. Delaware) will build, deploy, and operate the 3nd generation automated single-particle mass spectrometer system for near-real time constituent analysis Dr. Anthony Wexler will supervise the University of Delaware portion of the project and organize the UD portion of the field program. Dr. Murray Johnston will assist Dr. Wexler in supervising the Research Associate and Graduate Student with instrument construction and data analysis. **Dr. Phillip Hopke** (Clarkson Univ.) will assist in the finalization of the sampling design, data analysis, and interpretation of the results of the measurement campaign. He will be responsible for the "on-the-fly" multivariate data

reduction program to be used by RSMS III, hypothesis testing, data base development and management, and will serve as project quality assurance officer. As such, he will perform the QAQC audits. Dr. Hopke will be assisted by Dr. Ziad Ramadan and an external contractor. **Dr. Katherine Squibb** (UM, Baltimore) will be responsible for conducting cytokine assays on $PM_{2.5}$ samples. **Dr. Timothy J.. Buckley** (Johns-Hopkins Univ.) will oversee the planning and implementation of the monitoring campaigns at the community sites, and will be in charge of implementing the quality assurance procedures for the project. Dr. Buckley will also serve as a liaison between Supersite project investigators and epidemiology, toxicology, and exposure researchers at the Johns Hopkins School of Public Health. **Dr. MarcB. Parlange** (Johns Hopkins Univ.) will be responsible for deployment and operation of an advanced 3-wavelength scanning LIDAR system for 3- dimensional mapping of urban wind fields and relative PM concentrations. **Dr. Wolfgang Rogge** (Florida International Univ.) will be responsible for organic compound sampling and analysis for source identification.

Dr. Buckley is experienced in the design and conduct of community-based human exposure studies This field-based experience is complemented by laboratory studies investigating biomarkers of exposure . Dr. Buckley is currently involved in research on the exposure and effects of air pollution on children with asthma, exposure to air pollutants from an industry-impacted community, and the dermal absorption of VOCs in water and VOC biomarkers in breath.

Dr. Philip K. Hopke is Chair of the Department of Chemistry and holds a joint appointment in the Department of Civil and Environmental Engineering at Clarkson University. He has been a pioneer in the characterization of source/receptor relationships for ambient air pollutants and the use of multivariate statistical methods for data analysis. He is also currently involved in the development of measurement methods for characterizing ultrafine and radioactive particles. Prof. Hopke will be assisted by Dr. Alexandre Polissar. Dr. Polissar has been working with Prof. Hopke for the past 5 years on application of PMF and ME to various data sets.

Dr. Ondov has conducted multi-disciplinary projects for the U.S. DOE, Martin Marietta Corporation, and the University of Maryland. He has designed and built sampling systems for stack monitoring, including a 200 cfm system for size-segregating and collecting kg-quantities of stack-emitted aerosol; ambient $PM_{2.5}$ aerosol samplers, and, in a joint project with the Harvard School of Public Health, is responsible for development of the semi-continuous monitor. He developed unique methodology for apportioning fugitive emissions from industrial plants to specific processes and pioneered the development of extremely sensitive enriched rare-earth isotopic tracer techniques for use in source attribution and studies of aerosol particles over transport distances of 100s of km. He has conducted several receptor modeling studies using intentional tracers and tracers of opportunity, including studies to determine the sources and fluxes of toxic substances depositing onto surface waters of Lake Michigan and the Chesapeake Bay. Ondov also pioneered the application of highly-size resolved sampling to elucidate urban aerosol sources, age, and deposition.

Dr. Marc Parlange, Professor at Johns Hopkins University in the Department of Geography and Environmental Engineering, holds joint appointments in the Departments of Mechanical Engineering

and Earth and Planetary Science at Hopkins. He has extensive research experience in fluid mechanics in the environment, atmospheric boundary layer, turbulence, LIDAR (light detection and ranging), Large Eddy Simulation, aerosol transport, hydrology, and flow in porous media.

Dr. Rogge is a leading expert on tracing fine particulate source emissions in the urban atmosphere using fine particle-associated organic marker compounds. He identified and verified several source-derived marker compounds. Two of his journal papers received appreciable publicity in national and international newspapers, radio, and TV throughout the United States of America and Europe. Other sources investigated include gasoline and diesel powered vehicles, dual fuel powered vehicles operating on natural gas and gasoline; road dust, brake dust, and tire dust, leaf surface abrasion products, natural gas home appliances, hot asphalt roofing tar pot fume, boilers burning No.2 distillate fuel oil, wood burning in open fireplaces and campfires, restaurant type hamburger frying and charbroiling, residential charbroiling, residential cooking using natural gas and electricity. Furthermore, Dr. Rogge generated one of the most extensive ambient data set on fine particle-associated organic compound concentrations presently available for the Los Angeles area and Southern Florida. The organic tracer technique developed by Dr. Rogge was tested in many ways and showed remarkable results when using a Lagrangian type dispersion model as well as a Chemical Mass Balance (CMB) model to predict fine particle associated organic compound concentrations for the greater Los Angeles area.

Dr. Squibb has over 20 years of experience conducting research on mechanisms of the toxic effects of metals in mammalian whole animal and cellular systems at the National Institute of Environmental Health Sciences, the Institute of Environmental Medicine at NYU, and the University of Maryland, Baltimore. Her research has included studies of the effects of metals on lung tissue following inhalation exposure and effects of metal ions on macrophage activity.

Drs. Wexler and Johnston have been working together on single particle instruments for analyzing atmospheric particles since 1991. They have built the only instrument currently available for routine on-line analysis of ultrafine particles. They have published over 15 papers together that describe single particle instruments, characterizing their performance in the laboratory, and investigating atmospheric aerosol issues. They will be performing fine and ultrafine measurements at the Atlanta supersite during August 1999.

Facilities and Equipment
UMCP. Facilities available at UMCP include a well-equipped Nuclear Analysis Laboratory (120 m^2) with 7 intrinsic Ge detectors (24 to >40% efficiencies relative to $3^{\parallel}$ x $3^{\parallel}$ NaI) with resolutions (FWHM at the 1332 keV photopeak of ^{60}Co) of from 1.76 to 1.88 kev., a cold room (4^0C) for sample storage, a 120 m^2 Class 100 Clean Room complex, a 100 m^2 aerosol measurements laboratory, and newly-renovated 39-m^2 clean chemistry laboratory. The latter contains a Millipore MilliQ+ water purification system., 3 laminar flow clean benches, two laminar-flow clean air hoods (one is equipped with a scrubber to permit perchloric acid digestions), a computer-controlled Mettler UMT2 electronic balance installed in a sealed, environmental enclosure for gravimetric analysis at 50% relative humidity. The Class-100 room contains a 6.7 m^2 particle-free work surface for sample

packaging and preparation includes a laminar-flow clean bench dedicated to coating aerosol collection substrates. Neutron irradiations are performed at fluxes of from 7.7×10^{13} to 1×10^{14} n/cm/sec at the 20 MW research reactor located at the National Institute for Standards and Technology (NIST) in Gaithersburg, MD. A Dionex Ion chromatography and PE ICP-MS are available at UMCP.

Relevant equipment available for use in this project include: i) one SEAS, complete with SIMAA6000 analysis platform, ii) the computer-controlled UM Ultra High-Volume Sampler; iii) one 24-ft towable field laboratory trailer; iv) 5 hp PM2.5 high-volume sampler with 1000 LPM volumetric flow sensing system; iv) 2 meteorological stations each with wind speed and direction, temperature, and humidity sensors, and Campbell CR10 data logger; v) collapsible 10-m met tower; vi) a PMS high-volume forward-scattering laser spectrometer, vii) TSI differential mobility analyzer with continuous condensation nuclei counter, viii) 3 ten stage micro-orifice impactors; and ix) an 8.5 m plexiglass aerosol chamber ($1 \ m^2$ cross-sectional area) for testing particle generators and samplers, and xii) a low background counting facility. Particle generation equipment includes nebulizers with ^{85}Kr dischargers and diffusion dryers. Available software packages include: StatMost v3.5; Lotus SmartSuite 97, Word Perfect Office 8, Microsoft Office 97; Sigma Plot, v5; Mathcad v8.0; Matlab, v5, and the UM data management and analysis system which controls sample data entry (including data-logger files) and INAA analysis functions.

University of Delaware. Dr. Wexler and Dr. Johnston have separate laboratories. Dr. Wexler's laboratory is oriented toward building and fielding single particle instruments. The portion of the laboratory dedicate to single particle analysis is about 800 square feet. In addition, it has a 8 foot by 14 foot portable laboratory for transporting aerosol instrumentation to field sites and housing them there. Both single phase and three phase power distribution systems are available. The laboratory includes a single particle instrument that has been used in the field. A significant fraction of Dr. Johnston's laboratory is oriented towards developing new analytical chemical techniques for use in single particle analysis. About half of his laboratory, around 1500 square feet, is dedicated to single particle analysis and includes a laboratory-based TOF single particle analysis instrument and one under development based on ion mobility mass spectrometry. Both laboratories share a range of aerosol instruments including a TSI APS, SMPS, VOAG, nebulizer, and powder dispenser, and a custom-made radial DMA. Both laboratories are outfitted with laser warning lights, light curtains, fume hoods, a range of power sources, compressed gas, cooling water, and wet lab facilities. Each laboratory has independent single particle analysis instrumentation. The instrument in Dr. Johnston's laboratory is dedicated to laboratory applications. The one in Dr. Wexler's laboratory can be used in the laboratory or in the field.

Florida International University. Currently, two air pollution laboratories are available with together 1,000 ft^2. One of the laboratories is exclusively dedicated for trace organic compound analysis. Current equipment includes : i) 1 HP 6890 gas chromatograph with FID detector ii) 1 HP 5973 MSD interfaced with HP6890 GC; iii) 1 Buechi rotary evaporator; iv) 1 Micro-balance; v) 7 PC computers; vi) 1 API CO-analyzer, 300 Series; vii) 1 API NO/NO_2/NO_x-analyzer, 200A Series; viii) 2 MSP PM2.5 samplers; ix) 2 MSP PM10 samplers; x) 3 Grasby-Anderson 6-Stage Cascade

Impactors; xi) 2 2HP air sampling pumpsl xii) 4 1/2HP air sampling pumps; xiii) 1 Data acquisition station; xiv) 2 Temperature sensors; xv) 1 Humidity sensor; xvi) 1 Large dry gas meter; xvii) 1 Small dry gas meter; xviii) 1 Dehumidifier; xix) A number of volume flow controllers; xx) 1 stainless steel dilution tunnel; xxi) 1 large indoor stainless steel environmental chamber (27 m^3)**.**

University of Maryland, Baltimore. Laboratory space available for this project includes two Program in Toxicology laboratories located at the University of Maryland, Baltimore County (UMBC) Technology Center at the UMBC South Campus. One 300 sq. ft laboratory is a fully equipped tissue culture facility. The second laboratory (500 sq ft) is a well equipped biochemistry lab. Equipment available for the project includes a Beckman L8-80 ultracentrifuge, a GPKR centrifuge, a Sorval RC2B centrifuge, a Hewlett-Packard UV/UVS spectrophotometer, a Virtis Freeze-Dryer, and a PerSeptive Biosystems Cytofluor Series 4000 fluorescence multi-well plate reader. Five IBM/PC Pentium Processor computers located in the offices and laboratories at UM,B and UMBC are available. These are linked to the Unix Main Frame computers at the two campuses providing access to the Internet. The Program in Toxicology has one full time secretary and one business manager available to support the administrative aspects of this project. The project also has the full facilities of the UM,B Department of Pathology available to it, which includes tissue and organ culture, immunology, electron microscopy, and histology labs.

Johns Hopkins University. Equipment available: i) Model 3320 and 3300 Aerodynamic Particle Sizers (APS); ii) Anderson Dichotomous Samplers; iii) MSP PM10 and PM2.5 personal impactors; iv) LIDAR: The Hopkins LIDAR that will be used in this study is a duplication of the miniature elastic LIDAR system developed by Los Alamos National Laboratory. This LIDAR has been selected as a "Popular Science Best of What's New" and has won an R&D100 award for its design and controlling/analysis software (this award is an international award, given annually by R&D magazine, and is considered to be the most prestigious award for engineering). The system possesses a sophisticated computer control system to essentially operate the entire system independent of operator control and a well-developed analysis package (developed in part by Parlange). The system consists of a 1.064 micron ND:YAG laser, operating at approximately 125 mJ/pulse, 50 pulses per second, coupled to a 10 inch Cassegrain telescope and is capable of taking monostatic, elastic scattering measurements with 1.5 m range resolution (adjustable) out to a range of 3 to 12 km (depending on ambient particulate loading and upon the number of averaged pulses). Incoming light is focused at the back of the telescope on an IR-enhanced Silicon Avalanche Photodiode detector (APD) operating in current mode that is used to convert the light to a voltage signal. Data collection is via a 100 MHz transient digitizer card installed inside a PC. A computer-controlled motor system scans the atmosphere in azimuth and elevation, depending on the type of scan desired. A user-friendly control system operates the laser, scanner motor, detector gains, and digitization equipment. On-site graphics are presented in a color display of spatial concentrations.
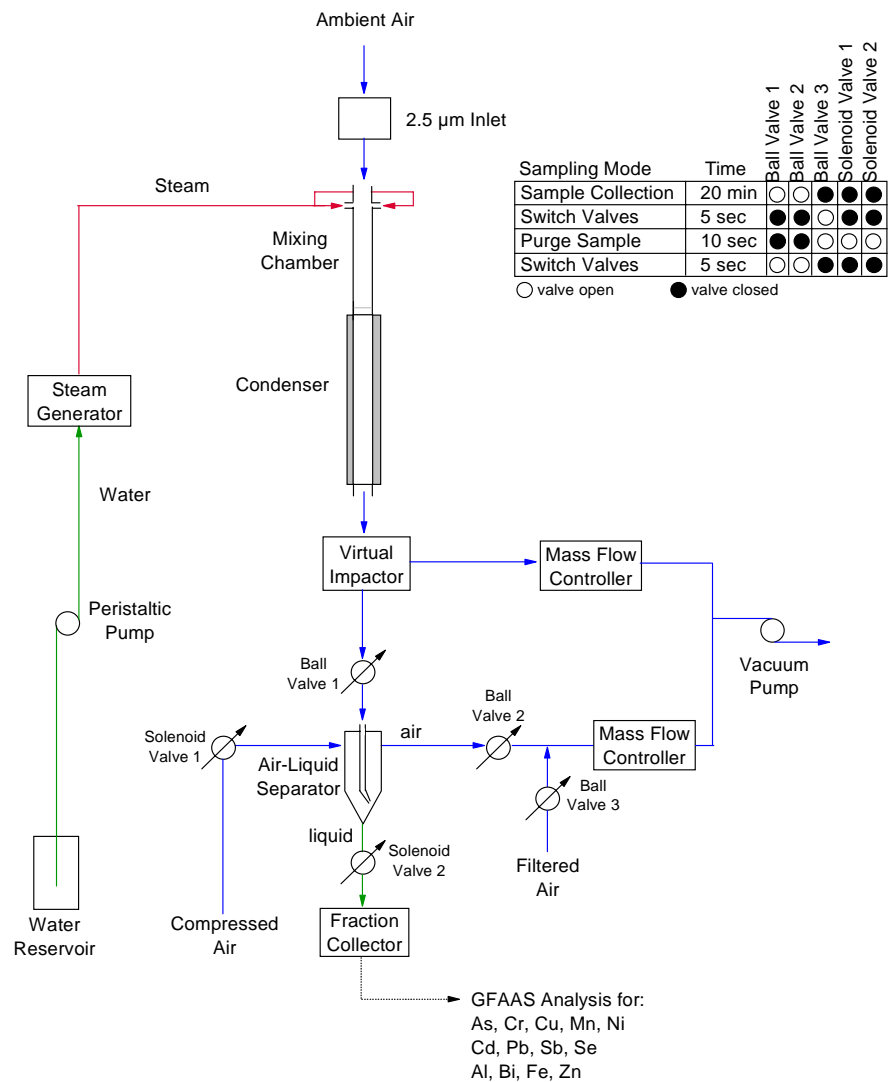
ATTACHMENT 1: Summary of Proposed Measurements

Instrument/Sampler		Instrument	Sites	Frequency	Duration
Commercial Continuous/Semicontinuous Monitors					
Ultrafine/near accumulation aerosol	0.02 to 0.5 μm	Scanning Mobility Particle Spectrometer, Forward Scanning Laser Spectrometer	1	5 min	12 months
Far accumulation aerosol/coarse size spectrum	0.5 to > 10 μm	Optical Particle Counter	1	5 min	12 months
Accumulation aerosol vs. aerodynamic size spectra	0.5 to > 10 μm	Aerodynamic Particle Spectrometer	2	5 min	community Intensives
Light Scattering	entire range	Integrated Nephalometer, Radiance Res.	1	2 sec	12 months
Mass concentration	PM2.5	TEOM, 1400A	1,2	5 min	12 months
Sulfate concentration	PM2.5	To be determined (e.g. R&P, HSPH)	1	10 min	12 months
Nitrate concentration	PM2.5	To be determined (e.g. R&P, HSPH)	1	10 min	12 months
EC/OC	PM2.5	R&P Series 5400-99-004-743-0025	1	30 to 60 min	12 months
Temp (2 heights), RH, Wind speed and direction, barometric pressure, solar insulation		RM Young/Campbell Sci. met station	1		12 months
Sensible latent heat and momentum fluxes		3-D Sonic Annemometer & Krypton hygrometer	1		12 months
Ozone		TECO	1		12 months
NOx,		TECO	1		2 months
SO$_2$		TECO	1		12 months
VOC		Hewlet Packard GC	1		12 months
Special Measurements			1	1 hr	12 months
As, Cu, Mn, Ni, Cr	PM2.5	UMCP SEAS	1	1 hr	12 months
Cd, Se, Ag, Pb, Al, Fe, Zn, Ca, V, Ti, Be, Ba	PM2.5	UMCP SEAS, retrospective analysis	1	1 hr	Intensives
Single particle classification by composition and size (most metals,e.g., Na, Mg, K, Cr, Cu, Zn, Cd, Cs, La, Pb, some valence information, NH$_4$SO$_4$, sulfites, hydroxymethane sulfonic acid, methane sulfonic acid, EC/OC, polynuclear aromatic hydrocarbons)	10nm to 2.5 μm	UDE RSMS III	1	approx 1 min every 10 min	12 months
3-D PM/wind fields, and mixing height		JHU 3-wavelength Lidar	area	1 scan every 6 hrs	12 months
210 scan at 5 intervals horizontal by 75 vertical, 8 km range		JHU Eye-Safe Lidar	area	1 scan every hour	Intensives
210 scan at 1/2 intervals horizontal by 75 vertical, 8 km range		JHU Eye-Safe Lidar	area	1 scan every hour	Intensives
Selective plume mapping and time series scans		JHU Eye-Safe Lidar	area	1 scan every hour	Intensives
Collections for Off-Line Analyses					
FRM Mass Conc.	<2.5 μm	RAAS 2.5 - 100	1,2	24 hr	12 months
Speciation Sampler (for elemental and EC/OC analysis)	<2.5 μm	RAAS 2.5 - 400	1	24 hr	12 months
Size Segregated Aerosol	<0.3 to 10 μm	3 Stage RDI	1	24 hr	12 months
Highly-Size Resolved Aerosol	<0.069 to 10 μm	3 Stage RDI	1	24 hr hrly resolution	12 months
PM2.5 for Cytokine/ROS assays	<2.5 μm	UMHFAS	1	1 hr	12 months
Bulk PM	<2.5 μm	UMUHVS	1	1 week	12 months
Organic Compounds	<2.5 μm	2-HP HVS	1	24 hr	12 months
			1	1 to 2 hrs	Intensives

ATTACHMENT II: ORGANIC MARKER SPECIES

Table 2. Organic Species to be Determined in Source Profiles

Emission Source	Potential Organic Tracer Compounds	Refs. (see page 39)
Motor Vehicles	n-alkanes, especially n-pentacosane; total hopanes and steranes	1
Non-catalytic converter-equipped vehicles	coronene, benzo[g,h,i]perylene	2
Heavy-duty diesel trucks	hydrocarbon 'fingerprints,' based on emission profiles	1
Secondary organic aerosol	C3-C9 aliphatic dicarboxyilic acids; aromatic polycarboxylic acids	3, 4
Wood comubstion	n-alkanoic acids >C18; total resin acids, especially dehydroabietic, isopimaric, and primaric acids and retene	2, 5, 6
Vegetative detritus	predominance of odd over even n-alkanes, especially C29, C31, and C33; predominace of odd over even n-alkanoic acids	7, 8
Meat cooking	oleic acid	9
Cigarette smoke	high MW branched alkanes, especially isohentriacontane and anteisodotriacotane	10
Hot asphalt roofing tar and road asphalt	Characteristic hopane or sterane in local petroleium sources	11
Road dust, brake linings, tire debris	No unique organic tracers, use Al and Si for road dust	12
Fuel oil	No unique organic tracers, use elemental tracers	13
Natural gas combustion	hydrocarbon 'fingerprints,' based on emission profiles	14

Ambient Air

2.5 µm Inlet

Steam

Mixing Chamber

Condenser

Steam Generator

Water

Peristaltic Pump

Water Reservoir

Compressed Air

Solenoid Valve 1

Air-Liquid Separator

liquid

Solenoid Valve 2

Ball Valve 1

Virtual Impactor

Mass Flow Controller

Vacuum Pump

air

Ball Valve 2

Mass Flow Controller

Ball Valve 3

Filtered Air

Fraction Collector

GFAAS Analysis for:
As, Cr, Cu, Mn, Ni
Cd, Pb, Sb, Se
Al, Bi, Fe, Zn

Sampling Mode	Time	Ball Valve 1	Ball Valve 2	Ball Valve 3	Solenoid Valve 1	Solenoid Valve 2
Sample Collection	20 min	○	○	●	●	●
Switch Valves	5 sec	●	●	○	●	●
Purge Sample	10 sec	●	●	○	○	○
Switch Valves	5 sec	○	○	●	●	●

○ valve open   ● valve closed

ATTACHMENT IV: Estimated Detection Factors for SEAS

| Element | Ambient Air Concentration (1) ng/m³ | | DL | Factor Above DL | |
	average	minium	pg	for minimum ambient air concentrations	for average ambient air concentrations
Ag	0.059	0.006	1	12	118
Al	121	24.8	6	827	4,033
As	0.69	0.337	10	67	138
Cd	0.131	0.0119	0.4	60	655
Co	0.159	0.051	8	13	40
Cr	0.79	0.039	1.6	49	988
Cu	2.35	0.31	5	16	118
Fe	117	33	6	165	585
Mn	3.09	0.05	1.8	5	309
Mo	0.712	0.057	4	3	36
Ni	2.92	0.36	16	45	365
Pb	4.13	0.316	3	6	75
Sb	0.495	0.185	8	5	12
Se	1.53	0.592	8	148	383
Sn			14		
Ti	12	0.017	10	1.7	1,200
V	3.24	0.564	18	63	360
Zn	13.5	4.7	6	1,567	4,500

(1) UMCP data for rural Maryland sites.

APPENDIX I
LETTERS FROM COLLABORATORS

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Marsha Wills-Karp
Johns Hopkins University
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Barbara Sattler, Director
Environmental Health Education Center
University of Maryland School of Nursing

1.   **Active: EPA/NIEHS Center for Childhood Asthma in the Urban Environment.**
        Overarching goal is to examine how exposures to environmental pollutants **and** allergens
        may relate to airway inflammation and respiratory morbidity in children with asthma
        living in the inner city of Baltimore.

        A.   **Mechanisms: Particulate Matter Induced Exacerbations of Allergic Asthma.**
                The overall goal of this proposal is to establish a causal relationship between PM
                exposure and asthma morbidity and to determine the mechanisms by which PM
                elicits these effects. Studies will be conducted using a murine model of
                susceptibility to allergic asthma. Sensitized mice will be exposed to PM and
                airway response, eosinophilic inflammation, Th2 cytokine (IL-4), and elevated
                IgE will be measured in order to test the hypothesis that PM exposure exacerbates
                allergic asthma. Preliminary studies suggest that ambient urban Baltimore
                particulate elicits a more toxic response than coal fly ash (Walters et al. 1999).
                The availability of well characterized (chemistry, size, and source) Baltimore
                urban particulate would provide a significant resource to advance this research.
                P.I.: Marsha Wills-Karp; Project Period 12/1/98 - 11/30/03.

Walters DM; Breysse PN; Wills-Karp M (1999): Outdoor air particulates composition and
effects. Abstract and Poster Discussion presented at the American Thoracic Society Annual
Meeting in San Diego.

        B.   **The Relationship of Air Pollutants and Allergens to Asthma Morbidity.** The
                proposed case / control epidemiologic study aims to eludicate the relationship
                between exposures to allergens and air pollutants and asthma morbidity among
                inner city children with asthma. Study design is a case control with a sample size
                of 300. Children aged 6-11 years will be recruited from five inner-city schools in
                East Baltimore within 1 km of Clifton and near the Johns Hopkins University
                School of Public Health. Children's exposure will be assessed based on indoor
                residential monitoring with personal monitoring conducted in a subset of
                individuals. Target pollutants measured include $PM_{2.5}$, $PM_{10,}$ NO_2, and $O_{3.}$ PM
                will be measured at 4 lpm over a three day period using MSP™ impactors.
                Outcome assessment will include spirometry and reported symptoms. PI: Jouni
                Jaakkola; Project Period 12/1/98 - 11/30/03; Data Collection Period: 9/99 - 9/02.
        C.   **Community Environmental Intervention Trial.** In this community-based
                randomized controlled clinical trial the effectiveness of current treatments for
                home allergen and pollutant control recommendations in reducing allergen and
                pollutant exposure in inner city homes will be tested (n=100). Air pollution
                control measures will include a program in cigarette smoking cessation and use of
                an in-home air cleaner. Air pollution exposure will be measured as described in
                1C above. The effectiveness of the intervention will be evaluated based on
                measurements of exposure and health at four time periods over a one year period.
                PI: Peyton A. Eggleston; Project Period 12/1/98 - 11/30/03; Data Collection
                Period: 9/99 - 9/02.

D. **Evaluation of Indirect PM$_{10}$ Exposure Assessment in a Case Control Epidemiological Study of Asthma Exacerbation in Urban Children.** This study is designed to complement the epidemiologic case control investigation by making direct measurements of PM$_{10}$ exposure for a nested subset of children for comparison to the indirect exposure estimate (n=30). Personal PM exposure will be measured as described in 1B. Furthermore, this project will entail indoor measurements at schools and residential air exchange rate measurements using perfluorocarbon tracers. PI: Timothy J. Buckley; Project Period 12/1/98 - 11/30/00; Data Collection Period: 9/99 - 9/00.

2. **Pending: EPA/National Center for Environmental Toxicology and Epidemiology.** This Center will address indoor exposures resulting from motor vehicle emissions and their health risk to adult asthmatics.

    A. **Indoor/Outdoor Relationships and Exposure Among Asthmatic Adults in the Urban Environment.** This study will test two hypotheses: 1) mobile sources are a primary determinant of indoor air pollution in the urban environment; and 2) among asthmatic adults living in an urban inner-city traffic corridor, mobile sources are a primary determinant of air pollution exposure. This study will conducted in central Baltimore in a residential area south and east of the train station. The air pollutants measured include PM$_4$, PM$_{10}$, PM$_{100}$ (TSI Respicon™ sampler), NO$_2$, VOCs, and O$_3$. Samples will collected as 24-h periods and related to peak flow measurements and reported symptoms defined in 2C below. PI: Timothy J. Buckley; Project Period: 1/00 - 1/03; Field Collection Period: 6/00 - 6/02

    B. **Mobile Source Air Pollution: Biomarkers of Exposure and Effect.** Biomarker development with a project designed to examine markers of polycyclic aromatic hydrocarbons (e.g., 1-hydroxypyrene) and benzene (e.g., *trans, trans*-muconic acid) as well as biomarkers of oxidative damage. PI: Paul T. Strickland; Project Period: 1/00 - 1/03; Field Collection Period: 6/00 - 6/02.

    C. **Respiratory Health Effects of Exposure to Urban Air Pollution from Vehicles in Adults with Asthma.** The primary objective of this study is to examine the effects of short-term exposure to urban air pollution from vehicles on ventilatory lung function and respiratory systems in adults with asthma. The exposure measurements are described in 2A. Asthmatic adults subjects (n=50) will be monitored over 14 consecutive days using 24h integrated measurements. PI: Jouni J.K. Jaakkola; Project Period: 1/00 - 1/03; Field Collection Period: 6/00 - 6/02.

3. **Active: Johns Hopkins Center in Urban Environmental Health.** To develop prevention strategies to reduce morbidity and mortality induced by environmental agents prevalent in urban areas. Baltimore City and its environs are our prime target, but our research will be relevant to many urban settings. Project Period: 3/98 - 3/03

    A. **Environmental Epidemiology and Human Exposure Assessment**. To identify the environmental factors associated with increased disease risk in residents of Baltimore City. Director: J.M. Samet.

    B. **Biomarkers and Prevention.** To develop mechanistically based, validated biomarkers for use in molecular epidemiology investigations of populations and individuals at high-risk from environmental exposures and to use these biomarkers to assess the efficacy of intervention/prevention strategies. Director: T.W. Kensler.

C.   **Molecular Toxicology.** To conduct research targeted towards a mechanistic understanding of the toxicological impact of environmental chemicals on biologic systems at the molecular level. Director: J.A. Yager.

D.   **Environmental Lung Disease.** To understand the role of inhaled pollutants and allergens on pulmonary function in humans and experimental models. Director: W. Mitzner.

E.   **Pilot Project Program.** To support innovative new research that supports the mission of the Center providing preliminary data for the development of competitive research proposals. Director: M.A. Trush.

4.   **Active: Molecular Basis of PM-Induced Respiratory Toxicity.** The long-term goal of the proposed research project is to elucidate the molecular basis of particulate matter (PM)-induced respiratory toxicity. This hypothesis will be tested by using a human primary airway epithelial cell culture system as a model to isolate and characterize genes that are regulated by PM. Recent advances in the development of high-density cDNA microarrays have facilitated studies designed to simultaneously profile gene expression patterns and clone differentially expressed genes related to various biological processes and diseases. This project is being conducted as a pilot project under 3.E. shown above. P.I.: S.P.M. Redddy.

5.   **Active: The Inner-City Environment and Asthma**. This is an asthma case-control study where approximately 150 asthmatics and 275 controls will be recruited in order to provide additional evidence that cockroach allergy has a causal relationship to asthma and to asthma severity. Subjects will include both adults and children. The study is designed to investigate changes in respiratory function associated with relocation from old to new public housing where allergen loading will be measured. The investigators are considering provisions for including measures of air pollution exposure. P.I. A. Togias; Project Period 4/1/99 - 3/31/04; Data Collection Period: 4/1/00 - 3/31/03.

6.   **Active: VOC Exposure in an Industry Impacted Community** The primary goal of the proposed study is to provide exposure information to a community concerned over their health hazard due to the intensity and proximity of industrial sources. VOC and $PM_{2.5}$ will be measured indoors and on parent / child pairs in 40 homes in the industry-impacted community (South Baltimore) and for 25 homes in a control location. VOCs will be sampled onto 3M OVM badges while $PM_{2.5}$ will be collected using a MSP™ impactor sampling at 4 lpm. Sampling will be conducted over a three day period during two seasons. P.I. T.J. Buckley; Project Period: 8/1/99 - 7/30/01; Data Collection Period: 9/99 - 2/01.

7.   **Pending: Effect of Urban Pollutants on Peripheral Airway Function.** The long term goal of this research is to identify potential mechanisms that can account for the clinical manifestations associated with episodes of high particulate air pollution. A well established canine model will be used to examine in the smallest airways of the lung the interactive effects of co-exposure to respirable particulate matter (PM) and an ambient gaseous co-pollutant. P.I.: A. Freed.

Multivariate Calibrations and Data Quality Analyses Methods
Partial Least Squares. The theory and properties of the partial least squares (PLS) have been extensively studied and reported over the years [1,2,3]. A brief description of the partial least squares (PLS2) algorithm (with more than one dependent variable) will be presented. The basic idea in PLS is to find a set of latent variables in the measurement variable space (X) that have a maximum covariance with the dependent variable space (Y). The advantage of this approach is that the latent variable analysis reduces the number and redundancy in the X block data by compressing the information into a limited number of components (latent variables). However, it is done in such a way as to optimize the prediction power of the resulting solution. Thus, linear combinations of the original variables are found that are rotated to have maximum ability to predict the Y block. The Y variables contain the information about the training objects. The PLS model can be formulated to resemble a regression equation:

$$\mathbf{Y} = \mathbf{XB} + \mathbf{E} \tag{1}$$

where $\mathbf{B}$ is the matrix of PLS regression coefficients, $\mathbf{E}$ is the matrix of residuals, and $\mathbf{X}$ is the matrix of independent variables.

The estimation of $\mathbf{B}$, $\hat{\mathbf{B}}$, can be obtained through the generalized inverse of $\mathbf{X}$, $\mathbf{X}^+$, provided by the PLS2 algorithm:

$$\hat{\mathbf{B}} = \mathbf{X}^+\mathbf{Y} = \mathbf{W}(\mathbf{P}'\mathbf{W})^{-1}\mathbf{Q}' \tag{2}$$

where $\mathbf{W}$ is the matrix of weights of the X-space, $\mathbf{Q}$ is the loadings matrix for the Y-space, and $\mathbf{P}$ is the X-space loadings matrix.

To obtain the PLS model with the best predictive performance, the optimal number of PLS components to be used in the model needs to be determined. Cross-validation will be applied. The performance criterion is the prediction residual sum of squares (PRESS). That is, within the training set, all of the objects are divided into several subgroups (called validation sets). For a problem such as this one, we would typically create at least 10 validation sets. Each validation set is left out of the training set and predicted by the model built from the remaining training objects. The process is repeated until all of the validation sets are predicted, and the overall PRESS value is calculated. The number of PLS components corresponding to the minimum PRESS is then used to build the final model to predict the additional new test objects.

After the estimation of the regression coefficients, $\hat{\mathbf{B}}$, is obtained from the training set, the prediction of dependent variables for a test set of objects is done by:

$$\mathbf{Y}_{\text{test}} = \mathbf{X}_{\text{test}}\hat{\mathbf{B}} \tag{3}$$

The final PLS model can then be used in the prediction of the values of the Y matrix. By looking at these relationships, we can begin to understand the response of the speciation or FRM sampler to various composition aerosols. We can also use the same methodology to understand the response of one instrument like light scattering to other appropriately time resolved data.

Artificial Neural Network Modeling. An artificial neural network is a mathematical model of a complex system. A schematic diagram of an artificial neural network is shown in Figure 1,

where the large circles are artificial neurons and the connections represent weights that describe the importance of the signal being transmitted along a given path. Thus, the net input to a given neuron would be given by

$$\text{Net}_i = \Psi\left(w_{s0} + \sum_{i=1}^{N} w_{si}\,\text{Inp}_i\right) \qquad (4)$$

where Inp_i is the total signal being transmitted from one neuron to the next along a single axon, w_{si} is the weight function for that connection, and $\Psi(\mathbf{x})$ is a transfer function. The conceptual basis for artificial neural networks has been in the literature for a long time [4, 5]. However, it was not until Hopfield [6] introduced the novel concept of non-linearity between the total input received by a neuron from the other neurons and the output produced and transferred onward to other neurons through the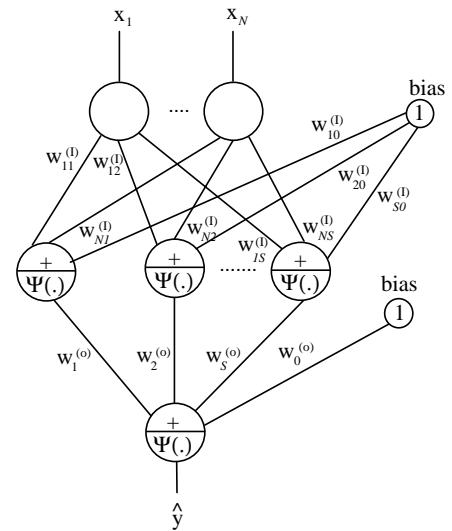 function $\Psi(\mathbf{x})$. The nonlinear output and the possible feedback coupling of outputs with inputs gave new flexibility to this old architecture and sparked a major new field of interest across a number of disciplines. A detailed description of artificial neural networks in chemistry has been provided by Zupan and Gasteiger [7].

Figure 6. Schematic outline of an artificial neural network.

The Neural Network Model. An artificial neural network (ANN) approximates a function of several variables in terms of the functions of one variable and summation. In most ANN applications, a network [8, 9] with one hidden layer is used (Figure 1):

$$\hat{y} = \Psi\left(w_0^{(o)} + \sum_{s=1}^{S} w_s^{(o)}\Psi\left(w_{s0}^{(I)} + \sum_{i=1}^{N} w_{si}^{(I)}x_i\right)\right) \qquad (5)$$

where x_i is the input value which combine to form a vector $\mathbf{x}$, $\hat{y}$ is the output from the model, f is the function connecting $\mathbf{x}$ and y, $\Psi(\mathbf{x})$ is the transfer function, usually a sigmoidal function, $\Psi(\mathbf{x}) = [1 + \exp(-x)]^{-1}$, $w_{si}^{(I)}$ is the weight connecting the input i with the hidden layer neuron s, $w_{s0}^{(I)}$ is a bias term for each neuron in the hidden layer, $w_s^{(o)}$ is the weight connecting the neurons in the hidden layers to the output layer, $w_0^{(o)}$ a bias term for the output, i=1,…,N is the counter for input neurons, and s=1,...,S is the counter for hidden neurons

For this type of network, the neurons are disposed in layers without feedback connections between layers. The transfer function $\Psi(\mathbf{x})$ in each neuron is usually a sigmoid function [8]. It has been proven by Cybenko [10], Hornik [11,12], Funahashi [13], and Bulsari [14] that such a network allows an accurate approximation to any continuous function in the interval [0,1]. The connection weights are adjusted during the learning cycles using the error back propagation rule [6, 15]. The updating rule minimizes the mean square error (MSE) function which is the difference between the initially known values of the approximated function over the discrete set of points and the neural network approximation of the function for the same set of points. For each training iteration, all of the synaptic weights are updated. The nonlinearizing function used in the neural net works only with data in the range [0,1] and therefore the data are range scaled to the [0,1] interval for the calibration data. However, this does not guarantee that the test set data

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will fall in this range and therefore a smaller range is used for range scaling the calibration data. The choice of this range is crucial for the functioning of the neural net. Calibration works best with the calibration data in the range [0,1], but data can be scaled to meet this criterion. Although the weights in the ANN are difficult to directly interpret, there are ways to linearize the problem and make them more interpretable [16]

Missing Data Values. All of the raw data will be archived. During the measurement period, some of the data will be missing, below detection lime (BDL), or otherwise suspect. These data must be handled carefully during subsequent statistical analysis. We have delt with this situation in the past and will use proven techniques in the proposed study [17][18].

Positive Matrix Factorization

Supposed **Y** is a n by m matrix consisting of the measurements of n chemical species in m samples. The objective of receptor modeling is to determine the number of pollutant sources, say p, the chemical compositions of each source and the amount that each of the p sources contribute to each sample. The corresponding factor model can be written as:

$$\mathbf{Y} = \mathbf{GF} + \mathbf{E} \tag{6}$$

where **G** is a n by p matrix of source compositions (source profiles) and **F** is a p by m matrix of source contributions to the samples. For the Alert data, each sample actually is a routine observation along the time axis, so **F** is actually the temporal variation of the sources. **E** represents the part of the data variance un-modeled by the p factors model.

PCA is the widely used technique for solving such a bilinear model. However, as previously described, Paatero and Tapper [1993] noted that the customary form of PCA is based on unrealistic assumptions about the errors in the elements of the data matrix, and such assumptions are unlikely to be realized in most physical or chemical situations. Conventional PCA is solved by an implicitly weighted least squares approach where weighting is based on such unrealistic error assumptions and thus poor fits may be produced [Paatero and Tapper, 1993]. Furthermore, there is no technique to chose a transformation from infinite candidates which guarantee to transform the abstract factors of PCA into a unique, physically meaningful solution. Therefore a new technique, PMF, was developed for solving the same bilinear model and avoiding such problems. In the PMF, sources are constrained to have non-negative species concentration, and no sample can have negative source contribution. Also, the error estimates of the observed data, which are usually available for the environmental measurements, were used as a more realistic scaling. The principle of PMF can thus be presented as:

$$\min_{G,F} Q(Y,\sigma,G,F) \tag{7}$$

where

$$e_{ij} = y_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \tag{8}$$

$$Q = \left\| \frac{(Y - GF)}{\sigma} \right\|^2 = \sum_{i} \sum_{j} \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2 \tag{9}$$

with $g_{ik} \geq 0$ and $f_{kj} \geq 0$ for $k = 1, ...,p$, and $\boldsymbol{\sigma}$ is the known matrix of uncertainties of **Y**. This form of factorization is quite different from the customary PCA. **G** and **F** are determined so that the Frobenius norm of **E** divided by $\boldsymbol{\sigma}$ (element-wisely) is minimized.

According to Paatero and Tapper [1993,1994], it is impossible to perform factorization by using singular value decomposition (SVD) on such a point-wise scaled matrix with inequality constraints. PMF uses a unique algorithm in which both matrices are varied simultaneous in each iteration step. The algorithm is described by Paatero [1997a]. The process continues until convergence.

The methods just described analyzes a series of samples analyzed for multiple chemical constituents at a single site. These data can be presented in a standard matrix. Alternatively, we can have data from a series of sites, collected over time and analyzed for multiple species. The resulting data would be a three-way array. There are other approaches whereby three-way arrays can be developed as will be discussed below. When a three-way data array is available, there are different methods to extend two-way factorization into three-way situations. One three-way data analysis technique fits the data into a trilinear model which is expressed as:

$$\underline{Y} = ABC + \underline{E} \tag{10}$$

or

$$y_{ijk} = a_{ih} b_{jh} c_{kh} + e_{ijk} \qquad \text{for} \quad h = 1,...,p \tag{11}$$

where $\underline{Y}$ is a n x m x q three-way data array, A, B, C are the resulting 2-way factor matrices in each of three modes and $\underline{E}$ is the un-modeled part of $\underline{Y}$. Based on the same non-negativity constraints and minimization criterion, PMF can solve the trilinear model [Paatero, 1997b].

Brief Description of the Multilinear Engine

The Multilinear Engine (ME) [Paatero, 1999] is a new concept for solving a variety of multilinear problems. The multilinear model can be written in the sums-of-products form:

$$y_i = \hat{y}_i + e_i = \sum_{k=1}^{K_i} \prod_{j \in \zeta_{ik}} f_j + e_i \tag{12}$$

where the index i enumerates the equations which form the model to be solved. Essentially each equation corresponds to each of the measured value x_i. Auxiliary equations can be used to represent any *a priori* information and/or some constraints such as smoothing, rotation, *etc* needed for the solution. M denotes the number of the equations which is the sum of the number of the measured values and the number of auxiliary equations, if any. The fitted value y_i for each data point x_i is represented as a sum of product of all factor elements f_j ($j \in z_{ik}$). K_i indicate the number of product terms in each equation. For equations corresponding to *pure* 2-way PCA and *pure* 3-way PARAFAC model, the values K_i equal to the number of factors. The elements j of the index sets z_{ik} are the indices of those factor elements f_j that form the kth product term of the ith equation. e_i is the unmodeled part of data y_i.

Determining the best fit to equation (7) is again equivalent to solving the appropriate minimization problem:

$$\lim_{f} Q(y,f) \tag{13}$$

where

$$Q(y,f) = \sum_{i=1}^{M} \left(\frac{e_i}{\sigma_i} \right)^2 = \sum_{i=1}^{M} \left(\frac{y_i - \sum_{k=1}^{K_i} \prod_{j \in \zeta_{ik}} f_j}{\sigma_i} \right)^2 \qquad f_j \geq 0 \quad (j \in 1,...,N) \tag{14}$$

where the values s_i are the uncertainties connected with the measurements; typically s_i is the standard deviation of the measured value y_i; N is the number of the elements of all the factors.

The formulation of the system of equations in equation (7) is extremely general. To facilitate the understanding of the principle of ME, a system of equations representing a mixed 2-way/3-way model is provided as a more practical example:

$$y_{ijk} = \sum_{q=1}^{Q} t_{ikq}\, g_{jq} + \sum_{p=1}^{P} a_{ip}\, b_{jp}\, c_{kp} + e_{ijk} \qquad \begin{pmatrix} i &=& 1,...,I \\ j &=& 1,...,J \\ k &=& 1,...,K \\ p &=& 1,...,P \\ q &=& 1,...,Q \end{pmatrix} \qquad (15)$$

The first term represents a customary Q factor 2-way PCA model with score and loading matrices **T** and **G**, while the second term is a P factor 3-way trilinear model with the **A**, **B**, and **C** matrices being the three modes, respectively. Hopke *et al.* [1999] has shown that there are data for which a mixed mode model as outlined in Equation 10 provides a superior fit to the data. In equation (10), y_{ijk} and e_{ijk} have the same meaning as x_i and e_i as in the general equation (1).

The importance of ME is that it has the same advantages as PMF in weighting individual data points, but provides a more flexible framework for imposing external constraints on solutions. Thus, any information that can be written as an auxiliary equation such as setting specific source contribution values to zero on days when it is known that the source cannot be affecting a sampling site can be easily incorporated into the analysis and thereby reduce the rotational ambiguities that otherwise exist in any factor analysis solution. Thus, we can offer both PMF and ME for solving the source/receptor modeling problem.

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QUALITY ASSURANCE NARRATIVE
PRINT FORM BUCKLEYS
This multi-investigator, multiple sampling and analytical method project will be developed with a carefully designed quality assurance/quality control program to ensure that there is comparability among the various measurements and that we will be able to test the various hypotheses outlined for the program. For each portion of the program, a complete quality assurance/quality control plan will be prepared.

8.   **Activities/Hypotheses**

Activities to be performed are to i) collect and analyze ambient PM2.5 samples at two different sites, and ii) perform preliminary multivariate statistical analysis to test the hypothesis that sub-hourly sampling frequencies will provide improvements in source resolution. These activities are directed to meet four primary objectives linked to seven hypotheses. The primary objectives are to i) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal, spatial, and chemical resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques: ii) provide appropriate ambient air pollution measurements linked with existing exposure and epidemiologic studies in order to evaluate relationships between ambient concentrations and sources with exposure and health outcome; iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, and v) test the specific hypothesis listed below.

1.   Reduced (i.e., hourly and sub-hourly) sampling/analysis times will immensely improve source attribution.
2.   Various health effects of PM are associated with its specific chemical, physical and time resolved (but mostly chemical) components that, owing to the vast number of these, a source based allocation of air toxins will provide the most useful information for PM standards and control (health data will be available from existing and proposed studies in Baltimore).
3.   Different aerosol constituents and properties would have different abilities to elicit cytokine responses and that these difference might reflect differences in the extent and mode of action in producing adverse health effects. For example, residual oil fly ash elicits a response largely attributed to V(despite the presence of larger amounts of Fe), whereas coal-fly ash elicits a lesser response.
4.   Aerosol age affects the size, chemistry, and health effects of PM. Thus spatially distant upwind, industrial area, and center-city aerosols differ significantly in temporal variability and biologically relevant composition.
5.   Taken together, detailed sub-hourly information of major, minor, and trace inorganic and organic aerosol constituents, size-resolved aerosol particle concentrations, and cytokine responses will permit unprecedented resolution of sources of toxic PM components and their toxic effects.
6.   24-hour and short-term concentrations, cytokine and ROS responses, and health effects of potentially toxic aerosol components in areas of Baltimore that are strongly influenced by heavy industry measurably exceed those observed in an urban downtown that is weakly influenced by industrial sources.

7. Some acute health responses are more closely associated with highly elevated short-term exposures than they are with 24h averages.
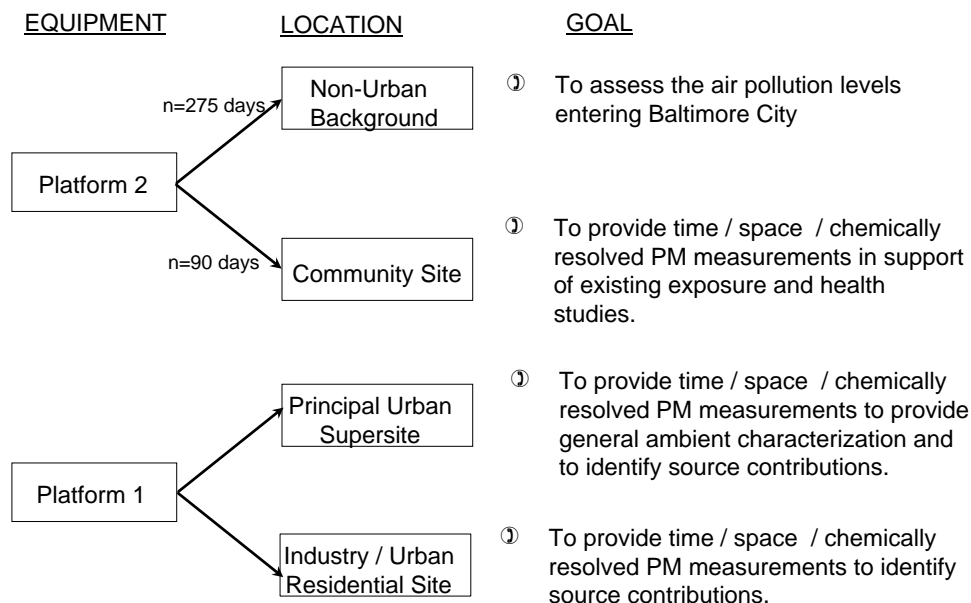
1a. Criteria of Data Acceptability

Acceptance criteria are as follows: analyte masses to be determined in filter samples shall be measured with an overall uncertainty of 12% or better, including random error (i.e. precision) and bias (i.e., accuracy), in at least 80% of the measurements. Samples will be selected for analysis on the basis of successful collection, i.e., when the sampling system successfully passes a leak test prior to aspiration of the sample and sampling parameters are properly recorded. Precision better than ±10% is expected; ±20% is acceptable. In general, we will require ±20% precision and accuracy for integrated sampling methods and 30% accuracy and precision for the direct reading measurements. For some assays such as the cytokine response and ROS, it may not be possible to evaluate the method accuracy. For all measurements, we expect complete >90% of our planned measurements.

Our study is designed to make highly time resolved measurements using several new innovative instrumental methods including the LIDAR, RSMS III, and SEAS. The results of these measurements will be compared with the parallel conventional measurements that are integrated over a 24 hour interval. For these new instruments/methods we do not yet have estimates on measurement precision. Thus, estimating the number of samples needed to make comparisons is not possible at this time. One of the initial tasks of characterizing the new monitoring methods will be determine the associated random and systematic errors. For the new instruments deployed including the , it will not be possible to assess precision or accuracy of the instrument because they are unique. The instrument measurement validation is provided by supporting methods publications described in the proposal under the instrument description.

Ancillary exposure / health study measurements including measurements of personal and indoor PM and related pollutant exposure will be achieve with an accuracy, precision and completeness similar to that identified for the ambient measurements. Measurements of pulmonary function including FEV_1 and peak expiratory flow will be achieved with a precision of ±10%.

2. **Study Design**

EQUIPMENT	LOCATION	GOAL

Platform 2 — n=275 days → **Non-Urban Background**
☽ To assess the air pollution levels entering Baltimore City

Platform 2 — n=90 days → **Community Site**
☽ To provide time / space / chemically resolved PM measurements in support of existing exposure and health studies.

Platform 1 → **Principal Urban Supersite**
☽ To provide time / space / chemically resolved PM measurements to provide general ambient characterization and to identify source contributions.

Platform 1 → **Industry / Urban Residential Site**
☽ To provide time / space / chemically resolved PM measurements to identify source contributions.

Factor analysis and MLA will be conducted on data for no fewer than 30 samples at each site.

3. **Sample Handling and Custody**

A number of measurement systems are direct reading including the LIDAR, RSMS III, SEAS, APS, integrating nephelometers, SMPS so that no sample handling is required.

PM Elemental Measurements. Proper identification of samples is assured by advance preparation of data collection forms containing spaces for all parameters to be recorded and documentation of "chain of command". Hard copies of all original data are maintained. Quality assurance procedures for elemental analyses include extensive characterization of field and laboratory blanks and replicate analyses. Field blanks are exposed in identical filter housings, but without air flow, and otherwise handled as samples. Field blanks will accompany 10% of the slurry samples collected. The quality of GFAAZ is assured through frequent analyses of NIST Standard Reference Materials (SRM) and comparisons with INAA. The quality of INAA is assured through i) rigorous detector calibrations using multielement standards, ii) frequent analysis of NIST standard reference materials (SRM), e.g., SRM 1648, "Urban Particulate Matter," iii) use of fixed internal calibration/county standard (i.e., ^{109}Cd) on all detectors in each and every spectrum, iv) flux monitors with every irradiation, v) collaborations with NIST to analyze new SRMs, and vi) and continuing personnel training.

Samples for elemental analysis will be handled in a clean room conditions using procedures developed during our EPA STAR Grant and during the College Park and Atlanta field tests. Samples are transferred to the UMCP laboratory in Styrofoam coolers. All samples are uniquely identified with a code assigned at the time of initial substrate preparation (e.g., when they are weighted) for filter samples and prior to the onset of sampling for PM suspension samples. To help prevent errors, the codes contain the date, time, and sampling site in readily identifiable format. This information is recorded electronically and in a notebook, together with the initials of the person collecting the samples. Following transportation to the laboratory, receipt of the samples will be recorded in a notebook with the date and time. The codes are entered into our

master data base where they are associated with sampling data and made available to our new analysis selection and control program.

Samples for cytokine and ROS analysis: $PM_{2.5}$ samples will be transferred to vials labeled with a sequential number and the date, time and place of collection. The sample number with the collection information will also be recorded in a notebook, together with the initials of the person collecting the samples. Following transportation of the samples to the laboratory, receipt of the samples ill be recorded in a notebook with the date and time. Each sample will then be lyophilized and stored in a desiccator at $-70^{\circ}C$. The location of the samples in the freezer will be recorded in the laboratory notebook.

PM samples for organic analysis (GC/MS) arriving from the study site in cooled storage containers at FIU are immediately stored in a dedicated freezer at a temperature £ -21 $^{\circ}C$ and are subjected to chemical analysis within 21 days upon arrival. Field blanks and laboratory blanks are stored and handled by exactly the same SOPs as used for the actual samples. Each sample batch to be extracted will be accompanied by a laboratory blank and field blank. Laboratory and field blanks are used to identify and monitor possible contaminants and used to suggest suitable modification to sample handling. Sample data will be corrected for contaminants observed in both field and lab blanks. Each handling and analysis step in the laboratory is monitored and written records maintained using chain-of-custody forms, sample receiving log book, cleaning log book, extraction log book, GC/MS log book, standard and response factor log book, instrument maintenance log book, and others. In addition to the logbooks, electronic records such as computer method files, raw data files, calibration files, and processed data files will be maintained. At the end of the project a copy of all computer files will be stored at FIU and University of Maryland.

4.   **Methods and Instrumentation**

A more complete description of the instrumentation and method can be found in the proposal.

Elemental analysis will be performed using a PE model 5100 GFAA with Zeeman (or pulsed source) background correction (or inductively-coupled plasma-mass spectrometer with a microconcentric or ultrasonic nebulizer. Quality control samples will be analyzed by Instrumental Neutron Activation Analysis at UMCP using state-of-the art multichannel analyzers.

The cytokine assay will be conducted by immunoassay using a microplate reader. Production of reactive oxygen species will be measured by fluorescence spectroscopy using a cytoflour multiplate reader.

RSMS III: The analytical procedures are described in the proposal and summarized here. Particles of a narrow size range are focused aerodynamically to the source region of a mass spectrometer. The size that is focused can be selected from 10 nm to 2 microns by adjusting the upstream pressure. An excimer laser beam colinear with the particle beam is periodically fired. If a particle is in the beam, it is desorbed and ionized. The ions are analyzed in a time-of-flight mass spectrometer .

Gas chromatography/ mass spectrometry (GC/MS) analyses will be conducted with high

sensitivity. Here, a HP 6890 GC interfaced with a HP5973 MSD will be used for sample extract analysis. The sensitivity of the instrument will be validated throughout sample analyses by conducting the HP sensitivity test, which includes the injection of 1 ml of octafluoronaphthalene with a concentration of 1pg/ml. If sensitivity is judged to be inadequate, corrective actions will be taken. For all standards available, the instrumental detection limit will be determined and routinely controlled. 1-Phenyldodecane will be used as coinjection standard. Before solvent extraction, all filter, and PUF samples will be spiked with an internal standard mixture of up to seven perdeuterated recovery standards that are necessary to obtain for each individual sample the extraction efficiency. Identifiable compound peaks are identified and quantified using authentic standards, as far as such standards are commercially available. Using extraction efficiencies determined for the internal standards, single compound recovery is monitored and used to correct for extraction losses.

Standard operating procedures (SOPs) for the analysis of trace organic compounds are in place and follow in essence ANSI/ASQC E4 as specified in EPA QA/R-5 and mentioned in EPA QA/G-4. Whenever state-of-the-art scientific knowledge becomes available, such knowledge is incorporated into SOPs with each revision. In short, quality assurance procedures for the identification and quantification of organic trace species in quartz fiber filters, and PUFs include the analysis of field blanks and laboratory blanks together with the actual samples. Field blanks consist of collection media transported to the field, installed in the sampler, but not exposed to airflow. Only high purity solvents will be used for the chemical extraction. The solvents will be analyzed for potential contaminants before use. All glassware used for sample handling, extraction, and solvent handling will be annealed at 250 °C for at least 8 hours after being cleaned, solvent rinsed, and packed in clean and annealed (550°C) aluminum foil. Before actual usage, each glass item is rinsed repeatedly with high purity solvents.

The LIDAR system has been used in numerous field studies, including city aerosol studies in Mexico City, Barcelona Spain (during the Olympics), Albuquerque and Las Cruces , New Mexico. It has also been used to track aircraft and missiles from their exhausts and to study clouds over the ocean as part of the Cepex studies. In all these studies, two detectors mounted in the periscope sample the outgoing laser pulse and produce signals which are used to correct for pulse-to-pulse variations in the laser energy and also serve as a timing marker to start the digitization process. Pulse averaging is used to increase the useful range of the system. A series of pulses are summed to make a single scan. A number of scans are used to build up a two or three-dimensional map of relative atmospheric aerosol concentrations. The plan is to take the data at the maximum collection rate possible and process the data off line.

5.   Calibration and Performance Evaluation of Sampling and Analytical Methods

A technical system audit (TSA) is the evaluation process used to measure the conformance of a measurement system to the criteria defined in the QAPP for a particular project. The TSA is a qualitative assessment of the measurement system that may be used to confirm that project implementation is occurring as planned. TSAs may be either self-assessments or independent assessments. In either case, the auditors/reviewers must have sufficient freedom, access to programs, and authority to: 1) identify and document problems affecting quality; 2) identify and cite noteworthy practices; and 3) propose recommendations (if requested).

The RSMS III will be run in parallel to analyze broader size ranges of composition and the

composition of many of the same compounds that RSMS-II will analyze. A mass balance will be performed between the RSMS-II measurements and those of other complementary instruments during the program.

The cytokine bioassay day to day measurement variability will be assessed from NIST SRM 1648 (urban particulate matter) included in each test run. Bioassays conducted on different days with different samples will be comparable to each other if the results obtained with the SRM particles vary by less than 10%.

Flow calibrations of ambient sampling flow meters will be conducted according to standard procedures before and after field measurements are made. Samplers will be calibrated in the field using a secondary reference electronic volume flow meter whose calibration is traceable to a NIST standard. Proper sampler operation is assured through the use of qualified personnel, preparation of detailed operational protocols, use of equipment check lists and logs, field calibrations, and regular site inspections by the PI.

6.   Procedures for Data Reduction and Reporting

Data validation is the process by which data are filtered and either accepted or flagged for further investigation following a predetermined set of criteria based on the study objectives and the type of data being examined. These procedures will be performed as soon as possible after data collection so that questionable data can be checked by recalling information on unusual events and on specific meteorological conditions that may have affected the environment being sampled. All of the project data will be put through appropriate validation procedures before being analyzed. Validation procedures will be used to identify problems that then result in prompt application of corrective actions. Such an iterative process will lead to a higher rate of capture of acceptable quality data.

Four different modes of data validation will be exercised:
- Routine check and review procedures which should be used to some extent in every data validation process,
- Tests for internal consistency of the data,
- Tests for consistency with previous data, (historical or temporal consistency), and
- Tests for consistency with other data sets, collected at the same time or under similar conditions (consistency of parallel data sets).

Data will be examined in a variety of ways including graphical displays, simple univariate, and multivariate methods at four levels: .

Level I.   Routine checks made during the initial data processing and generation of data, including proper data file identification, review of unusual events, review of field data sheets and result reports, instrument performance checks and deterministic relationships.

Level II.   Tests for internal consistency to identify values in the data which appear atypical when compared to values of the entire or whole data set.

Level III.   Comparison of the current data set with historical data to verify consistency over time. This level can be considered a part of the data interpretation or analysis process.

Level IV.   Tests for parallel consistency with data sets from the same population (region, period of time, air mass, etc.) to identify systematic bias. This level can also be considered a part of the data interpretation or analysis process.

The Level I validation will be done by the field personnel overseeing the data collection. Level II and Level III will be performed before the data are entered into the data base. Level IV analysis is part of the data analysis and interpretation work that will be performed to compare the results of the various measurement methods.

For the RSMS III, we have used a number of statistical chemometric techniques to identify and classify spectra, such as ARTs. Since the instrument is new and has not been used extensively in the field previously, data analysis and reporting methods will be developed.

Elemental measurement accuracy and precision will be evaluated based on repeated analysis of spiked samples and from the analysis of standards. Elemental analysis results will be expressed in ng m^{-3} of air at actual temperature and pressures. All analysis data are "blank" corrected and reported along with their one-standard-deviation measurement uncertainties propagated from counting statistics, replicate measurement standard deviations, blank uncertainties, and sample volume measurement errors, as appropriate.

Cytokine results will be reported as ng of the cytokine (IL-6, IL-8, TNFα, or GM-CFS) produced per hr per 10^5 cells/mg particles. The production of ROS will be reported as the change in absorption per hr per 10^5 cells/mg particles. The assays will be conducted in duplicate and the results averaged.

Statistical analyses to be used in the study are described more completely in the proposal. Data will be reviewed using descriptive statistics / univariate procedures as a preliminary assessment. More advanced multivariate factor methods will be used to test hypotheses.

7.   Intended Use of Data

The data will be used to identify source-receptor relations and to help identify particulate compounds which may have adverse health effects. More specifically, the cytokine bioassay will be used to determine whether the immunomodulating capacity of PM$_{2.5}$ samples correlates with the concentration of metals in the samples. The ability of the assays to serve as monitors of immunoactive particles in air will also be determined.

8.   Procedures to Evaluate Study Success

Study success will be evaluated based on the precision, accuracy and completeness of the data collection according to the criteria specified in no. 2 above and upon the ability to achieve the stated research objectives. The QA/QC objectives will be evaluated through periodic audits. Our ability to achieve the research objectives will be evaluated during meeting of study investigators and with the advisory committee.

9.   Peer Review of Study Design

We plan to assemble an advisory committee to include expertise in: 1) air pollution epidemiology, 2) toxicology, 3) policy/regulation (State and federal), 4) atmospheric chemistry (with expertise in network design and source attribution), and 5) meteorology. We will work with this advisory committee and our collaborators to improve the study design and coordinate our measurements. These activities will take place early in the project to maximize the benefit.

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