



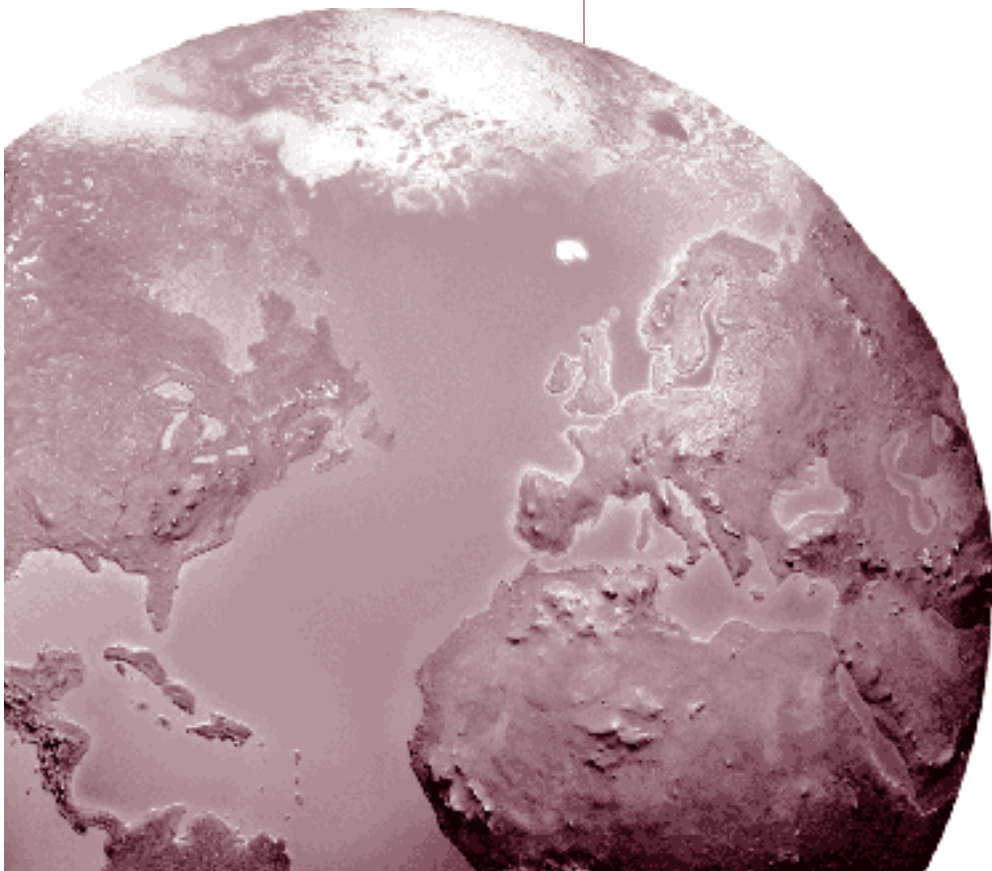
RESEARCH REPORT

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Evaluation of a Personal and Microenvironmental Aerosol Speciation Sampler (PMASS)

Alison S Geyh, Susanne Hering, Nathan Kreisberg,
and Walter John





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STATEMENT

Synopsis of Research Report 122

Evaluation of a Personal and Microenvironmental Aerosol Speciation Sampler

Over the last several decades, evidence has accumulated suggesting that exposure to ambient particulate matter (PM), which includes particles from different sources and of varying size and composition, may be associated with health effects on the cardiovascular and respiratory systems. Ambient PM tends to have a trimodal size distribution by diameter: coarse particles ($> 1 \mu\text{m}$), fine particles (0.1 to $1 \mu\text{m}$), and ultrafine particles ($< 0.1 \mu\text{m}$). The main components of ambient PM are elemental and organic carbon, inorganic ions (ammonium sulfate and ammonium nitrate), and trace elements. Because of concerns about health effects, the US Environmental Protection Agency regulates through the National Ambient Air Quality Standards ambient levels of PM with a diameter of $2.5 \mu\text{m}$ or less ($\text{PM}_{2.5}$).

Although a large body of epidemiologic research suggests that ambient PM may cause both acute and chronic health effects, lack of information on several key measures of exposure to particles complicates interpretation of this research, assessment of human risk, and design of control strategies. An important step in improving exposure estimates in epidemiologic studies is to characterize personal exposure to PM and its components, especially in individuals who may be sensitive to the effects of PM. Although portable, lightweight samplers have been developed for measuring PM personal exposure on a mass basis, the lack of an instrument that can measure specific PM components simultaneously has been a major limitation.

In September 2000, Dr Alison Geyh of Johns Hopkins University submitted an application entitled "Field Evaluation of the Personal Particle Speciation Sampler" for testing in the field a prototype personal sampler capable of measuring simultaneously $\text{PM}_{2.5}$ mass, elemental and organic carbon, sulfate, and nitrate. The prototype had been developed by Dr Susanne Hering with HEI funding (HEI Research Report 114).

APPROACH

The primary objective of this 14-month study was to evaluate the precision and accuracy of the Hering prototype used as a microenvironmental or personal sampler in two locations with different PM composition: Baltimore, Maryland, and Fresno, California. Geyh and coworkers also made a number of modifications to the prototype's design, which necessitated further laboratory tests. They renamed it the *personal and microenvironmental aerosol speciation sampler* (PMASS) to reflect its possible uses in the field.

The PMASS consists of a size-selective inlet with a size cutpoint of $2.5 \mu\text{m}$ through which ambient air is drawn at a flow rate of 4 L/min. Downstream from the inlet, the airflow splits between two channels to allow collection of particles on different substrates for compositional analysis. In the Geyh study, one channel contained a quartz fiber filter for measurement of elemental and organic carbon; the other channel contained a denuder, a primary Fiberfilm filter, and a backup filter for measurement of $\text{PM}_{2.5}$ mass, sulfate, and nitrate. The purpose of the backup filter was to capture nitrate that might be lost from the primary filter.

Dr Geyh and colleagues evaluated the precision and accuracy of the PMASS as a microenvironmental sampler in Fresno (outdoors) and Baltimore (indoors) and as a personal sampler in Baltimore. At the Fresno site, selected for its high ambient levels of nitrate, the PMASS was compared to the Air and Industrial Hygiene Laboratory (AIHL) cyclone. In Baltimore, the PMASS was compared to the Harvard impactor for microenvironmental sampling and to the personal environmental monitor (PEM) for personal sampling.

Precision was calculated as the percent variation among measurements taken in the same location at the same time by two or three PMASS units. Accuracy was expressed as the percent difference between

the PMASS measurements and the reference sampler measurements. Geyh and colleagues set a target of 10% precision and 10% accuracy for all species measured. However, high blank values precluded determination of PMASS precision and accuracy for sulfate in all field tests, and negative mass data for filters in the AIHL cyclone precluded determination of PMASS accuracy in Fresno. Accuracy was not determined for PMASS elemental and organic carbon and nitrate in comparison with the PEM.

RESULTS AND INTERPRETATION

The major modifications made to the Hering prototype included: (1) overall weight reduction of 50% (from 620 grams to 310 grams) by substituting low-density polyethylene for aluminum in the sampler body; (2) redesign of the size-selective inlet to fit into the new polyethylene body; (3) modification of the filter holders; and (4) use of orifice plates to compensate for differences in pressure drop across the filter media in the two channels.

Precision of the PMASS as a microenvironmental sampler was 13% to 18% for mass, 12% to 14% for nitrate, and less than 10% for elemental and organic carbon. When the PMASS was used as a personal sampler, precision was 8% for elemental carbon and around 20% for mass, nitrate, and organic carbon.

The best agreements for accuracy were reported between the PMASS and the Harvard impactor for

organic carbon and between the PMASS and the AIHL cyclone for organic carbon and nitrate. The PMASS and the PEM differed by more than 20% for mass. The observed biases for several of the species measured may be due to sampler differences (eg, in flow rate or in PM penetration efficiency). The reference samplers used in this study are not gold standards; they may have biases relative to one another as well as to the federal reference method for PM_{2.5}. Some tearing of Fiberglass filters when removed from the filter holders may be responsible for the poor precision and accuracy of PM_{2.5} mass measurements. The lack of data for sulfate should be addressed in future tests.

Overall, the PMASS is an improvement over the Hering prototype and is competitive with other recently developed samplers for assessment of personal exposure to PM_{2.5} and its chemical constituents. The field studies conducted revealed some limitations, however, such as problems with the Fiberglass filters, lower-than-targeted precision for mass and nitrate, and poor accuracy for mass and elemental carbon. These limitations need to be addressed before the PMASS is ready for use. The lack of appropriate samplers that can be used as gold standards is common to the testing of new PM samplers, especially those for personal exposure measurements. Until some form of validation of PM samplers is available, use of these samplers in epidemiologic studies should proceed with caution.



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Research Report 122

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HEI STATEMENT

This Statement is a nontechnical summary of the Investigators' Report and the Health Review Committee's Critique.

INVESTIGATORS' REPORT

When an HEI-funded study is completed, the investigators submit a final report. The Investigators' Report is first examined by three outside technical reviewers and a biostatistician. The report and the reviewers' comments are then evaluated by members of the HEI Health Review Committee, who had no role in selecting or managing the project. During the review process, the investigators have an opportunity to exchange comments with the Review Committee and, if necessary, revise the report.

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CRITIQUE Health Review Committee

The Critique about the Investigators' Report is prepared by the HEI Health Review Committee and staff. Its purpose is to place the studies into a broader scientific context, to point out strengths and limitations, and to discuss remaining uncertainties and implications of the findings for public health.

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RELATED HEI PUBLICATIONS

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ABSTRACT

In this study, an all-aluminum sampler was reconfigured to a lighter weight by using plastic for structural components not contacted by aerosol. Because the sampler body was made of plastic, the aluminum size-selective cyclone inlet was redesigned into a separate, removable unit.

The resulting personal and microenvironmental aerosol speciation sampler (PMASS*) is a small, compact sampler designed for assaying concentrations of each major chemical constituent of particulate matter less than or equal to 2.5 μm in aerodynamic diameter ($\text{PM}_{2.5}$) as well as its mass. The sampler consists of a miniature cyclone inlet and two parallel sampling channels, each of which may accommodate a denuder, particle filter, and backup filter. One channel serves to measure mass and inorganic ions; the other, organic and elemental carbon.

Six of these samplers were first evaluated in the laboratory to verify the 50% cutpoint of the redesigned cyclone inlet near the target flow rate of 4.0 L/min and to test the effect of sampler orientation, aerosol type, and flow rate on the 50% cutpoint. The six samplers were fabricated at two different times with slight modifications in construction that yielded slightly different 50% cutpoints. The units were then evaluated as microenvironmental samplers under field conditions against reference samplers in Fresno, California, and Baltimore, Maryland. Testing in Maryland also included deployment as a personal sampler.

* A list of abbreviations and other terms appears at the end of the Investigator's Report.

This Investigators' Report is one part of Health Effects Institute Research Report 122, which also includes a Critique by the Health Review Committee and an HEI Statement about the research project. Correspondence concerning the Investigators' Report may be addressed to Dr Alison S Geyh, Johns Hopkins Bloomberg School of Public Health, Environmental Health Engineering, 615 North Wolfe Street, Room E7035, Baltimore MD 21205-2179.

Although this document was produced with partial funding by the United States Environmental Protection Agency under Assistance Award R82811201 to the Health Effects Institute, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency, and no official endorsement by it should be inferred. The contents of this document also have not been reviewed by private party institutions, including those that support the Health Effects Institute; therefore, it may not reflect the views or policies of these parties, and no endorsement by them should be inferred.

In the laboratory, the mean (\pm SD) 50% cutpoint at a 4.1 L/min flow rate was $2.52 \pm 0.08 \mu\text{m}$. Sampler orientation did not affect performance of the cyclone. Small differences in penetration efficiency were found with different challenge aerosols. For flow rates between 3.1 and 4.9 L/min, the 50% cutpoint varied from 3.3 μm to 2.1 μm , respectively.

As a microenvironmental sampler, the PMASS performed well against relevant reference samplers for elemental carbon, organic carbon, and nitrate measurements but not for mass measurements, for which the PMASS showed a significant bias of -34% . Precision estimates for PMASS elemental carbon, organic carbon, nitrate, and mass, respectively, were 6.8%, 9.0%, 11.9%, and 12.7% in Fresno and 6.6%, 8.7%, 13.6%, and 17.5% in Baltimore.

For personal sampling, PMASS measurements of mass again showed a significant bias of -24% compared with the reference sampler. Precision estimates for the PMASS as a personal sampler for elemental carbon, organic carbon, nitrate, and mass were 8.1%, 19.3%, 19.1% and 24.2%, respectively. Sulfate data were not analyzable because of the large magnitude and variability of the sulfate blanks. Field testing revealed some deformation of components of the PMASS filter pack. These problems may have affected the integrity of the particle filter.

INTRODUCTION

Although particles are known to be complex mixtures of many compounds, current methods for measuring personal exposure to particles and microenvironmental concentrations of particles allow only a limited investigation of particle makeup. A particle is composed of various chemical constituents (including sulfates, nitrates, organic compounds, elemental carbon, and metals) that are contributed from many different sources (Christoforou et al 2000; Zheng et al 2002). The particle mixture varies depending on the magnitude of each source, geographic location, time of year, and even time of day. We do not yet understand which of the many particle constituents are important to human health and therefore where resources would be best used for control

technologies (US Environmental Protection Agency [EPA] 2001a,b). A complete understanding of particle composition would afford an opportunity to identify causative agents for observed health effects and would allow identification of particle sources.

CURRENT METHODS FOR MEASURING PERSONAL EXPOSURE

Most methods for measuring personal exposure to $PM_{2.5}$ use a size-selective inlet for removing particles greater than $PM_{2.5}$, followed by a single filter, usually 37 mm in diameter, for particle collection. The type of filter employed dictates to a large extent the type of analyses that can be conducted on a sample.

One such personal $PM_{2.5}$ sampler is the $PM_{2.5}$ personal environmental monitor (PEM) by MSP Corporation, which collects $PM_{2.5}$ by using an oiled impaction plate to remove particles greater than the desired cutpoint. Another is the single-filter $PM_{2.5}$ cyclone (BGI, Waltham MA), developed at the Finnish Institute of Public Health, which uses a cyclone inlet to select $PM_{2.5}$.

Both of these samplers generally use Teflon filters because Teflon is not hygroscopic, does not readily adsorb vapors such as sulfur dioxide, and is mechanically stable. These filters are suitable for analysis of mass, ions, and metals, but they cannot be analyzed for elemental and organic carbon, which are important components of particulate matter. To analyze for these constituents, samples must be collected on pre-fired quartz fiber filters. Another important constituent that cannot be measured with a single filter design is ammonium nitrate. Nitrate volatilizes from most filters and must be measured using both a denuder and a backup filter. The denuder removes nitric acid gas prior to nitrate particle collection on the front filter. The backup filter contains a reactive substance to capture any nitrate that evaporates from the collected nitrate particles.

Another approach to collecting information about the particle composition is the simultaneous use of several samplers. A system developed by the Koutrakis group at Harvard School of Public Health (now commercially available as the ChemPass model 3400 personal sampling system [Rupprecht and Patashnick Co, Albany NY]) incorporates several individual samplers into one unit. Although the resulting measurements yield information about mass, carbon content, and ions as well as ozone, nitrogen dioxide, and sulfur dioxide, the sampler is large and bulky. This unit can be burdensome for study subjects, especially children, and can ultimately lead to compliance problems.

ORIGINAL PERSONAL PARTICLE SPECIATION SAMPLER

The personal particle speciation sampler modified for this study was developed by Dr Susanne Hering's group, with funding from HEI, to monitor fine particles in both personal and microenvironmental settings (Hering et al 2003). This sampler was proposed in response to an increased interest in fine particles resulting from the EPA's decision to revise the National Ambient Air Quality Standard for $PM_{2.5}$ (EPA 1997). The design was chosen to allow a more complete characterization of fine particles than is currently possible with commercially available personal and microenvironmental methods.

Hering and colleagues developed their prototype sampler to meet measurement needs for each major constituent of $PM_{2.5}$ in a single, compact unit. The desired measurements— $PM_{2.5}$ mass and concentrations of elemental carbon, organic carbon, sulfates, and nitrates—could not be obtained by using a single filter medium.

For example, organic and elemental carbon must be measured on filters made of quartz, a medium that is not compatible with gravimetric mass determinations. However, particle nitrate must be collected on an adsorbing filter medium, such as Teflon, that will retain the nitrate volatilized during sampling. But adsorbing media cannot be used in the analysis of elemental and organic carbon. In addition, volatile components such as nitrates require both a denuder and an adsorbing backup filter to avoid evaporative losses during sampling.

To allow simultaneous assay of each of these constituents, the Hering prototype was designed with an oilless, greaseless size-fractionating cyclone inlet and two parallel filter channels. Each channel can accommodate a denuder, a particle filter, and a backup filter.

SPECIFIC AIMS

The current study involved modifying the Hering prototype and testing the new design, called PMASS, in the field. Elements of the sampler design and the reasons for them are summarized in Table 1. The specific aims of this study were:

- reduction of the overall sampler weight by manufacturing the body from low-density polyethylene;
- redesign of the aluminum $PM_{2.5}$ cyclone inlet to accommodate the new polyethylene body;
- verification of the 50% cutpoint of the redesigned cyclone inlet near the target flow rate and evaluation of

cutpoint performance under different sampler orientations, aerosol types, and flow rates;

- evaluation of PMASS performance as a microenvironmental PM_{2.5} sampler under field conditions (acceptable accuracy was preset at $\pm 10\%$ of that of the designated reference sampler);
- evaluation of PMASS performance as a personal PM_{2.5} sampler under field conditions (acceptable accuracy was preset at $\pm 10\%$ of that of the designated reference sampler); and
- evaluation of PMASS precision for measurements of mass, elemental and organic carbon, and inorganic ions (nitrate and sulfate) (acceptable precision was preset at $\pm 10\%$).

METHODS AND STUDY DESIGN

REDESIGN OF ORIGINAL SAMPLER

The PMASS is 10.7 cm long \times 6.2 cm tall \times 4.5 cm wide with a size-selective cyclone inlet and two parallel sampling channels (Figure 1). The inlet is an aluminum cyclone with a 50% cutpoint of 2.5 μm at a flow rate of 4 L/min. Downstream of the cyclone, the incoming air is passively split so that each channel samples at approximately 2 L/min. Each channel can hold a denuder and one or two filters. The sampler operates with one pump that pulls air through both channels.

The original Hering prototype sampler described in Hering and colleagues' 2003 report had the same cyclone

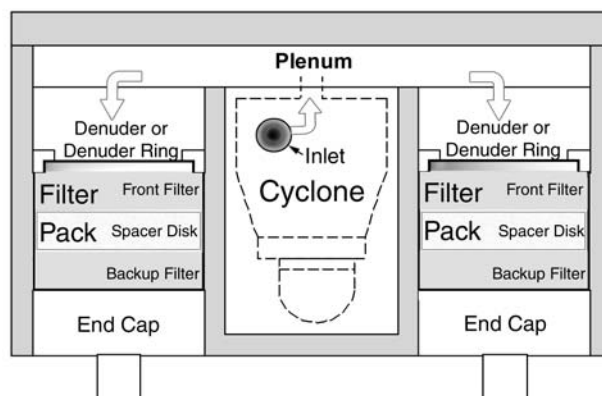
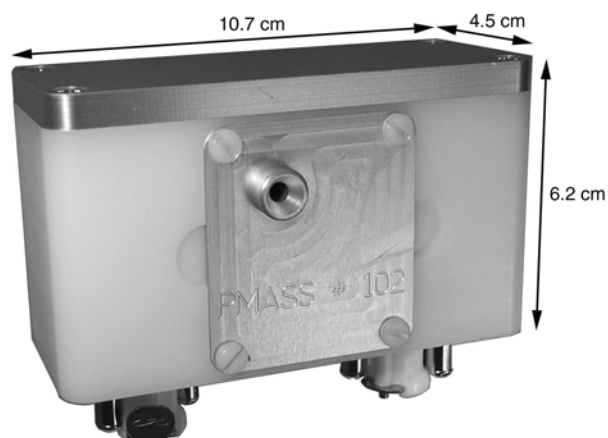


Figure 1. PMASS design. The inlet on the front face leads to the cyclone preseparator, plenum, and parallel particle collection channels. Configuration of each channel varies with the chemical analysis desired. Each channel can be configured with or without a denuder and with one or two filters in tandem.

Table 1. Design Elements of the PMASS^a

Two-channel sampling	No single filter medium is compatible with every analyte detection method, so a two-channel design is necessary. Total carbon concentration can only be determined using quartz filters, which are friable and thus not compatible with gravimetric mass determinations. Measurement of both mass and carbon requires parallel collection on a Teflon filter and a quartz filter.
Oilless, greaseless PM _{2.5} inlet	An oilless, greaseless PM _{2.5} inlet is desirable for precise measurement of organic carbon. Many commonly used inlets, such as the EPA FRM sampler or single-stage impactors, use oil or grease to prevent particle rebound. When measuring organic carbon, this possible source of contamination should be avoided.
Denuders and backup filters	Each channel should be able to incorporate a denuder for accurate measurement of semivolatile constituents such as ammonium nitrate. A denuder is used to remove interfering vapors and the primary filter (or a backup filter) usually consists of a reactive or adsorbing filter medium to prevent evaporation of deposited particles during sampling. Denuder filter methods are well developed for nitrate and are evolving for organic measurements as well.
Single-pump operation	Size, weight, and noise limitations dictate use of a single pump to operate both flow channels. All components must be packaged in a sampler that is small enough to be worn and that permits up to 24 hours of operation with a battery-powered personal sampling pump.

^a The PMASS is the personal particle speciation sampler described by Hering and colleagues (2003) and then modified as described in this report.

inlet and two-channel design (shown in Figure 1) but it differed in several ways from the PMASS units tested in this study. The prototype was fabricated entirely from aluminum and thus was heavier. The PMASS uses plastic for the body and for several of the non-aerosol-contacting internal components, which substantially decreases the weight. Additionally, the filter packs have been simplified and the passive split flow has been improved. These modifications were made prior to beginning tests in this study.

The PMASS is designed for complete chemical speciation of aerosol samples. Its parallel channels allow simultaneous measurement of $PM_{2.5}$ mass, elemental carbon, organic carbon, sulfates, and nitrates. A variety of configurations are possible. Figure 2 illustrates how the sampler was used in this study. Channel 1 collected samples on a 25-mm TFE-coated borosilicate glass fiber filter (Fiberfilm filter; Pallflex, Pall Corp, Ann Arbor MI), masked to a 1.27-cm diameter, that can be analyzed for mass and inorganic ions. This channel also contains an activated carbon honeycomb denuder to remove reactive gases (such as nitric acid) and a 25-mm cellulose backup filter impregnated with sodium chloride to capture any volatilized nitrate. Channel 2 collected samples on a masked 25-mm prefired quartz fiber filter (Pallflex, Pall Corp) for analysis of elemental and organic carbon. This sample collection area was 1.27 cm².

ADOPTION OF A PLASTIC BODY

For particle sampling, all sampler components upstream of the particle collection substrate require electrically conducting materials. Although Teflon is considered ideal for sampling gases, it is not suitable for particles because it readily retains an electric charge. This accumulation of charge leads to loss of particles by electrostatic deposition. Although some plastic materials can conduct electricity after being doped with carbon, such materials are not chemically inert.

For these reasons, we decided to make the PMASS components that are upstream of the particle collection filter from aluminum. Aluminum has the advantage of being electrically conducting while not contaminating samples for organic analysis. For ease of construction, the first Hering prototypes were fabricated entirely from aluminum, but from the outset of this project, we planned to reduce the weight of the sampler by using plastic materials where suitable.

The PMASS has a low-density polyethylene body and an aluminum cyclone body and plenum surface. This combination yields a lighter-weight sampler while maintaining metal surfaces for the portions of the sampler that contact the aerosol upstream of the particle collection filter. However, the use of two materials instead of one necessitated several changes in the construction details.

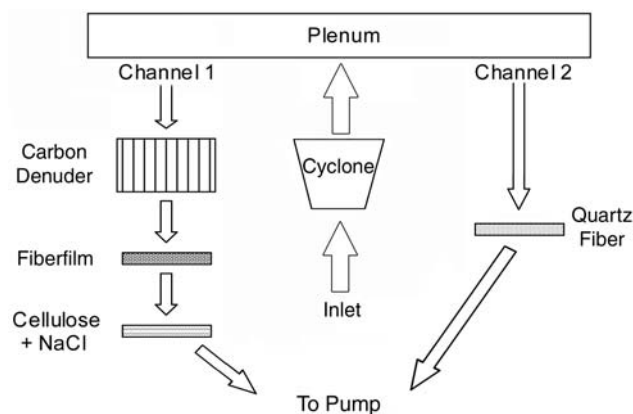


Figure 2. Airflow through the PMASS in this study. After removal of coarse particles by the cyclone, $PM_{2.5}$ particles are transported into the plenum and from there are split between the two particle collection channels. In this study, channel 1 contained an activated carbon denuder to remove reactive gases and a Teflon-coated fiber (Fiberfilm) filter and a cellulose backup filter impregnated with sodium chloride (NaCl) to collect particles for mass and inorganic ion analyses. Channel 2 contained a single quartz fiber filter to collect particles for analysis of elemental and organic carbon.

In the Hering prototype, the cyclone body was simply machined from the sampler body. In the PMASS, the cyclone is a separate piece that slips into the polyethylene body. The cavity that holds the cyclone has rounded bottom corners so that the cyclone cannot be installed upside down. A set of thumb notches facilitates removal of the cyclone. The bottom surfaces of the plenum chamber is lined with aluminum to avoid contact between the air sample and the plastic material of the body. The upper lid of the plenum chamber is made entirely of aluminum; we found that a plastic lid deformed with use and did not maintain a reliable seal.

The all-aluminum Hering prototype weighed approximately 620 g. The PMASS weighs 310 g, including the filter packs and denuder but not the pump (Figure 3).

FILTER PACK MODIFICATIONS

During initial development, we explored the determination of mass through β gauging. As reported by Hering and colleagues (2003), the β gauge only incrementally improved mass sensitivity while complicating filter handling. For these reasons, we decided to use gravimetric analysis of mass in this study and simplified the filter pack accordingly.

In the redesigned filter pack, the airstream passes through a denuder held in an aluminum denuder ring (or through an empty ring if no denuder is used) into the filter pack, composed of three parts (Figure 3): an aluminum cap, a Teflon spacer disk, and a Delrin base. The backup filter is held between the Delrin plastic base and the Teflon spacer disk, and the front particle filter is held between the spacer



Figure 3. Exploded view of the PMASS. From top to bottom: sampler body, aluminum denuder rings, filter cassette components—aluminum caps, Teflon spacer disks, and Delrin bases—and end caps.

disk and the aluminum cap. The Teflon spacer disk provides a seal for each filter as well as physically separating the two. A small relief at the edge of the disk accommodates ringed filters (such as Teflon filters) in addition to standard fiber or membrane filters. As in the original design, the filter packs prevent rotation of the component parts so that friable filters (such as quartz filters) are not damaged during loading.

As in the Hering prototype, the split flow between the two channels in the PMASS is handled passively to facilitate use of an ordinary, single-channel personal sampling pump. In the Hering prototype, the passive split flow was accomplished by unequally limiting the area of filter deposit. Although effective for a fixed selection of filter media, this approach does not offer flexibility for changing filter media and can create confusion between two nearly identical filter packs.

Tests with the Hering prototype showed that for high particle loadings the unequal filtration areas (described in Hering et al 2003) led to changes in flow balance during sampling. The PMASS has orifice plates that can be used to compensate for a difference in pressure drop across the selected filter media in the two channels if, for example,

an investigator changed the type or number of filters in one channel. A flow-balancing orifice plate is pressed to fit into the end cap in each channel.

We redesigned the end cap for each filter channel to reduce the number of o-rings from three to one and at the same time to eliminate the need for a bottom plate. A single o-ring now creates a seal between the end cap and the channel wall and between the channel and the outside (Figure 3). A 1/8-inch pipe thread at the outlets of the end caps allows each channel to be connected to the pump via a clip-lock connector.

We also constructed a special loading platform to allow filter packs to be easily loaded and placed in the sampler.

PENETRATION EFFICIENCY OF PMASS CYCLONE INLET

We evaluated the particle size-dependent penetration efficiency of the six new PMASS cyclone inlets using poly-dispersed and monodispersed test particles in a large chamber into which the PMASS was placed. Upstream and downstream particle concentrations were measured using an Aerodynamic Particle Sizer (model 3320, TSI, St Paul MN) as described by John and Kreisberg (1999). Tests were conducted with solid and liquid particles and to establish the effect of orientation and particle loading. Particle penetration tests were repeated for each PMASS unit to check for consistency among the cyclones and to compare them with the all-aluminum Hering prototype.

Particle Generation

Tests with solid particles were carried out using poly-dispersed and monodispersed polystyrene latex (Duke Scientific, Palo Alto CA) and Arizona road dust (item 415, Duke Scientific). The latex particles were in the form of a dry powder with particle diameters of 1 to 20 μm . A single monodispersed latex particle size was used: mean diameter 2.5 μm . The road dust was polydispersed with a diameter range of 1 to 80 μm . In these experiments, the number mean diameter of the polydispersed Arizona road dust and the polydispersed latex were both approximately 1 μm .

These particles were aerosolized using a fluidized bed constructed in the Aerosol Dynamics laboratory (Berkeley CA). The chamber of the fluidized bed was formed by sealing a flanged tube to the back half of a standard Gelman filter holder. The flanged tube was clear to permit visual observation. The bed particles were glass beads 320 to 420 μm in diameter (sieve size 60/80; part 5420, Alltech, Deerfield MI). These beads are normally used for gas chromatography; they are clean and relatively free of

fine particles. They are also capable of deagglomerating the test particles without damaging them like the larger metallic beads typically used in fluidized beds.

The bed held approximately 17 g of the beads, which were supported by a 47-mm etched stainless steel screen backed by a glass fiber filter. The support screen and filter were mounted in reverse to protect against breakage of the filter. For particle generation, approximately 20 mg of the latex or Arizona road dust was added as a batch to the beads and the fluidized bed was slightly shaken to mix the particles. Airflow through the bed was increased until the bed had the appearance of boiling. Flow rates through the bed varied from 1 to 5 L/min.

Tests with liquid aerosol were conducted using oleic acid particles generated by direct nebulization. The resulting geometric number mean diameter was 1.0 μm (GSD 1.6).

PMASS Cyclone Testing

In the experimental configuration, aerosol flowing upward from the particle generator turned 90° to enter a horizontal tube (Figure 4). After passing a pair of polonium-210 (^{210}Po) charge-neutralizer strips, the flow was diluted by incoming air and was introduced to a 50 × 50 × 60 cm chamber. The chamber had a large volume, 150 L, to stabilize the aerosol concentration. A pair of fans symmetrically stirred the aerosol in the chamber. The aerosol was sampled from the chamber by two vertical parallel tubes:

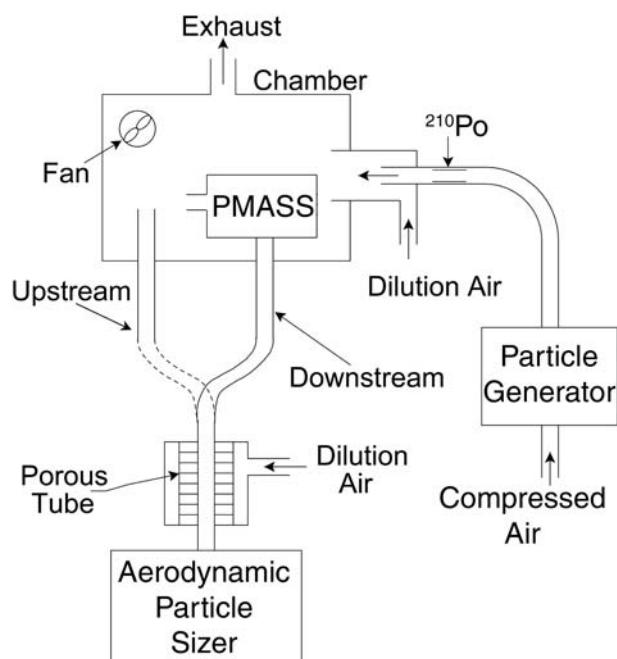


Figure 4. Experimental setup for testing particle penetration of the PMASS inlet.

the bypass, or upstream, tube sampled the aerosol directly (called the *upstream aerosol*); the other, downstream tube sampled the aerosol after passing through the PMASS cyclone (called the *downstream aerosol*).

An Aerodynamic Particle Sizer was used to measure the particle concentrations and size distributions upstream and downstream of the PMASS cyclone inlet. Two short pieces of electrically conducting flexible tubing were used as sampling lines to connect the Aerodynamic Particle Sizer to the flow. By avoiding valves, large losses of particles were avoided. Because the Aerodynamic Particle Sizer samples at a fixed flow rate of 5 L/min, the aerosol flow had to be augmented or diluted depending on the flow rate being tested. This flow compensation was achieved by introducing a 1 to 3 L/min flow of air via a porous tube surrounding the inlet of the Aerodynamic Particle Sizer (Figure 4).

The cyclones were tested in situ within the PMASS units, which were placed one at a time inside the chamber. The PMASS filter channels were left empty and only one side was tested at a time. The exhaust from the test channel of the PMASS was coupled directly to the Aerodynamic Particle Sizer. To maintain proper total inlet flow and split flow through the sampler, 2 L/min makeup flow was maintained for the filter channel not being tested. Care was taken to match the aspiration efficiencies of the downstream aerosol and upstream aerosol.

Each measurement consisted of a 1-minute count of the upstream aerosol, followed by a 1-minute count of the downstream aerosol and then another 1-minute count of the upstream aerosol. The two counts of the upstream aerosol were averaged to compensate for changes in aerosol concentration in each particle size bin during measurement. The measurement was discarded if the aerosol concentration changed more than approximately 15%. The sampling efficiency was obtained by dividing the downstream aerosol counts by the average upstream aerosol count for each particle size bin.

PMASS FIELD PERFORMANCE

We tested the performance of the PMASS for microenvironmental monitoring and precision of the PMASS in two different locations: Fresno, California, and Baltimore, Maryland. In each location, the PMASS was collocated with $\text{PM}_{2.5}$ samplers that have been well characterized and used extensively to monitor fine particles in ambient air: the Air and Industrial Hygiene Laboratory (AIHL) cyclone in Fresno and the Harvard impactor in Baltimore. The PMASS was also tested as personal sampler in Baltimore, where it was compared with the PEM.

Field Preparation

Sampler Cleaning Before each use in the field, all components of the PMASS filter pack except the carbon honeycomb denuders were cleaned by 30 minutes of sonication in ultrapure water and either Alconox powdered detergent (Alconox, White Plains NY) or isopropanol and then were rinsed with isopropanol. All Harvard impactor and PEM components except their oiled impaction plates were cleaned in the same way. Oiled impaction plates were cleaned by 15 minutes of sonication twice in Alconox and twice in ultrapure water followed by an isopropanol rinse. All components were allowed to air dry and were then stored in plastic resealable bags until needed.

Before each use in the field, the interior of each PMASS sampling channel was wiped clean with a damp Kimwipe (Kimberly-Clark Corp, Neenah WI). Prior to sampling in each location, PMASS cyclone inlets were disassembled and cleaned by sonication in ultrapure water and isopropanol. Once testing had commenced, the inlet was left in place; it was not cleaned during the testing period. Before each use in the field, the 25-mm carbon honeycomb denuders were baked for 1 hour at 150°C in aluminum foil. After cooling, the denuders were wrapped in the baked foil and stored in plastic resealable bags until needed.

Filter Handling All 25-mm Fiberfilm filters and 37-mm and 47-mm Teflo filters were stored in a weighing room with controlled temperature and humidity prior to gravimetric analysis to allow equilibration. When the postfield weights had been determined, the filters were stored in sealed plastic petri dishes in the weighing room until they were analyzed for nitrate and sulfate.

Quartz fiber filters of 25, 37, and 47 mm diameters were purchased prefired and were then refired at 500°C for minimum of 2 hours. Before use in the field, the refired quartz fiber filters were stored in resealable glass containers cleaned by autoclave. After sampling, the filters were placed in plastic petri dishes lined with aluminum foil that had been baked at 500°C for 2 hours and stored in a refrigerator until they were analyzed for elemental and organic carbon.

Cellulose filters for the PMASS and the AIHL cyclone were 25-mm and 47-mm in diameter (grade 41; Whatman, Clifton NJ), respectively. They were impregnated with 240 µg and 700 µg sodium chloride, respectively, using a 2% sodium chloride 50:50 methanol-ultrapure water solution. The filters were impregnated and allowed to dry either in a clean air hood or in an oven at 200°C for 1 hour. Before use in the field as backup filters, the cellulose filters were stored in a clean resealable glass container that had been

cleaned by autoclave. After sampling, the filters were placed in plastic petri dishes and stored in the refrigerator until they were analyzed for nitrate and sulfate.

Sampler Assembly and Disassembly In Fresno, assembly and disassembly of all samplers was conducted on a bench top covered with aluminum foil baked at 500°C for 2 hours. In Baltimore, the assembly and disassembly of all samplers was conducted in a glass static-air shelter. All components were handled with gloves and all filters were handled with forceps. To minimize static effects, a ²¹⁰Po charge-neutralizer strip was placed in the shelter.

Pumps AIHL cyclone sampling was carried out using an oilless piston pump (model 627CE44, Thomas Industries, Sheboygan WI) with free air displacement of 0.5 standard cubic feet per minute at 20 inches Hg vacuum. Harvard impactor sampling was accomplished using a twin-head diaphragm pump with volume-based flow control as well as temperature and pressure compensation from 4 to 28 L/min. On the basis of recommendations by the manufacturer (Air Diagnostics and Engineering) regarding flow stability, Harvard impactor sampling was conducted at approximately 10 L/min.

PMASS and PEM sampling was accomplished using personal sampling pumps (model 400-4, BGI) with flow rates of 4 to 6 L/min; the target flow rate for both was 4 L/min. For microenvironmental sampling, pumps used house power. For personal sampling, pumps were powered with nickel hydride 24-hour battery packs (model 403, BGI). The nickel hydride batteries were charged for a minimum of 16 hours before each use to a target voltage of 5.4 to 5.7 V.

Flow Measurements Total sampling flow for the PMASS and all reference samplers were measured using either DryCal DC-lite primary flowmeter or a DryCal DC-1 flow calibrator (BIOS International, Pompton Plains NJ). Individual channel flows for the PMASS were measured using a split flow test stand, which consisted of two 5 L/min air rotameters (Cole Parmer Instrument Co, Vernon Hill IL) and one Magnehelic pressure gauge with a range of 0 to 20 inches water (Dwyer, Michigan City IN).

For the PMASS and AIHL cyclone, flow per channel was calculated as the fraction of flow per channel determined by the split flow measurements multiplied by the total flow rate measured at the sampler inlet. For all methods, the total flow volume was calculated as the product of sampling duration and the average of the beginning and ending flow rates.

Microenvironmental Sampling

For purposes of performance evaluation, microenvironmental sampling locations were selected to ensure PM_{2.5} concentrations well above the limit of detection with adequate and easily accessible power. Durations of microenvironmental sampling were purposefully varied to provide a wide range of collected analyte masses and thus to simulate a wide range of ambient concentrations. Because some aspects of the sampler, such as the passive split flow, could depend on the collected mass, we deemed it important to assess performance while varying this parameter.

In each location, PMASS units were collocated with PM_{2.5} samplers that have been well characterized and used extensively to monitor fine particles in ambient air: the AIHL cyclone in Fresno and the Harvard impactor in Baltimore.

The AIHL cyclone (John and Reischl 1980) is used as the precut for the EPA speciation sampler (Andersen Instruments, Smyrna GA; John and Wall 1983; Solomon et al 1988; Eldred et al 1990). It is nearly dimensionally equivalent to the cyclone precut used in the Interagency Monitoring of Protected Visual Environments (IMPROVE) network and in the EPA speciation sampler marketed by Andersen Instruments (the Reference Ambient Air Sampler, or RAAS). Laboratory studies (Peters et al 2001) and field studies (Solomon et al 2000; Peters et al 2001) have shown that the AIHL cyclone inlet is equivalent to the FRM for PM_{2.5} under a wide range of conditions. The field-tested AIHL inlet serves as a good reference standard for the precut of a speciation sampler because it does not use oil; the oiled FRM inlet is not suitable for the chemical analyses employed in this study.

The Harvard impactor (Air Diagnostics and Engineering, Harrison ME), which has been used for many years as an ambient air sampler, was used for microenvironmental sampling in Baltimore. Although it is not a designated EPA FRM because it has not been tested in wind tunnels, researchers often use this sampler for PM_{2.5} measurements when an FRM is not required. Harvard impactor measurements of PM_{2.5} have compared well with FRM measurements in method comparison studies conducted by the EPA (Pitchford 1997; Turner et al 2000; Liu et al 2003).

To evaluate the precision of the PMASS, two to three units were set up at each microenvironmental monitoring location in Fresno and Baltimore for each sampling period.

Fresno The Fresno site was the EPA Supersite located at the California Air Resources Board monitoring site at 3425 First St. As part of the EPA Supersites program, the Desert Research Institute has collaborated with the California Air Resources Board to conduct intensive PM_{2.5} measurements

there since June 1999. The site is within 1 km of a freeway and within 2 km of downtown Fresno.

In Fresno, microenvironmental sampling was conducted on the roof of the monitoring station, approximately 10 m (two stories) above ground level. For this phase of the study, three PMASS units were operated alongside a single reference AIHL sampler. The three PMASS units and the AIHL cyclone were mounted under a sunshade 1.5 m above the roof. Over 2 weeks (July 2–13, 2003), 12 sets of measurements were collected, each over approximately half a day (537–770 minutes).

For the first two sets of samples, the PMASS units were operated using BGI pumps. To maintain flow stability, the remaining 10 sets were collected by using a BGI pump and a single 4 L/min critical orifice to control the flow through each PMASS. The AIHL cyclone reference sampler was operated on an independent Thomas pump with separate in-line flowmeters for each sampling line.

Total inlet flow and split flow measurements for the PMASS were taken inside the monitoring station before sample collection on the roof and again at the end of sample collection, immediately after removal of the PMASS from the roof. A low pressure drop filter was placed on the PMASS inlet to prevent any unwanted sampling while the split flow and pressure drop measurements were taken. For the two AIHL cyclone sampling lines, in-line rotameters were used to measure split flow before and after each sample collection.

The AIHL reference sampler was operated at the standard flow rate of 24 L/min to give a 50% cutpoint of 2.5 μm. The flow from the cyclone was split into two sampling lines to provide parallel collection for aerosol carbon and for mass and inorganic ions. In the first line, samples were collected for organic and elemental carbon analysis on prefired 47-mm quartz fiber filters at a flow rate of 18 L/min. The filters were mounted in Gelman filter holders with a masking ring that provided a clean 35-mm diameter deposit. In the second line, samples were collected for mass and nitrate and sulfate analysis at a flow rate of 6 L/min. These samples were collected onto 47-mm Fiberfilm filters (and 47-mm backup filters impregnated with sodium chloride) preceded by a magnesium oxide (MgO) denuder of the type used in the spiral aerosol speciation sampler (SASS; Met One Instruments, Grants Pass OR).

Baltimore Microenvironmental monitoring in Baltimore was conducted on the second floor of a residential row house located in midtown on a main commuting street that carries approximately 15,000 vehicles per day. The house is the site of an air quality monitoring station maintained by the Division of Environmental Health Engineering of the Johns Hopkins Bloomberg School of Public Health.

The site was selected for PMASS testing because it could guarantee consistently elevated indoor concentrations of PM_{2.5}, weekly concentrations of which have been documented at 7 to 37 µg/m³ (unpublished results).

Over 6 weeks in Baltimore, 15 sets of measurements were collected, each over 1 to 2 days (963–3490 minutes) from October 16 to November 13, 2002. For each sampling period, two to three PMASS units were collocated with two Harvard impactors containing either 37-mm Telfo or prefired quartz fiber filters. Immediately before sampling, total flow rates for all samplers were measured and set to within 2.5% of the target flow rate. After setting the total flow rate, PMASS channel flows and total pressure drops were measured and recorded. At the end of sampling, all total flows and the PMASS channel flows and total pressure drops were measured and recorded.

The Harvard impactor consists of an inlet and an impaction surface configured to exclude all particles greater than 2.5 µm in aerodynamic diameter and to allow an airstream path of correct length and diameter to achieve laminar flow. The configuration also allows a collection substrate of either a 37-mm stretched Teflon filter when particles are collected for gravimetric and inorganic ion analysis or a 37-mm prefired quartz fiber filter when particles are collected for elemental and organic carbon analysis. For this study, the Harvard impactor was run at a flow rate of approximately 10 L/min.

Personal Sampling—Baltimore

The PEM by the MSP Corporation has been used for many years as a personal monitor for PM_{2.5}.¹ This lightweight sampling device consists of a multiholed inlet, a single-stage impactor, and a final filter. The PEM is designed to run at a flow rate of 4 L/min. Aerosol particles are sampled through the single-stage impactor to remove particles above the 50% cutpoint of 2.5 µm aerodynamic diameter. Particles smaller than 2.5 µm in aerodynamic diameter are collected on a 37-mm filter.

To evaluate the PMASS as personal sampler, four field staff were hired to carry either a PMASS and a PEM (MSP Corporation; purchased from SKC, Eighty Four PA) or two PMASS

units simultaneously from October 25 to November 30, 2002. Two staff were technicians from the Johns Hopkins Bloomberg School of Public Health; two were individuals with no technical experience. Each sampler was attached to a dedicated personal pump so that each person carried a total of two samplers and two personal pumps attached to one 24 hour battery pack each. Samplers were carried using either a back pack or a shoulder bag that was large enough to carry the two personal pumps and sound-dampening foam. Staff were required to carry the samplers with them at all times during waking hours. At night, they were asked to place the sampling bags near them, but if the pump noise was bothersome, they were allowed to place the bags in another room.

Personal sampling was conducted over 6 weeks in Baltimore, Maryland. A total of 17 sets of samples were collected by staff who wore one PMASS and one PEM sampler and 14 sets of samples were collected by staff who wore two PMASS units. The sampling period for each set was approximately 1 day (1018–1568 minutes).

As with the microenvironmental sampling, total flow rates for each sampler were measured and set to within 2.5% of the target flow rate immediately before sampling. After setting the total flow rate, PMASS channel flows and total pressure drops were measured and recorded. At the end of sampling, all total flows and the PMASS channel flows and total pressure drops were measured and recorded.

SAMPLE ANALYSIS

Mass

All filters were weighed at Johns Hopkins Bloomberg School of Public Health. Filters were stored at room temperature in petri dishes. They were shipped to Fresno by overnight delivery services. Filters were returned to Johns Hopkins by overnight delivery service at the end of each week of sampling.

Fiberfilm and Teflon filters were weighed in laboratories of the Division of Environmental Health Engineering at the Johns Hopkins Bloomberg School of Public Health according to the EPA protocol for mass evaluation of PM_{2.5} (EPA 1999). Specifically, filters were weighed in a room with controlled temperature and humidity within 10 days before and after field sampling using a microbalance with a precision of ± 0.001 mg (Mettler T5, Mettler-Toledo International, Toledo OH). For each mass measurement, filters were weighed twice and the average of the two measurements was used. If the difference between the first and second measurement was greater than 0.003 mg, however, the filter was reweighed and the two nearest measurements were averaged.

1. No reference method exists for monitoring personal exposure to PM_{2.5}. Currently two monitors are available for use as a PM_{2.5} personal sampler: the MSP PM_{2.5} PEM and the Harvard PM_{2.5} PEM, developed by Demokritou and colleagues (2001). Researchers at the EPA and the University of Washington found variable performance with both PEMs compared with the Harvard impactor and FRM. In a study conducted in Baltimore, the MSP PEM was biased by -12% compared with a collocated PM_{2.5} FRM (Williams et al 2000). The Harvard PEM showed a bias of +13% relative to a collocated Harvard impactor (Wallace et al 2003) and -12% relative to a collocated FRM (Liu et al 2003). The reason for the variability in performance is unknown, but it most likely results from a combination of factors (including sensitivity to differences in sampler assembly, handling, and environmental conditions).

Elemental and Organic Carbon

Quartz fiber filters were sent to the Desert Research Institute in Reno, Nevada. These filters were analyzed for both elemental and organic carbon content by thermal optical reflectance (Chow et al 1993, 2001).

Nitrate and Sulfate

After mass determination, all Fiberfilm and Teflon filters were extracted and the samples analyzed by ion chromatography for nitrate and sulfate content, as were the cellulose filters impregnated with sodium chloride. This analysis was conducted at the Johns Hopkins Bloomberg School of Public Health according to the method developed at the Harvard School of Public Health for anion analysis by ion chromatography (Wolfson 1999). We used an integrated single-column ion chromatograph (model DX-600; Dionex, Sunnyvale CA) that performs isocratic separations using suppressed conductivity detection. Standard curves were generated for each set of analyses. Uniformly spaced replicate standard measurements were included in each run for quality control.

The extraction method involves wetting the filter with 0.15 μL of 100% ethanol and then extraction with 5 mL of ultrapure water. The filter is then sonicated for 15 minutes. Unlike the Teflo filter, which is a single layer of Teflon fabric, the Fiberfilm filter is a multilayer pad of compressed TFE-coated glass fibers. The pad thus contains interior spaces surrounded by hydrophobic material, which may present a barrier to efficient aqueous extraction. Quartz fiber filters were selected as the comparison collection medium because they present no such barrier.

DATA ANALYSIS

Accuracy of the PMASS was assessed by comparing PMASS measurements with those of the reference sampler using simple least squares linear regression of PMASS measurements against reference measurements and as the ratio of means (mean of PMASS values/mean of reference values). For microenvironmental sampling, PMASS performance was evaluated for measurement of mass and of elemental carbon, organic carbon, and nitrate and sulfate concentrations. For personal sampling, the PMASS was evaluated for measurement of mass. Because of the small dynamic range of values for all measurements, the ratio of means was thought to be less sensitive to the effects of values at the high end of the distribution.

Precision of the PMASS was estimated as the percent precision calculated according to the root mean squared error (RMSE) method, which allows comparisons of differences (d) among more than two collocated samplers (Harvard School of Public Health 1994):

$$\text{RMSE} = \sqrt{\frac{\sum d_i^2}{N}},$$

where $d_i = x_i - m_i$ for $n = 1 \dots i$ collocated samples; x_i = measurement $n = 1 \dots i$; m_i = mean of collocated samples within the test run; and N = total number of samples collected.

Percent precision was estimated as follows:

$$\% \text{ Precision} = \frac{\text{RMSE}}{M} \times 100,$$

where

$$M = \frac{\sum m_i}{N},$$

RESULTS

PMASS CYCLONE INLET TESTING

Tests for the size cut of the cyclones for the six PMASS units were carried out with Arizona road dust at a flow rate of 4.1 L/min with the samplers held in a normal, upright position (Figure 5). For all six units, the mean 50% cutpoint (defined as the aerodynamic diameter of particles collected with an efficiency of 50%) was 2.52 μm (SD = 0.08 μm).

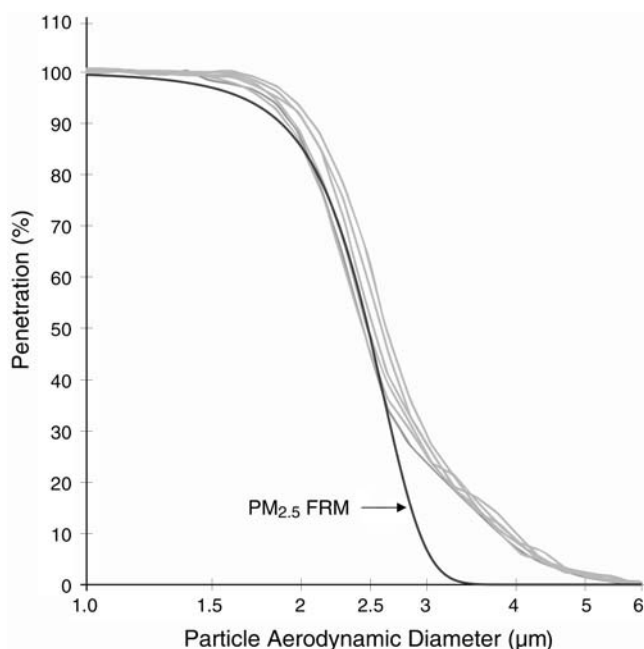


Figure 5. Size-dependent penetration of Arizona road dust through six upright PMASS cyclone inlets compared with the FRM curve (Peters et al 2001). Flow rate was 4.1 L/min. Mean (\pm SD) PMASS cutpoint = 2.52 \pm 0.08 μm . X-axis uses a log scale.

The cyclone curves show somewhat greater penetration efficiency of particles of 3 to 4 μm diameters than specified by the FRM curve.

Figure 6 compares penetration curves for a cyclone in one PMASS held at different orientations: upright (the normal orientation), inverted, and sideways. These tests were done at a flow rate of 4.0 ± 0.1 (SD) L/min. Again, the challenge aerosol was Arizona road dust. The resulting curves are the same within the precision of the measurement: the 50% cutpoints varied by ± 0.02 μm , or less than 1% of the mean.

The penetration curves of the same PMASS cyclone were then calculated after loading for 6 hours with Arizona road dust challenge aerosol at a flow rate of 4.1 L/min. (Figure 7). Coarse loading within the cyclone was approximately 100 μg as estimated from the size distribution of the challenge aerosol, the size-dependent collection by the cyclone, and the exposure time. Penetration curves for the loaded cyclone for upright, inverted, and sideways orientations as well as the average curve from Figure 6 were within the estimated measurement precision of 0.1 μm .

The penetration curves for Arizona road dust at five different flow rates from 3.1 to 4.9 L/min revealed the consequent changes in the 50% cutpoint: it increased with decreasing flow rate, from 2.1 μm at 4.9 L/min to 3.3 μm at 3.1 L/min (Figure 8).

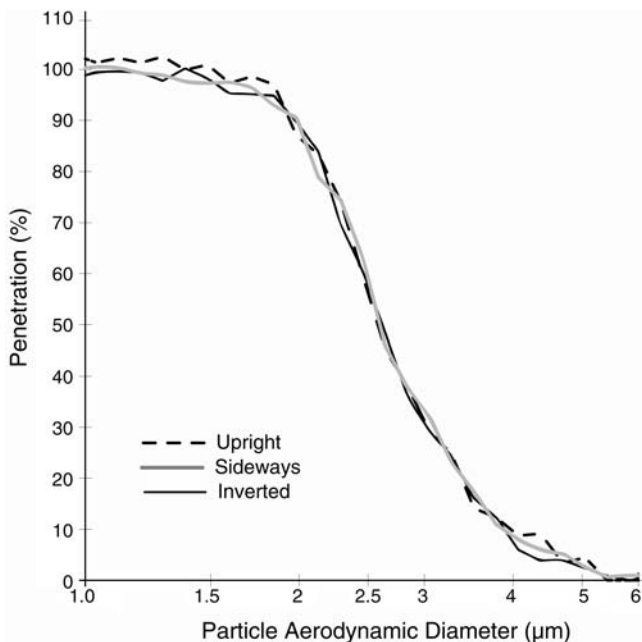


Figure 6. Size-dependent penetration of Arizona road dust through one PMASS cyclone inlet at different orientations. Flow rate was 4.0 L/min. X-axis uses a log scale.

Penetration curves at 4.1 L/min were calculated for three types of challenge aerosols: polystyrene latex, oleic acid, and Arizona road dust (Figure 9). Oleic acid, a liquid particle, gives a 50% cutpoint similar to that found for the solid particles that comprise Arizona road dust. The polystyrene latex gives a somewhat smaller cutpoint. We could not ascertain whether this difference was real or due to a difference in aerodynamic sizing of the different particles. Above 3 μm , all three types of aerosol were collected with equal effectiveness by the cyclone.

PASSIVE SPLIT FLOW

The split flow between the two channels was measured before and after each sample was taken. Stability of the split flow was measured as the absolute value of the change in the fraction of flow per channel expressed as a percentage of the channel flow fraction. Let f be the fraction of flow through the Fiberfilm filter channel. The relative change in the PMASS flow split was computed as follows:

$$[|f_2 - f_1| / (f_1 + f_2)] \times (2 \times 100),$$

where 1 and 2 refer to the initial and final flow splits, respectively.

The average changes in split flow for microenvironmental sampling in Fresno and Baltimore and personal sampling in Baltimore were 1.6%, 2.8%, and 3.2%, respectively. The corresponding uncertainty in flow volume, calculated as

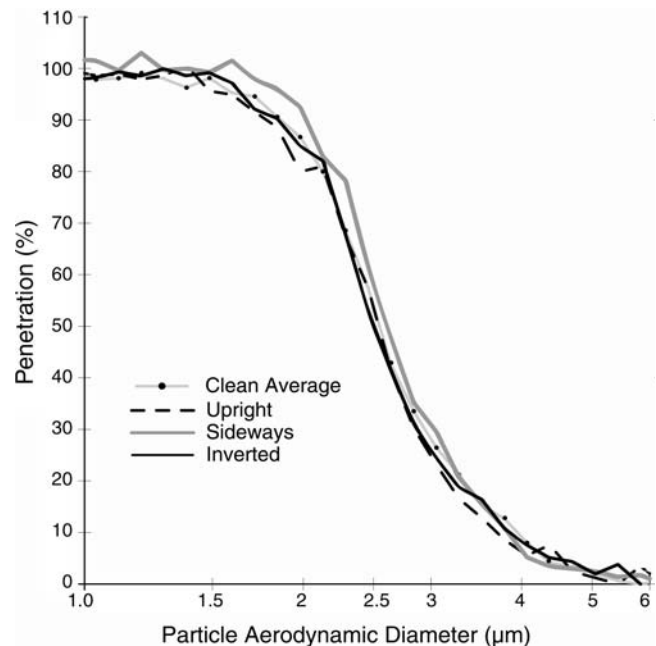


Figure 7. Size-dependent penetration of Arizona road dust through one PMASS cyclone inlet at different orientations after 6 hours of dust loading. Flow rate was 4.1 L/min. Clean average = penetration data for the clean inlet (Figure 6) averaged over all three orientations. X-axis uses a log scale.

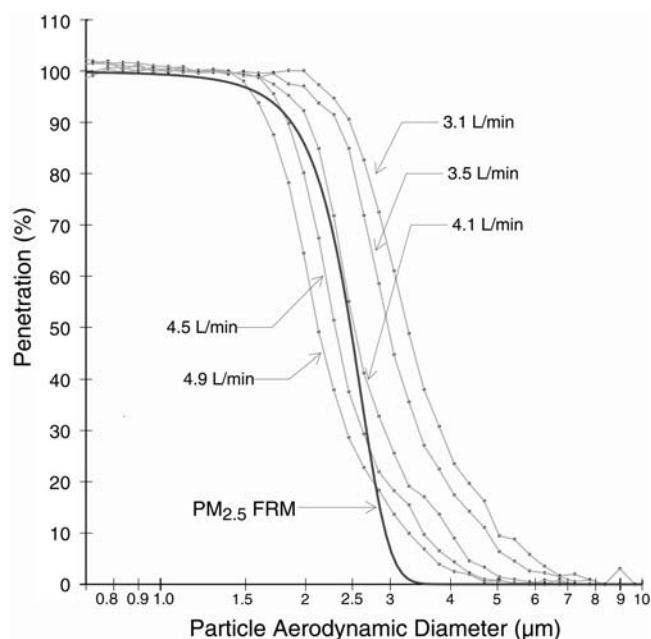


Figure 8. Penetration curves of Arizona road dust through one PMASS cyclone inlet at different flow rates compared with the FRM curve (Peters et al 2001). X-axis uses a log scale.

the average of the initial and final flows, was one half of the average change in the split flow, or 0.8%, 1.4%, and 1.6%, respectively.

QUALITY ASSURANCE AND QUALITY CONTROL

Excluded Samples

In Fresno, a total of 12 sets of samples were collected. For the AIHL cyclone, 50% of the 47-mm Fiberfilm filters analyzed showed negative mass, rendering the entire set of AIHL cyclone mass values suspect. None of these mass samples were used for analysis. However, chemical analyses were not compromised because the filter deposition areas were intact. In Baltimore, a total of 15 sets of microenvironmental samples and 31 sets of personal samples (14 sets of PMASS/PMASS and 17 sets of PMASS/PEM) were collected. Of these, eight PMASS samples were invalidated: one (microenvironmental) owing to suspect flow calibration, five (one microenvironmental, one personal from PMASS/PEM sets, and three personal from PMASS/PMASS sets) owing to pump failure, and two (microenvironmental) owing to imbalanced channel flow. Five additional PMASS personal mass samples (from PMASS/PMASS sets) were invalidated owing to torn Fiberfilm filters. Two Harvard impactor samples were invalidated; one owing to a void pre-weight and one owing to suspect flow calibration. Two PEM samples were invalidated; one owing to pump failure and one owing to a broken connection to the pump.

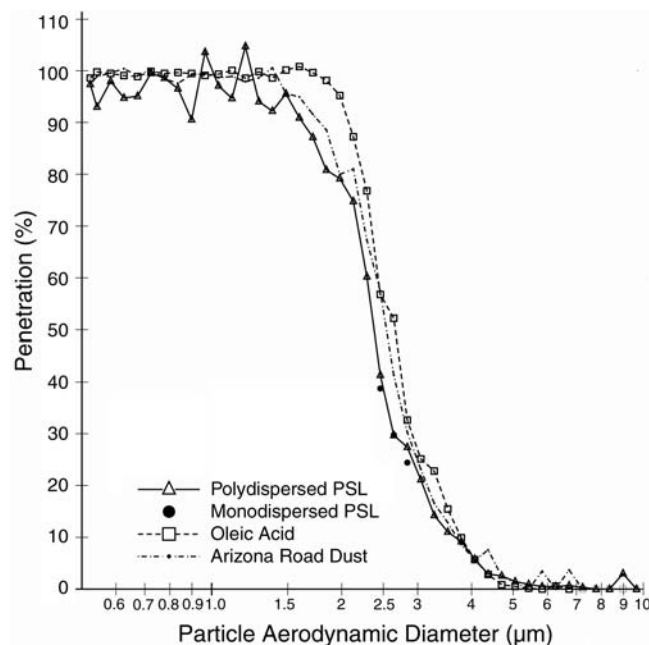


Figure 9. Penetration curves for three types of challenge aerosols for the PMASS inlet. Inlet flow rate was 4.1 L/min. PSL = polystyrene latex. X-axis uses a log scale.

Blank Samples

Blank filters were handled exactly as sample filters were except no flow was pulled through the filter.

An additional 10% of PMASS and Harvard impactor samples were collected as blank samples. No blank samples were collected for the AIHL cyclone. Elemental and organic carbon blank values were estimated for the AIHL cyclone as the product of elemental and organic carbon values, respectively, from the PMASS quartz fiber blanks and a scaling factor defined by the ratio of the filter areas. Mass blanks were not estimated for the AIHL cyclone because all AIHL mass measurements were found to be unusable for analysis (see previous section). No PEM blanks were collected. The Harvard impactor blank average was used to correct all 37-mm Teflo filter samples.

Table 2 shows averages and standard deviations for the blank values for each analyte. For each analyte, sample values were corrected for background by subtracting the average of the blank samples.

Blank values for the Fiberfilm filters used for gravimetric mass measurements resulted in variability equal to 12% [calculated as (blank mass SD/mean PMASS mass) \times 100] of the mean mass concentrations for microenvironmental sampling, which accounts for the 12.7% (Fresno) to 17.5% (Baltimore) variation in precision of microenvironmental mass measurements.

Table 2. Filter Blank Results and Limits of Detection

Sampler/ Analyte	<i>N</i>	Average Blank Value ± SD (µg/filter)	Limit of Detection ^{a,b} (µg)	Minimum Detectable Concentration (µg/m ³) ^b
PMASS				
Mass	5	-7.0 ± 3.7	11.0	3.82
Elemental carbon	5	0.033 ± 0.058	0.17	0.059
Organic carbon	5	0.50 ± 0.17	0.51	0.18
Nitrate	5	Not detected	0.15	0.052 ^a
Sulfate	5	2.0 ± 0.63	1.89	0.66
AIHL				
Mass ^c	ND ^d	ND	ND	ND
Elemental carbon ^e	2	0.23 ± 0.46	1.38	0.053
Organic carbon ^e	2	3.80 ± 1.29	3.87	0.050
Nitrate	ND	ND	ND	ND
Sulfate	ND	ND	ND	ND
Harvard impactor				
Mass	2	8.2 ± 3.9	11.7	0.81
Elemental carbon	2	0.05 ± 0.07	0.21	0.014
Organic carbon	2	4.80 ± 0.99	2.97	0.21
PEM				
Mass	ND	ND	ND	ND

^a Calculated as $3 \times$ standard deviation of average blank value, except for nitrate, for which limit of detection was that of the ion chromatography method.

^b Based on nominal flow rates and a 24-hour monitoring period.

^c Mass blank data were not estimated because AIHL mass data were excluded from analyses.

^d ND = not determined.

^e Calculated as analyte blank values from PMASS quartz blanks multiplied by a scaling factor defined by the ratio of the filter areas.

The average PMASS sulfate blank value represented 91% of the sulfate concentration found on PMASS sample filters.

Limits of Detection

Limits of detection for all analytes were set at three times the standard deviation of field blanks except for nitrate (Table 2). For all monitoring methods, nitrate background was below the limit of detection of the analytical method. Therefore, the limit of detection for nitrate was set at the limit of detection for ion chromatography. Limits of detection and minimum detectable concentrations were based on nominal flow rates and 24-hour monitoring.

Table 3. Comparison of Reference Sampler Mass Data

Comparison	<i>N</i>	Precision			<i>r</i> ²
		(%)	Slope ± SE	Intercept ± SE	
HI vs HI ^a	5	3.21	0.94 ± 0.12	0.65 ± 1.38	0.98
PEM vs PEM	3	5.73	0.92 ± 0.10	0.52 ± 1.83	0.99
PEM vs HI ^a	4	NA ^b	1.22 ± 0.12	-1.36 ± 2.13	0.99

^a HI = Harvard impactor.

^b Not applicable.

Comparison of Harvard Impactor and PEM

For purposes of quality assurance, a limited number of duplicate Harvard impactor and PEM mass samples were collected. In addition, Harvard impactor and PEM performances were compared to determine whether the chosen reference samplers agreed within accepted limits (Table 3). Percent precision estimated by the RMSE method was 3.21% for the Harvard impactor and 5.73% for the PEM. In comparison with the Harvard impactor, the PEM demonstrated a measurement bias of +22%. Therefore, all PEM mass measurements were adjusted downward by 22%.

Efficiency of Aqueous Extraction

Extraction efficiency for nitrate and sulfate from Fiberfilm filters was evaluated. The extraction method was developed by the Harvard School of Public Health for extraction of inorganic ion particles collected on Teflo filters (Wolfson 1999).

For this evaluation, particle samples were collected on Fiberfilm and quartz fiber filters simultaneously (one filter in each channel) using the PMASS. Both sets of filters were extracted according to protocol. Mass values for nitrate and sulfate collected on the different filters were normalized by collection volumes.

Nitrate concentrations ranged from 1.096 to 3.135 µg/m³ (Table 4). The average difference between the Fiberfilm and quartz fiber filter nitrate concentrations was 0.125 µg/m³. The average extraction efficiency for nitrate from Fiberfilm relative to quartz fiber was 105%. Sulfate concentrations ranged from 1.830 to 4.373 µg/m³. The average difference between the Fiberfilm and quartz fiber filter sulfate concentrations was 0.439 µg/m³. The average extraction efficiency of sulfate from Fiberfilm relative to quartz fiber was also 105%. On the basis of these similar results between the two types of filters, we concluded that the method was effective for extracting nitrate and sulfate ions from Fiberfilm filters.

Table 4. Results of Aqueous Extraction

Analyte	Filter		Efficiency ^a (%)
	Fiberfilm ($\mu\text{g}/\text{m}^3$)	Quartz Fiber ($\mu\text{g}/\text{m}^3$)	
Nitrate	3.135	2.915	108
	2.903	2.913	100
	1.944	2.150	90
	1.935	1.920	101
	1.368	1.221	112
	1.328	1.179	113
	1.225	1.096	112
	1.225	1.096	112
Sulfate	4.373	3.976	110
	4.301	3.640	118
	4.207	3.566	118
	2.569	2.174	118
	2.325	2.226	104
	2.270	2.621	87
	1.830	2.358	78
	1.830	2.358	78

^a Efficiency = [Fiberfilm sample ($\mu\text{g}/\text{m}^3$) - quartz fiber sample ($\mu\text{g}/\text{m}^3$)] \times 100.

PMASS PERFORMANCE

Microenvironmental Sampling

Evaluation of the PMASS as a microenvironmental sampler was conducted over 2 weeks in Fresno and 6 weeks in Baltimore. In Fresno, sampling periods ranged from 537 to 770 minutes; in Baltimore, from 963 to 3490 minutes.

Accuracy of PMASS measurements for mass, elemental and organic carbon, and nitrate were evaluated against the relevant reference sampler (Table 5). All results were blank corrected using values in Table 2. Error bars were determined from the standard deviations of replicate PMASS measurements. The precision of PMASS measurement for each analyte was also determined (Table 6).

For the AIHL cyclone, 50% of the 47-mm filters yielded negative mass measurements, rendering the entire set of AIHL mass values suspect. For this reason, no mass comparisons between the AIHL cyclone and the PMASS were conducted. PMASS mass measurements were in modest agreement with those of the Harvard impactor: the PMASS demonstrated a measurement bias relative to the Harvard impactor of approximately -33% (Figure 10); the ratio of means was 0.81. The precision of PMASS microenvironmental measurements collected in both locations was similar (12.7% in Fresno; 17.5% in Baltimore).

Table 5. Summary Statistics for PMASS and Reference Samplers^a

	N	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	Min ^b ($\mu\text{g}/\text{m}^3$)	Max ^c ($\mu\text{g}/\text{m}^3$)
Microenvironmental Sampling^{d,e}					
PMASS—Fresno					
Mass	36	13.5	12.8	8.1	24.4
Elemental carbon	36	1.2	1.2	0.6	1.8
Organic carbon	36	6.7	6.8	3.8	11.5
Nitrate	36	1.4	0.9	0.5	6.8
PMASS—Baltimore					
Mass	33	9.4	10.1	3.1	70.4
Elemental carbon	23	1.9	1.6	0.4	5.0
Organic carbon	23	4.9	4.8	2.8	9.0
Nitrate	33	1.4	1.3	0.4	3.9
AIHL cyclone ^f —Fresno					
Elemental carbon	12	1.3	1.3	0.6	1.8
Organic carbon	12	5.8	5.7	3.9	8.3
Nitrate	12	1.5	1.1	0.8	5.0
Harvard impactor—Baltimore					
Mass	19	11.4	11.6	3.6	20.1
Elemental carbon	9	2.0	1.8	0.8	4.4
Organic carbon	9	5.0	4.8	2.3	9.1
Personal Sampling^{d,g}					
PMASS—Baltimore					
Mass	35	41.7	26.1	7.6	123.2
Elemental carbon	23	1.8	0.8	0.1	6.4
Organic carbon	23	16.8	6.0	3.0	81.4
Nitrate	31	0.7	0.7	0.1	1.6
Adjusted PEM ^h —Baltimore					
Mass	15	58.7	61.8	2.5	166.4

^a For all valid samples.

^b Minimum.

^c Maximum.

^d Sulfate data were not analyzable because of the large magnitude and variability of the sulfate blanks.

^e Microenvironmental sampling was conducted over 2 weeks in Fresno and 6 weeks in Baltimore. Sample sets were collected for 537–770 minutes in Fresno and 963–3490 minutes in Baltimore.

^f Mass data from the AIHL cyclone were excluded from analysis because half of the filters had negative mass.

^g Personal sampling was conducted over 6 weeks in Baltimore, with each sample set collected for 1018–1568 minutes.

^h PEM mass measurements were adjusted downward by 22% to eliminate measurement bias compared with the Harvard impactor.

PMASS elemental carbon measurements showed a bias of -26% with respect to the AIHL cyclone and +24% with respect to the Harvard impactor on the basis of the slope (Figures 11 and 12). The ratios of means were 0.94 and 0.90,

Table 6. PMASS Precision

	Fresno		Baltimore	
	N (sets)	Precision (%)	N (sets)	Precision (%)
Microenvironmental sampling ^a				
Mass	36 (12)	12.7	29 (13)	17.5
Elemental carbon	36 (12)	6.8	20 (9)	6.6
Organic carbon	36 (12)	9.0	20 (9)	8.7
Nitrate	33 (11) ^b	11.9	27 (12)	13.6
Personal Sampling ^a				
Mass			18 (9)	24.2
Elemental carbon			22 (11)	8.1
Organic carbon			22 (11)	19.3
Nitrate			18 (9)	19.1

^a Sulfate data were not analyzable because of the large magnitude and variability of the sulfate blanks.

^b One of the 12 nitrate sets was not analyzed because the backup filters yielded high and variable data. With the anomalous set included, precision was estimated to be 22.1%.

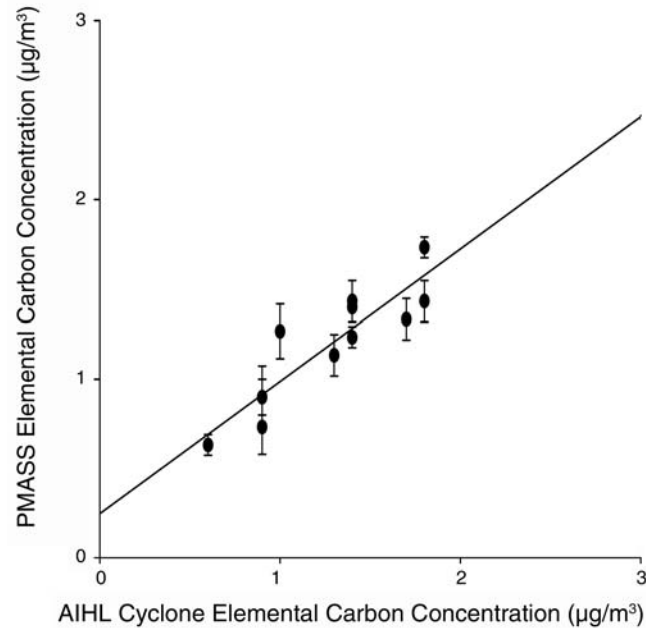


Figure 11. Accuracy of microenvironmental sampling in Fresno: PMASS versus AIHL cyclone elemental carbon measurements. Slope = 0.74 ± 0.075 , $r^2 = 0.74$; intercept = 0.25 ± 0.10 , $P = 0.02$. Each error bar = 1 SD. Both the SD and r^2 were calculated from the original PMASS data.

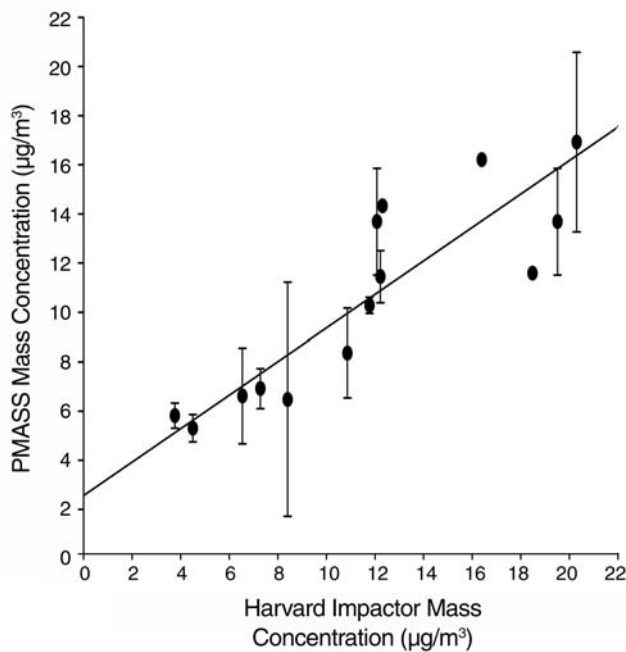


Figure 10. Accuracy of microenvironmental sampling in Baltimore: PMASS versus Harvard impactor mass measurements. Slope = 0.66 ± 0.09 , $r^2 = 0.67$; intercept = 2.20 ± 1.11 , $P = 0.06$. Each error bar = 1 SD. Both the SD and r^2 were calculated from the original PMASS data.

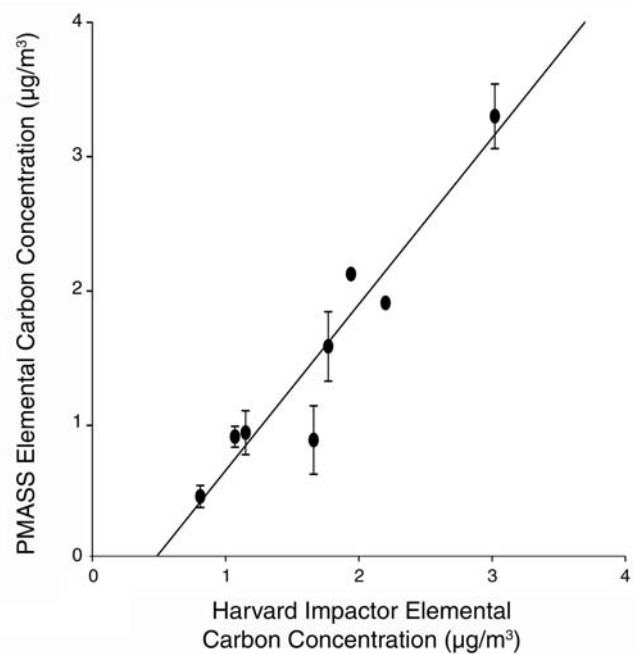


Figure 12. Accuracy of microenvironmental sampling in Baltimore: PMASS versus Harvard impactor elemental carbon measurements. Slope = 1.24 ± 0.11 , $r^2 = 0.90$; intercept = -0.57 ± 0.19 , $P = 0.01$. Each error bar = 1 SD. Both the SD and r^2 were calculated from the original PMASS data.

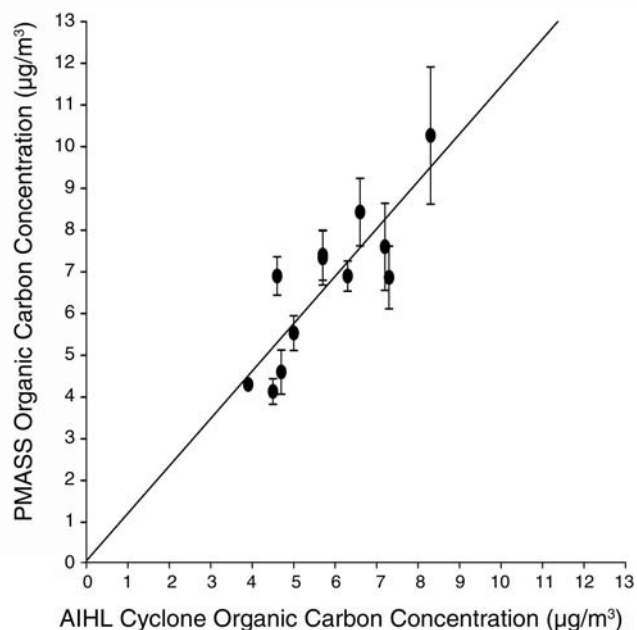


Figure 13. Accuracy of microenvironmental sampling in Fresno: PMASS versus AIHL cyclone organic carbon measurements. Slope = 1.03 ± 0.16 , $r^2 = 0.58$; intercept = 0.50 ± 0.92 , $P = 0.60$. Each error bar = 1 SD. Both the SD and r^2 were calculated from the original PMASS data.

respectively. The precision of PMASS microenvironmental measurements collected in each location was essentially equivalent: 6.8% for Fresno; 6.6% for Baltimore.

PMASS microenvironmental organic carbon measurements agreed with measurements of the AIHL cyclone and the Harvard impactor on the basis of the slope (Figures 13 and 14). The ratios of means were 1.15 and 0.98, respectively. Precision estimated for the PMASS microenvironmental organic carbon measurements in both locations was again essentially equivalent: 9.0% in Fresno; 8.7% in Baltimore.

PMASS measurement of nitrate was in good agreement with the AIHL cyclone on the basis of the slope (Figure 15). The ratio of means was 0.96. Precision estimates for the PMASS microenvironmental nitrate measurements were similar in both locations: 11.9% in Fresno; 13.6% in Baltimore. The precision and accuracy of the Fresno PMASS nitrate data were estimated from 11 of the 12 runs. For one run, the backup cellulose filters had exceedingly high and variable values; the standard deviation was calculated to be 1.3 to 20.1 times higher than that of the remaining 11 runs. With the anomalous run included, PMASS precision was estimated to be 22.1%. PMASS nitrate measurements were not evaluated against Harvard impactor nitrate measurements as the Harvard impactor is not designed to measure particle-bound nitrate correctly.

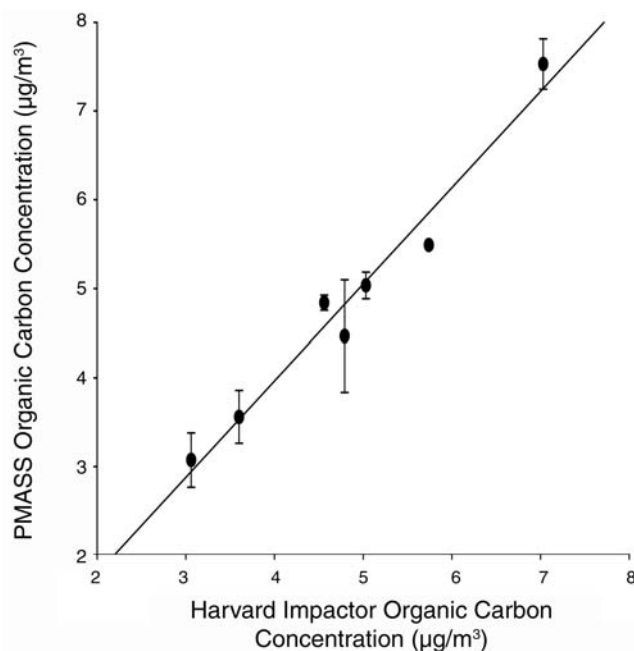


Figure 14. Accuracy of microenvironmental sampling in Baltimore: PMASS versus Harvard impactor organic carbon measurements. Slope = 1.08 ± 0.08 , $r^2 = 0.93$; intercept = -0.38 ± 0.40 , $P = 0.36$. Each error bar = 1 SD. Both the SD and r^2 were calculated from the original PMASS data.

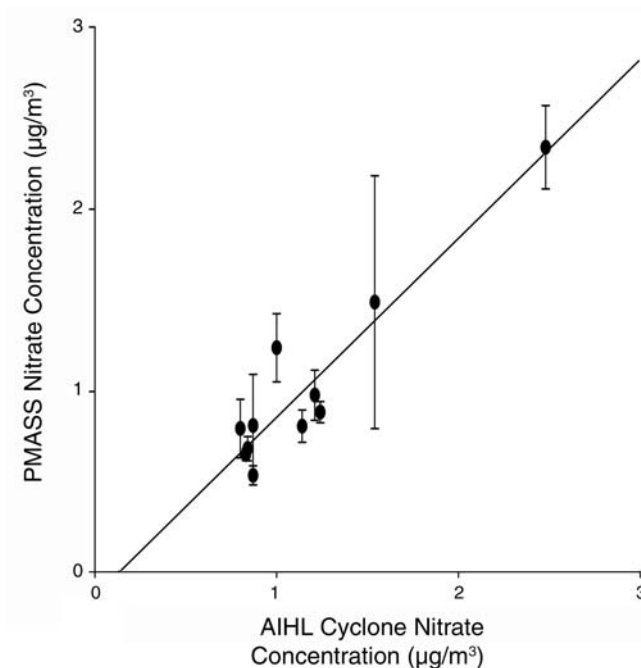


Figure 15. Accuracy of microenvironmental sampling in Fresno: PMASS versus AIHL cyclone nitrate measurements. Slope = 0.99 ± 0.10 , $r^2 = 0.75$; intercept = -0.12 ± 0.13 , $P = 0.35$. Each error bar = 1 SD. Both the SD and r^2 were calculated from the original PMASS data.

Sulfate data were not analyzable as a result of the large magnitude and variability of the sulfate blanks resulting from an analytical problem in the laboratory (which has since been resolved). The average PMASS sulfate blank value represented 91% of the sulfate concentration found on PMASS sample filters.

Personal Sampling

Evaluation of the PMASS as a personal sampler was conducted over 6 weeks in Baltimore. Sampling periods ranged from 1018 to 1568 minutes. The accuracy of PMASS mass measurements was estimated from least squares linear regression against PEM measurements (Table 5). The measurement precision for each analyte was determined by the RMSE method (Table 6).

PMASS mass measurements were in modest agreement with adjusted PEM values; the PMASS showed a measurement bias of -24% (Figure 16). PMASS measurement precision for mass was estimated to be 24.2% .

PMASS measurement precision for elemental carbon was 8.1% , essentially equivalent to that found for microenvironmental sampling. PMASS measurement precision for organic carbon was estimated at 19.3% .

PMASS measurement precision for nitrate was estimated to be 19.1% .

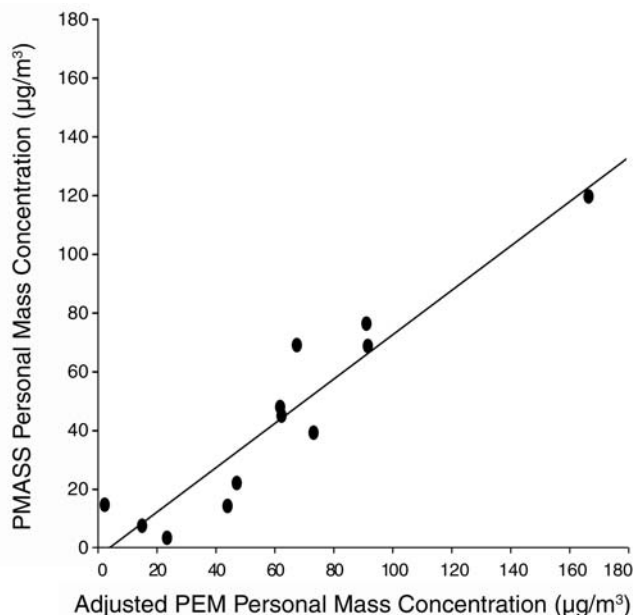


Figure 16. Accuracy of personal sampling in Baltimore: PMASS versus adjusted PEM personal mass measurements. Slope = 0.76 ± 0.09 , $r^2 = 0.89$; intercept = -2.82 ± 6.38 , $P = 0.67$. PEM mass measurements were adjusted downward by 22% to eliminate measurement bias compared with the Harvard impactor. Each error bar = 1 SD. Both the SD and r^2 were calculated from the original PMASS data.

DISCUSSION

PMASS CYCLONE INLET PERFORMANCE

The internal dimensions of the PMASS cyclone inlets are identical to those of the Hering prototype, so we expected the performance to be the same. Because construction details differed in order to accommodate the plastic sampler body, however, laboratory tests were necessary to verify the 50% cutpoint, to assess similarity among the six PMASS units, and to examine their performance under several operational conditions.

Because the PMASS is designed to be worn by a person, the sampler was tested in different orientations—upright, sideways, and inverted. These orientation tests were done with a clean cyclone and with the same cyclone loaded with Arizona road dust. The performance of the cyclone was the same before and after loading with dust. No difference was seen among any of the sampler orientations with or without loading (Figures 6 and 7).

For all six PMASS units, the mean (\pm SD) 50% cutpoint (or aerodynamic diameter of particles that penetrated with an efficiency of 50%) was $2.52 \pm 0.08 \mu\text{m}$ at a flow rate of 4.1 L/min . The six samplers were fabricated at two different times with slight modifications in construction. The first two samplers had a mean (\pm SD) 50% cutpoint of $2.61 \pm 0.03 \mu\text{m}$; the remaining four samplers had a mean 50% cutpoint of 2.48 ± 0.03 .

The shapes of the PMASS cyclone penetration curve and the FRM curve for $\text{PM}_{2.5}$ were not exactly the same. The PMASS cyclone allowed somewhat greater penetration from 3 to $5 \mu\text{m}$ in aerodynamic diameter (Figure 5). This difference occurred because the FRM curve is based on an impactor, which has an inherently sharper cutpoint than does a cyclone. The disadvantages of impactors (such as the required application of oil or grease to minimize rebound and the change in cutpoint with particle loading on the impaction surface) made them a poor choice for the speciation application desired in this study, however.

We evaluated whether the difference between the PMASS and the FRM in the shape of the $\text{PM}_{2.5}$ penetration curve was important by using the FRM criteria. The FRM criteria for an equivalent $\text{PM}_{2.5}$ method specify a tolerance of $0.2 \mu\text{m}$ for the 50% cutpoint (mean \pm SD = $2.5 \pm 0.2 \mu\text{m}$) and a penetration of $\text{PM}_{2.5}$ mass for three aerosol size distributions within 5% of that obtained in the FRM curve (Peters et al 2001). The three test size distributions—labeled *coarse*, *typical*, and *fine*—correspond to bimodal size distributions in which the fractions of mass above $2.5 \mu\text{m}$ were 73% , 45% , and 6% of the mass of particulate matter $\leq 10 \mu\text{m}$ in aerodynamic diameter (PM_{10}), respectively.

When the PMASS was operated at 4.1 L/min such that its 50% cutpoint was 2.5 μm , it met the FRM criteria for both typical and fine aerosol. For the coarse size distribution, particles that penetrated the PMASS cyclone were 7% larger than for the FRM curve, exceeding the specified 5% tolerance. This result indicates that the PMASS inlet curve was equivalent to the FRM curve under most circumstances. When the mass of airborne particles was dominated by those above 2.5 μm in aerodynamic diameter, however, the more gradual slope of the PMASS cyclone penetration curve led to an oversampling bias of a few percent.

The 50% cutpoint of the cyclone inlet depends on flow rate (Figure 8). These data are fit by a curve of the form:

$$D_{50} = 9.56Q^{-0.94}.$$

where D_{50} is the aerodynamic 50% cutpoint (in microns) and Q is the flow rate (in liters per minute). As extrapolated from the above equation, for flow rates between 3.8 and 4.6 L/min, the PMASS cyclone 50% cutpoint varied from 2.3 μm to 2.7 μm , which is within the 2.5 ± 0.2 μm tolerance specified by the FRM criteria. Over this same range, the ratios of mass that penetrated the cyclone for typical and fine size distributions are within the 5% of that which would penetrate the idealized FRM curve. At the lowest flow rate we tested, 3.1 L/min, the PMASS cyclone allowed 15% more mass penetration for the coarse size distribution than penetrates the idealized FRM curve.

As in an earlier study (Hering et al 2003), both liquid and solid particles were tested in the laboratory. Solid particles are prone to bounce and reentrainment, leading to penetration of particles larger than the 2.5 μm 50% cutpoint. These larger particles are then collected on the sampler filter, leading to an artifact termed *oversampling*. On the other hand, liquid particles are more susceptible to impaction on the walls of the cyclone, which leads to undersampling. Reliable performance of the inlet requires nearly equal performance for both liquid and solid particles.

When particle rebound and reentrainment become problems, the discrepancies between solid and liquid particle collection are evident for large particles. Figure 9 shows no difference in penetration of liquid and solid particles for particle sizes above the 50% cutpoint. Thus we conclude that particle rebound does not affect the size-selective characteristics of the PMASS cyclone inlet.

Polystyrene latex showed a somewhat smaller cut size than either the road dust or oleic acid aerosols. The reason for this discrepancy is not yet resolved; it might be a systematic difference in the aerodynamic sizing of these particles by the Aerodynamic Particle Sizer.

The laboratory measurements of inlet penetration also indicate a slight difference between the two types of solid particles and the liquid oleic acid particles between 1.5 and 2.3 μm , with greater penetration indicated for the liquid aerosol. We know of no mechanism by which liquid particles are collected less efficiently than solid particles, so we must assume that this difference is due to a limitation in measurement. Whereas precision of the size cut measurements indicated by replicate measurements with the same test aerosol was ± 0.02 μm , the differences found between different types of tests (data not shown) limit the accuracy of the size cut measurement of ± 0.1 μm .

FIELD TESTING

Field tests of the PMASS as a personal sampler demonstrated that it is small enough to be worn easily by a person undergoing a typical personal sampling field protocol. The sampler is very lightweight and compact.

The areas of the filter deposits were clearly demarcated on the filter. This precisely defined filtration area is important to area-specific assays (such as analysis of organic and elemental carbon).

The passive split flow between the two channels was stable, introducing less than 1.5% uncertainty in the sample volume per channel. This stability supports the use of a single pump for operation of both channels, reducing both weight and cost of personal sampling. The ability to collect multiple samples using a single pump is a distinct advantage in any personal particle exposure study because the pump contributes a large fraction of the total weight of the sampling system.

The absence of valving to control the flow through each channel allows for sample collection on multiple filters using a single pump. This feature is a distinct advantage over the only other personal particle sampler, which uses a small, valved, four-port manifold to connect a set of individual particle samplers to one pump. To attain the desired flow rate for each filter, the flow through each port must be balanced because a flow adjustment for one filter affects the flow through all the others. Preparing that personal sampler for deployment in the field can be fairly time consuming.

During the initial development of the PMASS, the filtration medium for the inorganic sampling channel was selected to be compatible with mass determinations by β gauging. Teflo filters, which are often used for gravimetric mass determinations, were not used in the PMASS because they are too nonhomogeneous for β gauging. We did not conduct β gauging in this study because prior work did not show that the approach sufficiently improved the precision of mass determinations to justify its complications (Hering

et al 2003). Our continued use of Fiberfilm filters, however, complicated the gravimetric mass measurements. In some instances the filters were not mechanically stable, tending to shred or tear, which invalidated those gravimetric assays. These complications did not, however, affect nitrate and sulfate determinations.

Field testing uncovered some difficulties with extended use of the PMASS. The Teflon spacers between the front and backup filters did not retain their size tolerance with use, making the filter packs difficult to disassemble. In addition, the o-rings in the end caps tended to bind in the end caps, creating difficulty in sampler assembly and disassembly. The Fiberfilm filters were sometimes damaged during disassembly.²

Aerosol chemistry data showed that the PMASS results were best for organic and elemental carbon. PMASS precision for both microenvironmental and personal sampling for elemental carbon met our target of 10%. Linear regression analysis of PMASS compared with the AIHL cyclone and Harvard impactor data for elemental carbon indicated a negative and a positive bias, respectively. On the other hand, the ratios of mean elemental carbon concentration measured by the PMASS to those measured by the AIHL cyclone and Harvard impactor were 0.94 and 0.90, respectively, indicating a bias of less than 10% and a change in bias direction for the Harvard impactor. These contradictory assessments of bias arise from the small dynamic range and the small absolute values in elemental carbon concentrations observed in this study (Table 5).

Precision of the PMASS measurements for organic carbon was within our target of 10% for microenvironmental sampling but was 19.3% for personal sampling. The greater imprecision in personal organic carbon measurements is attributable to the exceptionally high organic carbon values found for two of the indoor samples, which were heavily influenced by environmental tobacco smoke.

2. The mechanical problems contributing to losses of Fiberfilm filter mass have since been resolved through improved machining of parts and substitution of a stiffer, glass-impregnated Teflon material for the spacer. To evaluate the success of the remachined components, we conducted another evaluation of the PMASS. Two samplers were operated side by side at the Aerosol Dynamics laboratory (Berkeley CA). Teflo filters were used in place of Fiberfilm filters because they provided a more stringent test of excessive sealing pressure; the stretched membrane has a greater tendency to tear under abrasion. In addition, other investigators have expressed interest in using the Teflo filter. Each channel of the samplers was loaded with a 25-mm Teflo filter for replicate mass sampling. All four channels were connected individually to critical orifice-controlled pump lines so that flow rate uncertainty was minimized. Each flow line was individually calibrated and the total inlet flow was measured before and after each run to correct for flow rate drift. Filter samples were handled as in the field study with the addition of a 24-hour equilibration under the prevailing moderate humidity and temperature in the laboratory. Three sampling sessions were conducted for a total of 12 samples over 22 to 44 hours. Visual inspection of each filter after sampling showed no holes or tearing, indicating that the problem had been corrected. Collected mass was 5 to 13 μg per filter with a mean of 6.9 μg . The pooled SD of the 6 pairs of samples was 1.1 μg , a level of precision on the order of the microbalance itself.

Regression analysis of the PMASS organic carbon data against the AIHL cyclone and Harvard impactor data yield slopes that do not differ significantly from 1. The lack of PMASS bias is in part attributable to the similar filter face velocity for the PMASS, AIHL cyclone, and Harvard impactor (26 cm/sec, 31 cm/sec and 20 cm/sec, respectively). Artifacts that arise from adsorption of organic vapors or loss of volatile organic aerosols depend on filter face velocity. Denuder methods designed for more accurate collection of organic aerosols is a current area of research. As effective denuders are developed, they can be incorporated into the PMASS.

Precision for particulate nitrate collected during microenvironmental sampling—11.9% for Fresno and 13.6% for Baltimore—just exceeded our target value of 10%. The nitrate concentrations are derived from the sum of the front and backup filters in the denuded sampling channel. The relatively poor precision for nitrate is consistent with prior work (Hering et al 2003) and in part reflects the low nitrate concentrations collected.

PMASS nitrate values were compared with those from the AIHL reference sampler, which also had a denuder and backup filter. The regression slope (0.99 ± 0.10) and the ratio of mean PMASS nitrate measurements to mean AIHL reference nitrate measurements (0.94) showed no systematic bias between the two methods. In contrast, PMASS nitrate values did not agree with Harvard impactor and PEM nitrate samples, highlighting the necessity of the denuder-backup filter system when sampling for nitrate.

Comparison of the front and backup filters for nitrate also underscores the importance of the denuder-backup filter method for this volatile species. The Fresno samples were collected during a period of high ambient temperatures (daytime highs of 36°C to 41°C), resulting in lower-than-normal nitrate concentrations. On July 9, when ambient temperatures reached 41°C, the backup filter collected 66% of the total nitrate collected by the PMASS and 21% of that collected by the AIHL cyclone. Although the total particulate nitrate concentrations collected by the PMASS and by the AIHL reference sampler were similar (2.3 and 2.5 $\mu\text{g}/\text{m}^3$, respectively), the distribution between the front and backup filters differed. Without the denuded backup filter, the nitrate concentrations from these two samplers would have differed by more than a factor of 2. This example shows that a denuded backup filter is important for providing consistency among samplers of differing designs as well as providing a more accurate measure of particulate nitrate.

For sulfate, the blank values were as high as those of the sulfate mass loadings. This result was unexpected because precision for sulfate measurements is generally good by comparison with other analytes.

CONCLUSIONS

In many respects, the PMASS was found to be suitable for use as a personal or microenvironmental sampler. Its cyclone inlet performed well in the laboratory and in the field, and it met the FRM criteria for a PM_{2.5} inlet for typical size distributions when operated at a flow rate between 3.8 and 4.6 L/min. The inlet performed equally well for upright and inverted orientations and it was not sensitive to the amount of deposit within the inlet. The passive split flow was stable within 1.5%, permitting operation of both channels by a single sampling pump. The personal sampling staff appreciated the compact and light-weight PMASS.

Recovery of volatilized nitrate was crucial in measuring particulate nitrate. The PMASS results agreed with those of the reference sampler (AIHL cyclone) even when the amount of volatilization off the primary filter differed between the two samplers by more than a factor of 2. The summed front and backup filter nitrate mass was equivalent for the PMASS and reference AIHL cyclone. Accurate nitrate sampling was thus demonstrated under adverse conditions.

Collocation experiments with reference samplers during microenvironmental sampling demonstrated that PMASS accuracy based on ratio of means was within or near the target level of 10% of the reference sampler for all species in Fresno and Baltimore, excepting organic carbon collected in Fresno (15% bias). In contrast, the best agreement between the PMASS and a reference sampler was for the same species, organic carbon, in Baltimore (2%). Without an accepted method for recovery of volatilized organic vapor, as for nitrate, accurate measurement of organic carbon is difficult in hot environments such as in Fresno. Under appropriate conditions, however, the PMASS was accurate to within 10% as assessed by ratio of means of the reference sampler for microenvironmental sampling of nitrate and organic and elemental carbon.

Our goal of precision within 10% was met for elemental carbon and organic carbon at both sampling sites. Nitrate and mass precision were estimated at 11.9% and 12.7% in Fresno and 13.6% and 17.5% in Baltimore, respectively. We experienced problems with the Fiberfilm filters for gravimetric mass analysis: the PMASS improperly applied excess sealing force and caused loss of filter fiber and negative mass biases. Multiple design corrections and modifications were discovered in the course of this study, all of which have since been addressed.

Precision for PMASS microenvironmental sampling was, therefore, approximately 10% for carbonaceous aerosols and 15% for nitrate. We may infer a precision level of 10% for sulfate, as measured in a previous study (Hering et

al 2003), because measurement of this species traditionally has been one of the most precise.

In summary, the PMASS was found to possess the following characteristics:

- *Size and ease of use.* At approximately 310 g and 300 cm³, the PMASS is a compact, light sampler for personal sampling. The need for only a single pump to provide two parallel sets of filter samples further reduces the wearer's burden.
- *Fine-particle collection.* The PMASS inlet has undergone thorough laboratory testing with liquid and solid particles. It collects particles in agreement with the FRM for fine and typical aerosol distributions and is only slightly biased for coarse aerosol distributions.
- *Design.* To accurately sample volatile species such as nitrate, the PMASS can be equipped with a denuder or backup filter or both in either channel. These additions remove gaseous interferants and reduce particle volatilization. The shared inlet for the two channels is ideally suited for replicate sampling during personal exposures.
- *Accuracy and precision.* The PMASS is accurate and precise for microenvironmental sampling of organic carbon, elemental carbon, and nitrate at the approximately 10% level. Similar levels of accuracy have been inferred for sulfate on the basis of prior work. Precision for personal sampling was estimated from 8% to 24%, but further testing is needed to more accurately define a specification.

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 ABOUT THE AUTHORS

Alison S Geyh is assistant professor at the Johns Hopkins Bloomberg School of Public Health, Department of Environmental Health Sciences. Her work related to the World Trade Center disaster has included air monitoring and exposure assessment of one group of workers at the site in addition to a health assessment of approximately 4500 workers who were involved in the cleanup and recovery effort. Her other research interests include assessing the impact of vehicle-related air pollution on the health and environment of inner-city residents and an exploration into the specific chemical composition of metal species found in particulate matter. She holds a PhD in physical organic chemistry from Brandeis University.

Susanne Hering is founder and president of Aerosol Dynamics Inc, a small research firm specializing in the development of measurement methods for fine, airborne particles. She holds an AB in physics from the University of California at Santa Cruz and a doctorate in physics in 1974 from the University of Washington, with an experimental thesis in the field of low-temperature physics. At Aerosol Dynamics Inc she codeveloped an automated system for high-time resolution measurement of fine particulate nitrate and sulfate (commercialized by Rupprecht and Patashnick) and a two-week integrated sampler for ambient fine particle mass and ionic species. She has directed numerous air quality field studies and is currently president of the American Association for Aerosol Research.

Nathan Kreisberg received an AB in physics from the University of California at Berkeley in 1983 and a PhD in physics from the University of Texas at Austin in 1991. His postdoctoral work was conducted at Los Alamos National Laboratory from 1991 to 1993 in numerical simulations of aerosol particle transport. Employed at Aerosol Dynamics Inc since 1994, he is involved with development of aerosol measurement techniques for atmospheric and laboratory sampling of airborne particles. His current research interests

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Walter John has a BS in physics from California Institute of Technology and a PhD in physics from the University of California at Berkeley. He was an instructor at the University of Illinois and professor and chairman of the Physical Sciences Department, California State College at Stanislaus. His principal career appointments were at the Lawrence Livermore National Laboratory from 1958 to 1971, where he was Nuclear Reactor Research Group leader and at the California Department of Health Services from 1974 to 1992, where he headed the aerosol and microscopy laboratories. He is presently retired and consults part time on the development of aerosol sampling instruments. His research interests include studies of the basic properties of aerosols in the laboratory and in the atmosphere as well as the technology of aerosol sampling and analysis. He has been a director of the American Association for Aerosol Research and on the editorial boards of several journals. He has over 100 publications in journals and books. He is a fellow of the American Physical Society.

 ABBREVIATIONS AND OTHER TERMS

AIHL	Air and Industrial Hygiene Laboratory
EPA	Environmental Protection Agency (US)
FRM	federal reference method
PEM	personal environmental monitor
PM	particulate matter
PM _{2.5}	PM \leq 2.5 μm in aerodynamic diameter
PM ₁₀	PM \leq 10 μm in aerodynamic diameter
PMASS	personal and microenvironmental aerosol speciation sampler
r^2	coefficient of determination for bivariate analysis
RMSE	root mean squared error

Over the last several decades, evidence has accumulated suggesting that exposure to ambient particulate matter (PM*), which includes particles from different sources and of varying size and composition, may be associated with health effects on the cardiovascular and respiratory systems (Pope and Dockery 1999). Ambient PM tends to have a trimodal size distribution by diameter: coarse particles (> 1 µm), fine particles (0.1 to 1 µm), and ultrafine particles (< 0.1 µm). The main components of ambient PM are elemental and organic carbon, inorganic ions (ammonium sulfate and ammonium nitrate), and trace elements. Because of concerns about health effects, US Environmental Protection Agency (EPA) regulates through the National Ambient Air Quality Standards ambient levels of PM with a diameter of 2.5 µm or less (PM_{2.5}) (EPA 1997).

Although a large body of epidemiologic research suggests that ambient PM may cause both acute and chronic health effects (Pope and Dockery 1999), lack of information on several key measures of exposure to particles complicates interpretation of this research, assessment of human risk, and design of control strategies. An important step in improving exposure estimates in epidemiologic studies is to characterize personal exposure to PM and its components, especially in individuals who may be sensitive to the effects of PM. Although portable, lightweight samplers have been developed for measuring PM personal exposure on a mass basis, the lack of an instrument that can measure specific PM components simultaneously has been a major limitation.

Through Requests for Preliminary Applications (RFPAs), HEI supports studies that are compatible with its overall research priorities but that are outside the areas currently targeted in its Requests for Applications. In September 2000, Dr Alison Geyh of Johns Hopkins University submitted a preliminary application in response to RFPA 98-6, entitled "Field Evaluation of the Personal Particle Speciation Sampler." The application proposed testing a personal sampler in the field for simultaneous measurement of PM_{2.5} mass, elemental and organic carbon, sulfate, and nitrate. A prototype sampler had been developed by Dr Susanne Hering with HEI funding (Hering et al 2003). After evaluating the preliminary application, the HEI Health Research Committee requested a full application and subsequently recommended that HEI fund the Geyh

study.[†] The Committee believed that the sampler's initial development was promising and that, if properly evaluated, the sampler could be useful for personal exposure assessment, especially in children, because of its lightweight construction. This Critique is intended to aid HEI sponsors and the public by highlighting the strengths of the study, pointing out alternative interpretations, and placing the research into scientific perspective.

SCIENTIFIC BACKGROUND

MEASURING PERSONAL EXPOSURE TO PM

Most epidemiologic studies of the health effects of air pollution have used measurements of PM mass taken at stationary monitoring sites as surrogate values of personal exposure. When Dr Geyh submitted her application, there was a need to improve exposure assessment in epidemiologic studies not only to assess the assumption that ambient PM level could be used as an indicator of personal exposure (within a subject's breathing zone) but also to characterize personal exposure to PM and to identify the components of that exposure.

Because identification of different particle components require different analytic methods and collection substrates, a personal sampler must collect sufficient material on multiple substrates and it also must be lightweight enough to be carried by study participants during their daily activities. If personal exposure is measured by determining pollutant concentrations in the microenvironments in which subjects spend most of their time, however, sampler weight is less of an issue because the sampler is stationary.

SAMPLING AND MEASURING PM

Currently, two approaches are used to measure PM. One is based on time-integrated analysis of PM collected on a substrate over a specified period of time, and the other is based on in situ analysis, which yields real-time, continuous measurements of some PM components. Time-integrated measurement can be biased due to sampling artifacts (losses

* A list of abbreviations and other terms appears at the end of the Investigators' Report.

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[†] Dr Geyh's 14-month study, "Field Evaluation of the Personal Particle Speciation Sampler," began in November 2001. Total expenditures were \$138,027. The draft Investigators' Report from Geyh and colleagues was received for review in January 2003. A revised report, received in September 2003, was accepted for publication in October 2003. During the review process, the HEI Health Review Committee and the investigators had the opportunity to exchange comments and to clarify issues in both the Investigators' Report and in the Review Committee's Critique.

or gains of semivolatile components) and does not allow good time resolution. It does allow, however, collection of sufficient material for analysis of components present in small amounts. In situ measurement provides real-time information, but the instruments used (especially for compositional analysis) are heavy and complex.

Samplers used for time-integrated analysis of PM generally contain a size-selective inlet that separates out the desired size fraction of PM, a collecting filter, and a pump that draws air through the inlet and the filter at a constant rate.

Size-selective inlets are characterized by two features: (1) the size cutpoint, defined as the particle diameter at which 50% of particles pass through the inlet for collection and the other 50% are trapped in the inlet, and (2) the sampling effectiveness (or penetration efficiency), the fraction of particles in the air that actually penetrate the inlet as a function of diameter (Chow 1995). Because these two parameters depend highly on flow rate, testing conditions, and inlet type, the samplers used for PM_{2.5} compliance monitoring need to conform to the EPA's federal reference method criteria (EPA 1997). These criteria specify both the cutpoint range and the penetration efficiency.

The most common size-selective inlets used to sample fine and coarse particles are cyclones and impactors (Critique Figure). A cyclone is a conical chamber that causes circular airflow. This flow creates a centrifugal force that causes particles above a certain size to impact the chamber walls and the bottom while smaller particles flow out of the chamber through a cylindrical tube perpendicular to the flow, where they can be collected (Chow 1995; McMurry et al 2004). An impactor uses an impaction plate in the path of the airflow, on which large particles deposit. Smaller particles follow the flow as it bends at the plate and can be collected downstream. Because some large particles can bounce off the impaction surfaces, in both

cyclones and impactors these surfaces are generally oiled or greased to retain the particles. Several types of cyclones and impactors that operate at different flow rates are available commercially.

Denuders are often placed upstream of the collecting filter to remove gases (such as sulfur dioxide and nitrogen dioxide) that may interfere with collection of PM and with measurement of mass and some particle components (such as sulfate and nitrate) (Chow 1995). Moreover, because nitrate distribution between the gas phase and PM phase is very sensitive to small changes in temperature, nitrate may evaporate (in the form of ammonium nitrate) from the particles collected during the sampling period. Thus, to accurately measure nitrate, a backup filter impregnated with a nitrate-reactive compound is placed downstream of the primary filter to absorb any volatilized nitrate (McMurry et al 2004). Total particle nitrate is determined by summing the nitrate measured on the primary and the backup filters.

PM Mass

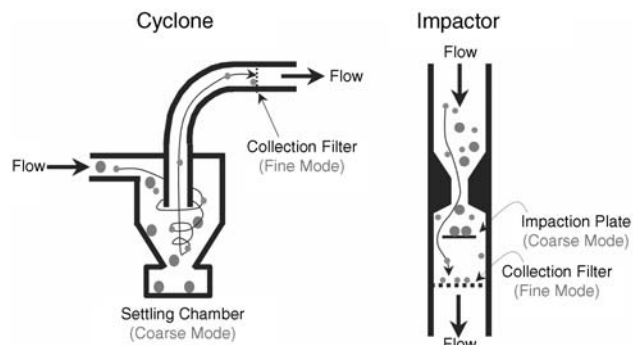
Particle mass can be measured using several techniques: gravimetric measurement, β attenuation, and vibrational microbalance methods. Gravimetry, the most common method, provides time-integrated measures, typically over several hours. It is also used to determine regulatory compliance. Gravimetry measures the net weight of particles collected on a filter, generally Teflon, after sampling (under conditions of controlled temperature and humidity).

In β attenuation, a β -gauge device measures attenuation of high-energy electrons (β radiation emitted from a radioactive source) through the filter sample (McMurry et al 2004). Measurement error may arise because β absorption is calibrated for mass and actual weight is not directly measured.

Vibrational microbalance techniques include the one used in the tapered element oscillating microbalance (TEOM). The TEOM optically measures the frequency shift of an element's oscillation caused by increasing inertial PM mass accumulating on a substrate mounted on the thin end of a tapered oscillating hollow element (McMurry et al 2004).

PM Composition

Various filters are available for collecting PM for compositional analysis (for a review, see Chow 1995), but no single filter medium is appropriate for all desired analyses. Inorganic ions, metals, and individual organic compounds can be analyzed in the PM collected on the filter used for mass determination. Analysis of elemental and total organic carbon requires collecting particles on a noncarbonaceous quartz fiber filter, which does not interfere with thermal analyses of these species.



Critique Figure. Two inlets commonly used for particle size separation, illustrating separation of smaller (fine mode) particles from larger (coarse mode) particles. Geyh and colleagues' PMASS uses a cyclone inlet. Figure adapted from McMurry et al 2004 and printed with permission from NARSTO.

PERSONAL PM SAMPLERS

Personal samplers are designed to be carried by an individual and to sample the local air, possibly from the breathing zone, over a given period of time. They must be lightweight, stable under different conditions (eg, varied orientations and rates of airflow), and able to collect sufficient PM on multiple substrates for compositional analyses.

When this study was funded, several personal samplers were available for collecting PM on a single filter for mass, sulfate, and nitrate determination but none were designed to collect particles simultaneously on multiple substrates. The Harvard personal sampler uses a PM_{2.5} impactor followed by a two-filter pack containing a primary Teflon filter (Koutrakis et al 1988; Brauer et al 1989) and a backup filter to collect volatilized ammonium nitrate. The personal environmental monitor (or PEM; MSP Corp, Minneapolis MN) is a similarly lightweight sampler available with either a PM_{2.5} or a PM₁₀ impactor but it lacks a denuder and a backup filter. Janssen and colleagues (2000) used a PM_{2.5} cyclone (BGI, Waltham MA) with a single filter to measure personal exposure to PM_{2.5}.

The first version of a multipollutant personal sampler used two PEMs (one for PM_{2.5} and one for PM₁₀) operated by a single pump and also used passive samplers for gaseous species (Chang et al 1999; Sarnat et al 2000).

Before Geyh and colleagues' study, Dr Susanne Hering and colleagues developed, with HEI funding, a prototype multipollutant sampler named the *personal particle speciation sampler* (or PPSS; Hering et al 2003). By splitting airflow into two channels, the sampler allowed collection of particles on one substrate for determination of PM_{2.5} mass, nitrate, and sulfate and on a second substrate for elemental and organic carbon. This sampler was tested to evaluate various size-selective greaseless inlets, the β attenuation method for determining PM mass, and the precision of passive split flow between the two channels (Hering et al 2003). In addition, a small number of field tests were conducted in Fresno, California, to evaluate the sampler's field performance.

TECHNICAL EVALUATION

STUDY AIMS

The primary objective of Geyh's 14-month study was to evaluate the precision and accuracy of the Hering prototype used as a personal or a microenvironmental sampler in Baltimore, Maryland, and Fresno, California. Precision refers to the variation in measurements under constant conditions, calculated in this study as percent difference.

Accuracy refers to a sampler's ability to correctly measure the true amount of a species in the air, calculated as percent difference from measurements of reference samplers. Geyh and colleagues set a target of achieving 10% precision and 10% accuracy for all species measured.

Although not part of the original study aims, Geyh and coworkers made a number of modifications to the sampler's design after the study began, which necessitated further laboratory tests. They also renamed it the *personal and microenvironmental aerosol speciation sampler* (PMASS) to reflect its possible uses in the field. The PMASS provides time-integrated measurements of PM mass and PM components.

STUDY DESIGN AND METHODS

PMASS Design

The PMASS consists of a cyclone with a size cutpoint of 2.5 μm through which ambient air is drawn at a flow rate of 4 L/min. Downstream of the cyclone, the airflow splits between two channels. In the design tested by Geyh and colleagues, one channel contained a quartz fiber filter; the other channel contained a denuder and, downstream of the denuder, two filters separated by a Teflon spacer disk: a primary Fiberfilm filter and a sodium chloride-impregnated cellulose backup filter to capture volatile material (in particular, volatilized nitrate) that might be lost from the primary filter.

Major modifications of the Hering prototype included: (1) overall weight reduction from 620 grams to 310 grams, accomplished by manufacturing the body from low-density polyethylene rather than aluminum (with aluminum still being used for the cyclone and the internal surfaces); (2) redesign of the cyclone size-selective inlet to fit into the new polyethylene body, (3) modification of the filter holders to accommodate gravimetric analysis of mass rather than β gauging; and (4) use of orifice plates to compensate for differences in pressure drop across filter media in the two channels.

Laboratory Tests of Size-Selective Inlet

In order to determine that the redesigned inlet conforms to the federal reference method for PM_{2.5}, the investigators measured the size-dependent PM penetration efficiency as a function of flow rate, inlet orientation, and particle load on the impaction plate. These tests used solid particles (polydispersed polystyrene latex particles with diameters from 1 to 20 μm and Arizona road dust with diameters from 1 to 80 μm) and liquid particles (monodispersed oleic acid particles with a mean diameter of 1 μm). An aerodynamic particle sizer sampled the flow upstream and

downstream of the cyclone to measure the PM size distributions in both locations. One channel was tested at a time in the absence of a filter.

Field Sampling to Measure Precision and Accuracy

Dr Geyh evaluated the PMASS as a microenvironmental sampler in Fresno (outdoors) and Baltimore (indoors) and as a personal sampler in Baltimore. The Fresno site was selected for its high ambient levels of nitrate.

Precision was calculated as the percent variation among measurements taken in the same location at the same time by two or three PMASS units. Accuracy was evaluated using two approaches. In one approach, regression analysis was used to quantify the correlation between the PMASS measurements and the reference sampler measurements. In this case, accuracy was expressed as the percent difference between the observed slope and the ideal target slope of 1 (if the PMASS agreed perfectly with the reference sampler). In the other approach, accuracy was calculated as the ratio of the means of the PMASS measurements and the reference sampler measurements. A ratio of 1 would indicate perfect agreement between the two samplers. The comparisons made and the numbers of samples collected were as follows.

- **Baltimore microenvironmental sampling (October–November 2002):** The reference sampler was the Harvard impactor (first described by Marple et al 1987) operating at a flow rate of 10 L/min. Two Harvard impactors (one containing a Teflon filter and one containing a quartz fiber filter) and two to three PMASS were used for each measurement. Because neither Harvard impactor had a denuder or a backup filter, accuracy was not determined for nitrate. Sampling periods ranged from 16 to 58 hours. Nine to thirteen sets of PMASS measurements were used to determine precision of the various species, and 13 sets of PMASS/Harvard impactor measurements (of 15 sets collected) were used to determine accuracy.
- **Fresno microenvironmental sampling (July 2003):** The reference sampler was the Air and Industrial Hygiene Laboratory (AIHL) cyclone operating at a flow rate of 24 L/min. Like the PMASS, this sampler has two channels. One contained a denuder, a Fiberfilm filter, and a backup filter; the other, a quartz fiber filter. Sampling periods ranged from approximately 9 to 13 hours. Twelve sets of measurements were obtained by three PMASS and one AIHL cyclone for determination of precision and accuracy.
- **Baltimore personal sampling (October–November 2002):** The reference sampler was the PEM operating at a flow rate of 4 L/min. The PEM has a single channel

containing a Teflon filter. For this study, four volunteers (two of whom were technicians at the Johns Hopkins School of Public Health) wore either two PMASS units or a PMASS and a PEM. Each sampling session lasted approximately 17 to 26 hours. Nine sets of PMASS/PMASS measurements (of 14 collected) were used to determine precision for mass only and 16 sets of PMASS/PEM measurements (of 17 collected) were used to determine accuracy of mass only. In addition, Geyh and colleagues compared the PEM (used as microenvironmental sampler) with the Harvard impactor.

Total inlet flow and split flow measurements were made at the monitoring sites before and after each sampling session for all PMASS samplers. Additional samples (10% of the total number of field samples) were collected as blanks by using the PMASS and the Harvard impactor operating at zero flow.

Analytic Methods

At the Johns Hopkins Bloomberg School of Public Health in Baltimore, mass on Fiberfilm and Teflon filters was determined gravimetrically. Nitrate and sulfate were extracted from the primary filter and the backup filter (when present) and their concentrations determined by using ion chromatography (nitrate concentrations were not determined in samples collected by the Harvard impactor and the PEM). Elemental and organic carbon concentrations were determined by using thermal optical reflectance of the quartz fiber filters by a contract laboratory. The values were corrected by subtracting blank values obtained from the additional samples collected at zero flow. Blank values were determined for all species collected by the PMASS and for mass for the Harvard impactor. They were estimated for elemental and organic carbon collected by the AIHL cyclone. No blank samples were collected or estimated for mass, nitrate, or sulfate measured by the AIHL cyclone or for mass measured by the PEM. Nitrate values for all blank samples were below the limit of detection.

RESULTS

Verification of Inlet Cutpoint and Split Flow

The average cutpoint of the PMASS was $2.52 \pm 0.08 \mu\text{m}$ at a flow rate of 4.1 L/min, and it increased with decreasing flow rate. This average value is very close to the target federal reference method cutpoint for $\text{PM}_{2.5}$, which is based on sampling by an impactor (EPA 1997). In comparison with the federal reference method penetration curve, the cyclone allowed 5% to 7% greater penetration for particles 3 to 5 μm in aerodynamic diameter. Some differences in cutpoint

Critique Table. Summary of Precision and Accuracy Data

	Mass	Sulfate	Nitrate	Elemental Carbon	Organic Carbon
PMASS precision					
Baltimore microenvironmental	17.5%	ND ^a	13.6%	6.6%	8.7%
Fresno microenvironmental	12.7%	ND	11.9%	6.8%	9.0%
Baltimore personal	24.2%	ND	19.1%	8.1%	19.3%
Accuracy comparisons					
PMASS vs Harvard impactor	-33%	ND	NM ^b	+24%	+8%
PMASS vs AIHL cyclone	ND	ND	-1%	-26%	+3%
PMASS vs PEM	-24%	ND	NM	NM	NM
PEM vs Harvard impactor	+22%	ND	NM	NM	NM

^a ND = not determined.

^b NM = not measured by sampler (either Harvard impactor or PEM).

were found for the three aerosols, with the inlet having a slightly smaller cutpoint for polystyrene latex particles. Inlet performance was not affected by sampler orientation or by preloading of the cyclone with Arizona road dust.

The average difference in flow between the two PMASS channels for all tests was 1.7% to 3.2%, indicating that air-flow was split evenly.

PEM Versus Harvard Impactor

The average PEM mass measurements were 22% higher than the average Harvard impactor measurements. The investigators corrected all data collected by the PEM by subtracting 22%.

PMASS Precision and Accuracy

Results of comparisons made between collocated PMASS samplers or collocated PMASS and reference samplers are summarized in this section and in the Critique Table. Neither precision nor accuracy for sulfate could be determined because the sulfate blank values were very high (owing to analytic problems). After extended use of the PMASS, Geyh and colleagues also reported difficulty in removing Fiberfilm filters, owing to deformation of some spacer disks.

- **Baltimore microenvironmental sampling:** Precision of the PMASS measurements was 17.5% for mass, 6.6% for elemental carbon, 8.7% for organic carbon, and 13.6% for nitrate. Mass measured by the PMASS was on average 33% lower than that measured by the Harvard impactor, elemental carbon was 24% higher, and organic carbon was 8% higher.
- **Fresno microenvironmental sampling:** Precision of the PMASS measurements was similar to that determined in Baltimore: 12.7% for mass, 6.8% for elemental carbon, 9.0% for organic carbon, and 11.9% for nitrate

(one sample excluded). Accuracy of the PMASS mass data could not be determined because some AIHL cyclone Fiberfilm filters used to determine mass weighed less after sampling than before sampling (possibly due to tearing). Elemental carbon values for the PMASS were 26% lower than those for the AIHL cyclone, whereas organic carbon and nitrate values were in good agreement.

- **Baltimore personal sampling:** Precision of the PMASS measurements was 24.2% for mass, 8.1% for elemental carbon, 19.3% for organic carbon, and 19.1% for nitrate. Agreement between the PMASS and the PEM was modest. PMASS mass values were 24% lower than the corrected PEM values.

DISCUSSION

Dr Geyh and colleagues conducted a carefully designed study to test in the field a portable lightweight PM_{2.5} sampler—the PMASS—for simultaneous measurement of levels of various PM components to which people are exposed. The prototype sampler was developed by Dr Hering and colleagues in a previous HEI study (Hering et al 2003) and was modified by Geyh and colleagues before their field tests. The authors present their results clearly and discuss their limitations honestly.

Considerable changes were made to the Hering prototype, in particular reducing its weight by half, which made it more practical as a personal sampler. Laboratory tests showed that the cutpoint of the redesigned sampler was within design guidelines, but field studies revealed some limitations that will need to be addressed before it is ready for use. These include problems with the Fiberfilm filters, lower than targeted precision for mass and nitrate, and

poor accuracy for mass and elemental carbon. High blank values precluded determination of PMASS precision and accuracy for sulfate in all field tests and negative mass data for filters in the AIHL cyclone precluded determination of PMASS accuracy in Fresno. The lack of data for sulfate should be addressed in future tests.

The Fiberfilm filter was chosen because it is more suitable than the Teflon filter for use in a β gauge, which was used in the Hering study and was planned for use in this study to improve the precision of mass determination. Early in this study, the investigators decided to use the gravimetric method to determine mass because β attenuation did not appear to yield substantial advantages. They continued to use the Fiberfilm filter, however, which turned out to tear when removed from some of the filter holders. Problems with Fiberfilm may be responsible for the poor precision and accuracy of $PM_{2.5}$ mass measurements. Tests conducted after the final report was submitted to HEI seem to indicate that these problems are solvable.

With regard to accuracy, no general trend in bias was found for values of any PM component. The best agreements were reported between the PMASS and the Harvard impactor for organic carbon and between the PMASS and the AIHL cyclone for organic carbon and nitrate. The observed biases for other species (Critique Table) may be due to differences among the samplers, such as in flow rate and PM penetration efficiency. The investigators did not compare the performance of the PMASS for nitrate with the PEM and the Harvard impactor because they lack the backup filter.

Geyh and coworkers used two approaches to evaluate accuracy of the PMASS relative to the reference samplers. One approach was to plot the PMASS measurements against the reference measurements and compare the slopes of the regression line to the ideal value of 1. The other was to compute the ratio of the means of PMASS measurements and the reference sampler measurements. The ratio of means method gives better accuracy evaluations for PMASS, but the HEI Health Review Committee believes that accuracy based on the regression method is more appropriate because it compares the two sets of measurements across a range of measured values rather than just comparing two central means.

Accuracy of PMASS mass based on the difference in slope was -24% for personal sampling (relative to the PEM) and -33% for microenvironmental sampling (relative to the Harvard impactor). However, the PEM mass values were reduced by 22% (to correct for the difference between the PEM and the Harvard impactor in microenvironmental sampling). It is not clear whether this correction is appropriate. Without it, the agreement between the PMASS and the PEM would have been poorer. Other studies have also reported a difference between the PEM and the Harvard

impactor or the PEM and the federal reference method, albeit one lower than 22% (Chang et al 1999; Williams et al 2000; Liu et al 2003; Meng et al 2004). Liu and colleagues also noted that the Harvard impactor agreed well with the federal reference method (-3%).

The reference samplers used in this study are not gold standards; they may have biases relative to one another as well as to the federal reference method. The Harvard impactor and the AIHL cyclone were not compared directly to determine the extent to which their measurements agreed. The PMASS was tested as a personal sampler on a limited number of adult volunteers who were aware of the scope of the study. How the PMASS would perform in the general population and children in particular is not yet known. Precision and accuracy of the PMASS as a personal sampler across a range of individuals would be subject to a different degree of variability.

While this study was ongoing, an integrated multipollutant sampler was developed for simultaneous measurement of PM_{10} and $PM_{2.5}$ mass and composition and of gaseous copollutants (Demokritou et al 2001). This sampler consists of one $PM_{2.5}$ and one PM_{10} impactor-based sampler for mass determination, as well as two miniature $PM_{2.5}$ impactors. One miniature impactor samples PM for analysis of elemental carbon and organic carbon. The other consists of a denuder and a single glass fiber filter coated with a nitrate reagent; it samples PM for analysis of sulfate and nitrate. Passive substrates for collecting ozone, sulfur dioxide, and nitrogen dioxide also can be attached to the unit. This sampler (presently marketed by Rupprecht & Patashnick Co under the trade name ChemPass) is quite bulky, however, and data comparing it to other samplers are not yet available.

Another sampler recently developed by Pang and colleagues (2002) is a simple, lightweight personal sampler using carbon-impregnated foam as a size selective inlet and denuder. It can measure mass and organic carbon simultaneously.

Overall, the PMASS is an improvement over the Hering prototype and is competitive with existing samplers for assessment of personal exposure to $PM_{2.5}$ and its chemical constituents. At the present time, however, use of the PMASS without further testing is premature because of the accuracy and precision reported in this study, the need for additional design modifications, and the lack of testing in the general population. A difficulty common to testing of new PM samplers, especially those for personal exposure measurements, is the lack of samplers that can be used as gold standards. Until some form of validation of PM samplers is available, use of these samplers in epidemiologic studies should proceed with caution.

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