Environmental Technology Verification Report

THERMO ANDERSEN CONTINUOUS AMBIENT MASS MONITOR (CAMM)

Prepared by

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ETV Joint Verification Statement

TECHNOLOGY TYPE: Continuous Ambient Mass Monitor

APPLICATION: **MEASURING FINE PARTICULATE MASS IN AMBIENT AIR**

TECHNOLOGY NAME: **Continuous Ambient Mass Monitor**

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The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations; with stakeholder groups that consist of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Advanced Monitoring Systems (AMS) Center, one of six technology centers under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center has recently evaluated the performance of continuous monitors used to measure fine particulate mass and species in ambient air. This verification statement provides a summary of the test results for the Thermo Andersen continuous ambient mass monitor (CAMM).

VERIFICATION TEST DESCRIPTION

The objective of this verification test is to provide quantitative performance data on continuous fine particle monitors under a range of realistic operating conditions. To meet this objective, field testing was conducted in two phases in geographically distinct regions of the United States during different seasons of the year. The first phase of field testing was conducted at the ambient air monitoring station on the Department of Energy's National Energy Technology Laboratory campus in Pittsburgh, PA, from August 1 to September 1, 2000. The second phase of testing was performed at the California Air Resources Board's ambient air monitoring station in Fresno, CA, from December 18, 2000, to January 17, 2001. Specific performance characteristics verified in this test include inter-unit precision, accuracy and correlation relative to time-integrated reference methods, effect of meteorological conditions, influence of precursor gases, and short-term monitoring capabilities. The CAMM reports measurement results in terms of $PM_{2.5}$ mass and, therefore, was compared with the federal reference method (FRM) for $PM_{2.5}$ mass determination. Additionally, comparisons with a variety of supplemental measurements were made to establish specific performance characteristics.

Quality assurance (QA) oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a data quality audit of 10% of the test data, and performance evaluation audits were conducted on the FRM samplers used in the verification test. Battelle QA staff conducted an internal technical system audit for Phase I and Phase II. EPA QA staff conducted an external technical systems audit during Phase II.

TECHNOLOGY DESCRIPTION

The CAMM is a continuous ambient air monitor that determines fine particulate mass by measuring the increase in pressure drop across a membrane filter during particle sampling. The CAMM reports $PM_{2.5}$ concentrations in micrograms per cubic meter of air ($\mu g/m^3$). A new section of filter tape is exposed every measurement period, allowing particles to remain in or close to equilibrium with the sample air during collection. The CAMM measures at ambient temperature to minimize losses due to volatilization and has a short sampling duration and low face velocity to reduce sampling artifacts. The CAMM consists of a conventional FRM PM_{10} inlet, a $PM_{2.5}$ Sharp Cut Cyclone, a diffusion dryer, a filter tape, a tape transfer mechanism, and a data acquisition and control unit. Fine particle monitoring is accomplished by a filter tape transport system and an array of pressure trans-ducers. The monitoring system includes a microprocessor-controlled drive to advance the tape and a mechanism to release and reseal the filter tape during each advance. Automatic filter changes and enclosure design both support sample equilibration with ambient conditions and optimize the reduction of sampling artifacts. Sensor calibrations are stored via internal memory. Built-in diagnostic features, analog outputs, and instrument interfaces provide the user with advanced quality control features through local or remote access.

VERIFICATION OF PERFORMANCE

Inter-Unit Precision: Only one of the duplicate CAMMs provided usable data during Phase I. The second unit had a leak in the sampling system, and the collected data were invalidated. Consequently, no measure of inter-unit precision is available for Phase I. During Phase II, regression analysis showed r^2 values of 0.918 and 0.930, respectively, for the hourly data and the 24-hour averages from the duplicate monitors. The slopes of the regression lines were 0.903 (0.024 95% confidence interval) and 0.774 (0.086), respectively, for the hourly data and 24-hour averages, indicating a statistically significant difference between the duplicate CAMMs. The intercepts were 5.8 (2.8) $\mu g/m^3$ and 16.1 (9.9) $\mu g/m^3$, respectively. The calculated coefficient of variation (CV) for the hourly data was 17.2% and for the 24-hour averages, the CV was 13.8%.

Comparability/Predictability: During Phase I, comparisons of the 24-hour averages with $PM_{2.5}$ FRM results showed a slope of the regression line for Monitor 1 of 0.45 (0.26) and an intercept of 13.5 (5.4) $\mu g/m^3$. The regression results show an r^2 value of 0.386. During Phase II, comparison of the 24-hour averages with $PM_{2.5}$ FRM results showed slopes of the regression lines for Monitor 1 and Monitor 2 of 1.46 (0.30) and 1.20 (0.22),

respectively, and no statistically significant intercept was observed in either case at the 95% confidence level. The regression results show r^2 values of 0.809 and 0.843 for Monitor 1 and Monitor 2, respectively.

Meteorological Effects: Multivariable analysis shows that none of the meteorological parameters measured during Phase I influenced the readings of the CAMM relative to the FRM at the 90% confidence level. Multi-variable analysis showed that, during Phase II, relative humidity had a statistically significant (90% confidence) influence on the readings of one of the duplicate CAMMs. However, this effect was largely canceled out by the intercept of the regression analysis, and was of no practical significance.

Influence of Precursor Gases: None of the precursor gases had a statistically significant effect (90% confidence) on the readings of the CAMM during Phase I or Phase II.

Short-Term Monitoring: In addition to 24-hour FRM samples, short-term sampling was performed on a five-sample-per-day basis during Phase II only. The results from the duplicate CAMMs were independently averaged for each of the sampling periods and compared with the gravimetric results. Considering all of the short-term data together, linear regression showed slopes of 1.27 and 1.15, respectively, for Monitor 1 and Monitor 2. The intercepts of the regression lines were 13.1 and 15.6 $\mu g/m^3$, respectively; and the r^2 values were 0.716 and 0.666, respectively.

Other Parameters: The CAMMs required some maintenance during both phases of verification testing. During Phase I, the virtual impactors on the two CAMMs were cleaned approximately weekly. Additionally, the filter tape in each CAMM was changed several times during Phase I. Some additional troubleshooting was performed on one of the units to identify the source of problems indicated by the error codes on the display of the monitor. As noted previously, a leak in this monitor that invalidated all data. With the exception of several power outages, approximately 90% data recovery was achieved from the one CAMM that operated in Phase I. During Phase II of the verification test, the virtual impactors required cleaning approximately every one to two days as a result of the high $PM_{2.5}$ concentrations. An external timer mechanism was added to each of the CAMMs to allow data collection on a two-minute time scale rather than the default one-hour time scale.

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Thermo Andersen
Continuous Ambient Mass Monitor (CAMM)

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Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency and recommended for public release. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

Foreword

The U.S. EPA is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/07/07_main.htm.

Acknowledgments

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List of Abbreviations

ADQ	audit of data quality
AMS	Advanced Monitoring Systems
CAMM	continouous ambient mass monitor
CARB	California Air Resources Board
CI	confidence interval
cm	centimeter
CO	carbon monoxide
CV	coefficient of variation
DPI	digital pressure indicator
DRI	Desert Research Institute
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FRM	federal reference method
H_2S	hydrogen sulfide
IMPROVE	Interagency Monitoring for Protection of Visual Environments
in.	inch
L/min	liters per minute
mg	milligram
mm	millimeters
NETL	National Energy Technology Laboratory
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
O_3	ozone
ppb	parts per billion
QA/QC	quality assurance/quality control
QMP	Quality Management Plan
R&P	Rupprecht & Patashnick
SCC	Sharp Cut Cyclone
SFS	sequential filter sampling system
SLAMS	state and local air monitoring stations
SO_2	sulfur dioxide
TOR	thermal optical reflectance
TSA	technical systems audit
WINS	well impactor ninety six

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in designing, distributing, permitting, purchasing, and using environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of regulators, buyers, and vendor organizations; and with the full participation of individual technology developers. The program evaluates the performance of innovative tech-nologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of fine particle monitors for use in continuous monitoring of ambient fine particle matter. This verification report presents the procedures and results of the verification test for the Thermo Andersen continuous ambient mass monitor (CAMM).

Chapter 2
Technology Description

The following description of the CAMM is based on information provided by the vendor.

The CAMM is a continuous ambient air monitor that determines fine particulate mass by measuring the increase in pressure drop across a membrane filter during particle sampling. Ambient $PM_{2.5}$ mass concentrations are reported by the CAMM in microgram per cubic meter ($\mu g/m^3$) units. A new section of filter tape is exposed every measurement period, allowing particles to remain in or close to equilibrium with the sample air during collection. The CAMM measures at ambient temperature to minimize losses due to volatilization and has a short sampling duration and low face velocity to reduce sampling artifacts. The CAMM consists of a conventional federal reference method (FRM) PM_{10} inlet, a $PM_{2.5}$ Sharp Cut Cyclone, a diffusion dryer, a filter tape, a tape transfer mechanism, and a data acquisition and control unit. Two virtual impactor stages, with different size cutpoints, are used to reduce the number of smaller particles that reach the filter tape, thereby making the pressure drop linearly proportional to the particle diameter. Fine particle monitoring is accomplished by a filter tape transport system and an array of pressure transducers. The monitoring system includes a microprocessor-controlled drive to advance the tape and a mechanism to release and reseal the filter tape during each advance. Automatic filter changes and enclosure design both support sample equilibration with ambient conditions and optimize the reduction of sampling artifacts. Sensor calibrations are stored via internal memory. Built-in diagnostic features, analog outputs, and instrument interfaces provide the user with advanced quality control features through local or remote access.

Figure 2-1. Thermo Andersen CAMM

The CAMM has a four-line display, internal data storage, two analog outputs (0-10V; 0-20 mA), two RS-232 interfaces for remote control, and built-in quality assurance status and logbook features.

Chapter 3
Test Design and Procedures

3.1 Introduction

The objective of this verification test is to provide quantitative performance data on continuous fine particle monitors under a range of realistic operating conditions. To meet this objective, field testing was conducted in two phases in geographically distinct regions of the United States during different seasons of the year. Performing the test in different locations and in different seasons allowed sampling of widely different particulate matter concentrations and chemical composition. At each site, testing was conducted for one month during the season in which local $PM_{2.5}$ levels were expected to be highest. The verification test was conducted according to the procedures specified in the *Test/QA Plan for Verification of Ambient Fine Particle Monitors.*[1]

The first phase of field testing was conducted at the ambient air monitoring station on the Department of Energy's (DOE's) National Energy Technology Laboratory (NETL) campus in Pittsburgh, PA. Sampling during this phase of testing was conducted from August 1 to September 1, 2000. The second phase of testing was performed at the California Air Resources Board's (CARB's) Air Monitoring Station in Fresno, CA. This site is also host to one of the EPA's $PM_{2.5}$ Supersites being managed by Desert Research Institute (DRI). This phase of testing was conducted from December 18, 2000, to January 17, 2001.

3.2 Test Design

Specific performance characteristics verified in this test include

- Inter-unit precision
- Agreement with and correlation to time-integrated reference methods
- Effect of meteorological conditions
- Influence of precursor gases
- Short-term monitoring capabilities.

To assess inter-unit precision, duplicate CAMMs were tested in side-by-side operation during each phase of testing. During Phase I, the CAMMs tested were Serial Numbers 106 and 107. During Phase II, the CAMMs tested were Serial Numbers 121 and 123. Collocation of the CAMMs with reference systems for time-integrated sampling of fine particulate mass and chemical speciation provided the basis for assessing the degree of agreement and/or correlation between the continuous and reference methods. Each test site was equipped with continuous

monitors to record meteorological conditions and the concentration of key precursor gases (ozone, nitrogen oxides, sulfur dioxide, etc.). The data from the meteorological and gas monitors were used to assess the influence of these parameters on the performance of the fine particle monitors being tested. Reference method sampling periods of 3, 5, and 8 hours were used in Phase II of this test to establish the short-term monitoring capabilities of the continuous monitors being tested. Statistical calculations, as described in Chapter 5, were used to establish each of these performance characteristics.

Additionally, other performance characteristics of the technologies being verified, such as reliability, maintenance requirements, and ease of use, were assessed. Instrumental features that may be of interest to potential users (e.g., power and shelter requirements and overall cost), are also reported.

3.3 Reference Method and Supplemental Measurements

Since no appropriate absolute standards for fine particulate matter exist, the reference methods for this test were well established, time-integrated methods for determining particulate matter mass or chemical composition. It is recognized that comparing real-time measurements with time-integrated measurements does not fully explore the capabilities of the real-time monitors. However, in the absence of accepted standards for real-time fine particulate matter measurements, the use of time-integrated standard methods that are widely accepted was necessary for performance verification purposes. It should be noted that there are necessary differences between continuous and time-integrated, filter-based techniques. For example, in time-integrated sampling, particulate matter collected on a filter may remain there for up to 24 hours, whereas continuous monitors generally retain the particulate sample for one hour or less. Thus, the potential for sampling artifacts differs. Also, in the case of particle mass measurements, the mass of particulate matter is determined after equilibration at constant temperature and humidity, conditions that are almost certain to differ from those during sampling by a continuous monitor.

The CAMM reports measurement results in terms of $PM_{2.5}$ mass concentration in $\mu g/m^3$ units and, therefore, was compared with the FRM for $PM_{2.5}$ mass determination.[2] Additionally, comparisons with a variety of supplemental measurements were made to establish specific performance characteristics. Descriptions of the reference method and supplemental measurements used during the verification test are given below.

3.3.1 $PM_{2.5}$ Mass

The primary comparisons of the CAMM readings were made relative to the FRM for $PM_{2.5}$ mass determination, i.e., the 24-hour time-averaged procedure detailed in 40 CFR Part 50.[2] This method involves manual sampling using any of a number of designated commercially available filter samplers, followed by gravimetric analysis of the collected sample. In this method, a size-selective inlet is used to sample only that fraction of aerosol of interest (i.e., < 2.5 µm aerodynamic diameter). The air sample is drawn into the sampler at a fixed rate over 24 hours, and the aerosol is collected on an appropriate filter for gravimetric analysis. After equilibration of the

sample and filter in a temperature- and humidity- controlled environment, the sample is weighed on an appropriate microbalance. The particulate sample weight is determined by subtracting the weight of the filter alone, determined prior to sampling after similar equilibration. Protocols for sample collection, handling, and analysis are prescribed by the EPA[2] and were followed for this verification test.

Filter samples for the PM$_{2.5}$ FRM were collected daily during each phase of the testing using a BGI FRM Sampler (RFPS-0498-116), and the PM$_{2.5}$ mass was determined according to the procedures mentioned above. In Phase I, a single BGI FRM sampler (SN 311) was operated daily from noon to noon to collect the FRM samples. During Phase II, two BGI FRM samplers (SN 287 and SN 311) were used and were operated on alternate days to facilitate a midnight-to-midnight sampling schedule.

Collocated samples were collected during each phase to establish the precision of the FRM. A discussion of the collocated sampling is presented in Section 4.4 of this report.

3.3.2 Supplemental Measurements

Various supplemental measurements were used to further establish the performance of the continuous monitors being tested. Meteorological conditions were monitored and recorded continuously throughout each phase of the verification test. These measurements included temperature, relative humidity, wind speed, direction, barometric pressure, and solar radiation. These data were provided to Battelle for Phase I by DOE/NETL and for Phase II by DRI. Likewise, the ambient concentrations of various precursor gases including ozone and nitrogen oxides also were measured continuously during the verification test and used to assess the influence of these parameters on the performance of the monitors tested. Continuous measurements of sulfur dioxide, hydrogen sulfide, nitric oxide, nitrogen dioxide, nitrogen oxides, and ozone were provided for Phase I by DOE/NETL; and continuous measurements of carbon monoxide, ozone, nitric oxide, nitrogen dioxide, and nitrogen oxides were provided for Phase II by DRI. These gases were of interest as potential chemical precursors to aerosol components, and as indicators of ambient pollutant levels.

During Phase I, samples for chemical speciation were collected using an Andersen RAAS speciation sampler configured with five sample trains (one channel at 16.7 L/min and four channels at approximately 8 L/min). The 16.7 L/min channel was operated with a Teflon filter for PM$_{2.5}$ mass determination. Samples for carbon analysis were collected at 8 L/min on quartz filters and analyzed by the IMPROVE thermal optical reflectance method at DRI. Nitrate and sulfate samples were collected on nylon filters downstream of a magnesium-oxide-coated compound annular denuder, and analyzed by ion chromatography at Consol.

To supplement the 24-hour samples, additional samples for PM$_{2.5}$ mass were collected at the Fresno site over shorter sampling periods (i.e., 3-, 5-, 8-hour) to assess the capabilities of the monitors being tested in indicating short-term PM$_{2.5}$ levels. A medium-volume sequential filter sampling system (SFS) sampling at a flow rate of 113 L/min was used to collect the short-term mass and speciation samples during Phase II. The SFS was configured to take two simultaneous samples (i.e., Teflon-membrane/drain disk/quartz-fiber and quartz-fiber/sodium-chloride-

impregnated cellulose-fiber filter packs) at 20 L/min through each sampling port. Anodized aluminum nitric acid denuders were located between the inlets and the filters to remove gaseous nitric acid. The remaining 73 L/min required for the 113 L/min total inlet flow was drawn through a makeup air sampling port inside the plenum. The timer was set to take five sets of sequential samples every 24 hours. Solenoid valves, controlled by a timer, switched between one to five sets of filters at midnight each day. A vacuum pump drew air through the paired filter packs when the valves were open. The flow rate was controlled by maintaining a constant pressure across a valve with a differential pressure regulator.

The filters were loaded at the DRI's Reno, NV, laboratory into modified Nuclepore filter holders that were plugged into quick-disconnect fittings on the SFS. One filter pack contained a 47-mm-diameter Teflon-membrane filter with quartz-fiber backup filter. A drain disc was placed between the Teflon-membrane and quartz-fiber filters to ensure a homogeneous sample deposit on the front Teflon-membrane filter and to minimize fiber transfer from one filter to the other. The Teflon-membrane filter collected particles for mass and elemental analysis. The other filter pack contained a 47-mm-diameter quartz-fiber filter with a sodium-chloride-impregnated cellulose-fiber backup filter on a separate stage. The deposit on the quartz-fiber filter was analyzed for ions and carbon. The sodium-chloride-impregnated cellulose-fiber backup filter was analyzed for nitrate to estimate losses due to volatilization of ammonium nitrate from the front filter during sampling.

This sequential filter sampler was operated from midnight to 5:00 a.m. (0000-0500), from 5:00 a.m. to 10:00 a.m. (0500-1000), from 10:00 a.m. to 1:00 p.m. (1000-1300), from 1:00 p.m. to 4:00 p.m. (1300-1600), and from 4:00 p.m. to midnight (1600-2400). These short-term sampling measurements were appropriately summed over 24 hours for comparison with the corresponding 24-hour results of the FRM reference samplers to establish the relationship between the two sets of measurements.

3.4 Data Comparisons

The primary means used to verify the performance of the CAMM was comparison with the 24-hour FRM results. Additional comparisons were made with the supplemental meteorological conditions and precursor gas measurements to assess the effects of these parameters on the response of the monitors being tested. The short-term monitoring results from Phase II of the verification test also were used to assess the capabilities of the CAMM to indicate short-term levels of ambient $PM_{2.5}$. The comparisons were based on statistical calculations as described in Section 5 of this report.

Comparisons were made independently for the data from each phase of field testing; and, with the exception of the inter-unit precision calculations, the results from the duplicate monitors were analyzed and are reported separately. Inter-unit precision was determined from a statistical intercomparison of the results from the duplicate monitors.

3.5 Site Layout/Instrument Installation

In each phase of testing, the two CAMMs were installed outside. A PM_{10} head and $PM_{2.5}$ Sharp Cut Cyclone (SCC) were used with each CAMM to provide particle size selection. Data generated by the CAMMs were recorded internally and downloaded several times throughout each phase of testing as described in Section 4.6.2.

3.5.1 Phase I

Phase I verification testing was conducted at the DOE/NETL facility within the Bruceton Research Center. The facility is located in the South Park area of Pittsburgh, PA, approximately 7 miles from downtown. The air monitoring station where testing was conducted is located on the top of a relatively remote hill within the facility and is impacted little by road traffic. The layout of the testing facility is illustrated schematically in Figure 3-1.

For this test, Battelle provided temporary facilities to augment the permanent facilities in use by the DOE/NETL air monitoring staff. These temporary facilities included a temporary Battelle/ ETV platform (16-foot by 14-foot scaffold construction) and a Battelle instrument trailer. The Battelle trailer was positioned parallel with, and approximately 25 feet from, the DOE/NETL instrument trailer. The Battelle/ETV platform was located between the two trailers, with the surface at a height of approximately 2 meters (6 feet).

Most of the DOE/NETL continuous monitoring equipment, including the continuous precursor gas monitors, was located inside the DOE/NETL instrument trailer. A DOE/NETL Rupprecht & Patashnick (R&P) Co. Partisol FRM sampler used to evaluate FRM precision was located outside on a DOE/NETL platform. The CAMMs (serial number 106 and serial number 107) were installed within three meters of the BGI FRM sampler on the Battelle/ETV platform. The height of the inlets of the CAMMs were within one meter of the height of the BGI FRM sampler. A 10-meter (33-foot) meteorological tower was located approximately 20 meters (65 feet) to the north of the DOE/NETL trailer.

3.5.2 Phase II

Phase II of verification testing was conducted at the CARB site on First Street in Fresno. This site is located in a residential/commercial neighborhood about three miles north of the center of Fresno. The two BGI FRM samplers and a 3-meter (10-foot) meteorological tower were located on the roof of the two-story building housing the CARB office. Continuous precursor gas monitors were located inside the CARB office space and sampled through a port in the roof of the building. The two BGI FRM samplers were located on the southernmost edge of the rooftop, to be as close as possible to the instrument trailer. The Battelle trailer used during Phase I of this verification test also was used during Phase II. For Phase II, the Battelle trailer was located in the parking lot adjacent to the building in which the CARB site is located. The trailer was positioned approximately 25 meters (80 feet) to the south of the building, as shown in Figure 3-2. A difference in elevation of approximately 20 feet existed between the top of the trailer and the roof of the building housing the CARB site. In addition to the two BGI FRM samplers used to collect the

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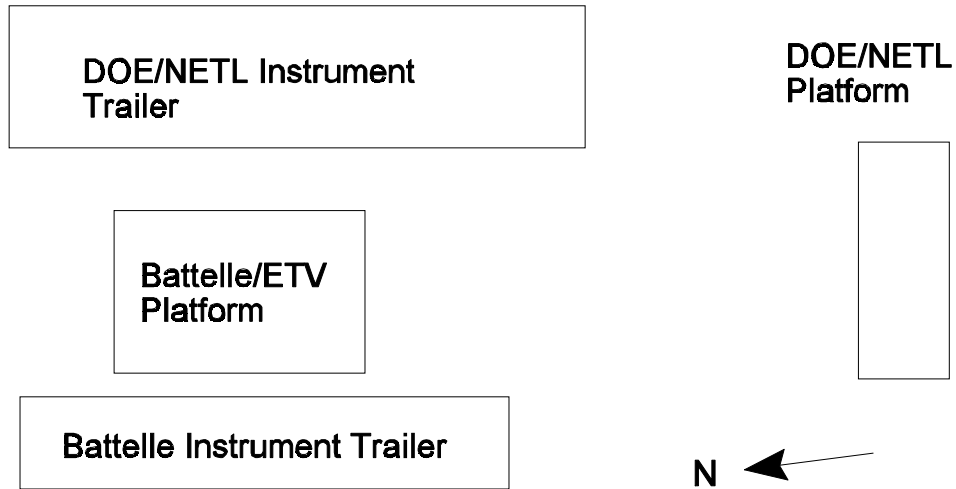
Figure 3-1. Site Layout During Phase I of Verification Testing (not drawn to scale)
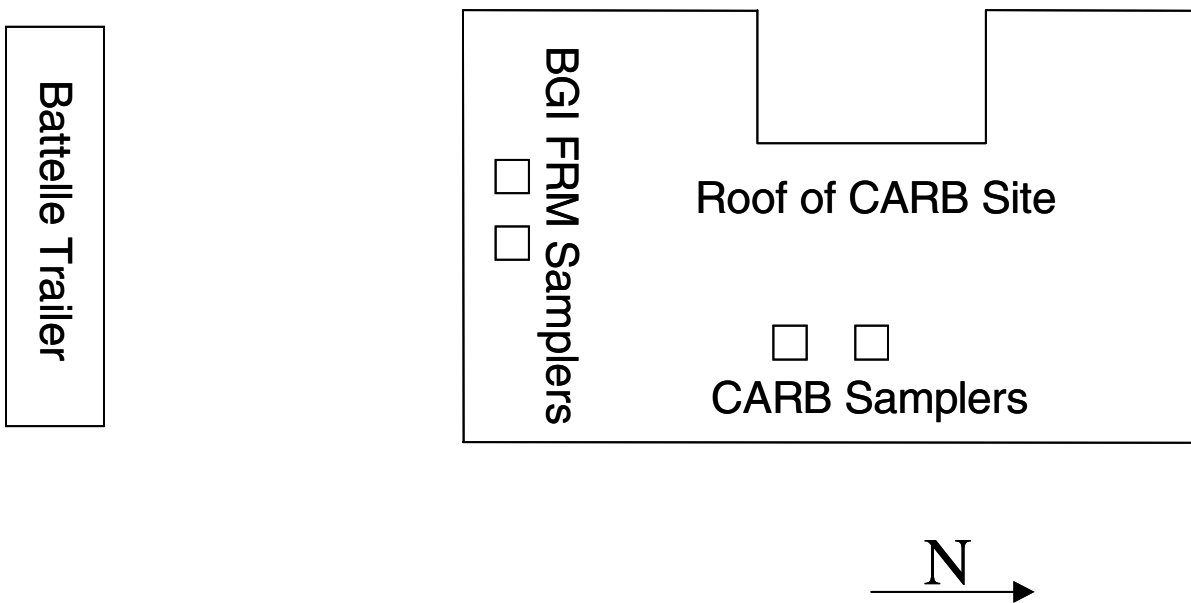
Figure 3-2. Site Layout During Phase II of Verification Testing (not drawn to scale)

reference samples, an R&P Partisol FRM sampler was operated on the rooftop by CARB. This sampler was positioned approximately 25 meters (65 feet) to the northeast of the BGI FRM samplers. The sequential filter sampler used to collect the short-term samples was located near the R&P FRM sampler. The CAMMs (serial number 121 and serial number 123) were located on the rooftop next to the BGI FRM samplers, with their inlets within one meter vertically of the BGI FRM inlets.

Chapter 4
Quality Assurance/Quality Control

4.1 Data Review and Validation

Test data were reviewed and approved according to the AMS Center quality management plan (QMP),[3] the test/QA plan,[1] and Battelle's one-over-one policy. The Verification Test Coordinator, or the Verification Test Leader or designee reviewed the raw data, laboratory notebook entries, and the data sheets that were generated each day and approved them by initialing and dating the records.

Data from the CAMMs were validated by a representative of Thermo Andersen and reviewed by the Verification Test Coordinator before being used in statistical calculations. Data were checked for error flags and not used if flagged for power or instrument failure. Daily $PM_{2.5}$ concentration averages calculated from the continuous CAMM data were considered valid if the percent data recovery for the 24-hour sampling period (i.e., noon to noon for Phase I, midnight to midnight for Phase II) was 75% or greater. However, high particle loadings clogged the CAMM filter tapes during hourly sampling in the first half of Phase II, resulting in the loss of a substantial amount of data. Consequently, a shorter CAMM sampling period was adopted, and this completeness criterion was relaxed to 40% as necessary in Phase II to present the most complete data set possible.

4.2 Deviations from the Test/QA Plan

The following deviations from the test/QA plan were documented and approved by the AMS Center Manager. None of these deviations had any deleterious effect on the verification data.

- Calibration checks of the temperature and pressure sensors were not performed within one week of the start of Phase II. Subsequent checks of these sensors indicated proper calibration.

- The distance between the reference samplers and the monitors being tested was increased to about 25 meters to accommodate changes in the overall site layout for Phase II.

4.3 Calibration and Parameter Checks of Reference Sampler

The BGI FRM samplers provided by Battelle for this verification test were calibrated using National Institute of Standards and Technology (NIST)-traceable flow meters and temperature and pressure sensors. The calibration and verification of these samplers are described below.

4.3.1 Flow Rate Calibration and Verification

Prior to Phase I of the verification test, a three-point calibration of the sampler flow rate was performed on June 22, 2000. Flows were measured at three set points (16.7 L/min and approximately +10% and -10% of 16.7 L/min) using a dry gas meter (American Meter Company, Battelle asset number LN 275010, calibrated January 21, 2000). If necessary, the flows were adjusted manually until agreement with the dry gas meter fell within ±2% of the sampler's indicated flow reading.

The on-site operators checked the flow rate of the BGI FRM sampler both before and after Phase I of the verification test using an Andersen dry gas meter (identification number 103652, calibrated March 30, 2000). The flow rate was checked prior to testing on both July 19, 2000, and July 30, 2000. In both cases, the measured flow rate was verified to be within 4% of the flow rate indicated by the sampler. After testing, the flow rate was again checked on September 11, 2000, using the same Andersen dry gas meter. In this case, the flow rate did not fall within the 4% acceptance limit. This failure is probably linked to the failure of the ambient temperature thermocouple on September 7, 2000, after completion of the Phase I sampling (see Section 4.3.2).

Prior to Phase II of the verification test, single-point calibration checks of the duplicate BGI FRM samplers were performed at 16.7 L/min on December 15, 2000. These flow rate checks were performed using a BGI DeltaCal calibrator (BGI Inc., serial number 0027, calibrated October 24, 2000), and the measured flow rates were within 4% of the indicated flow on each sampler. Weekly flow rate checks also were performed throughout Phase II using the DeltaCal flow meter. In each case, the measured flow rates were within ±4% of the indicated reading of the BGI FRM and within 5% of the nominal 16.7 L/min setpoint.

4.3.2 Temperature Sensor Calibration and Verification

Both the ambient temperature sensor and the filter temperature sensor of the BGI FRM sampler were checked at three temperatures (approximately 5, 22, and 45°C) on June 20, 2000. The sensor readings were compared with those from an NIST-traceable Fluke Model 52 thermocouple gauge (Battelle asset number LN 570068, calibrated October 15, 1999). Agreement between the sampler temperature sensors and the calibrated thermocouple was within ±2°C at each temperature.

The temperature sensors were also checked at the DOE/NETL site both before and after Phase I of the verification test by the on-site operators. Prior to testing, the sensors were checked on July 19, 2000, and July 30, 2000, against the readings from a mercury thermometer (Ever Ready, serial number 6419, calibrated October 29, 1999). For these checks, agreement between the sensors and the thermometer was within ±2°C. After the verification period, the ambient

temperature sensor suffered a malfunction on September 7. The filter temperature sensor was checked on September 11, 2000, and showed agreement with the mercury thermometer within ±2°C. The sensor was replaced, after completing Phase I, with a new factory-calibrated sensor provided by BGI.

The temperature sensors for the two BGI FRM samplers were checked on January 16, 2001, against readings from a Fluke Model 52 thermocouple gauge (Battelle asset number LN 570077, calibrated October 26, 2000). For each BGI FRM , both the ambient and filter temperature sensor readings agreed with the thermocouple readings within ±2°C.

4.3.3 Pressure Sensor Calibration and Verification

Before Phase I, the barometric pressure sensor in the BGI FRM sampler was calibrated against an NIST-traceable Taylor Model 2250M barometer (Battelle asset number LN 163610, calibrated January 12, 2000) and an NIST-traceable convectron gauge (Granville-Phillips Co., Battelle asset number LN 298084, calibrated August 25, 1999) on June 17 and 18, 2000. The sensor was calibrated at ambient pressure and under a reduced pressure (approximately 100 mm mercury below ambient).

Checks of the pressure sensor were performed at the DOE/NETL site both before and after Phase I of the verification test. The pressure sensor was checked on July 19, 2000, and July 30, 2000, using an NIST-traceable Taylor Model 2250M barometer (Battelle asset number LN 163609, calibrated January 12, 2000). On September 11, 2000, the pressure sensor of the BGI FRM sampler was again checked against the same barometer, but did not agree within the acceptance criterion of 5 mm mercury. This failure is possibly associated with the failure of the ambient temperature sensor on September 7, 2000.

The ambient pressure sensor for both BGI FRM samplers used in Phase II was checked against the pressure readings of a BGI DeltaCal on January 16, 2001. Agreement between the BGI FRM pressure readings and those of the DeltaCal was within ±5 mm mercury for both samplers.

4.3.4 Leak Checks

Leak checks of the BGI FRM sampler were performed every fourth day during Phase I of the verification test. These leak checks were conducted immediately following the cleaning of the WINS impactor and were performed according to the procedures in the operator's manual for the BGI FRM sampler. All leak checks passed the acceptance criteria provided in the operator's manual.

Leak checks of the BGI FRM samplers were performed daily during Phase II of the verification test. These leak checks were conducted during set-up for each 24-hour sampling period. All leak checks passed before the sampler set-up was completed.

4.4 Collocated Sampling

4.4.1 Phase I—Pittsburgh

To establish the precision of the $PM_{2.5}$ FRM, the BGI FRM sampler was collocated with an R&P FRM sampler for Phase I, including a period of two weeks prior to and one week after Phase I of the verification test. During the sampling periods before and after Phase I, the BGI and R&P FRM samplers were located on the same platform and within 4 meters of one another. During the Phase I testing period, these samplers were separated by a distance of approximately 25 meters. The samples from the BGI FRM sampler were collected and analyzed by Consol, and the samples from the R&P FRM sampler were collected and analyzed by on-site Mining Safety and Health Administration staff.

Figure 4-1 shows the results of the collocated FRM sampling conducted for Phase I. These data were compared by linear regression; and the calculated slope, intercept, and r^2 values are 0.939 (0.067), 1.28 (1.33) $\mu g/m^3$, and 0.957, respectively, where the values in parentheses are 95% confidence intervals (CIs). Despite completely independent operations (i.e., separate sampling staff and weighing facilities), these data show very good agreement between the BGI FRM and the R&P FRM samplers. The data also indicate that, although the humidity in the conditioning/ weighing room at Consol was not always within the specified FRM limits, the influence of the elevated humidity was not severe.

4.4.2 Phase II—Fresno

During Phase II of testing, duplicate BGI FRM samplers (SN 287 and SN 311) were used to collect the 24-hour FRM reference samples. These samplers were operated one at a time on alternate days to facilitate midnight-to-midnight sampling. Likewise, an R&P Partisol sampler was used by CARB to collect 24-hour FRM samples. The R&P FRM sampler was located approximately 25 meters from the BGI FRM samplers. The same on-site operators performed the sampling for the FRM samplers; however, DRI performed the gravimetric analyses for the BGI FRM samplers and CARB performed the analyses for the R&P FRM sampler.

Figure 4-2 shows the results for the collocated FRM sampling conducted for Phase II. Only 12 days of collocated sampling were available from the Fresno site. The linear regression of these data shows a slope of 1.096 (0.106) and intercept of -1.04 (4.7) $\mu g/m^3$ and r^2 value of 0.982, where the numbers in parentheses indicate the 95% CIs.

4.4.3 Summary

The results from the collocated FRMs in both Pittsburgh and Fresno show agreement that is consistent with the goals for measurement uncertainty of $PM_{2.5}$ methods run at state and local air monitoring stations (SLAMS). These goals are identified in Appendix A to 40 CFR Part 58, Section 3.5[4] which states: "The goal for acceptable measurement uncertainty has been defined as 10 percent coefficient of variation (CV) for total precision and ± 10% for total bias." Since the
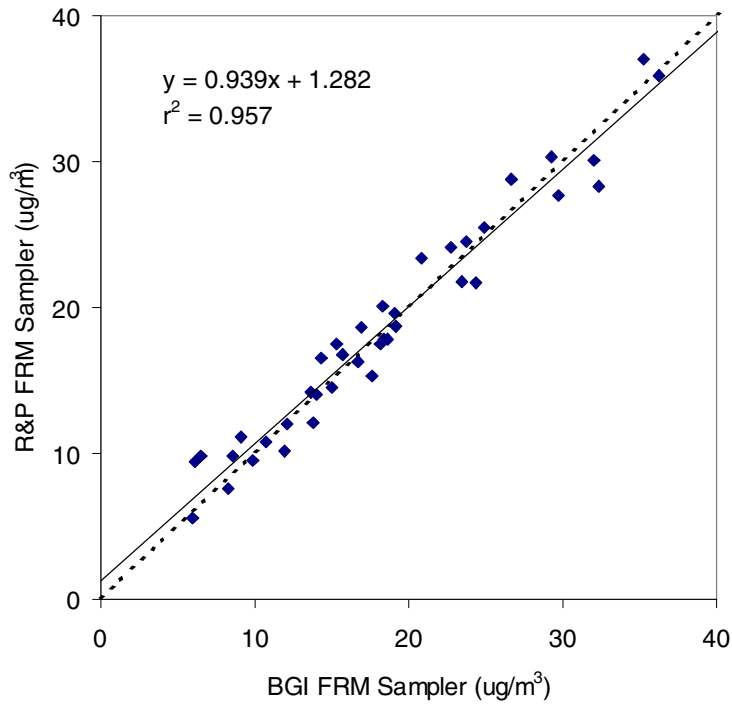
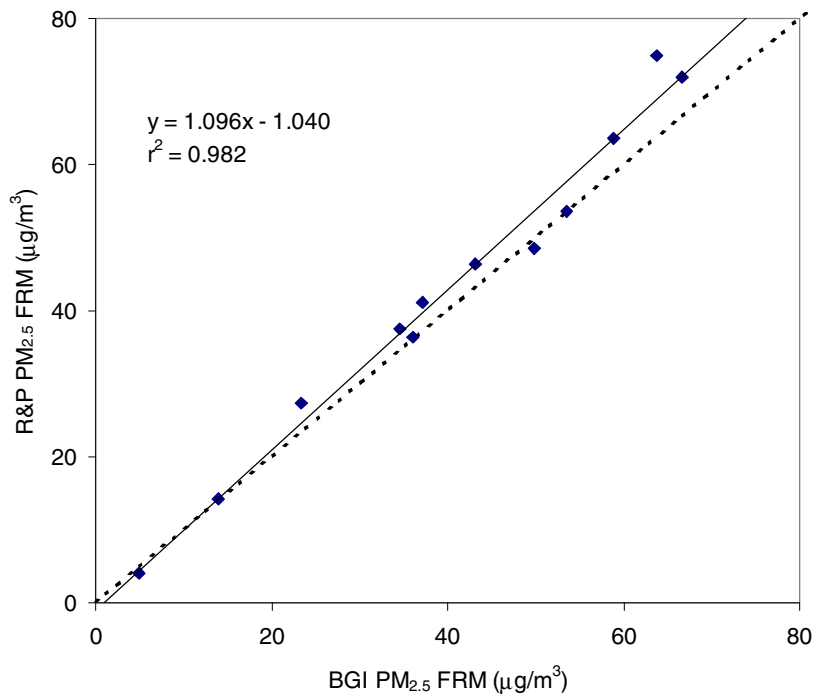**Figure 4-1. Comparison of Collocated PM$_{2.5}$ FRM Samplers for Phase I of Verification Testing**

Figure 4-2. Comparison of Collocated PM$_{2.5}$ FRM Samplers for Phase II of Verification Testing

collocated FRMs in both Pittsburgh and Fresno were operated by independent organizations, a comparison to the SLAMS data quality objectives for $PM_{2.5}$ is an appropriate way to assess whether the measurement systems were producing data of acceptable quality. In both Pittsburgh and Fresno, the results of the collocated sampling meet the data quality objectives for the total bias. In Fresno, the collocated sampling results show a CV of 6.3%, which meets the data quality objectives for precision. In Pittsburgh, the calculated CV was 10.5%. However, this value is driven largely by a single data pair. When this pair is removed, the CV becomes 9.1%, which meets the data quality objectives for total precision. (It should be noted, as well, that the Fresno collocated results consist of only 12 data points.) Thus, the collocated FRM results from Pittsburgh and Fresno show that the reference measurements were suitable for verifying the performance of continuous fine particle monitors.

4.5 Field Blanks

4.5.1 Phase I—Pittsburgh

During Phase I, at least 10% of the collected reference samples were field blanks. The observed filter mass difference of the field blanks ranged from -7 µg to 16 µg, and the corresponding $PM_{2.5}$ concentrations (which were determined using an assumed sample volume of 24 m^3) were all less than 0.7 µg/m^3, averaging 0.15 µg/m^3. FRM results for Phase I were not blank corrected.

4.5.2 Phase II—Fresno

During Phase II, at least 10% of the collected reference samples (for both the BGI FRM samplers and the DRI sequential filter sampler) were field blanks. The results were added to a database containing historical field blank data. On average, these blanks showed mass differences of 2 µg, with a standard deviation of 8 µg. Assuming a sample volume of 24 m^3 (i.e., FRM volume), these blanks account for ~ 0.1 µg/m^3. Assuming a sample volume of 3.6 m^3 (i.e., three-hour short-term sample from sequential filter sampler), these blanks account for ~ 0.6 µg/m^3. These blank values were negligible, even for the short-term sampling periods, in comparison with the $PM_{2.5}$ mass levels that were present during the Phase II testing (see Section 6.2). FRM results for Phase II were blank corrected using the data available from the historical database.

4.6 Data Collection

4.6.1 Reference Measurements

During Phase I, daily records of the sampling activities for the BGI FRM sampler were recorded on individual data sheets by the on-site operators, and summary data from the BGI FRM sampler were downloaded daily using portable data logging modules. Information recorded on the data sheets included identification of the sampling media (i.e., filter ID numbers) and the start and stop times for the sampling periods. Summary data from the sampler included the parameters listed

above, in addition to the sampling duration, volume sampled, and average temperature and pressure readings.

During Phase II, summary data from the BGI FRM samplers were logged daily on sampling sheets by the on-site operators. These data included sample identification, start times for the sampling period, sampling duration, volume sampled, and average temperature and pressure readings.

4.6.2 CAMMs

During Phase I, data from each of the CAMMs were recorded every hour and stored in an internal memory buffer. These data were stored in tabular format showing the date and time, the instrument status code, an error flag, and the hourly $PM_{2.5}$ concentration values ($\mu g/m^3$). During Phase II, the data were recorded every hour in the same format as Phase I until January 5. On January 5, an internal timing device was installed on each monitor, and readings were recorded every two minutes thereafter.

The recorded data were downloaded directly onto a computer and saved as text files. These data were imported into a spreadsheet for analysis, and copies of the data were stored by the Verification Test Coordinator on a floppy disk, as well as on a computer hard drive.

4.7 Assessments and Audits

4.7.1 Technical Systems Audit

Phase I—Pittsburgh

The technical systems audit (TSA) ensures that the verification tests are conducted according to the test/QA plan[1] and that all activities associated with the tests are in compliance with the ETV pilot QMP.[3] The Battelle Quality Manager conducted an internal TSA on August 3, 2000, at the Pittsburgh test site. All findings noted during this TSA were documented and submitted to the Verification Test Coordinator for correction. The corrections were documented by the Verification Test Coordinator and reviewed by Battelle's Quality Manager, Verification Testing Leader, and AMS Center Manager. None of the findings adversely affected the quality or outcome of this phase of the verification test. All corrective actions were completed to the satisfaction of the Battelle Quality Manager. The records concerning this TSA are permanently stored with the Battelle Quality Manager.

Phase II—Fresno

An internal TSA was conducted by the Battelle Quality Manager on January 9, 2001, at the Fresno test site. An external TSA was also conducted concurrently by EPA quality staff, Ms. Elizabeth Betz and Ms. Elizabeth Hunike. All findings noted during these TSAs were documented and submitted to the Verification Test Coordinator for corrective action. None of the findings adversely affected the quality or outcome of this phase of the verification test for the

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CAMM. All corrective actions were completed to the satisfaction of the Battelle Quality Manager and the EPA.

4.7.2 Performance Evaluation Audit

Phase I—Pittsburgh

The reference sampler provided by Battelle for this verification test was audited during Phase I to ensure that it was operating properly. During Phase I of the verification test, the flow rate of the BGI FRM sampler was audited on August 28, 2000, using a dry gas meter (American Meter Company, Battelle asset number LN 275010, calibrated April 17, 2000). The measured flow rate was within the ±4% acceptance criterion with respect to the internal flow meter and within the ±5% acceptance criterion with respect to the nominal flow rate.

Both temperature sensors in the BGI FRM sampler were checked on August 28, 2000, using a Fluke 52 thermocouple (Battelle asset number LN 570068, calibrated October 15, 1999). Agreement between each sensor and the thermocouple was within the ±2°C acceptance criterion.

Phase II—Fresno

A performance evaluation audit was conducted to ensure that the two BGI FRM samplers used during Phase II of testing were operating properly. The flow rates of the samplers were audited on January 16 and 17, 2001, using a dry gas meter (Schlumberger, SN 103620, calibrated July 6, 2000). For each sampler, the measured flow rate was within the ±4% acceptance criterion with respect to the internal flow meter and within the ±5% acceptance criterion with respect to the nominal flow rate.

The temperature readings for the two samplers were checked with a mercury thermometer (Fisher Scientific, SN 7116). Agreement between each sensor and the thermocouple was within the ±2°C acceptance criterion.

The pressure sensors for the two samplers were checked against a Druck digital pressure indicator (DPI) (SN 6016/00-2, calibrated June 28, 2000). Agreement between each sensor and the DPI was within the acceptance criterion of ±5 mm mercury.

4.7.3 Audit of Data Quality

Battelle's Quality Manager ensured that an audit of data quality (ADQ) of at least 10% of the verification data acquired during the verification test was completed. The ADQ traced the data from initial acquisition, through reduction and statistical comparisons, to final reporting. Reporting of findings followed the procedures described above for the Phase I TSA. All findings were corrected to the satisfaction of the Battelle Quality Manager, and none of the findings adversely affected the quality of the verification test for the CAMM.

Chapter 5
Statistical Methods

Performance verification is based, in part, on statistical comparisons of continuous monitoring data with results from the reference methods. A summary of the statistical calculations that have been made is given below.

5.1 Inter-Unit Precision

The inter-unit precision of the CAMM was determined based on procedures described in Section 5.5.2 of EPA 40 CFR 58, Appendix A, which contains guidance for precision assessments of collocated non-FRM samplers. Simultaneous measurements from the duplicate CAMM were paired, and the behavior of their differences was used to assess precision. For both the hourly and the 24-hour $PM_{2.5}$ measurements, the coefficient of variation (CV) is reported. The CV is defined as the standard deviation of the differences divided by the mean of the measurements and expresses the variability in the differences as a percentage of the mean. As suggested by the EPA guidance, only measurements above the limit of detection were used in precision calculations. Inter-unit precision was assessed separately for each phase of the verification test.

5.2 Comparability/Predictability

The comparability between the CAMM and the $PM_{2.5}$ FRM was assessed, since the CAMMs yield measurements with the same units of measure as the $PM_{2.5}$ FRM. The relationship between the two was assessed from a linear regression of the data using the $PM_{2.5}$ FRM results as the independent variable and the CAMM results as the dependent variable as follows:

$$C_i = \mu + \beta \times R_i + \varepsilon_i \tag{1}$$

where R_i is the ith 24-hour FRM $PM_{2.5}$ measurement; C_i is the average of the hourly CAMM measurements over the same 24-hour time period as the ith reference measurement; μ and β are the intercept and slope parameters, respectively; and ε_i is error unexplained by the model. The average of the hourly CAMM measurements is used because this quantity is most comparable to the reference sampler measurements.

Comparability is expressed in terms of bias between the CAMM and the $PM_{2.5}$ FRM and the degree of correlation (i.e., r^2) between the two. Bias was assessed based on the slope and

intercept of the linear regression of the data from the $PM_{2.5}$ FRM and the CAMM. In the absence of bias, the regression equation would be $C_i = R_i + \varepsilon_i$ (slope = 1, intercept = 0), indicating that the 24-hour average of hourly CAMM measurements is simply the $PM_{2.5}$ FRM measurement, plus random error. A value of r^2 close to 1 implies that the amount of random error is small; that is, the variability in the hourly measurements is almost entirely explained by the variability in the $PM_{2.5}$ FRM measurements.

Quantities reported include r^2, intercept, and slope, with estimates of their respective 95% CIs. Comparability to the FRM was determined independently for each of the two duplicate CAMM being tested and was assessed separately for each phase of the verification test.

5.3 Meteorological Effects/Precursor Gas Influence

The influence of meteorological conditions on the correlation between the CAMM and the $PM_{2.5}$ FRM reference samplers was evaluated by using meteorological data such as temperature and humidity as parameters in multivariable analyses of the reference/monitor comparison. The same evaluation was done with ambient precursor pollutant concentrations as the model parameters. The model used is as follows:

$$C_i = \mu + \beta \times R_i + \Sigma \gamma_j \times X_{ji} + \varepsilon_i \tag{2}$$

where X_{ji} is meteorological or precursor gas measurement for the ith 24-hour time period, γ_j is the associated slope parameter, and other notation is in Equation 1. Comparability results are reported again after these variables are adjusted for in the model. Additionally, estimates of γ_j are provided. Meteorological effects and precursor gas interferences were assessed independently for each of the two duplicate CAMMs tested, and were assessed separately for each phase of the verification test. In conducting these multivariable analyses, a significance level of 90% was used in the model selection. This significance level is less stringent than the 95% level used in other aspects of the verification, and was chosen so that even marginally important factors could be identified for consideration.

Note that the multivariable model ascribes variance unaccounted for by linear regression against the FRM to the meteorological or precursor gas parameters. The model treats all candidate parameters equally. The model discards the least significant parameter and is rerun until all remaining variables have the required significance (i.e., predictive power). The results of the model should not be taken to imply a cause-and-effect relationship. It is even possible that the parameters identified as significant for one unit of a monitoring technology may differ from those identified for the duplicate unit of that technology, due to differences in the two data sets.

5.4 Short-Term Monitoring Capabilities

This assessment was based on linear regression analysis of results from the CAMM monitors and the short-term (3-, 5-, and 8-hour) sampling results from the two BGI FRM samplers generated in Phase II only. The analysis was conducted, and the results are reported in a fashion identical to that for the comparability results for the 24-hour samples described in Section 5.2.

These comparisons were made only after establishing the relationship between the short-term sampling results and the corresponding 24-hour results. The relationship between the two sets of reference measurements was made by linear regression using the weighted sum of the results from the short-term sampling as the dependent variable and the 24-hour FRM results as the independent variable in the regression analysis. Comparability was assessed using Equation 1, replacing the average of hourly measures with the average of short-term sampler measurements. The short-term sampling results also have been used to assess the effects of meteorological conditions and precursor gas concentrations on the response of the monitors. These short-term results were used in place of the 24-hour measurements in the analysis described in Section 5.3 for Phase II only. Independent assessments were made for each of the duplicate CAMMs and the data from each phase of testing were analyzed separately.

Chapter 6
Test Results

6.1 Phase I—Pittsburgh (August 1 - September 1, 2000)

Samples were collected daily between August 1 and September 1, 2000, using a $PM_{2.5}$ FRM sampler. During this period, the daily $PM_{2.5}$ concentration as measured by the BGI FRM sampler ranged from 6.1 µg/m^3 to 36.2 µg/m^3, with an average daily concentration of 18.4 µg/m^3. Typically, the $PM_{2.5}$ composition was dominated by sulfate and carbon species. On average, the measured sulfate concentration, determined by ion chromatography, accounted for approximately 47% of the daily $PM_{2.5}$ mass. Total carbon, as measured by the IMPROVE thermal optical reflectance (TOR) method, accounted for approximately 38% of the $PM_{2.5}$ mass, with elemental carbon contributing approximately 22% and organic carbon contributing approximately 77% of the total carbon. Additionally, nitrate contributed about 8.3% of the daily $PM_{2.5}$ concentration.

Table 6-1 summarizes the meteorological conditions during Phase I, and Table 6-2 summarizes the observed concentrations of the measured precursor gases during this period.

Table 6-1. Summary of Daily Values for the Measured Meteorological Parameters During Phase I of Verification Testing

	Wind Speed (mph)	Vertical Wind Speed (mph)	Wind Direction (degrees)	Air Temp. @ 10 m (C)	Air Temp. @ 2 m (C)	RH (%)	Solar Radiation (W/m^2)	Press. (mbar)	Total Precip. (in.)
Average	3.35	0.09	196	20.0	16.6	89.4	162.8	979.7	0.0014
Max	6.45	0.29	298	24.1	22.5	95.8	246.1	986.7	0.03
Min	1.88	-0.03	106	14.6	12.1	80.2	47.9	974.5	0.00

Table 6-2. Summary of Daily Values for the Measured Precursor Gas Concentrations During Phase I of Verification Testing

	SO$_2$ (ppb)	H$_2$S (ppb)	NO (ppb)	NO$_2$ (ppb)	NO$_x$ (ppb)	O$_3$ (ppb)
Average	6.9	1.5	3.1	10.1	13.0	24
Max	12.8	2.9	10.4	17.4	27.4	51
Min	2.7	-0.6	0.1	5.3	5.3	5

6.1.1 Inter-Unit Precision

Fine particle mass concentration readings from the two CAMMs were recorded hourly during Phase I of the verification test. Unfortunately, a leak was present in the flow system of one of the two CAMMs during Phase I testing. As a result, the data from that monitor are not valid. Since the data from only one unit are available, no measure of inter-unit precision can be made for Phase I of the verification test.

6.1.2 Comparability/Predictability

Figure 6-1 shows the hourly readings from one CAMM for Phase I of testing. For comparison with the PM$_{2.5}$ FRM reference measurements, the hourly data were averaged from noon-to-noon for each day to correspond with the 24-hour sampling periods used in Phase I of the verification test. In Figure 6-2a, the noon-to-noon averages of the CAMM measurements are shown, along with the PM$_{2.5}$ FRM measurements for Phase I of the verification test. These PM$_{2.5}$ concentration values were analyzed by linear regression according to Section 5.2 to establish the comparability of the CAMM monitor with the PM$_{2.5}$ reference sampler. The resulting comparison is plotted in Figure 6-2b; and the calculated slope, intercept, and r^2 value of the regression analysis are presented in Table 6-3.

Although the slope [0.448 (0.257)] of the regression line indicates a negative bias of greater than 50% relative to the FRM, the regression results show a relatively large intercept [13.5 (5.4) μg/m^3]. Consequently, as can be seen in Figure 6-2a, the 24-hour averages from the CAMMs were sometimes, but not always, substantially greater than the corresponding PM$_{2.5}$ FRM results. The regression results show an r^2 value of 0.386.
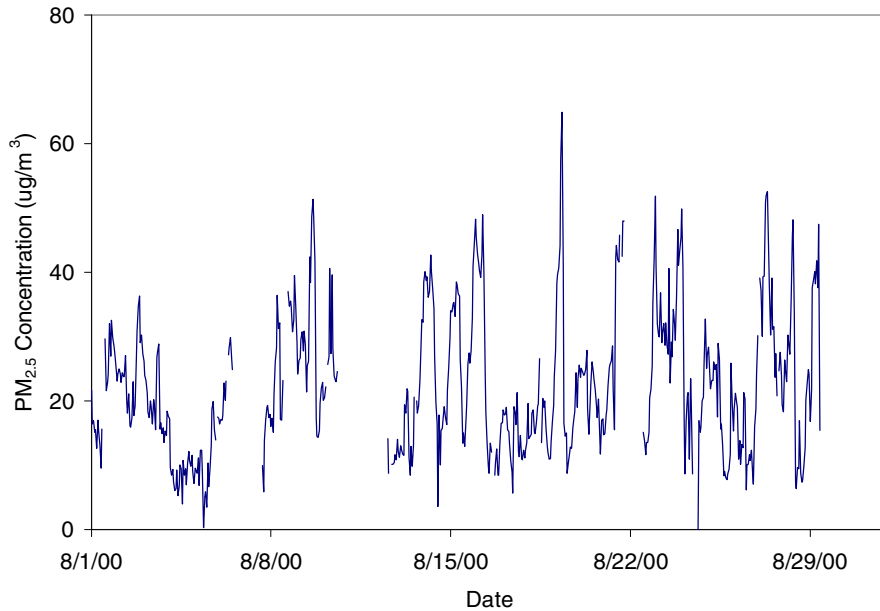
Figure 6-1. Hourly PM$_{2.5}$ Mass Concentrations from the CAMM During Phase I of Verification Testing

Table 6-3. Comparability of the CAMM with the PM$_{2.5}$ FRM Sampler for Phase I

Regression Parameter	Monitor 1	Monitor 2
Slope (95% CI)	0.448 (0.257)	NA
Intercept (μg/m^3) (95% CI)	13.5 (5.4)	NA
r^2	0.386	NA

NA = Not available.

6.1.3 Meteorological Effects

A multivariable model, as described in Section 5.3, was used to determine if the readings of the single CAMM could be accounted for by the meteorological conditions. This analysis involved a backward elimination process to remove from the analysis model those parameters showing no statistically significant influence on the results. This analysis indicated that, during Phase I, no meteorological effects were observed on the CAMM relative to the FRM at the 90% confidence level.
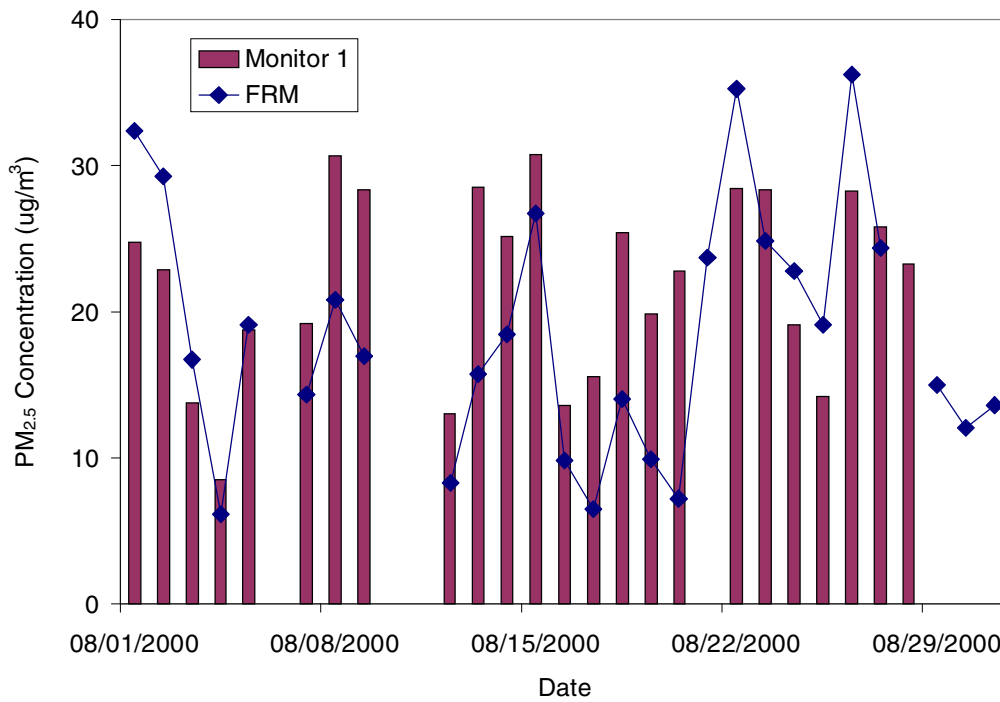
Figure 6-2a. Daily PM$_{2.5}$ FRM Concentrations and 24-Hour PM$_{2.5}$ Averages from the CAMM During Phase I of Verification Testing
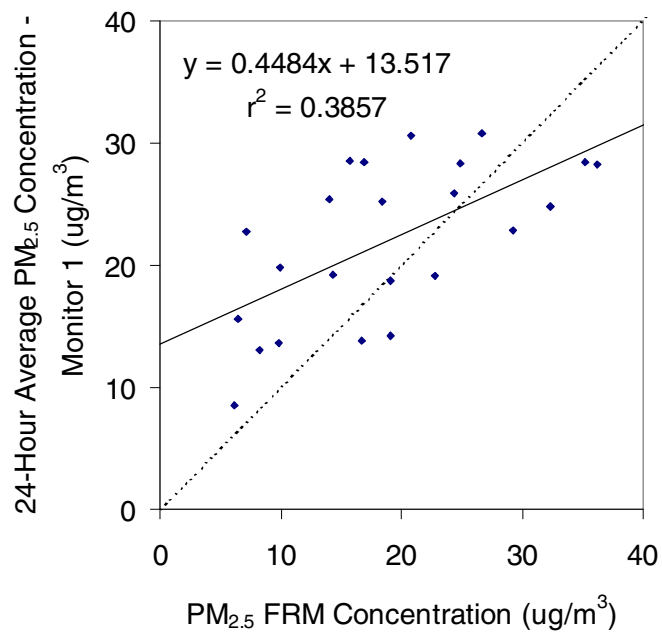

Figure 6-2b. Correlation Plot of the 24-Hour Averages from the CAMM and the PM$_{2.5}$ FRM During Phase I of Verification Testing

6.1.4 Influence of Precursor Gases

Multivariable analysis also was performed to establish if a relationship exists between precursor gases and the CAMM readings relative to the FRM. This analysis showed no influence of the precursor gases on the readings of the CAMM at the 90% confidence level.

6.2 Phase II—Fresno (December 18, 2000 - January 17, 2001)

During Phase II, daily 24-hour $PM_{2.5}$ concentrations averaged 74 µg/m^3 and ranged from 4.9 µg/m^3 to 146 µg/m^3. A strong diurnal pattern was observed in the $PM_{2.5}$ concentration, with the peak levels occurring near midnight. Particle composition was dominated by nitrate and carbon. On average, the overall $PM_{2.5}$ concentration comprised 22% nitrate and 40% total carbon. Sulfate accounted for only about 2% of the daily $PM_{2.5}$ mass. Both nitrate and sulfate were determined by ion chromatography, and carbon was determined by the IMPROVE TOR method.

Table 6-4 summarizes the meteorological conditions during Phase II, and Table 6-5 summarizes the observed concentrations of the measured precursor gases during this period.

Table 6-4. Summary of Daily Values for the Measured Meteorological Parameters During Phase II of Verification Testing

	Wind Speed (mps)	Wind Direction (Degrees)	Air Temp. (C)	RH (%)	Solar Radiation (W/m²)	Press. (mmHg)
Average	1.43	186	8.3	75.4	88.2	756.2
Max	4.18	260	12.8	92.0	123.5	761.7
Min	0.91	116	4.6	51.6	17.1	747.3

Table 6-5. Summary of Daily Values for the Measured Precursor Gas Concentrations During Phase II of Verification Testing

	CO (ppm)	O_3 (ppb)	NO (ppb)	NO_2 (ppb)	NO_x (ppb)
Average	1.9	13	61.8	32.6	94.4
Max	3.3	28	119.9	50.3	170.2
Min	0.4	6	4.1	14.8	18.9

6.2.1 Inter-Unit Precision

Between December 18, 2000, and January 3, 2001, hourly mass concentration readings were recorded from the two CAMMs. Unfortunately, the high $PM_{2.5}$ concentrations during this period were sufficient to cause clogging of the filter tape used by the CAMMs. To alleviate this problem, a representative of Thermo Andersen installed an external timing mechanism on the two CAMMs on January 6, which enabled sampling with a period of two minutes rather than one hour. From January 6 through January 17, the 2-minute data collected from the duplicate CAMMs were averaged to obtain hourly $PM_{2.5}$ readings. Figure 6-3a shows the hourly data for the duplicate CAMMs for Phase II. In Figure 6-3b, these same data are plotted to show the correlation between the two CAMMs.

For comparison with the $PM_{2.5}$ FRM reference measurements, the hourly data were averaged from midnight to midnight for each day to correspond with the 24-hour sampling periods used in Phase II of the verification test. In Figure 6-4a, the midnight-to-midnight averages for Phase II of the verification test are presented for the two CAMMs. A correlation plot of these data is shown in Figure 6-4b.

The results of a linear regression analysis of these data are presented in Table 6-6. The coefficient of variation for the hourly and the midnight-to-midnight average values were also calculated and are shown in Table 6-6.

Table 6-6 Linear Regression and Coefficient of Variation Results for Hourly and 24-Hour Average $PM_{2.5}$ Concentrations During Phase II of Verification Testing

Parameter	Hourly Data	24-Hour Average Data
Slope (95% CI)	0.903 (0.024)	0.774 (0.086)
Intercept ($\mu g/m^3$) (95% CI)	5.8 (2.8)	16.1 (9.9)
r^2	0.918	0.930
CV	17.2 %	13.8 %

The hourly data from the duplicate monitors show a slope of 0.903 (0.024); intercept of 5.8 (2.8) $\mu g/m^3$; and r^2 of 0.918. The calculated CV for the hourly data is 17.2%. A Student's t-test of the mean hourly data shows a statistically significant difference in the readings of the duplicate CAMMs, with Monitor 1 reading 3.2 $\mu g/m^3$ higher than Monitor 2 on average. This difference amounts to about 3.4% of the mean hourly CAMM reading of 93.3 $\mu g/m^3$.
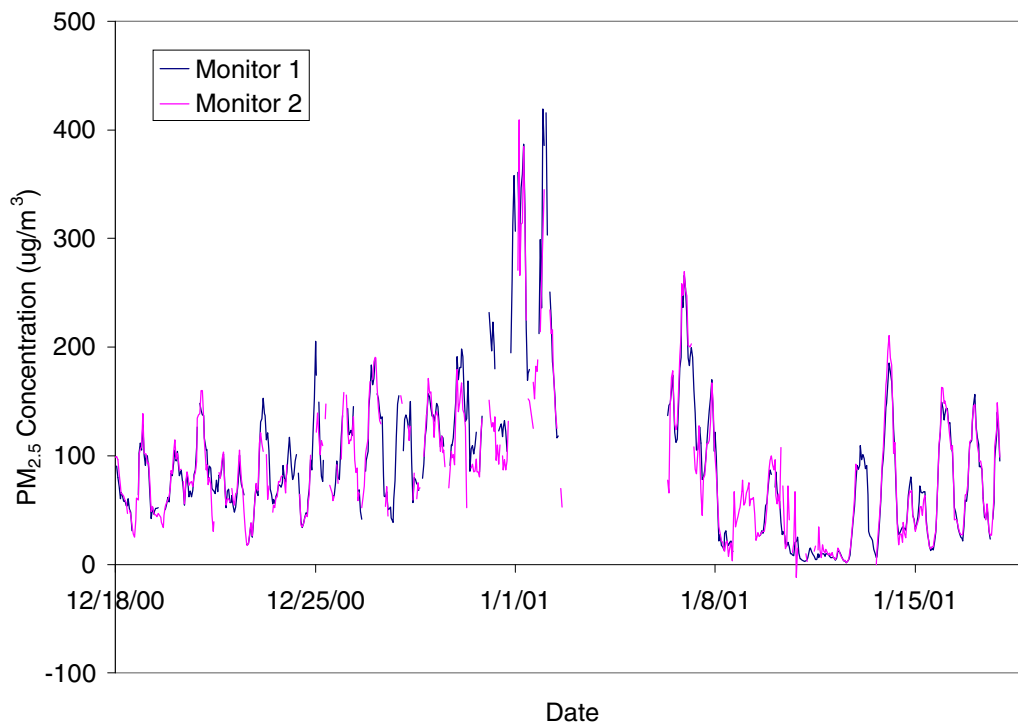
Figure 6-3a. Hourly PM$_{2.5}$ Concentrations from Duplicate CAMMs During Phase II of Verification Testing
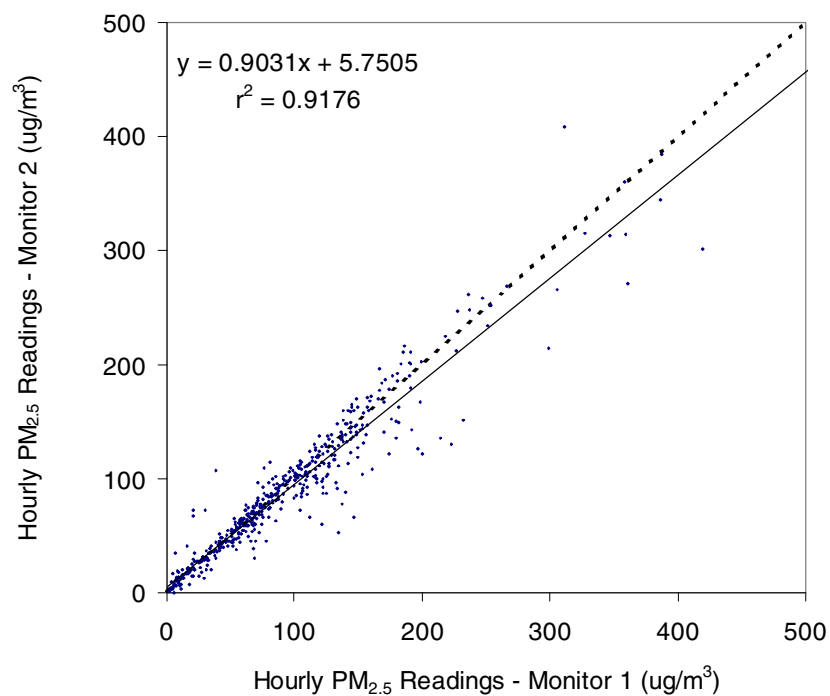

Figure 6-3b. Correlation Plot of Hourly PM$_{2.5}$ Measurements from Duplicate CAMMs During Phase II of Verification Testing
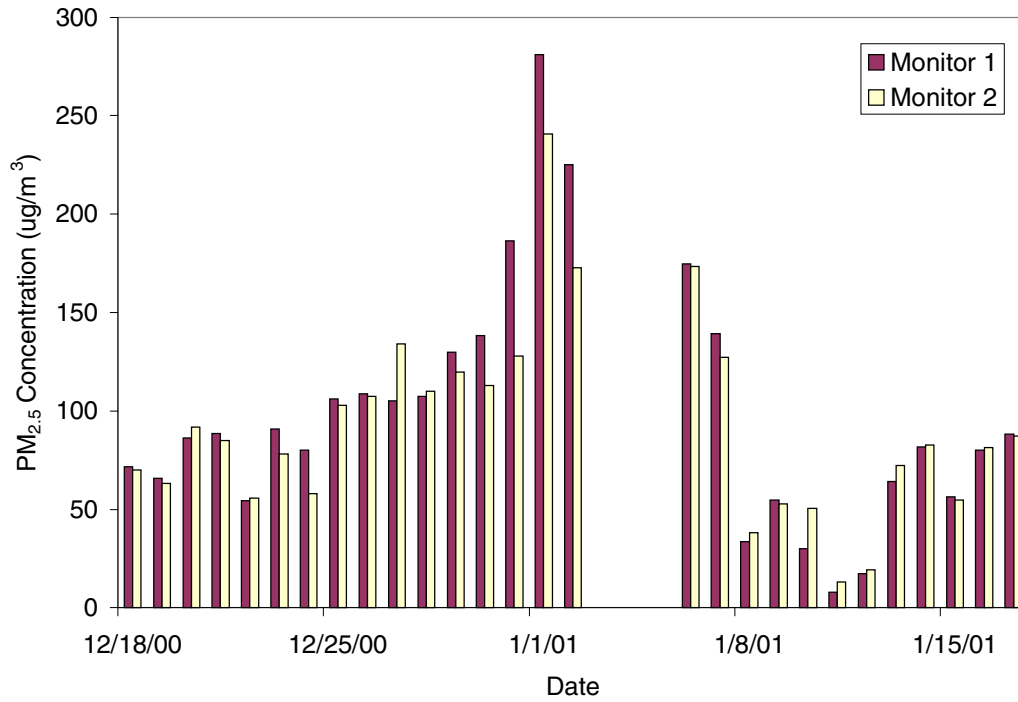
Figure 6-4a. Midnight-to-Midnight PM$_{2.5}$ Average Concentrations from Duplicate CAMMs During Phase II of Verification Testing
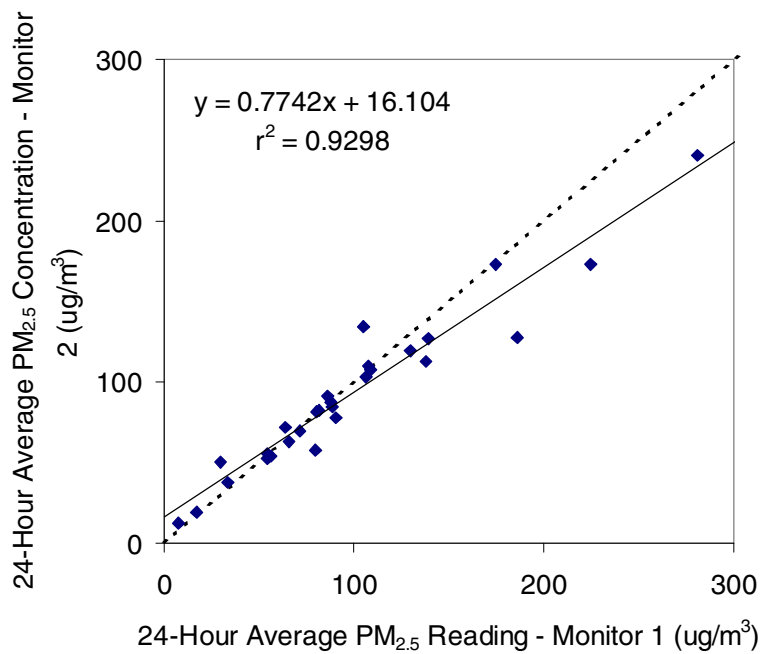

Figure 6-4b. Correlation Plot of the 24-Hour PM$_{2.5}$ Average Concentrations from Duplicate CAMMs During Phase II of Verification Testing

The 24-hour data show a slope of 0.774 (0.086); intercept of 16.1 (9.9) µg/m^3; and an r^2 of 0.930. A Student's t-test shows no statistically significant bias between the two monitors. The 24-hour average concentration results show somewhat less quantitative agreement between the duplicate monitors compared with the hourly data.

6.2.2 Comparability/Predictability

In Figures 6-5a and 6-5b, the midnight-to-midnight averages of the CAMM measurements are shown, along with the PM$_{2.5}$ FRM measurements for Phase II of the verification test. Since a large amount of data was lost during hour-long sampling in the first half of Phase II because of clogging of the filter tape, days that did not meet the 75% acceptance criterion were included in this analysis. (All days used in this analysis had at least 40% data completeness.) These PM$_{2.5}$ concentration values were analyzed by linear regression according to Section 5.2 to establish the comparability of each of the CAMMs and the PM$_{2.5}$ reference sampler. The calculated slope, intercept, and r^2 value of the regression analyses are presented in Table 6-7 for each monitor.

The r^2 values of the regression analyses of the 24-hour averages were 0.809 for Monitor 1 and 0.843 for Monitor 2. Monitor 1 showed a significant positive bias in slope relative to the FRM [slope = 1.46 (0.30)]. The slope of the regression line for Monitor 2 was not statistically different from unity [slope = 1.20 (0.22)]. The intercepts of the regression lines were not statistically different from zero at the 95% confidence level.

Historically, during the winter period in which Phase II was conducted, organic material from wood smoke has been a substantial source of PM$_{2.5}$ in Fresno. The vendor has suggested that the positive bias of the two CAMMs relative to the FRM may be attributable to volatile smoke-related components of the ambient aerosol that are measured by the CAMMs, but that volatilize prior to gravimetric analysis of the FRM samples.

6.2.3 Meteorological Effects

As with the data from Phase I, multivariable analysis was performed to determine if the meteorological conditions had an influence on the readings of the CAMMs. This analysis involved a backward elimination process to remove from the analysis model those parameters showing no statistically significant influence on the results. This analysis indicates that, during Phase II, no meteorological effects were observed on Monitor 2 relative to the FRM at the 90% confidence level. However, relative humidity had a statistically significant influence on the readings from Monitor 1 relative to the FRM values at 90% confidence. The regression analysis indicates a relationship of the form:
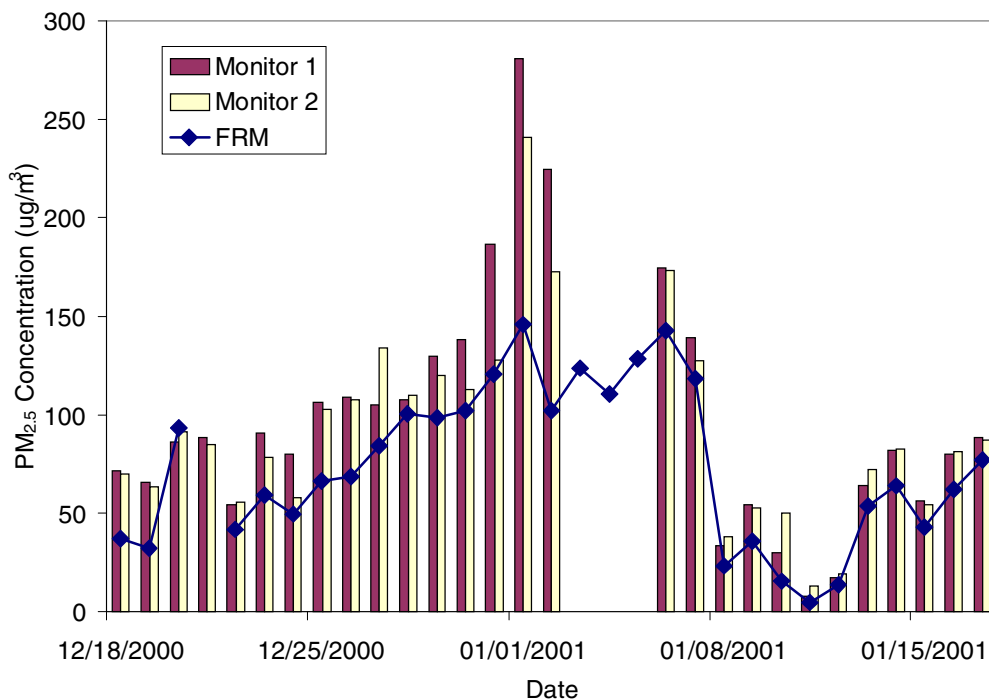
Monitor 1 = 1.55*FRM + 1.41*RH - 114.7 µg/m^3

Figure 6-5a. Midnight-to-Midnight Average Concentrations from Duplicate CAMMs and the PM$_{2.5}$ FRM Results During Phase II of Verification Testing
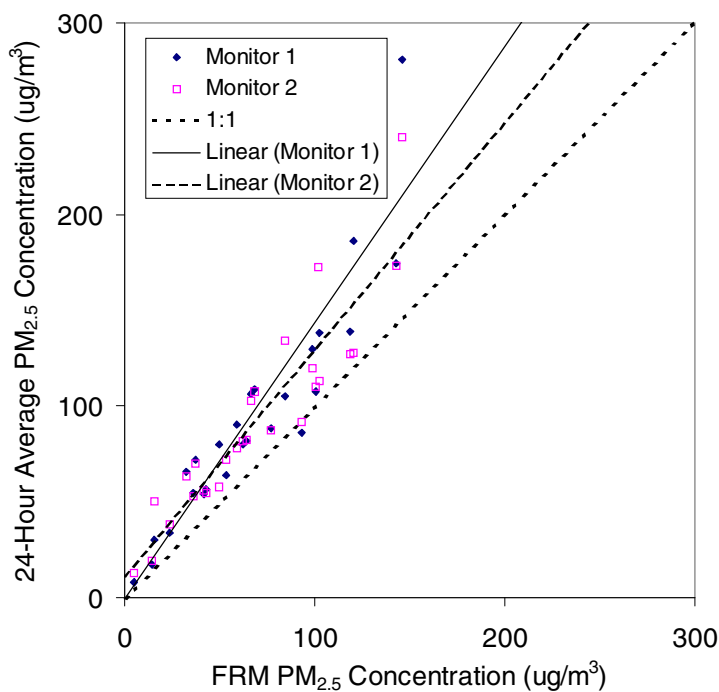

Figure 6-5b. Correlation Plot of 24-Hour Average Concentrations from Duplicate CAMMs and the PM$_{2.5}$ FRM During Phase II of Verification Testing

Table 6-7. Comparability of the CAMMs with the PM$_{2.5}$ FRM for Phase II

Regression Parameter	Monitor 1	Monitor 2
Slope (95% CI)	1.462 (0.300)	1.197 (0.218)
Intercept (95% CI) (μg/m^3)	-2.7 (23.9)	9.6 (17.4)
r^2	0.809	0.843

where FRM represents the measured PM$_{2.5}$ FRM values in μg/m^3, and RH represents the relative humidity in percent. This equation indicates that the effect of relative humidity on the CAMM readings largely canceled out the calculated intercept, and the slope of the regression relationship changed by less than 10% from the value shown in Table 6-7. The impact of relative humidity on CAMM readings predicted by the multivariate equation is negligible. For example, using the average values for PM$_{2.5}$ and relative humidity during Phase II, the multivariate equation would predict an average PM$_{2.5}$ reading of 106.3 μg/m^3 for Monitor 1, i.e.:

$$\text{Monitor 1} = 1.55*74 + 1.41*75.4 - 114.7$$

$$= 106.3 \ \mu g/m^3.$$

Based on the linear regression results (Table 6-7) and the average PM$_{2.5}$ concentration during Phase II, Monitor 1 would read

$$\text{Monitor 1} = 1.462*74 - 2.7$$

$$= 105.5 \ \mu g/m^3$$

i.e., a difference of less than 1%.

6.2.4 Influence of Precursor Gases

Multivariable analysis also was performed to determine if a relationship exists between precursor gases (carbon monoxide, nitrogen dioxide, nitric oxide, nitrogen oxides, and ozone) and the CAMM readings relative to the FRM. This analysis showed no influence of the precursor gases on the readings of either monitor at the 90% confidence level.

6.2.5 Short-Term Monitoring

During Phase II of the verification test, short-term monitoring was conducted on a five-sample-per-day basis throughout the test period. Table 6-8 presents the averages and the ranges of the time-integrated PM$_{2.5}$ concentrations for these sampling periods during Phase II. Figure 6-6 shows the correlation between the time-weighted sum of the short-term measurements from the sequential filter sampler and the 24-hour FRM measurements. The slope and intercept of the regression line are

Table 6-8. Summary of PM$_{2.5}$ Levels During Phase II of Verification Testing

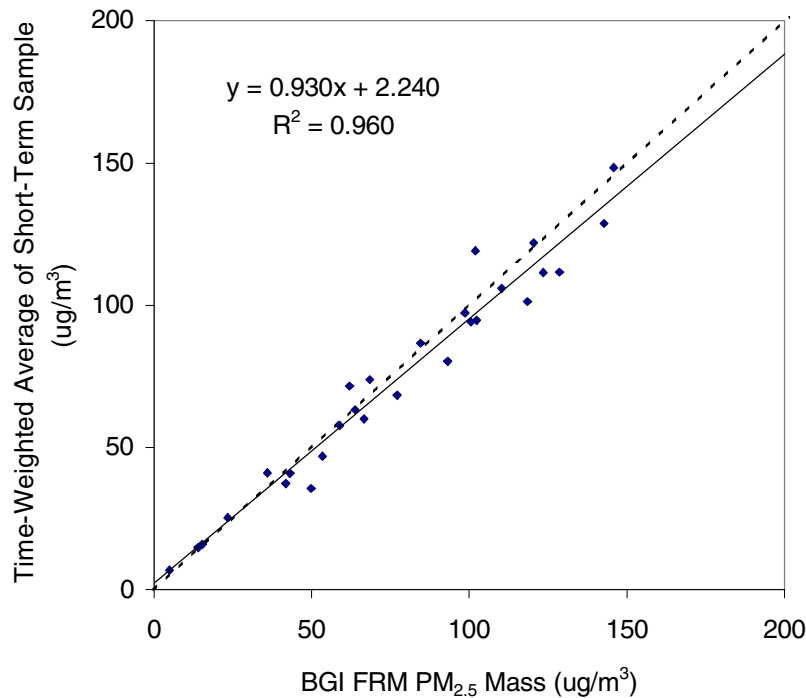| PM$_{2.5}$ Concentration (µg/m³)	Sampling Period				
	0000-0500	0500-1000	1000-1300	1300-1600	1600-2400
Average	81.0	52.2	56.8	46.7	87.7
Maximum	163.2	131.4	140.9	136.6	180.7
Minimum	3.4	7.7	4.8	2.2	7.2

Figure 6-6. Correlation Plot of the Time-Weighted Average for the Short-Term Samples and the PM$_{2.5}$ FRM

0.930 (0.077), and 2.2 µg/m³ (6.6), respectively, with an r² value of 0.960, where the numbers in parentheses are 95% CIs.

In Figure 6-7, the averages of the CAMM readings for all the short-term monitoring periods are plotted versus the corresponding PM$_{2.5}$ concentration values from the sequential filter sampler. Linear regression analysis of these data was performed separately for each CAMM, and the results are presented in Table 6-9. Regression analyses also were performed separately for each
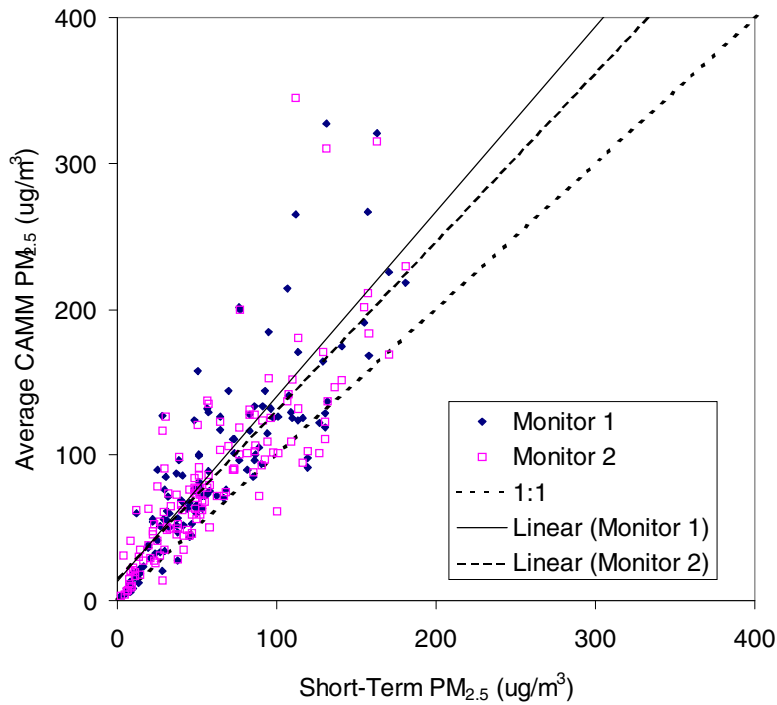
Figure 6-7. Correlation Plot of Short-Term Monitoring Results and the Corresponding Averages from the Duplicate CAMMs During Phase II of Verification Testing

Table 6-9. Regression Analysis Results for the Short-Term Monitoring

Short-Term Monitoring Period	Monitor 1			Monitor 2		
	Slope	Intercept ($\mu g/m^3$)	r^2	Slope	Intercept ($\mu g/m^3$)	r^2
All	1.27	13.1	0.716	1.15	15.6	0.666
0000-0500	1.30	27.2	0.688	1.33	25.1	0.654
0500-1000	1.90	8.4	0.751	1.52	17.2	0.599
1000-1300	1.18	5.4	0.958	1.09	4.9	0.920
1300-1600	1.26	2.5	0.925	0.90	15.2	0.795
1600-2400	1.14	3.1	0.802	0.98	12.9	0.862

of the five time periods during which the short-term samples were collected.(i.e., 0000-0500, 0500-1000, 1000-1300, 1300-1600, and 1600-2400). These regression results also are presented in Table 6-9.

The short-term monitoring results indicate that the response of the CAMMs relative to the short-term reference measurements varies with time of day. Overall, the slopes of the regression lines were 1.27 and 1.15 for Monitor 1 and Monitor 2, respectively. The slopes of the regression lines for the different sampling periods range from 1.14 to 1.90 for Monitor 1, and from 0.90 to 1.52 for Monitor 2. (It should be noted that the reference measurements have not been corrected to account for the observed difference between the time-weighted average of the short-term samples and the FRM.)

6.3 Instrument Reliability/Ease of Use

The CAMMs required some maintenance during Phase I. Approximately weekly, the virtual impactors on the two CAMMs were cleaned. Additionally, the filter tape in each CAMM was changed several times during Phase I. Some additional troubleshooting was performed on one of the units to identify the source of problems indicated by the error codes on the display of the monitor. As noted previously, a leak was present in this monitor that invalidated all data. With the exception of several power outages, approximately 90% data recovery was achieved from the one CAMM that operated in Phase I.

During Phase II of the verification test, the virtual impactors required cleaning approximately every one to two days as a result of the high $PM_{2.5}$ concentrations. An external timer mechanism was added to each of the CAMMs to allow data collection on a two-minute time scale rather than the default one-hour time scale.

6.4 Shelter/Power Requirements

The CAMMs were installed and operated outside during each phase of testing. The monitors and pumps were run on a single 15 A circuit. Vendor literature indicates a range of operating temperatures from -10°C to 40°C; however, this was not verified during this test.

6.5 Instrument Cost

The price of the CAMM as tested is approximately $15,000. Filter tape for the CAMM is the only consumable associated with this technology. Though not verified in this test, Thermo Andersen suggests that a roll of filter tape is expected to last approximately 60 days of continuous monitoring at a one-hour sample rate.

Chapter 7
Performance Summary

The CAMM is designed to provide hourly indications of the ambient particulate matter concentration. Duplicate CAMMs were evaluated under field test conditions in two separate phases of this verification test. The collocated monitors were operated outside and were installed with a PM_{10} head and $PM_{2.5}$ Sharp Cut Cyclone to provide size selection of the aerosol. The results from each phase of this verification test are summarized below.

7.1 Phase I—Pittsburgh (August 1 - September 1, 2000)

Only one of the duplicate CAMMs provided usable data during Phase I. The second unit had a leak in the sampling system, and the collected data were invalidated. Consequently, no measure of inter-unit precision is available for Phase I.

Comparisons of the 24-hour averages with $PM_{2.5}$ FRM results showed a slope of the regression line for Monitor 1 of 0.45 (0.26) and an intercept of 13.5 (5.4) $\mu g/m^3$, where the values in parentheses are 95% CIs. The regression results showed an r^2 value of 0.386. A substantial negative bias relative to the FRM was indicated by these data.

Multivariable analysis showed that none of the meteorological parameters measured during Phase I influenced the readings of the CAMM relative to the FRM at the 90% confidence level. Likewise, none of the precursor gases were shown to have a statistically significant effect on the readings of the CAMM during Phase I.

The CAMMs required some maintenance during Phase I. Approximately weekly, the virtual impactors on the two CAMMs were cleaned. Additionally, the filter tape in each CAMM was changed several times during Phase I. Some additional troubleshooting was performed on one of the units to identify the source of problems indicated by the error codes on the display of the monitor. As noted previously, a leak was present in this monitor that invalidated all data. With the exception of several power outages, approximately 90% data recovery was achieved from the one CAMM that operated in Phase I.

7.2 Phase II—Fresno (December 18, 2000 - January 17, 2001)

The duplicate CAMMs correlated closely with one another at both the hourly level and in terms of the 24-hour averages during Phase II. Regression analysis showed r^2 values of 0.918 and 0.930, respectively, for these hourly data and 24-hour averages. The slopes of the regression lines were 0.903 (0.024) and 0.774 (0.086), respectively, for the hourly data and 24-hour averages; and the intercepts were 5.8 (2.8) $\mu g/m^3$ and 16.1 (9.9) $\mu g/m^3$, respectively. The calculated CV for the hourly data was 17.2%, and for the 24-hour data the CV was 13.8%.

Comparison of the 24-hour averages with $PM_{2.5}$ FRM results showed slopes of the regression lines for Monitor 1 and Monitor 2 of 1.46 (0.30) and 1.20 (0.22), respectively. The regression results showed r^2 values of 0.809 and 0.843 for Monitor 1 and Monitor 2, respectively.

Multivariable analysis showed that relative humidity influenced the readings of one of the duplicate CAMMs during Phase II. However, the overall effect was small (approximately 1% on average) and of little practical importance. None of the precursor gases measured during Phase II were shown to have a statistically significant influence on the results of the CAMMs relative to the FRM.

In addition to 24-hour FRM samples, short-term monitoring was performed on a five-sample-per-day basis. The CAMM results were averaged for each of the sampling periods and compared with the gravimetric results. Linear regression of these data, including all short-term sampling periods, showed slopes of 1.27 and 1.15, respectively, for Monitor 1 and Monitor 2. The intercepts of the regression lines were 13.1 and 15.6 $\mu g/m^3$, respectively; and the r^2 values were 0.716 and 0.666, respectively.

During Phase II of the verification test, the virtual impactors required cleaning approximately every one to two days as a result of the high $PM_{2.5}$ concentrations. An external timer mechanism was added to each of the CAMMs to allow data collection on a two-minute time scale rather than the default one-hour time scale.

Chapter 8
References

1. *Test/QA Plan for the Verification of Ambient Fine Particle Monitors*, Battelle, Columbus, Ohio, June 2000.

2. "National Ambient Air Quality Standards for Particulate Matter; Final Rule," U.S. Environmental Protection Agency, 40 CFR Part 50, *Federal Register,* 62 (138):38651-38701, July 18, 1997.

3. *Quality Management Plan (QMP) for the Advanced Monitoring Systems Pilot*, Version 2.0, Battelle, Columbus, Ohio, October 2000.

4. "Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS)." Appendix A to 40 CFR Part 58, *Federal Register*, 62 (138), p.65, July 18, 1997.