Environmental Technology Verification Report

ECOCHEM ANALYTICS PAS 2000 PARTICULATE PAH MONITOR

Prepared by

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ETV Joint Verification Statement

TECHNOLOGY TYPE: Continuous Ambient Fine Particle Monitor

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

**TECHNOLOGY
NAME:** **PAS 2000 Particulate PAH Monitor**

COMPANY: **EcoChem Analytics**

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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 EcoChem Analytics Photoelectric Aerosol Sensor (PAS) 2000 particulate polycyclic aromatic hydrocarbon (PAH) monitor.

VERIFICATION TEST DESCRIPTION

The objective of this verification test was to provide quantitative performance data on a variety of 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. For verification of the PAS 2000 monitors, 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 May 10 to 23, 2001. Specific performance characteristics to be verified in this test included inter-unit precision, agreement with and correlation to time-integrated reference methods, effect of meteorological conditions, and influence of precursor gases. The PAS 2000 measures electron current associated with ionization of particulate-bound PAH species, and, therefore, was compared to a reference procedure for determining ambient concentrations of particulate-bound PAHs. Additionally, comparisons with a variety of supplemental measurements were made to establish specific performance characteristics. Unfortunately, in both phases of testing, both reference and PAS 2000 data indicated that the ambient PAH levels were often near or below the nominal 3 ng/m^3 detection limit of the monitors. As a result, the quantitative evaluation of PAS 2000 performance was limited.

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 systems audit for Phase I and Phase II. EPA QA staff conducted an external technical systems audit during Phase II.

TECHNOLOGY DESCRIPTION

The PAS 2000 works on the principle of photoionization of particle-bound PAH. Using a 220-nm excimer lamp, the aerosol flow is exposed to high-intensity, narrow band ultraviolet radiation. The narrowly restricted wavelength of the light allows only particulate PAH having ionization potentials of 5.6 eV or less to be ionized, while gas molecules and non-carbon aerosols remain neutral. The aerosol particles that have PAH molecules adsorbed on their surfaces emit electrons as a result of the photoionization process that are removed when an electric field is applied. The remaining positively charged particles are then collected on a filter inside an electrometer, where the charge is measured. The resulting electric current establishes a signal that is proportional to the concentration of total particle-bound PAH. Source-specific calibration curves are available, or can be generated by comparing the monitor output to an analytically determined PAH concentration, based on sampling the source emissions. A source-specific calibration curve can provide greater accuracy for the particle size, charge, and PAH distribution specific to the source. In addition to the source-specific curves, an approximate universal calibration curve can be used for screening and real-time trending applications. That universal calibration curve was used in all PAS 2000 monitoring in this verification test. A specially designed sample conditioning system for monitoring PAH in source emissions consists of a heated probe and a dilution system. These features permit the PAS 2000 to handle emission streams with high particle loading from stacks. The PAS 2000 also can be connected to a rotating disk dilution system. As used in this study for monitoring particle-bound PAH in ambient air, the PAS 2000 had a nominal detection limit of 3 ng/m^3 The PAS 2000 incorporates no internal particle size selection. In this verification, no external particle size selection was used either, because of the predominant occurrence of ambient atmospheric particle-bound PAH in the fine particle size range (i.e., $PM_{2.5}$).

VERIFICATION OF PERFORMANCE

Inter-Unit Precision: During Phase I , the duplicate PAS 2000 monitors showed the same temporal pattern of ambient PAH levels for both the 15-minute data and 24-hour averages. Regression analysis showed $r^2 = 0.989$ for the 15-minute data and $r^2 = 0.979$ for the 24-hour averages. The slopes of the regression lines were 0.779 (0.002) and 0.782 (0.023), respectively, for the 15-minute data and 24-hour averages, indicating a significant bias of

about 22% between the two monitors. The intercept of the regression line was -0.66 (0.01) ng/m^3 for the 15-minute data, and was -0.68 (0.10) ng/m^3 for the 24-hour data. The calculated coefficient of variation (CV) for the 15-minute data was 60.4%; and, for the 24-hour averages, the CV was 40.8%. Much of these CV values may be attributed to the bias between the monitors and to the fact that the ambient PAH concentrations were comparable to the 3 ng/m^3 nominal detection limit of the monitors, making even small inter-unit differences relatively large contributors to the CV.

During Phase II, the duplicate PAS 2000 monitors again showed the same temporal trends when 15-minute average data were considered. Regression analysis showed an r^2 of 0.812, a slope of 0.875 (0.010) and an intercept of -1.98 (0.04) ng/m^3. The calculated CV for these data was 101%, much of which is attributed to an offset (~2 ng/m^3) between the two monitors. No conclusive statistical measure of precision was available for the 24-hour averages, as all the results from one monitor were below the nominal detection limit. However, a linear regression analysis of these data show an r^2 of 0.406, a slope of 0.475 (0.382), and an intercept of -0.65 (1.46) ng/m^3. The calculated CV for these data was 84.3%. In light of the low ambient PAH levels present (comparable to the 3 ng/m^3 nominal detection limit of the monitors), the substantial offset between the two monitors undoubtedly was a major contributor to these CV values.

Comparability/Predictability: In both phases of the verification test, both the reference method and the PAS 2000 data indicated that ambient particulate PAH levels were usually near or below the nominal 3 ng/m^3 detection limit of the PAS 2000 monitors. Consequently, quantitative comparisons to the reference data were not conducted, although the ranges of the reference and PAS 2000 data were similar, and some agreement in temporal trends was observed.

Meteorological Effects: Because the ambient PAH levels were comparable to the nominal detection limit of the monitors, no conclusions could be made from multivariable analysis concerning the influence of meteorological conditions on PAS 2000 readings.

Influence of Precursor Gases: Because the ambient PAH levels were comparable to the nominal detection limit of the monitors, no conclusions could be made from multivariable analysis concerning the influence of precursor gases on PAS 2000 readings.

Other Parameters: The two monitors required no maintenance during either phase of testing. Some periods of data were lost because of recurrent difficulties with the data collection system in the form of failure to restart data collection after power outages. Overall data recovery was approximately 90%.

Gabor J. Kovacs	Date	Gary J. Foley	Date
Vice President		Director	
Environmental Sector		National Exposure Research Laboratory	
Battelle		Office of Research and Development	
		U.S. Environmental Protection Agency	

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

ECOCHEM ANALYTICS PAS 2000 PARTICULATE PAH MONITOR

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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

Contents

Figures

Tables

List of Abbreviations

ADQ	audit of data quality
AMS	Advanced Monitoring Systems
CARB	California Air Resources Board
CI	confidence interval
CO	carbon monoxide
CV	coefficient of variation
DOE	U.S. Department of Energy
DPI	digital pressure indicator
DRI	Desert Research Institute
EC	elemental carbon
EPA	U.S. Environmental Protection Agency
eV	electron volt
ETV	Environmental Technology Verification
FRM	federal reference method
Hg	mercury
H_2S	hydrogen sulfide
IMPROVE	Interagency Monitoring for Protection of Visual Environments
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
PAH	polycyclic aromatic hydrocarbon
PAS	photoelectric aerosol sensor
ppb	parts per billion
QA/QC	quality assurance/quality control
QMP	Quality Management Plan
SO_2	sulfur dioxide
TOR	thermal optical reflectance
TSA	technical systems audit

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 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 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 fine particulate matter in ambient air. This verification report presents the procedures and results of the verification test for the EcoChem Analytics Photoelectric Aerosol Sensor (PAS) 2000 particulate polycyclic aromatic hydrocarbon (PAH) monitor.

Chapter 2
Technology Description

The following description of the PAS 2000 is based on information provided by the vendor.

The PAS 2000 works on the principle of photoionization of particle-bound PAH. Using a 220-nm excimer lamp, the aerosol flow is exposed to high-intensity, narrow band ultraviolet radiation. The narrowly restricted wavelength of the light allows only particulate PAH having ionization potentials of 5.6 eV or less to be ionized, while gas molecules and non-carbon aerosols remain neutral. The aerosol particles that have PAH molecules adsorbed on their surfaces emit electrons as a result of the photoionization process that are removed when an electric field is applied. The remaining positively charged particles are then collected on a filter inside an electrometer, where the charge is measured. The resulting electric current establishes a signal that is proportional to the concentration of total particle-bound PAH. Source-specific calibration curves are available, or can be generated by comparing the monitor output to an analytically determined PAH concentration, based on sampling the source emissions. A source-specific calibration curve can provide greater accuracy for the particle size, charge, and PAH distribution specific to the source. In addition to the source-specific curves, an approximate universal calibration curve can be used for screening and real-time trending applications. That universal calibration curve was used in all PAS 2000 monitoring in this verification test. A specially designed sample conditioning system for monitoring PAH in source emissions consists of a heated probe and a dilution system. These features permit the PAS 2000 to handle emission streams with high particle loading from stacks. The PAS 2000 also can be connected to a rotating disk dilution system. As used in this study for monitoring particle-bound PAH in ambient air, the PAS 2000 had a nominal detection limit of 3 nanograms per cubic meter (ng/m^3). The PAS 2000 incorporates no internal particle size selection. In this verification, no external particle size selection was used either, because of the predominant occurrence of ambient atmospheric particle-bound PAH in the fine particle size range (i.e., $PM_{2.5}$).

Figure 2-1. EcoChem Analytics PAS 2000 Particulate Monitor

The PAS 2000 has the following housing options: standard desktop, rack-mounted, or wall-mounted. It has an liquid crystal panel display, with 128

by 64 pixel resolution, and operates on 115 volts AC/ 60 Hz or 220 volts AC / 50 Hz. The desktop unit is 4.5 in, high, 9.3 in. wide, and 12.5 in. deep and weighs 20 pounds.

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. 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 testing of the PAS 2000 PAH monitors 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). For the EcoChem PAS 2000, this phase of testing was conducted from May 10-23, 2001.

3.2 Test Design

This verification test was designed to assess the following specific performance characteristics:

- Inter-unit precision
- Agreement with and correlation to a time-integrated reference method for particulate PAH
- Effect of meteorological conditions
- Influence of precursor gases
- Correlation with elemental carbon measurements.

To assess inter-unit precision, duplicate PAS 2000 monitors were tested in side-by-side operation during each phase of testing. Collocation of the PAS 2000 monitors 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. In addition, at the vendor's requests, the correlation of PAS 2000 readings with particulate elemental carbon (EC) was assessed in Phase I of testing. Statistical calculations, as described in Chapter 5, were designed to quantify each of these performance characteristics. However, as will be shown in Chapter 6, the ambient levels of particle-bound PAH were usually close to the nominal detection limit of the PAS 2000 (i.e., 3 ng/m^3). As a result, quantitative treatment of some performance characteristics was not feasible.

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 used in the field periods were well-established methods for determining particulate matter mass or chemical composition. It is recognized that comparing real-time measurements with time-averaged 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-averaged standard methods that are widely accepted was necessary for performance verification purposes.

The PAS 2000 measures electron current associated with ionization of particle-bound PAH species. While widely used in source-related PAH monitoring, the PAS 2000 monitor is not yet widely used for ambient monitoring. The low concentrations of particulate PAH typical of ambient air present a challenge for the PAS 2000 monitor, as well as for any reference method used for comparison. In particular, the semivolatile nature of PAH compounds requires that the vapor and particle phases of ambient PAH be separated so that the particle-bound PAH may be determined. The cost and complexity of such PAH phase distribution measurements have severely limited the number of particle-phase PAH data available. Many reported "particulate PAH" results are not obtained with the appropriate phase separation to isolate and preserve the particulate PAH fraction. The few reliable particulate PAH data indicate ambient levels of a few ng/m^3. Thus, a sensitive sampling and analytical method is needed to determine particle-phase PAH with proper phase separation. Consequently, for verification purposes, a reference method was chosen that is capable of determining low ambient concentrations of particle-bound PAHs. A summary of this method is given below.

3.3.1 Particle-Bound PAH

For particle-bound PAH measurements, sample collection and analysis procedures based on ASTM Method D-6209-98[2] were used. This method uses a filter/adsorbent resin combination to collect particulate PAHs, preceded in the sample flow path by a denuder to remove vapor-phase PAHs. Battelle supplied filter/XAD resin sampling trains and appropriate denuders to determine

the particle-phase PAH species. After removing the vapor phase material in the denuder, the total particle-phase PAH was collected on a quartz fiber filter followed by an XAD-2 resin bed. Particulate matter collected on the combined filter/XAD trains was analyzed for 22 target PAH compounds and their isomers by solvent extraction and subsequent gas chromatography/mass spectrometry procedures. Further detail on the PAH species measured is provided in Section 3.4. It must be stressed that the reference method used in this verification is not a fully developed Federal Reference Method, such as that for $PM_{2.5}$ determination. Ambient atmospheric PAH measurements are a research topic rather than a routine monitoring task, and no FRM-level standard method exists.

Particulate matter samples for PAH determination were collected daily over 24-hour periods at each test site and were used to verify the performance of the commercial particulate PAH monitor. In Phase I PAH reference sampling took place from noon to noon, and in Phase II from 2:30 p.m. to 2:30 p.m., to avoid conflicts with other activities at the test site. During each phase of testing, these samples were collected using an Andersen RAAS $PM_{2.5}$ speciation sampler (Serial Number 0212). A sample flow rate of 8 L/min was used in both phases of testing. With a 24-hour sampling period, the detection limit for each of the 22 target PAH compounds was 0.09 ng/m^3.

During Phase I of testing, a supply of compound annular XAD-coated denuders[3] was used to remove gaseous PAH species from the air stream in the PAH reference samples. Each denuder was used for three successive days, rinsed with methylene chloride to remove the adsorbed species, and reused after drying. The results of Phase I suggest that, as used, these denuders may not have provided sufficient capacity or lifetime for the full duration of Phase I. That is, the removal efficiency of the denuders declined after successive cycles of use, rinsing, and drying. During Phase II, activated charcoal denuders provided by DRI were used instead of the XAD-coated denuders. Those charcoal denuders had a large capacity for PAH adsorption, and no regeneration of the denuders was required.

A small number of collocated PAH samples were collected during each phase to investigate the precision of the reference method. A discussion of the collocated sampling is presented in Section 4.4 of this report.

3.3.2 Supplemental Measurements

Various supplemental measurements were made in order to further investigate 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, were measured continuously during the verification test for use in investigating the influence of these parameters on the performance of the monitors tested. Additionally, 24-hour elemental carbon reference measurements were made during Phase I. These measurements were made using an Andersen RAAS speciation sampler, with quartz fiber filters that had been heated in a muffle furnace to remove organic binders and contamination. Those filters were analyzed by

DRI using the IMPROVE thermal optical reflectance technique. These EC measurements were used to test the correlation of the PAS 2000 readings with the EC content of the aerosol.

3.4 Data Comparisons

As noted in Chapter 2, the PAS 2000 monitors respond to the sum of particle-bound PAH with ionization potentials of 5.6 eV or less. To achieve the most relevant comparison, those 12 PAHs measured with the reference method and having ionization potentials in that range were summed for each 24-hour PAH sample. Those 12 PAHs were anthracene, pyrene, methylpyrene isomers, benz(a)anthracene, methylbenz(a)anthracene isomers, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, and dibenzo(a,h)anthracene. Thus, in all cases, the reference PAH data refer to the sum of these 12 compounds from the reference measurements. These 12 compounds were selected from a much larger list of PAH-type compounds potentially present, as accounting for most of the particle-bound PAH with ionization potentials in the requisite range. It must be pointed out that no site-specific calibration curve was established for the PAS 2000 response for either phase of the verification test. The verification results are based on use of the approximate universal calibration curve for the PAS 2000 monitors.

Additional comparisons were made with the supplemental meteorological conditions and precursor gas concentrations to assess the effects of these parameters on the response of the monitors being tested. Correlation of PAS 2000 and $PM_{2.5}$ EC results was also investigated in Phase I of the verification. To the extent feasible, 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 reported separately. Inter-unit precision was determined from a statistical inter-comparison of the results from the duplicate monitors.

3.5 Site Layout/Instrument Installation

In Phase I, the two PAS 2000 monitors were installed in Battelle's instrument trailer, which is a converted 40-foot refrigerator semi-trailer. The PAS 2000 monitors were placed on a counter top, below a 7.6-cm (3 in.) port through the roof of the trailer. During Phase II, the duplicate monitors were located inside the CARB office. Flexible plastic tubes were used to supply the sampled air to the duplicate monitors in both phases. No size-selective inlet was used in either phase. Data generated by the PAS 2000 monitors were recorded on laptop computers during 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. The PAS 2000 monitors were installed inside the Battelle trailer, and the Andersen RAAS sampler was installed on the Battelle/ETV platform. A vertical separation of approximately 2 to 3 meters and a horizontal separation of approximately 3 meters existed between the inlets of the PAS 2000 monitors and the Andersen RAAS sampler. A 10-meter (33-foot) meteorological tower was located approximately 20 meters (65 feet) to the north of the DOE/NETL instrument trailer.
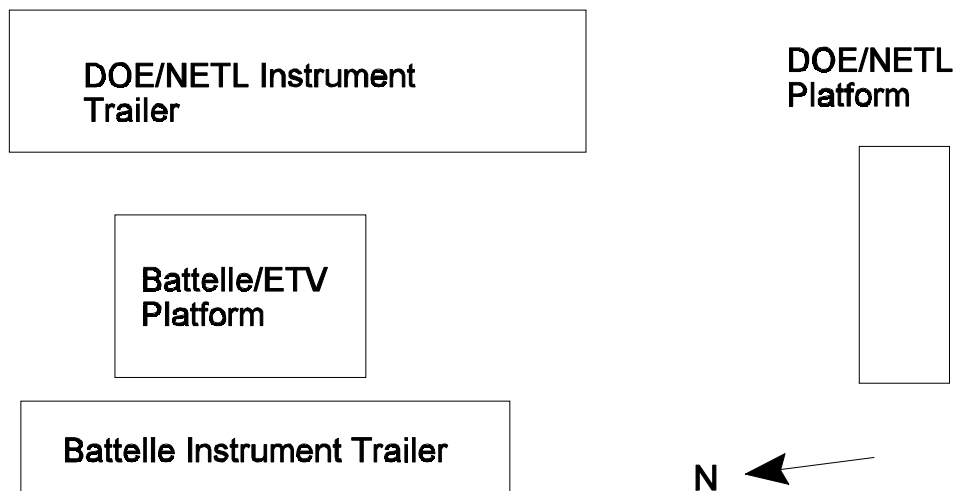
Figure 3-1. Site Layout During Phase I of Verification Testing (not drawn to scale)

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. During testing the two PAS 2000 monitors were positioned on a countertop inside the CARB site and sampled through a port in the roof of the building. Flexible plastic tubing was used to supply the sampled air to the duplicate monitors. The Andersen RAAS speciation sampler used to collect the reference samples was located on the roof of the building, approximately five meters from the inlet of the PAS 2000 monitors. A vertical separation of approximately 1 to 2 meters existed between the inlets of the PAS 2000 and the Andersen RAAS sampler.

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], and the test/QA plan.[1] The Verification Test Coordinator or the Verification Testing Leader or designee reviewed the raw data, laboratory notebook entries, and data sheets that were generated each day and approved them by initialing and dating the records.

Data from the PAS 2000 monitors were reviewed by the Verification Test Coordinator before being used in statistical calculations.

4.2 Deviations from the Test/QA Plan

The following deviations from the test/QA plan relate to verification of the PAS 2000 monitors, and were documented and approved by the AMS Center Manager.

- As a result of problems associated with reference sample documentation for verification of the PAS 2000 during the originally scheduled Phase II period (December 18, 2000, through January 17, 2001), sampling for Phase II was repeated (May 10 through 23, 2001).

- With the agreement of the vendor, only two weeks of sampling were repeated for Phase II. Consequently, only two sets of duplicate samples, rather than five, were collected during Phase II because of the shortened sampling schedule.

4.3 Calibration and Parameter Checks of Reference Sampler

The Andersen RAAS speciation sampler provided by Battelle for this verification test was calibrated using National Institute of Standards and Technology (NIST)-traceable flow meters and temperature and pressure sensors. The calibration and verification of this sampler is described below.

4.3.1 Flow Rate Calibration and Verification

Prior to Phase I of the verification test, a single-point calibration of the flow rate for each channel of the Andersen RAAS sampler was performed on July 20, 2000. Flows were measured using a dry gas meter (American Meter Company, Battelle asset number LN 275010, calibrated January 21, 2000).

For Phase II measurements, the flow rates for the PAH channels of the Andersen RAAS sampler were calibrated and verified on May 9, 2001, using a dry gas meter (Schlumberger, Serial No. 103620. Agreement between the measured flow rate and the indicated flow rate was within 5%.

4.3.2 Temperature Sensor Calibration and Verification

The temperature sensors in the Andersen RAAS sampler were 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 18, 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 $\pm 2^\circ$C. On August 28, a Performance Evaluation Audit of the temperature sensors (Section 4.7.2) confirmed proper operation of the sensors. After the verification period was completed, the ambient temperature sensor suffered a malfunction on September 7.

For Phase II measurements, the calibration of the temperature sensors in the Andersen RAAS was verified both before and after the verification period, on May 9 and May 25, 2001, respectively, using a mercury thermometer (Fisher Scientific, serial number 7116). Agreement between the sensors and the thermometer readings was within $\pm 2^\circ$C in all cases.

4.3.3 Pressure Sensor Calibration and Verification

Checks of the pressure sensor in the Andersen RAAS sampler 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) and the results agreed within the acceptance criterion of 5 mm of mercury. On September 11, 2000, the pressure sensor was again checked against the same barometer, but did not agree within the acceptance criterion of 5 mm of mercury. This failure is possibly associated with the failure of the ambient temperature sensor on September 7, 2000.

For Phase II measurements, the ambient pressure sensor for the Andersen RAAS sampler was checked against the pressure readings of a digital pressure indicator (Druck DPI 705, serial number 6016/00-2) both before and after the verification period, on May 9 and May 25, 2001, respectively. Agreement between the pressure readings from the RAAS sampler and those of the DPI 705 were within 5 mm of mercury in both cases.

4.3.4 Leak Checks

Leak checks of the Andersen RAAS sampler were performed every fourth day during Phase I of the verification test. These leak checks were conducted during sampler set-up and were performed according to the procedures in the operator's manual for the RAAS sampler. All leak checks passed the acceptance criteria provided in the operator's manual.

Leak checks of the Andersen RAAS sampler 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 the acceptance criteria.

4.4 Collocated Sampling

4.4.1 Phase I—Pittsburgh

To establish the precision of the PAH reference method, the Andersen RAAS sampler was collocated with the DOE/NETL RAAS sampler both before and after Phase I of the verification test. During these sampling periods, the two RAAS samplers were located on the same platform and were within four meters of one another. The collected particulate PAH samples from these periods were stored cold at Consol and shipped on dry ice to Battelle for extraction and analysis.

These duplicate samples showed good agreement for the period prior to the Phase I verification, but poor agreement after the Phase I verification. Prior to Phase I, the agreement between the duplicate samples (difference divided by mean) ranged from 4% to 40%, with an average of about 16%. After Phase I, the average difference was approximately 140%. Inspection of the individual sample results suggests that the denuders used during Phase I became less efficient at removing gaseous PAH species over the course of testing. This possibility was taken into account in evaluating the PAS 2000 verification data.

4.4.2 Phase II—Fresno

During Phase II of testing, duplicate trains in the Andersen RAAS sampler were used to establish the precision of the reference method. These trains were used to collect two sets of simultaneous reference samples. These samples were stored in a freezer in Fresno until shipment on dry ice to Battelle for extraction and analysis.

The analysis shows that the percent difference (difference divided by mean) for the two sets of duplicate samples was 0% (2.7 and 2.7 ng/m^3) for one set and approximately 22% (1.6 and 1.9 ng/m^3) for the second set.

4.5 Field Blanks

Ten percent of the reference samples collected during Phase I were field blanks. These field blanks showed PAH mass ranging from 1.1 to 1.5 ng, with an average PAH mass of 1.3 ng for those 12 PAHs to which the PAS 2000 responds (i.e., those with ionization potentials 5.6 eV) Assuming a sample volume of 10 m^3, these blanks account for approximately 0.11 to 0.15 ng/m^3 of the reference PAH values.

Three of the reference samples collected during Phase II were also field blanks. One blank sample container was broken in transit from Fresno and was likely contaminated. The two other blank samples showed a PAH mass of 1.2 and 1.5 ng. Assuming a sample volume of 10 m^3, these blanks would account for approximately 0.12 to 0.15 ng/m^3 of the reference PAH concentration.

4.6 Data Collection

4.6.1 Reference Measurements

During Phase I, daily records of the sampling activities for the Andersen RAAS sampler were recorded on individual data sheets by the on-site operators, and summary data from the RAAS 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 Andersen RAAS sampler 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 PAS 2000 Monitors

Data from each of the PAS 2000 monitors were recorded about every eight seconds on an on-site laptop computer. These data were saved daily as text files that were imported into a spreedsheet for statistical analysis. 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 the TSA are permanently stored with the Battelle Quality Manager.

Phase II—Fresno

The Phase II TSA was conducted by the Battelle Quality Manager at the Fresno test site on January 9, 2001, in conjunction with Phase II tests of other $PM_{2.5}$ monitoring devices. An independent audit was completed concurrently by EPA auditors, Ms. Elizabeth Betz and Ms. Elizabeth Hunike. Findings of this TSA primarily addressed documentation of the PAH reference sampling, and the Battelle and EPA Quality Managers requested that the Verification Test Coordinator take several corrective actions. All findings and related corrective actions were documented and reviewed as described above for the Phase I TSA. All corrective actions were completed to the satisfaction of the Battelle Quality Manager and the EPA. However, in order for the PAH test documentation to reach the quality objectives of the ETV AMS Center QMP and the verification test/QA plan, it was necessary to repeat that portion of the verification that addressed the PAS 2000 monitors. The repeat PAH verification, conducted May 10-23, 2001, is Phase II of the PAS 2000 verification reported here.

4.7.2 Performance Evaluation Audit

Phase I—Pittsburgh

The performance evaluation audit challenges the reference measurement systems with independent standards or comparisons as a check on data quality. During Phase I of the verification test, the flow rate of the Andersen RAAS sampler was audited on August 28, 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.

The temperature sensors in the RAAS sampler were checked on August 28, 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

The flow rates of the PAH channels in the RAAS sampler were audited on May 9, 2001, using a flow calibrator (Chinook, serial number 10961) and manometer. For each of the PAH channels, the measured pressure drop was converted to a sample flow rate and compared with the flow rate indicated by the sampler. In each case, the calculated flow rate was within the ±4% acceptance criterion with respect to the internal flow meter.

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 outlined in the Phase I TSA. All findings were minor, and 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 PAS 2000 monitors.

Chapter 5
Statistical Methods

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

5.1 Inter-Unit Precision

The inter-unit precision of the PAS 2000 monitors 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 PAS 2000 monitors were paired, and the behavior of their differences was used to assess precision. For both the 15-minute average readings and the 24-hour average measurements, the coefficient of variation (CV) is reported. The CV is defined as the standard deviation of the differences between paired measurements divided by the mean of the measurements, and expresses the variability in the differences as a percentage of the mean.

5.2 Comparability/Predictability

The comparability between the PAS 2000 results and the reference PAH measurements was assessed, since the PAS 2000 responds to the same particulate PAH measured by the reference method. The relationship between the two was assessed from a linear regression of the data using the PAH reference results as the independent variable and the PAS 2000 monitor 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 PAH reference measurement; C_i is the average of the 15-minute PAS 2000 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 24-hour average of the PAS 2000 measurements is used because this is the quantity that is most comparable to the reference sampler measurements.

Comparability is expressed in terms of bias between the PAS 2000 monitor and the PAH reference method, and by 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 PAH reference method and the PAS 2000 monitor. 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 PAS 2000 measurements is simply the PAH reference 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 PAH reference measurements.

Quantities reported include r^2, intercept and slope with their respective 95% confidence intervals (CIs) for the intercept and slope. Comparability to the reference method was determined independently for each of the duplicate PAS 2000 monitors being tested and was assessed separately for each phase of the verification test.

The comparison of PAS 2000 data and EC results in Phase I was limited to the correlation between these data, since quantitatively they are very different. The r^2 value characterizing the correlation between the 24-hour average PAS 2000 results and the EC results from 24-hour samples was calculated.

5.3 Meteorological Effects/Precursor Gas Influence

The influence of meteorological conditions on the correlation between the PAS 2000 monitors and the PAH reference samplers was evaluated by using meteorological data such as temperature and humidity as parameters in multivariable analyses of the data. The same evaluation was done with ambient precursor pollutant concentrations as the model parameters. The model used is as follows:

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

where X_{ji} is the meteorological or precursor gas measurement for the ith 24-hour time period, γ_j is the associated slope parameter, and other notation is as in Equation 1. Comparability results are reported again after these variables are adjusted for in the model. Meteorological effects and precursor gas interferences were assessed independently for each of the two duplicate PAS 2000 monitors tested, and were assessed separately for each phase of the verification test.

Note that the multivariable model ascribes variance unaccounted for by linear regression against the reference method 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.

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 BGI $PM_{2.5}$ FRM sampler to determine $PM_{2.5}$ mass and the Andersen RAAS for reference PAH sampling. 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, which on average accounted for 47% and 38% of the daily $PM_{2.5}$ mass, respectively. Additionally, nitrate contributed about 8.3% to 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	0.0397
Min	1.88	-0.03	106	14.6	12.1	80.2	47.9	974.5	0.0000

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

|	SO_2 (ppb)	H_2S (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	0.14	5.3	5.3	5

6.1.1 Inter-Unit Precision

Particle-bound PAH concentration measurements were recorded about every eight seconds by the duplicate PAS 2000 monitors during Phase I of the verification test. These PAH concentration readings were averaged to obtain 15-minute results. Figure 6-1a shows the 15-minute average PAH data from the two PAS 2000 monitors for Phase I of the verification test. Gaps in the data indicate periods during which power outages at the test site occurred or in which no data from the PAS 2000 monitors were available. Figure 6-1a shows that the two PAS 2000 monitors gave similar readings throughout Phase I. Although Monitor 1 consistently read somewhat higher than Monitor 2, the two PAS 2000 monitors showed the same temporal pattern of PAH levels throughout Phase I. In a few cases, peak 15-minute average PAH values exceeded 30 ng/m^3, but the great majority of the data were less than 5 ng/m^3. Figure 6-1b is a scatter plot of the 15-minute average data from the two monitors, illustrating the correlation of the two readings.

For comparison with the PAH reference measurements, the 15-minute 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 for Phase I of the verification test are presented for the two PAS 2000 monitors. A scatter plot of these data is shown in Figure 6-2b. These figures also show the correlation of the readings from the two monitors, with Monitor 1 generally reading higher than Monitor 2. This close correlation of readings is noteworthy given that most of the 24-hour average PAS 2000 readings were near or below the nominal 3 ng/m^3 detection limit of the PAS 2000 monitors.

These data were analyzed by linear regression, and the results of this analysis are presented in Table 6-3. The CV values for these data were also determined according to Section 5.1, and the calculated CV is shown in Table 6-3. The regression analysis of the 15-minute data shows an r^2 value of 0.989 and a slope of 0.779 (0.003). This slope, which is statistically different from unity at 95% confidence, indicates a substantial bias between the two monitors, with Monitor 1 generally reading higher than Monitor 2. The regression results for the 15-minute data also show that the intercept of the correlation plot is -0.66 (0.02) ng/m^3, which is significantly different from zero at the 95% confidence interval. The calculated CV for the 15-minute data is 60.4%, much of which may be attributable to the bias between the two monitors, rather than to random differences in the readings.

The 24-hour average results in Table 6-3 are similar to the 15-minute average results. As with the 15-minute data, the 24-hour average results indicate an r^2 value of 0.979. The slope of the correlation plot is 0.782 (0.048), which is statistically different from unity at the 95% confidence level. These data show an intercept of -0.68 (0.2) ng/m^3, which is statistically significant at the 95% confidence level. The calculated CV for the 24-hour averages is 40.8%, much of which may be attributable to the bias between the duplicate monitors rather than to random differences in the readings.
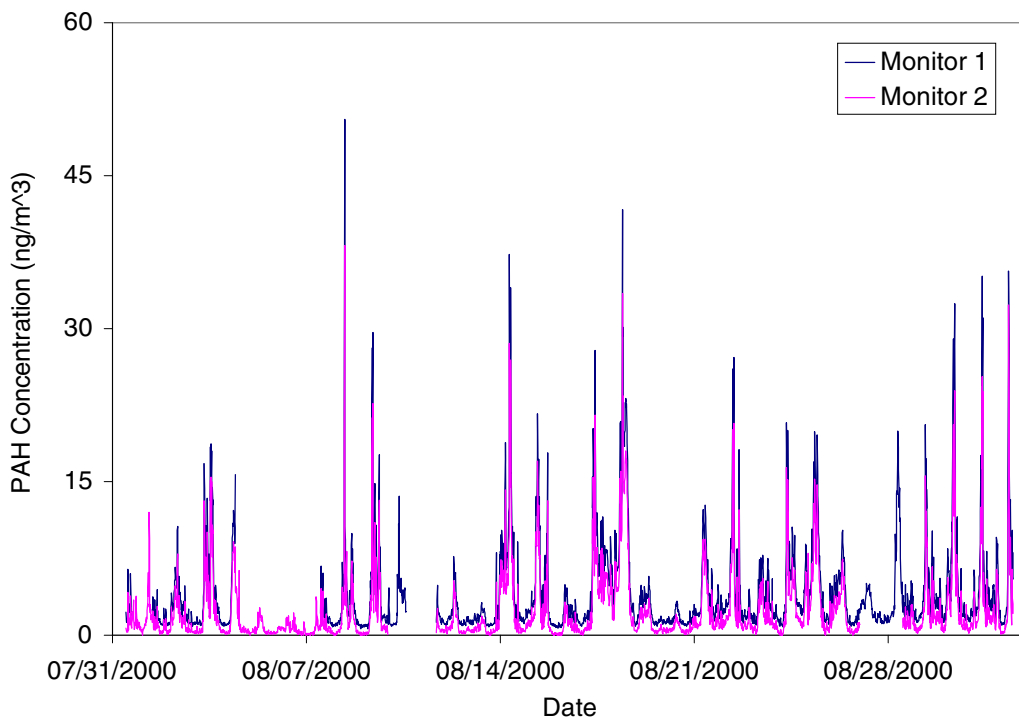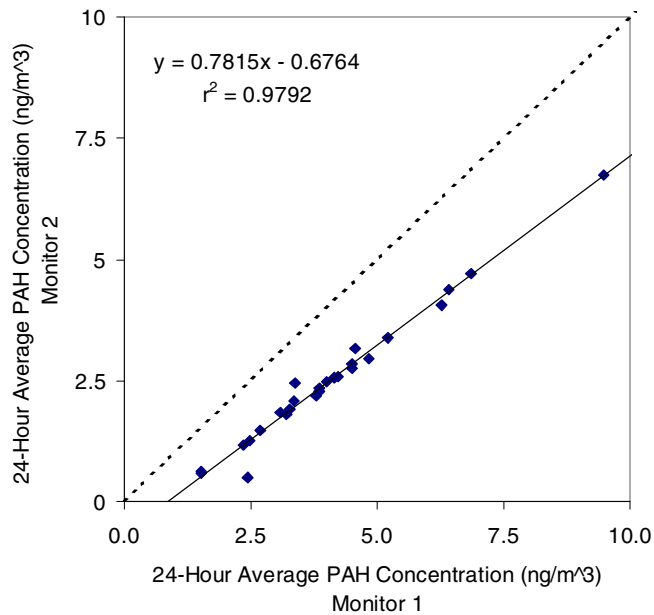
Figure 6-1a. 15-Minute Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase I
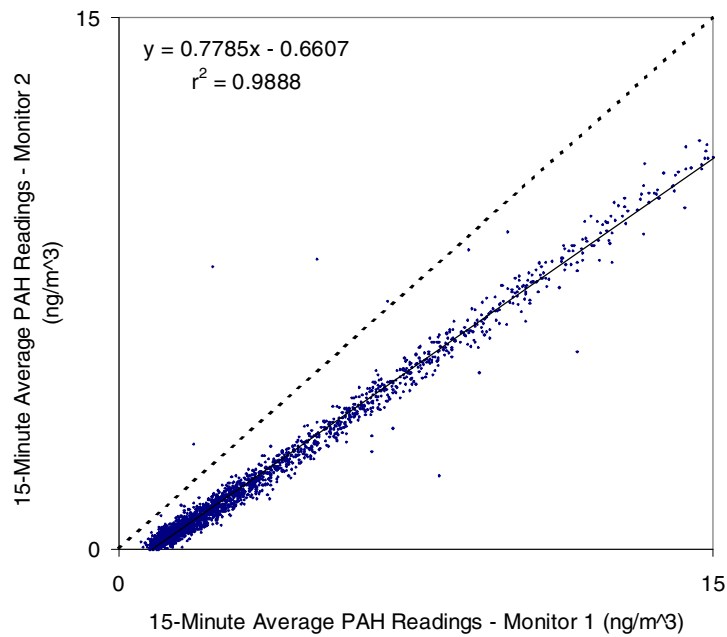
Figure 6-1b. Correlation Plot of 15-Minute Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase I
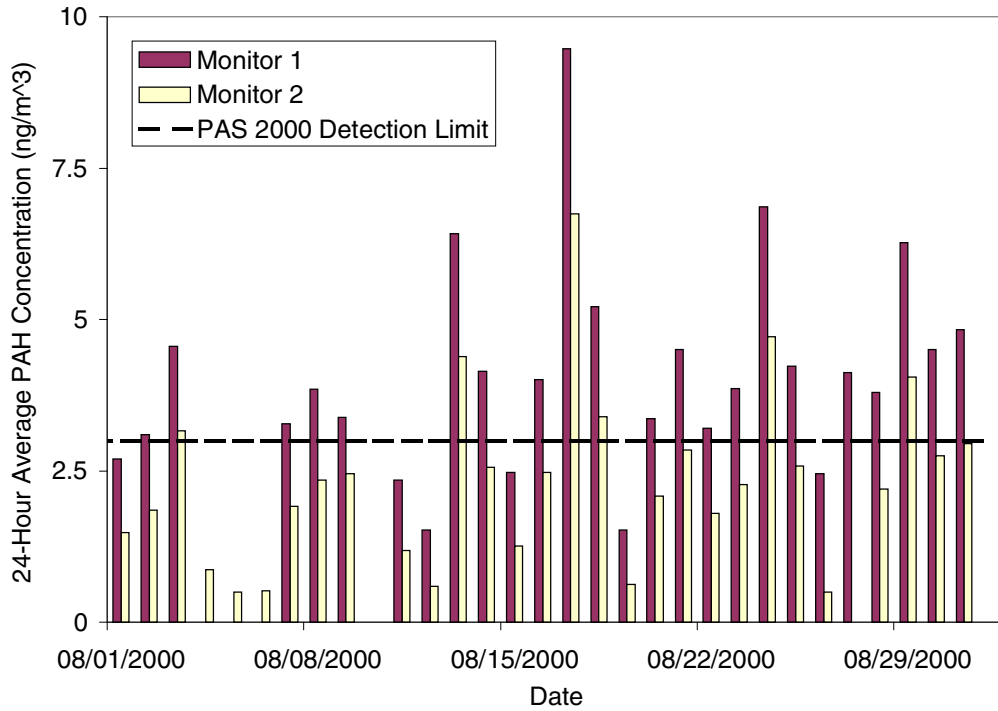
Figure 6-2a. 24-Hour Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase I (nominal PAS 2000detection limit of 3 ng/m^3 indicated by horizontal line)

Figure 6-2b. Correlation Plot of 24-Hour Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase I

Table 6-3. Linear Regression and Coefficient of Variation Results for 15-Minute and 24-Hour Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase I

Parameter	15-Minute Data	24-Hour Average Data
Slope (95% CI)	0.779 (0.003)	0.782 (0.048)
Intercept (ng/m^3) (95% CI)	-0.66 (0.02)	-0.68 (0.21)
r^2	0.989	0.979
CV	60.4%	40.8%

6.1.2 Comparability/Predictability

The reference method used long-term sample collection of 24 hours. While the PAS 200 analyzers frequently indicated measurable levels of PAH, those were periodic in nature (presumably tied in with local source activity) and, when averaged with long periods of near zero PAH conditions, the results were very low. ASTM given uncertainty bands of 30 to 50% for the reference method used; and, at the low ambient PAH levels encountered, the impact of these uncertainties is also substantial. As a result, quantitative comparisons of PAS 2000 readings with the reference method results were not made.

Comparisons to the PAH reference data were made using the 24-hour average PAS 2000 results. In Figure 6-3, the noon-to-noon averages of the PAS 2000 measurements are shown, along with the corresponding PAH reference measurements for Phase I of the verification test. Also shown in Figure 6-3 is the nominal 3 ng/m^3 detection limit of the PAS 2000 monitors.

Figure 6-3 shows that, with few exceptions, both the reference and PAS 2000 24-hour averages were near or below the nominal 3 ng/m^3 detection limit of the monitors. Although the PAS 2000 values are similar to those of the reference results and, in some cases, show similar temporal trends, the low ambient PAH levels hinder any quantitative comparison. As a result, no quantitative calculations were carried out to assess comparability with the reference data from Phase I.

6.1.3 Meteorological Effects

No influence of meteorology on the PAS 2000 monitors could be established, because the ambient levels of particulate PAH were usually below the nominal detection limit of the monitors.

6.1.4 Influence of Precursor Gases

No influence of precursor gases on the PAS 2000 monitors could be established because the ambient levels of particulate PAH were usually below the nominal detection limit of the monitors.
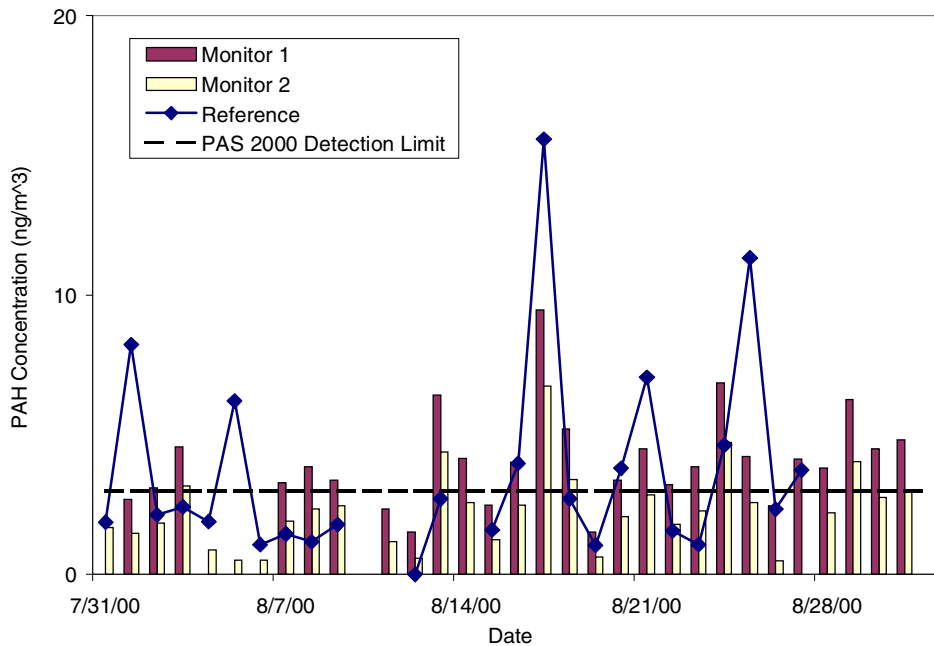
Figure 6-3. PAH Reference Concentrations and the 24-Hour Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase I (nominal PAS 2000 detection limit of 3 ng/m³ indicated by horizontal line)

6.1.5 Correlation with Elemental Carbon Measurements

At the request of the vendor, the 24-hour average PAH concentrations from the duplicate PAS 2000 monitors were compared with 24-hour EC measurements recorded during Phase I. Figure 6-4 shows comparisons of the PAH readings and the reference EC measurements. This figure shows the PAH data in ng/m³ and the EC data in µg/m³, and illustrates that the PAS 2000 monitors show similar temporal features as the EC reference measurements.

6.2 Phase II—Fresno (May 10-23, 2001)

6.2.1 Inter-Unit Precision

During Phase II, average particle-bound PAH concentration readings were recorded every 15 minutes by the duplicate PAS 2000 monitors. The 15-minute average PAH concentration readings from the two PAS 2000 monitors for Phase II of the verification test are shown in Figure 6-5a. Also shown in Figure 6-5a is the nominal PAS 2000 detection limit of 3 ng/m³. As was the case in Phase I, the great majority of ambient particulate PAH readings were near or below that nominal detection limit. From this figure, it is apparent that, although the two monitors indicated the same temporal trends, Monitor 1 consistently read about 2.5 to 3 ng/m³
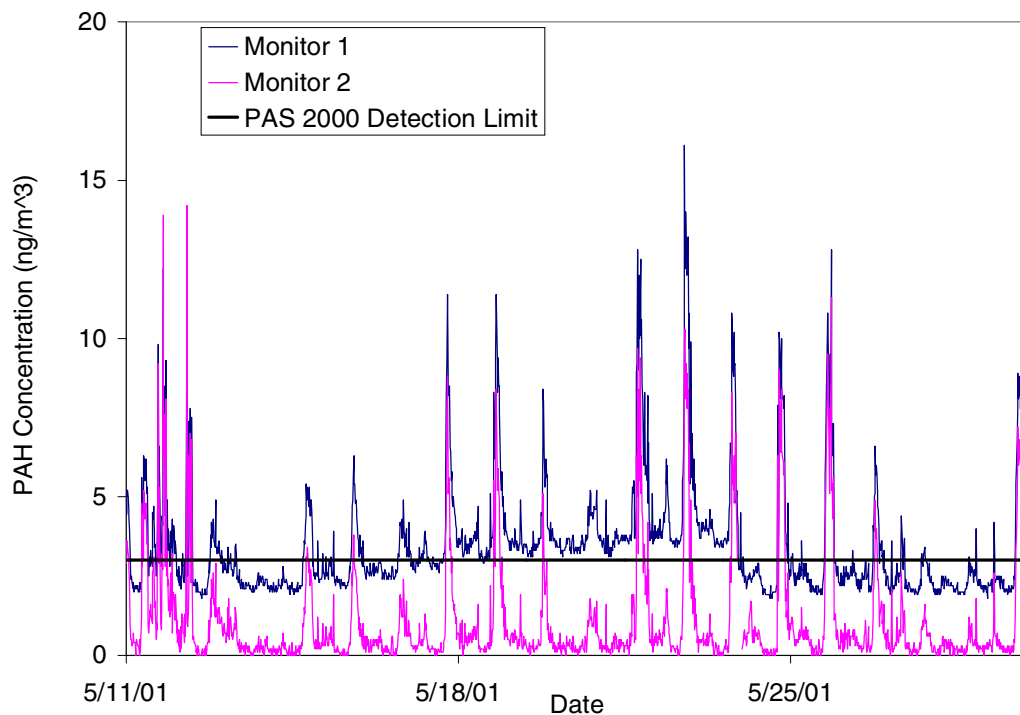
23
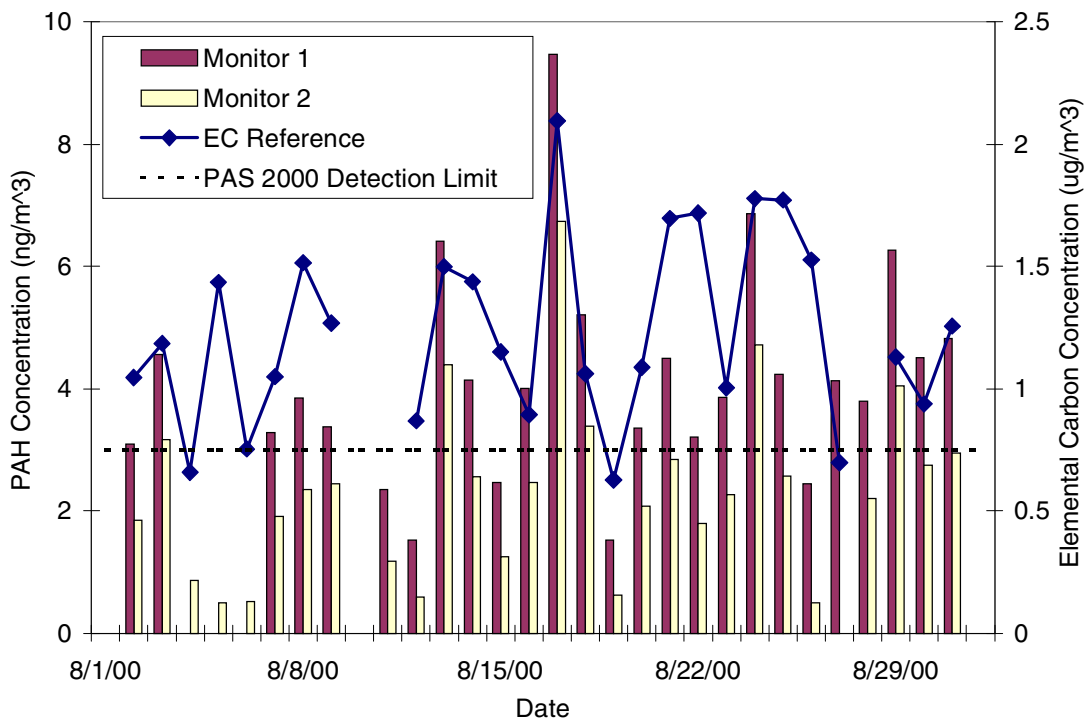
Figure 6-4. Comparison of 24-Hour Average PAH Concentrations and 24-Hour EC Reference Concentrations During Phase I (nominal PAS 2000 detection limit of 3 ng/m³ indicated by horizontal line)

higher than Monitor 2. The reason for this difference is not known, but it appears to be a straightforward offset in the zero settings of the two units. In Figure 6-5b, these data are plotted against one another to illustrate the correlation between the two monitors.

For comparison with the PAH reference measurements, the 15-minute average data were averaged each day to correspond with the 24-hour sampling periods used in Phase II of the verification test. In Figure 6-6a, the 24-hour averages for Phase II of the verification test are presented for the two PAS 2000 monitors, along with an indication of the 3 ng/m³ nominal detection limit of the monitors. Figure 6-6b is a scatter plot of these data, showing the correlation between the two monitors.

The results of a linear regression analysis of the 15-minute data and 24-hour averages are presented in Table 6-4. The CV values for these data were also calculated and are shown in Table 6-4.
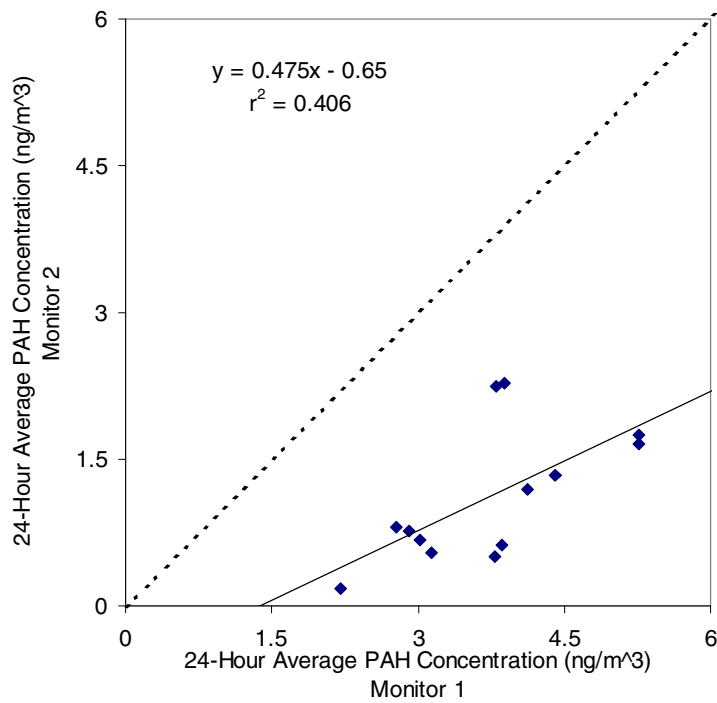
Figure 6-5a. 15-Minute Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase II (nominal PAS 2000 detection limit of 3 ng/m^3 indicated by horizontal line)
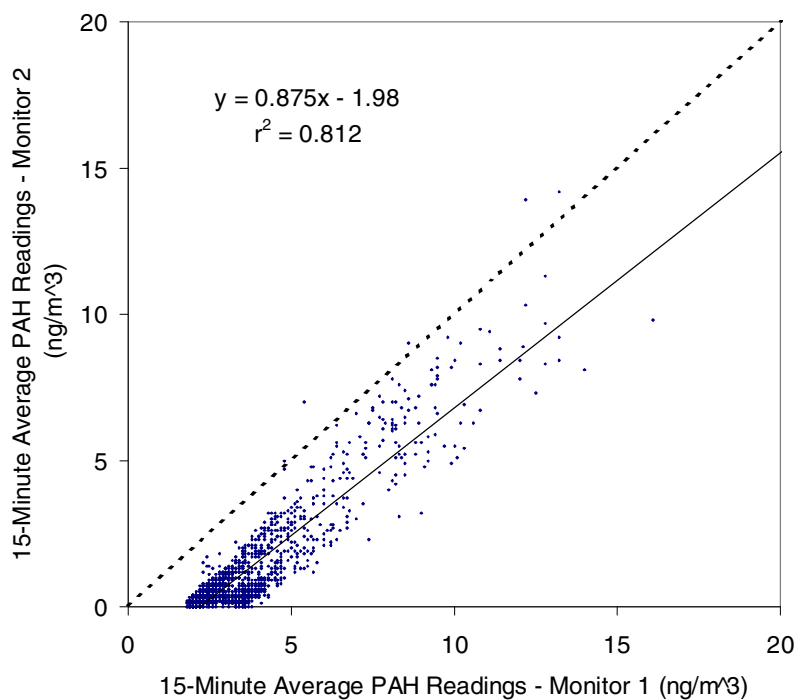
Figure 6-5b. Correlation Plot of 15-Minute Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase II
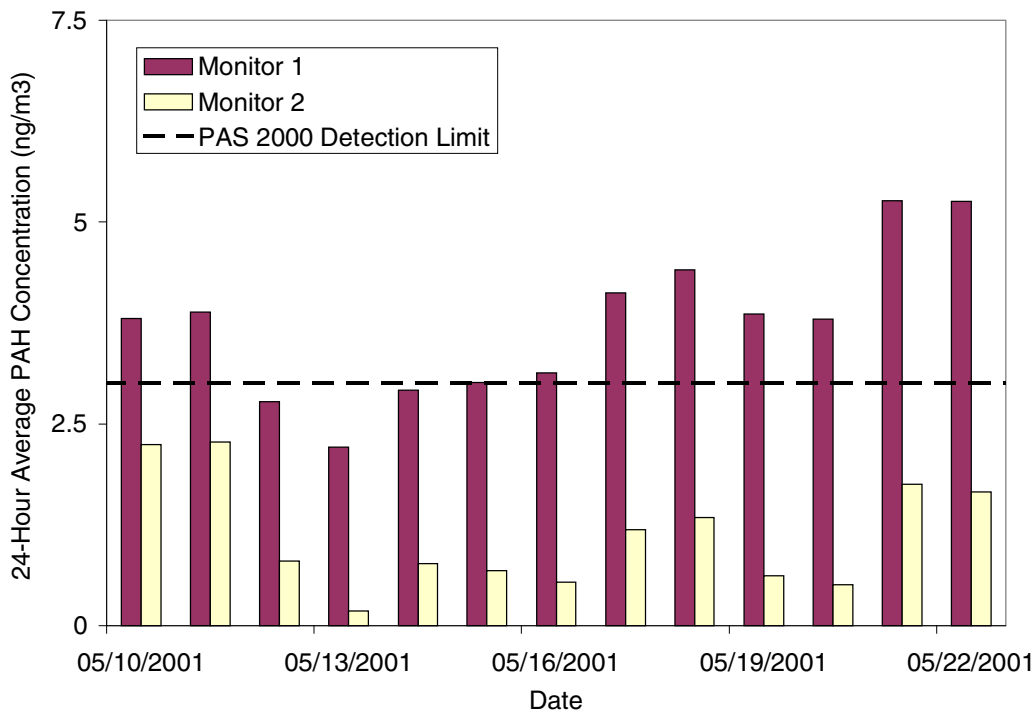
Figure 6-6a. 24-Hour Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase II (nominal PAS 2000 detection limit of 3 ng/m^3 indicated by horizontal line)

Figure 6-6b. Correlation Plot of 24-Hour Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase II

Table 6-4. Linear Regression and Coefficient of Variation Results for 15-Minute and 24-Hour Average PAH Concentrations from Duplicate PAS 2000 Monitors During Phase II

Parameter	15-Minute Data	24-Hour Average Data
Slope (95% CI)	0.875 (0.019)	0.475 (0.382)
Intercept (ng/m^3) (95% CI)	-1.98 (0.07)	-0.65 (1.46)
r^2	0.812	0.406
CV	101%	84.3%

The 15-minute data from the duplicate monitors show an r^2 value 0.812, but show a bias between the two monitors, with Monitor 1 reading higher than Monitor 2 [slope = 0.875 (0.019)]. The intercept of -1.98 ng/m^3 clearly results from the offset between the two units, as noted above. The calculated CV for the 15-minute data is 101%. Much of the calculated CV is attributable to the substantial bias between the duplicate monitors, rather than to random differences in the readings. Since the measured PAH concentrations are small, even small absolute differences between the two monitors result in large relative differences. The offset between PAS 2000 monitors could presumably be prevented by appropriate adjustment of the zero settings or calibration curves.

The regression results of the 24-hour data show an r^2 value of 0.406, a slope of 0.475 (0.382), and an intercept of -0.65 (1.46) ng/m^3. The calculated CV for these data is 84.3%. It should be noted that all of the 24-hour averages for one of the monitors fell below the stated detection limit of 3 ng/m^3.

6.2.2 Comparability/Predictability

In Figure 6-7, the 24-hour averages of the PAS 2000 measurements are shown, along with the reference PAH measurements for Phase II of the verification test. It is apparent from Figure 6-7 that, as in Phase I, the reference ambient PAH concentrations during Phase II were usually near or below the 3 ng/m^3 nominal detection limit of the PAS 2000 monitors. Consequently, once again no quantitative comparison could be made between the PAS 2000 and reference PAH measurements.

6.3 Instrument Reliability/Ease of Use

No maintenance was performed on either monitor, and both monitors ran largely unattended throughout the two phases of testing. The only problems encountered were with data loss after power outages. During both Phase I and Phase II, some periods of data were lost as a result of problems with the datalogging computers. Although the PAS 2000 monitors restarted after power outages, the datalogging computers were not set up with that capability. The data acquisition program required a manual restart. In some cases this was not performed promptly and periods of data were lost. Overall data recovery was approximately 90%.
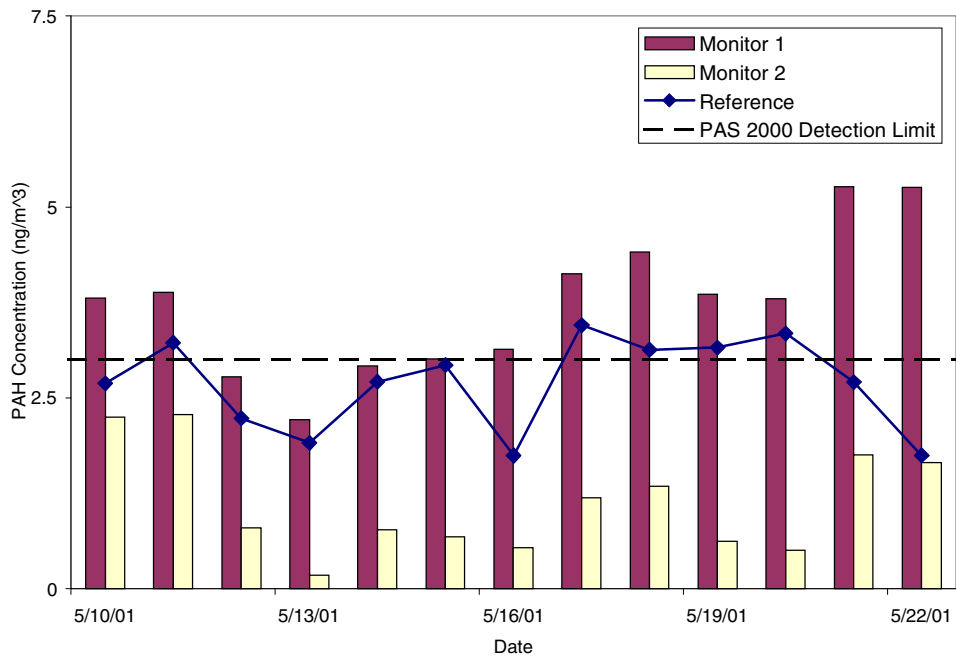
Figure 6-7. 24-Hour Average PAH Concentrations from Duplicate PAS 2000 Monitors and PAH Reference Method During Phase II (nominal PAS 2000 detection limit of 3 ng/m³ indicated by horizontal line)

6.4 Shelter/Power Requirements

As recommended by the vendor, the PAS 2000 monitors were installed and operated inside the shelter of Battelle's trailer during each phase of testing. Both instruments and their associated data collection computer were run on a single 15 A circuit. Vendor literature indicates an operative range of temperatures from 5 to 40°C; however these limits were not verified in this test.

6.5 Instrument Cost

The price of the PAS 2000 monitor, as tested, is approximately $16,000.

Chapter 7
Performance Summary

The PAS 2000 monitor is a continuous particle monitor designed to indicate the ambient particulate PAH concentration at time periods as short as a few seconds. Duplicate PAS 2000 monitors were evaluated under field conditions in two separate phases of this verification test. The locations and time periods of those two phases were chosen to provide different particle compositions and particulate matter concentrations for testing a variety of fine particle monitoring instruments. In these tests, the PAS monitors were operated using a universal calibration factor that approximately relates instrument response to the ambient particulate PAH concentration. Unfortunately, the ambient levels of particulate PAH were approximately the same as the 3 ng/m^3 nominal detection limit of the PAS 2000 monitors in both phases of this verification test. As a result, quantitative evaluation of the performance of the PAS 2000 PAH monitors was limited. The results from each phase of this verification test are summarized below.

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

In Phase I the duplicate PAS 2000 monitors showed the same temporal behavior of particulate PAH levels, for both the 15-minute data and 24-hour averages. Regression analysis showed r^2 = 0.989 for the 15-minute data and r^2 = 0.979 for the 24-hour averages. The slopes of the regression lines were 0.779 (0.003) and 0.782 (0.048), respectively, for the 15-minute data and 24-hour averages, indicating a substantial bias of about 22% between the two monitors (Monitor 1 reading higher than Monitor 2). The intercept of the regression line was -0.66 (0.02) for the 15-minute data, and was -0.68 (0.21) for the 24-hour data. The calculated CV for the 15-minute data was 60.4%; and, for the 24-hour averages, the CV was 40.8%. Much of these CV values may be attributed to the bias between the monitors and to the fact that the ambient PAH concentrations were comparable to the 3 ng/m^3 nominal detection limit of the monitors, making even small inter-unit differences relatively large contributors to the CV.

The ambient PAH concentrations in Phase I were generally near the detection limit of the PAS 2000 monitors and, as a result, no quantitative comparison of reference and PAS 2000 results can be made. However, the reference and PAS 2000 results agreed in terms of the low range of the ambient levels.

Because ambient PAH levels were so low, multivariable analysis of the 24-hour average data could not establish any influence of either meteorological conditions or ambient precursor gas concentrations on the readings of the PAS 2000 monitors.

7.2 Phase II—Fresno (May 10-23, 2001)

In Phase II, the duplicate PAS 2000 monitors again indicated the same temporal patterns in particulate PAH concentrations. Regression analysis of 15-minute data from the duplicate monitors showed an r^2 of 0.812, a slope of 0.875 (0.010) and an intercept of -1.98 (0.04) ng/m^3. The calculated CV for these data was 101%, much of which is attributed to the offset (~2 ng/m^3) between the two monitors. No conclusive measure of precision was available for the 24-hour averages, as all the results from one monitor were below the nominal detection limit of the monitors. However, a linear regression analysis of these data show an r^2 of 0.406, a slope of 0.475 (0.382), and an intercept of -0.65 (1.46) ng/m^3. The calculated CV for these data was 84.3%. The ambient PAH levels present were comparable to the 3 ng/m^3 nominal detection limit of the monitors, so the substantial offset between the two monitors undoubtedly was a major contributor to these CV values. That offset had the appearance of a simple difference in zero setting that might be eliminated by appropriate calibration.

As in Phase I, both the reference and PAS 2000 results indicated that ambient particulate PAH levels were near or below the nominal 3 ng/m^3 detection limit of the PAS 2000 monitors. As a result, no quantitative comparison of the reference and PAS 2000 data sets could be made.

7.3 Other Parameters

The two monitors required no maintenance during either phase of testing. Some periods of data were lost because of recurrent difficulties with the data collection system, in the form of a failure to restart data collection after power outages. Overall data recovery was approximately 90%.

Chapter 8
References

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

2. American Society for Testing and Materials, "Standard Test Method for Determination of Gaseous and Particulate Polycyclic Aromatic Hydrocarbons in Ambient Air (Collection on Sorbent-Backed Filters with Gas Chromatography/Mass Spectrometric Analysis)," ASTM Method D-6209-98, in *Annual Book of Standards*, Vol.11.03, West Conshohoken, PA, 1998.

3. L. A. Gundel, V. C. Lee, K. R. R. Mahanama, R. K. Stevens, and J. M. Daisey, *Atoms. Environ.*, **29**, 1719-1733, (1995).

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