August 2001

Environmental Technology Verification Report

THERMO ANDERSEN AETHALOMETER™ PARTICULATE CARBON MONITOR

Prepared by

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EPA U.S. Environmental Protection Agency

ETV ETV ETV

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

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ETV Joint Verification Statement

TECHNOLOGY TYPE:	**Continuous Ambient Particulate Carbon Monitor**
APPLICATION:	**MEASURING PARTICULATE CARBON CONCENTRATIONS IN AMBIENT AIR**
TECHNOLOGY NAME:	**Aethalometer™ Particulate Carbon Monitor**
COMPANY:	**Thermo Andersen**
ADDRESS:	**500 Technology Court, Smyrna, GA 30082** — **PHONE: 800-241-6898, FAX: 770-319-0336**
WEB SITE:	**http://www.AndersenInstruments.com**
E-MAIL:	**sales@AndersenInstruments.com**

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 Aethalometer™ particulate carbon monitor.

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, agreement with and correlation to time-integrated reference methods, effect of meteorological conditions, and influence of precursor gases. The Aethalometer™ reports measurement results in terms of particulate black carbon (BC) concentration and, therefore, was compared with the elemental carbon (EC) results of thermal/optical analysis of collected particulate mass samples. Ambient aerosol carbon levels differed markedly in the two phases of testing, with elemental carbon averages of 1.3 $\mu g/m^3$ in Phase I, and 6.1 $\mu g/m^3$ in Phase II. 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 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 Aethalometer™ uses a continuous filtration and optical transmission technique to measure the concentration of aerosol black carbon in near real time. The Aethalometer™ is fully automatic and completely self-contained. It is constructed in a standard 19-inch enclosed chassis and includes a filtration and analysis chamber with automatically-advancing quartz fiber tape, sample aspiration pump and air mass flow meter or controller, and temperature-stabilized optics and electronics. The Aethalometer™ is operated by an embedded computer with display screen and keypad that controls all instrument functions and records the data to a built-in 3.5 in. floppy disk. The Aethalometer™ measures, at regular intervals, the attenuation of a beam of light transmitted through a filter while the filter is continuously collecting an aerosol sample. The carbon black content of the aerosol deposit is determined at each measurement time by using the appropriate attenuation value for the particular combination of filter and optical components. For this test the Aethalometer™ results are based on the "Harvard" EC calibration factor. The increase in optical attenuation from one period to the next is due to the increment of aerosol black carbon collected from the air stream during the period. This increment is divided by the volume of air sampled during that time to calculate the mean carbon black concentration in the sampled air. The Aethalometer™ power consumption is approximately 60 W at either 115 or 230 V AC. Its weight is approximately 35 pounds and its rack width is 19 in. It is 11 in. high and 12 in. deep. During this verification test the 7-wavelength version of the Aethalometer™ was tested; however, only the results from the 880 nm channel are presented.

VERIFICATION OF PERFORMANCE

Inter-Unit Precision: During Phase I, regression analysis showed r^2 values of 0.932 and 0.982, respectively, for the 5-minute data and 24-hour averages for the duplicate monitors. The slopes of the regression lines (with Monitor 1 as the independent variable), were 0.914 (0.005) and 0.963 (0.049), respectively, for the 5-minute data and 24-hour averages (where the numbers in parentheses are 95% confidence intervals). The slope of the 5-minute data was statistically different from unity, and the slope of the 24-hour averages was not. For the 5-minute data, an intercept of 0.051 (0.007) $\mu g/m^3$ was observed and for the 24-hour data an intercept of -0.003 (0.058). The calculated CV for the 5-minute data was 17.8%; and, for the 24-hour averages, the CV was 4.2%. During Phase II, regression analysis showed r^2 values of 0.947 and 0.995, respectively, for the 5-minute and 24-hour average data. The slopes of the regression lines were 0.999 (0.007) and 1.004 (0.027), respectively, for the

5-minute data and 24-hour averages. In both cases, the slopes were not statistically different from unity at the 95% confidence level. A statistically significant intercept of 0.055 (0.038) $\mu g/m^3$ was observed for the 5-minute data; and an intercept of -0.052 (0.175) $\mu g/m^3$ was observed for the 24-hour averages. The calculated CV for the 5-minute data was 12.3%; and, for the 24-hour averages, the CV was 2.7%.

Comparability/Predictability: During Phase I, comparisons of the 24-hour averages with IMPROVE TOR reference results for EC showed intercepts indistinguishable from zero at 95% confidence and slopes of the regression lines of 0.815 (0.280) and 0.791 (0.270), respectively, for Monitor 1 and Monitor 2. The regression results show r^2 values of 0.590 and 0.593 for Monitor 1 and Monitor 2, respectively. During Phase II, comparison of the appropriately averaged data from the Aethalometers™ with reference EC results from all of the sampling periods showed slopes of the regression lines for Monitor 1 and Monitor 2 of 0.711 (0.031) and 0.735 (0.031) and intercepts of 0.54 (0.25) $\mu g/m^3$ and 0.47 (0.25) $\mu g/m^3$, respectively, indicating a bias between the Aethalometer™ monitors and the IMPROVE TOR results for EC. The regression results show r^2 values of 0.930 and 0.934 for Monitor 1 and Monitor 2, respectively. Correlation of the BC and refrence EC results was best for samples from the 000-0500 time period, and lowest for time periods between 1000-1300 for Monitor 1 and from 1300-1600 for Monitor 2.

Meteorological Effects: Multivariable model analysis was used to establish if meteorological conditions influenced the readings of the duplicate Aethalometers™ relative to the reference EC measurements during Phase I. This model ascribed to wind speed and air temperature a statistical effect on one of the Aethalometers™, and to wind direction a statistical effect on the other. For one monitor, the multivariable results differed from the linear regression results by approximately 2.5% on average. For the other monitor, a difference of approximately 60% was seen. During Phase II, this analysis ascribed to wind speed, wind direction, the standard deviation of wind direction, relative humidity, solar radiation, and barometric pressure an influence on the two Aethalometers™ relative to the reference results at the 90% confidence level. The multivariable results differed from the linear regression results by 14% for Monitor 1; for Monitor 2, the difference was negligible.

Influence of Precursor Gases: Multivariable analysis also was performed during Phase I to determine whether the presence of precursor gases had an effect on the Aethalometer™ readings. This analysis ascribed to both nitric oxide and nitrogen oxides a statistically significant (90% confidence) effect on the readings of both Aethalometers™ relative to the EC reference measurements. The effects of these gases were similar in magnitude and opposing in nature; the multivariable results were the same as the linear regression results for both monitors. Multivariable analysis also was performed during Phase II to determine whether the presence of precursor gases had an effect on the Aethalometer™ readings. As with the results from Phase I, this analysis ascribed to both nitric oxide and nitrogen oxides a statistically significant (90% confidence) effect on the readings of both Aethalometers™ relative to the EC reference measurements. The effects of these gases were similar in magnitude and opposing in nature. The multivariable and linear regression results in Phase II differed by 8.2% for Monitor 1 and 4.0% for Monitor 2.

Other Parameters: The Aethalometers™ ran almost unattended for the duration of each phase. Data disks were replaced in each instrument weekly to capture the data, but no maintenance on either Aethalometer™was required during either phase. Data capture during Phase I was near 100%. During Phase II, the high $PM_{2.5}$ concentrations resulted in the need to advance the filter tape on a frequent basis. As such, the data capture was approximately 75% during this phase of testing.

Gabor J. Kovacs Date
Vice President
Environmental Sector
Battelle

Gary J. Foley Date
Director
National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency

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August 2001

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

THERMO ANDERSEN AETHALOMETER™ PARTICULATE CARBON MONITOR

by

Kenneth Cowen
Thomas Kelly
Basil Coutant
Karen Riggs

Battelle
Columbus, Ohio 43201

Notice

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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
BC	black carbon
CARB	California Air Resources Board
cm	centimeter
CO	carbon monoxide
CV	coefficient of variation
DOE	U.S. Department of Energy
DRI	Desert Research Institute
EC	elemental carbon
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FRM	federal reference method
H_2S	hydrogen sulfide
Hg	mercury
IMPROVE	Interagency Monitoring for Protection of Visual Environments
in.	inch
L/min	liters per minute
µg	microgram
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
OC	organic carbon
ppb	parts per billion
QA/QC	quality assurance/quality control
QMP	Quality Management Plan
SFS	sequential filter sampler
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 Thermo Andersen Aethalometer™ particulate carbon monitor.

Chapter 2
Technology Description

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

The Aethalometer™ uses a continuous filtration and optical transmission technique to measure the concentration of aerosol black carbon in near real time. The Aethalometer™ is fully automatic and completely self-contained. It is constructed in a standard 19-inch enclosed chassis and includes a filtration and analysis chamber with automatically advancing quartz fiber tape, sample aspiration pump and air mass flow meter or controller (typical flow rates are 2 to 6 L/min), and temperature-stabilized optics and electronics. The Aethalometer™ is operated by an embedded computer with display screen and keypad that controls all instrument functions and records the data to a built-in 3.5 in. floppy disk. It has COM-port digital data stream output and an analog voltage terminal that can be programmed either to represent the measured concentration or to function as an on/off threshold alarm.

The Aethalometer™ measures, at regular intervals, the attenuation of a beam of light transmitted through a filter while the filter is continuously collecting an aerosol sample. The carbon black content of the aerosol deposit is determined at each measurement time by using the appropriate attenuation value for the particular combination of filter and optical components. For this test the Aethalometer™ results are based on this "Harvard" EC calibration factor. The increase in optical attenuation from one period to the next is due to the increment of aerosol black carbon collected from the air stream during the period. This increment is divided by the volume of air sampled during that time to calculate the mean black carbon concentration in the sampled air.

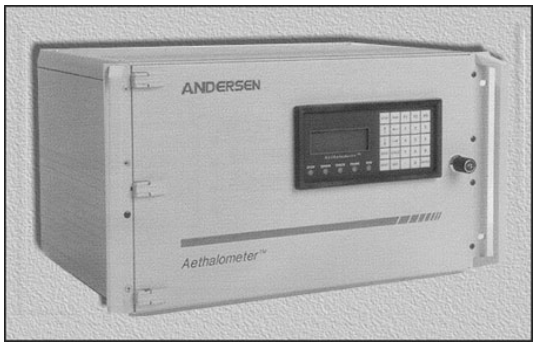

Figure 2-1. Aethalometer™ Particulate Carbon Monitor

The Aethalometer™ power consumption is approximately 60 W at either 115 or 230 V AC. Its weight is approximately 35 pounds and its rack width is 19 in. It is 11 in. high and 12 in. deep. In this verification test, the 7-wavelength version of the Aethalometer™ was tested.

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.

To assess inter-unit precision, duplicate Aethalometers™ were tested in side-by-side operation during each phase of testing. During Phase I, the monitors tested were Serial Number 268 and Serial Number 237. During Phase II, the monitors tested were Serial Number 251 and Serial Number 237. Collocation of the Aethalometers™ 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. 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 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 Aethalometer™ reports measurement results in terms of particulate black carbon (BC) concentration. As such, the measurements from the Aethalometers™ were compared with results of thermal/optical analysis of elemental carbon in collected particulate matter samples. 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 Thermal/Optical Carbon Reference Method

The primary comparisons of the Aethalometer™ readings were made relative to reference samples analyzed by the thermal/optical reflectance (TOR) method[2] for carbon used in the IMPROVE network.[3] This technique involves the preferential oxidation and detection of organic carbon (OC) and elemental carbon (EC) fractions at different temperatures. The Aethalometers™ results were compared to the EC results of the TOR method.

The TOR technique has been shown to differ from the NIOSH-5040 protocol in its results for the EC content of urban particulate matter samples, despite analytical similarities.[4] Its use in this verification test is as a methodological comparison rather than as an absolute standard. In the TOR method, a 0.5 cm^2 section is punched from a filter and then is subjected to successive temperatures of 120, 250, 450, and 550°C in a pure helium atmosphere. Organic material of successively lower volatility is driven from the filter section at each successive temperature. The temperature is then maintained at 550°C while the atmosphere is changed to 2% O_2/98% He. The filter section is then subjected to successive temperatures of 550, 700, and 800°C, at which carbonaceous material remaining on the filter is combusted in the O_2/He atmosphere. At each temperature step throughout the process, the carbon evolved is converted to methane and

determined with a flame ionization detector. The filters used for sampling are of quartz fiber, and are heated in a muffle furnace in air before use to remove any organic binders, thereby minimizing the filter carbon blanks.

Throughout the thermal evolution/combustion process, the optical reflectance of the particle deposit side of the filter section is monitored at 632.8 nm wavelength. The reflectance generally decreases from its original value during heating in the helium atmosphere, due to pyrolysis of organic material, and then increases during heating in the O_2/He atmosphere as carbon is combusted and removed. By definition, organic carbon is that evolved before reflectance returns to its original value, and elemental carbon is that evolved after the reflectance rises above its initial value. This operational definition means that the measured organic carbon consists of organic carbon species that do not absorb 632.8 nm light, and that the measured elemental carbon consists of organic and elemental carbon species that do absorb that light.

It must be stressed that the TOR method is based on operational definitions of the EC and OC fractions, and incorporates assumptions about the nature of the carbonaceous materials present. It is not a fully established, officially recognized reference method. However, it is a widely used and carefully documented research method that has been employed in numerous atmospheric monitoring studies.[4] As such, the TOR method is a suitable reference method for use in this verification. However, differences exist between the TOR method and the Aethalometers™ that should be noted. Most importantly, the Aethalometers™ do not use quartz filters, which may absorb vapor phase organics in some circumstances; the TOR method does use quartz filters. Differences in sampling conditions (i.e., flow rate) between the reference sampler and the Aethalometers™ may also be important.

During Phase I, 24-hour 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 TOR 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 by Consol Energy, under subcontract with Battelle.

A medium-volume sequential filter sampling (SFS) system 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 sets of filters at midnight each day. A vacuum pump drew air through the paired filter packs when the valves were open. Each set of filters was programmed to carry out sampling in five periods each day (0000-0500, 0500-1000, 1000-1300, 1300-1600, and 1600-2400). The flow rate was controlled by maintaining a constant pressure across a valve with a

differential pressure regulator. 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 sulfate, nitrate, 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.

In addition, collocated samples were collected during Phase I to establish the precision of the reference method. Estimates of precision for Phase II are based on previously reported results from duplicate SFSs collocated in Bakersfield, CA. A discussion of the collocated sampling is presented in Section 4.4 of this report.

A considerable amount of independent work has shown the close relationship between the optical determination of BC as performed by the Aethalometer™ and the thermochemical determination of EC as performed by the TOR method. In U.S. urban areas, the average ratio of BC to EC for 187 24-hour samples was 0.76 ±0.16, with a correlation coefficient r^2 of 0.97.[5, 6] At a remote location, the average ratio of BC to EC for 30 48-hour samples was 0.76 ±0.31, with a correlation coefficient r^2 of 0.92.[7]

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, wind 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.

3.4 Data Comparisons

The primary means used to verify the performance of the Aethalometers™ was comparison with the 24-hour EC results for Phase I and with the 3-, 5-, and 8-hour EC results for Phase II. 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. 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 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 both phases of testing, a Battelle-owned 40-foot semi-trailer was used to house the continuous monitors. The Aethalometers™ were placed on a counter top, with each monitor below a 7.6-cm (3") port through the roof of the trailer. Separate inlet tubes (conductive plastic) were run through the roof port and positioned in separate arms of a T-shaped PVC tube. A $PM_{2.5}$ sharp cut cyclone provided by the vendor was used with each Aethalometer™ to provide particle size selection. Data generated by the Aethalometers™ 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 the 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).

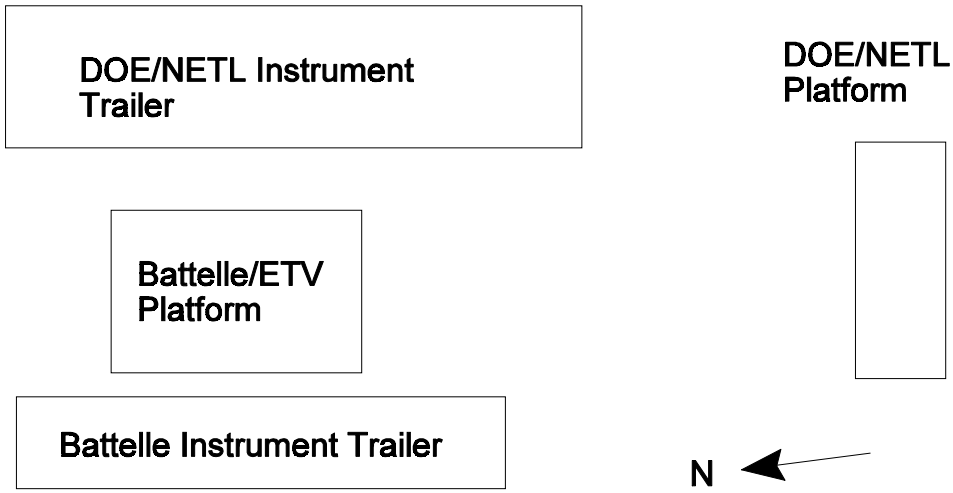

Figure 3-1. Site Layout During Phase I of Verification Testing (not drawn to scale)

Most of the DOE/NETL continuous monitoring equipment, including the continuous precursor gas monitors, was located inside the DOE/NETL instrument trailer. A Battelle-supplied Andersen RAAS sampler used to collect reference samples was located on the Battelle/ETV platform. The Aethalometers™ were installed inside the Battelle trailer. A vertical separation of approximately 2 meters and a horizontal separation of approximately 3 meters existed between the inlets of the two Aethalometers™ 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.

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 RAAS sequential filter sampler and a 3-meter (10-foot) meteorological tower were located on the roof of the two-story building housing the CARB office. The continuous gas monitors were located inside the CARB office space and sampled through a port in the roof of the building. The RAAS sequential filter sampler was located near the center of the rooftop location. The Battelle trailer used during Phase I of this verification test was also 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 6 meters (20 feet) existed between the top of the trailer and the roof of the building housing the CARB site.

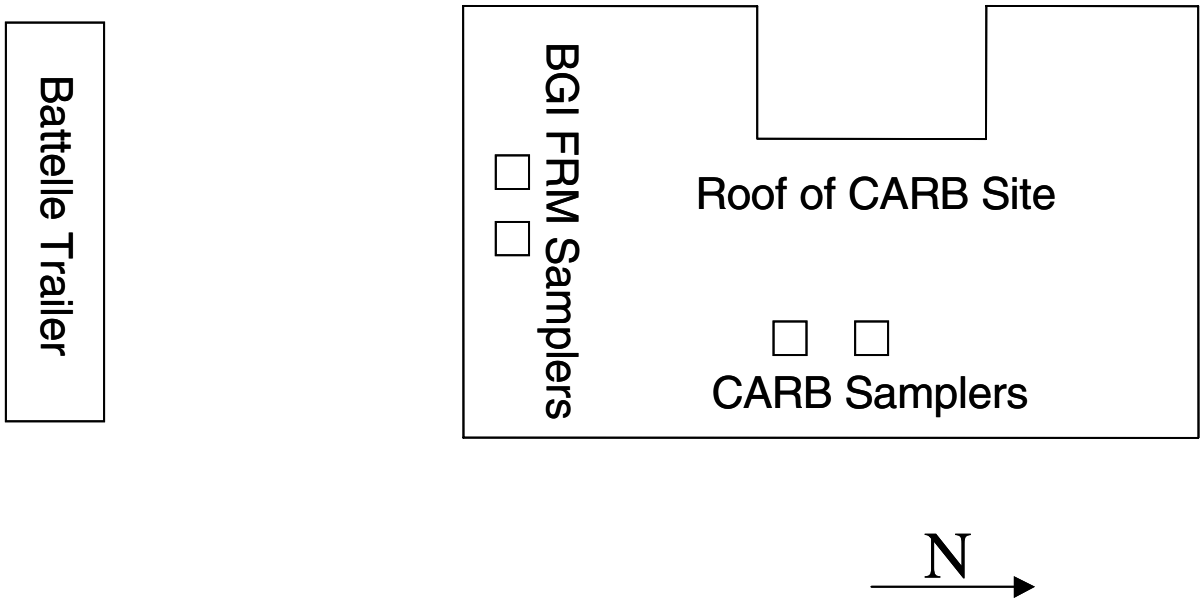

Figure 3-2. Site Layout During Phase II of Verification Testing (not drawn to scale)

One of the Aethalometers™ was located in the Battelle trailer and installed in the same fashion as in Phase I of the verification test. A vertical separation of approximately 6 meters and a horizontal separation of approximately 40 meters existed between the inlet of this Aethalometer™ and that of the SFS. The second Aethalometer™ was located inside the CARB facility and installed in a fashion similar to that of the other monitor. A vertical separation of approximately 1 meter and a horizontal separation of approximately 5 meters existed between the inlet of this Aethalometer™ and that of the SFS.

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 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 Aethalometers™ were validated by a representative of Thermo Andersen and reviewed by the Verification Test Coordinator before being used in statistical calculations.

4.2 Deviations from the Test/QA Plan

The following deviation from the test/QA plan related to verification of the Aethalometer™ was documented and approved by the AMS Center Manager. This deviation had no deleterious effect on the verification data.

- The distance between the sequential filter sampler and one of the Aethalometers™ being tested was increased to approximately 40 meters to accommodate changes in the overall site layout for Phase II.

4.3 Calibration and Parameter Checks of Reference Sampler

The Andersen RAAS sampler provided by Battelle for Phase I of 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 are 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 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).

The on-site operators checked the flow rate of the Andersen RAAS sampler both before and after Phase I of the verification test using an Andersen Ltd. dry gas meter (identification number 103652, calibrated March 30, 2000). The flow rate was checked prior to testing on July 30, 2000, and again checked on September 11, 2000, using the same Andersen dry gas meter. In both cases, the measured flow rate was verified to be within 4% of the flow rate indicated by the sampler.

Calibration of the flow rate for the SFS sampler used during Phase II was maintained by DRI through daily flow checks with a calibrated rotameter, and through independent performance evaluation audits conducted by Parson's Engineering. No additional flow verification was performed for this test.

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 ±2°C. After the verification period, the ambient temperature sensor malfunctioned on September 7. The sensor was replaced, after completing Phase I, with a new factory-calibrated sensor provided by BGI.

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, 2001). 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 mercury. This failure is possibly associated with the failure of the ambient temperature sensor on September 7, 2000.

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 performed according to the procedures in the operator's manual for the Andersen RAAS sampler. All leak checks passed the acceptance criteria provided in the operator's manual. Leak checks of the sequential filter sampler were performed daily during Phase II of the verification test. These leak checks were conducted during setup for each 24-hour sampling period. All leak checks passed before the sampler setup was completed.

4.4 Collocated Sampling

To establish the precision of the EC reference method for Phase I, the Battelle Andersen RAAS sampler was collocated with a DOE/NETL Andersen RAAS sampler for periods before and after Phase I of the verification test. During these sampling periods, the Battelle and DOE/NETL Andersen RAAS samplers were located on the same platform and within 4 meters of one another. A total of six sets of duplicate samples were collected from the two samplers during periods before and after Phase I. These collocated samples were analyzed for EC concentrations. The measured EC concentration for these samples ranged from 1 to 2 $\mu g/m^3$. On average, these collocated samples showed relative agreement (difference divided by mean) with one another within approximately 21%. The observed differences ranged from 6% to 41%.

Estimates of the precision of the reference method for Phase II are based on previously reported results from a study (IMS95 winter study) conducted in Bakersfield, CA. In this study, a series of 24 duplicate three-hour samples were collected from collocated SFSs and analyzed by the IMPROVE TOR method. The regression results for the elemental carbon show a slope of 0.58 (0.12); intercept of 1.75 (0.68); and correlation coefficient (r) of 0.72, where the values in parentheses are the standard errors.

4.5 Field Blanks

At least 10% of the samples collected throughout Phase I of the verification test were field blanks. None of these blanks showed any EC mass on the filter above the detection limit of 0.8 µg/filter. Assuming a sample volume of 11 m^3, the blank concentrations would not exceed 0.07 $\mu g/m^3$, which is approximately 10% of the lowest 24-hour reference EC measurement during Phase I. EC reference measurements were not corrected for field blanks in Phase I.

At least 10% of the samples collected throughout Phase II of the verification test were field blanks. None of these blanks showed any EC mass on the filter above the detection limit of 0.9 µg/filter. Assuming a sample volume of 3.6 m^3 (i.e., three-hour sample from SFS), the blank values would account for no more than 0.3 $\mu g/m^3$. For EC, the reference sample mass concentration ranged from nondetectable up to 22.9 $\mu g/m^3$ and averaged 6.1 $\mu g/m^3$. The maximum blank mass concentration of 0.3 $\mu g/m^3$ could be significant for some samples, but accounted for 5% or less of the reference sample mass, on average. Phase II carbon reference measurements are corrected for the field blanks.

4.6 Data Collection

4.6.1 Reference Measurements

During Phase I, summary data from the Andersen 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, sample flow rate, and average temperature and pressure readings.

During Phase II, summary data from the sequential filter 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, flow rate, and average temperature and pressure readings.

4.6.2 Aethalometer™

Data from each of the Aethalometers™ were recorded every 5 minutes on an internal floppy disk, which was changed once per week throughout each phase of the testing period. These data were recorded in tabular format showing the date and time and the 5-minute BC concentrations. These data were imported directly into a spreadsheet for analysis. Copies of the data were stored by the Verification Test Coordinator on 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.[8] 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, and all were resolved 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 Aethalometers™. All corrective actions were completed to the satisfaction of the Battelle Quality Manager and the EPA.

4.7.2 Performance Evaluation Audit

The Andersen RAAS sampler provided by Battelle for carbon reference measurements was audited during Phase I to ensure that it was operating properly. 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 for the carbon channel was within the ±4% acceptance criterion with respect to the internal flow meter.

The ambient and filter temperature sensors of the Battelle Andersen 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.

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 minor, and all were corrected to the satisfaction of the Battelle Quality Manager.

Chapter 5
Statistical Methods

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

5.1 Inter-Unit Precision

The inter-unit precision of the Aethalometers™ 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 Aethalometers™ were paired, and the behavior of their differences was used to assess precision. For both the 5-minute 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 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 Aethalometer™ results and the EC reference results was assessed, since the Aethalometer™ BC results have been shown to correlate well with EC results in previous studies[5-7]. The relationship between the two was assessed from a linear regression of the data using the EC reference results as the independent variable and the Aethalometer™ BC results as the dependent variable as follows:

$$C_i = \mu + \beta \times R_i + \varepsilon_i \qquad (1)$$

where R_i is the ith EC reference measurement; C_i is the average of the 5-minute Aethalometer™ BC measurements over the same 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 Aethalometer™ 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 Aethalometer™ and the EC reference method 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 EC reference results and the Aethalometer™. In the absence of bias, the regression equation would be $C_i = R_i + \varepsilon_i$ (slope = 1, intercept = 0), indicating that the average of 5-minute Aethalometer™ measurements is simply the EC 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 Aethalometer™ measurements is almost entirely explained by the variability in the EC reference measurements.

Quantities reported include r^2, intercept, and slope, with estimates of the 95% confidence intervals. Comparability to the reference method was determined independently for each of the two duplicate Aethalometers™ 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 Aethalometers™ and the EC reference measurements was evaluated by using meteorological data such as temperature and humidity as parameters in multivariable analyses of the reference/monitor comparison data. The same evaluation was conducted using measurements of ambient precursor pollutant gases 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 reference sample 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. Additionally, estimates of γ_j are provided. Meteorological effects and precursor gas interferences were assessed independently for each of the two duplicate Aethalometers™ 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 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 $PM_{2.5}$ 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. The average EC concentration was 1.3 µg/m^3. 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 (F)	Air Temp. @ 2 m (F)	RH (%)	Solar Radiation (W/m^2)	Press. (mbar)	Total Precip. (in.)
Average	3.35	0.09	196	68.0	61.9	89.4	162.8	979.7	0.0014
Max	6.45	0.29	298	75.4	72.5	95.8	246.1	986.7	0.0297
Min	1.88	-0.03	106	58.3	53.8	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

Light absorption readings were recorded at seven different wavelengths by the two Aethalometers™ every 5 minutes during Phase I of the verification test. Figure 6-1a shows the 5-minute data from the 880-nm channel for the two Aethalometers™. Light absorption at this wavelength is expected to correlate with ambient levels of particulate BC. Breaks in the data indicate episodes during which power outages occurred at the test site (August 6, 7, and 10 through 11), or periods during which data were not available from the Aethalometers™. The two Aethalometers™ agreed closely with one another throughout this phase of testing. In fact, the two traces in Figure 6-1a overlap almost completely. In Figure 6-1b, these same data are plotted against one another to illustrate the correlation between the two monitors.

For comparison with the EC reference measurements, the 5-minute data were averaged from noon to noon for each day to correspond with the 24-hour reference 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 Aethalometers™. A correlation plot of these data is shown in Figure 6-2b.

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 5-minute data shows a coefficient of determination (r^2) of 0.932 between the duplicate monitors. The results of the regression analysis of the 5-minute data indicate a bias between the two monitors, with Monitor 1 generally reading higher than Monitor 2 [slope = 0.914 (0.005)]. The regression results for the 5-minute data also show an intercept of the correlation plot [0.051 (0.007)] that is significantly different from zero at the 95% confidence interval.

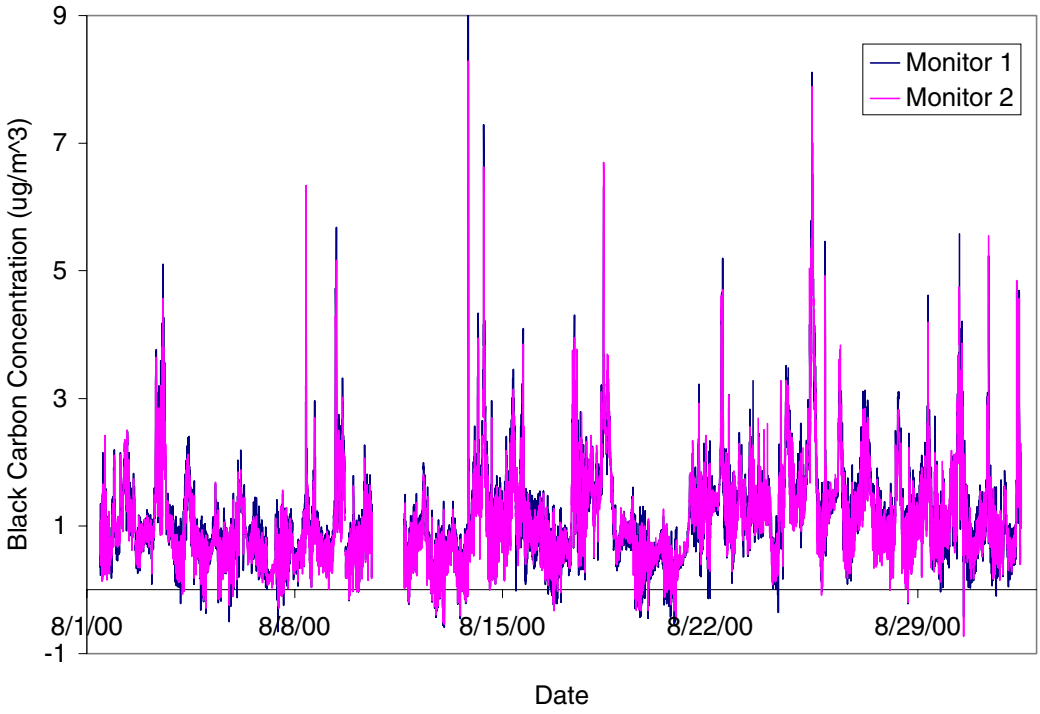

Figure 6-1a. 5-Minute BC Concentrations from Duplicate Aethalometers™ During Phase I

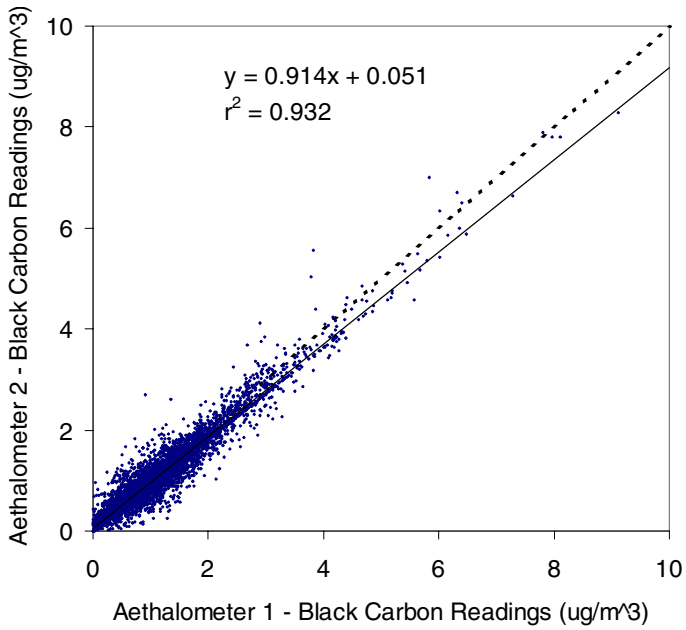

Figure 6-1b. Correlation Plot of 5-Minute BC Concentrations from Duplicate Aethalometers™ During Phase I

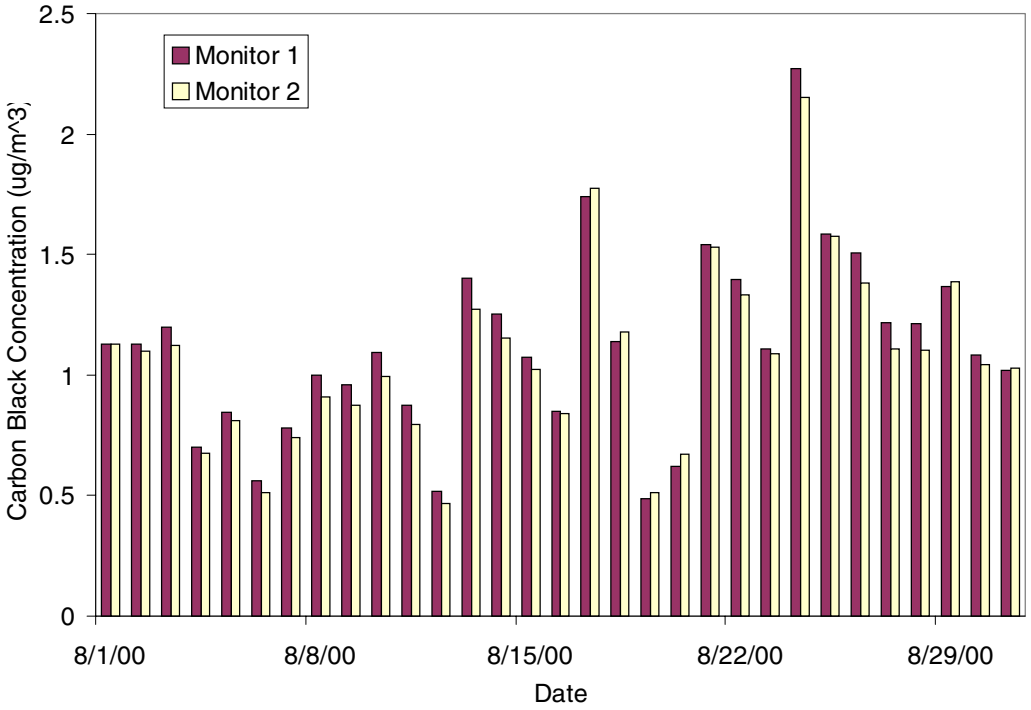

Figure 6-2a. 24-Hour Average BC Concentrations from Duplicate Aethalometers™ During Phase I

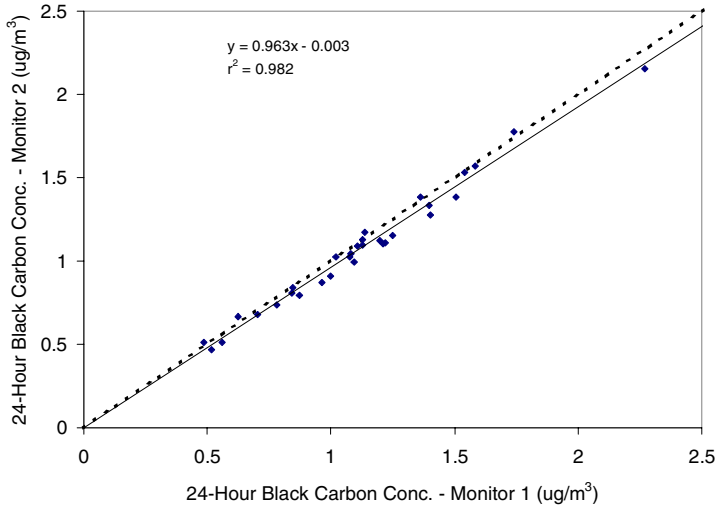

Figure 6-2b. Correlation Plot of 24-Hour Average BC Concentrations from Duplicate Aethalometers™ During Phase I

Table 6-3. Linear Regression and Coefficient of Variation Results for 5-Minute and 24-Hour Average BC Concentrations from Duplicate Aethalometers™ for Phase I

Parameter	5-Minute Data	24-Hour Average Data
Slope (95% CI)	0.914 (0.005)	0.963 (0.049)
Intercept (µg/m^3) (95% CI)	0.051 (0.007)	-0.003 (0.058)
r^2	0.932	0.982
CV	17.8%	4.2%

The 24-hour average concentration results in Table 6-3 indicate an r^2 value of 0.982. The slope of the correlation plot is not statistically different from unity at the 95% confidence level. These data show an intercept of -0.003 (0.058) µg/m^3, which is not statistically significant at the 95% confidence level.

6.1.2 Comparability/Predictability

In Figure 6-3a, the noon-to-noon average BC concentrations from the duplicate Aethalometers™ measurements are shown, along with the EC reference measurements for Phase I of the verification test. These EC concentrations were analyzed by linear regression according to Section 5.2 to establish the comparability of each of the Aethalometers™ with the EC reference measurements. (Note: The reference EC measurement for August 1, 2000, was not included in the analyses because it is an apparent outlier.) The resulting comparisons are plotted in Figure 6-3b; and the calculated slope, intercept, and r^2 value of the regression analyses are presented in Table 6-4 for each monitor.

Table 6-4. Comparability of the Aethalometers™ with the EC Reference Measurements for Phase I

Regression Parameter	Monitor 1	Monitor 2
Slope (95% CI)	0.815 (0.280)	0.791 (0.270)
Intercept (µg/m^3) (95% CI)	0.124 (0.360)	0.112 (0.347)
r^2	0.590	0.593

In each case, the 24-hour average BC measurements average approximately 80% of the reference measurements. For Monitor 1, the slope of the regression line is 0.815 (0.280); and, for Monitor 2, the slope is 0.791 (0.270). These slopes are close to the mean value of 0.76 ±0.16 reported for the mean ratio of BC to EC in U.S. urban areas.[5, 6] No statistically significant intercept is observed in either case at the 95% confidence level, and the r^2 values are 0.590 and 0.593, respectively, for Monitor 1 and Monitor 2.

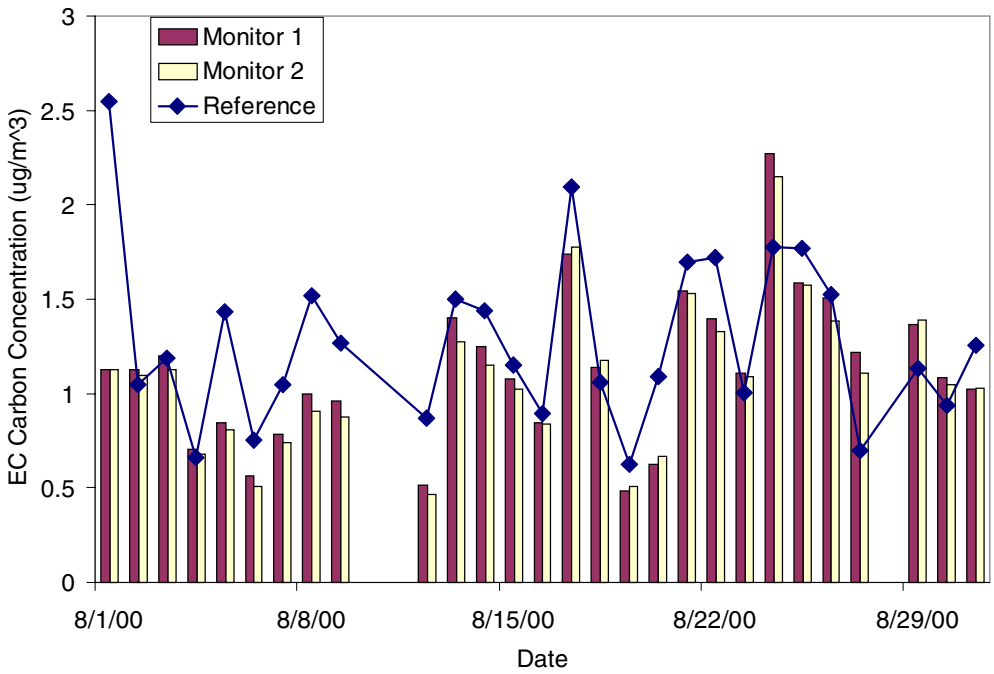

Figure 6-3a. EC Reference Concentrations and 24-Hour Average BC Concentrations from Duplicate Aethalometers™ During Phase I

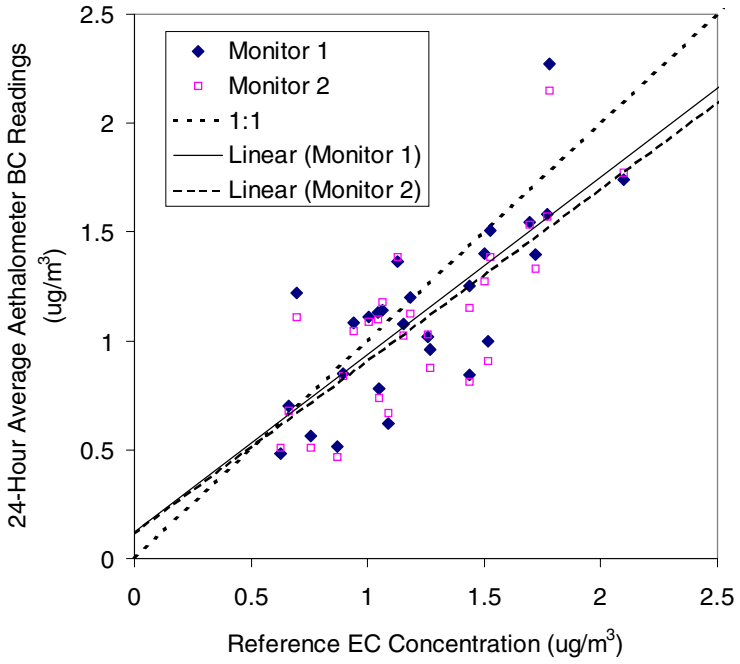

Figure 6-3b. Correlation Plot of 24-Hour Average BC Concentrations from Duplicate Aethalometers™ and EC Reference Concentrations During Phase I

6.1.3 Meteorological Effects

A multivariable model analysis, as described in Section 5.3, was used to determine if the meteorological conditions had an influence on the readings of the Aethalometer™ . This analysis involved a backward elimination process to remove from the analysis those parameters showing no statistically significant influence on the results. This model ascribed to wind speed and the ambient air temperature an effect on the results of one monitor relative to the EC reference measurements, and to the wind direction an influence on the results of the other monitor. The analysis shows the following relationships:

$$\text{Monitor 1} = 0.461*\text{Ref} - 0.273\ \mu g/m^3 - 0.236*\text{WS} + 0.0260*\text{T2}$$

and,

$$\text{Monitor 2} = 0.584*\text{Ref} - 0.333\ \mu g/m^3 + 1.06\times10^{-4}*\text{WD}$$

where Ref is the reference EC measurement in $\mu g/m^3$, WS is the wind speed in mph, T2 is the air temperature at 2 meters in °F, and WD is the wind direction in degrees.

The magnitude of the implied effects can be estimated by comparison of the predicted Aethalometer readings based on the multivariable model to those based on the simple linear regression against reference results. For example, using the average values for these parameters from Phase I (Section 6.1), the multivariable equations predict average BC concentrations of:

$$\text{Monitor 1} = 0.461*1.3 - 0.273 - 0.236*3.35 + 0.0260*61.9$$

$$= 1.15\ \mu g/m^3$$

and,

$$\text{Monitor 2} = 0.584*1.3 - 0.333 + 1.06*10^{-4}*\ 196$$

$$= 0.45\ \mu g/m^3.$$

Based on the linear regression results (Table 6-4) and the average EC concentration during Phase I, the predicted average BC readings would be:

$$\text{Monitor 1} = 0.815*1.3 + 0.124$$

$$= 1.18\ \mu g/m^3$$

and,

$$\text{Monitor 2} = 0.791*1.3 + 0.112$$

$$= 1.14\ \mu g/m^3$$

For Monitor 1, the multivariable model predicts average BC readings that differ by about 2.5% from the values predicted by the simple linear regression results. For Monitor 2, the average values predicted by the multivariable model are approximately 40% of those predicted by the linear regression results.

6.1.4 Influence of Precursor Gases

As with the meteorological data, a multivariable model analysis was used to test for any influence of the measured precursor gases on the readings of the Aethalometers™ relative to the reference measurements in Phase I. This analysis also involved backward elimination of parameters that were found to have no statistical effect. The analysis shows the following relationships:

$$\text{Monitor 1} = 0.373*\text{Ref} - 0.0468\ \mu g/m^3 - 0.122*\text{NO} + 0.0860*\text{NOx}$$

$$\text{Monitor 2} = 0.361*\text{Ref} - 0.0945\ \mu g/m^3 - 0.121*\text{NO} + 0.0877*\text{NOx}$$

where the concentrations of nitric oxide and nitrogen oxides are in ppb. These equations illustrate that the effects ascribed by the model to these gases on the Aethalometer™ readings are similar in magnitude for the two monitors; and, since the contributions of the two gases have opposite effects, their contributions largely cancel out one another.

Using the average values for these parameters from Phase I (Section 6.1), these multivariable equations predict average BC concentrations of:

$$\text{Monitor 1} = 0.373*1.3 - 0.0468 - 0.122*3.1 + 0.0860*13.0$$

$$= 1.18\ \mu g/m^3$$

and

$$\text{Monitor 2} = 0.361*1.3 - 0.0945 - 0.121*3.1 + 0.0877*13.0$$

$$= 1.14\ \mu g/m^3.$$

In both cases, the multivariable model results are identical to the values predicted by the simple linear regression results.

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

During Phase II, daily 24-hour $PM_{2.5}$ concentrations averaged 74 $\mu g/m^3$ and ranged from 4.9 $\mu g/m^3$ to 146 $\mu g/m^3$. 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. The average EC concentration was 6.1 $\mu g/m^3$. 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 6-5 summarizes the meteorological conditions during Phase II, and Table 6-6 summarizes the observed concentrations of the measured precursor gases during this period.

Table 6-5. Summary of Daily Values for the Measured Meteorological Parameters During Phase II of Verification Testing

	Wind Speed (m/sec)	Wind Direction (Degrees)	Air Temp. (C)	RH (%)	Solar Radiation (W/m^2)	Press. (mm Hg)
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 6-6. 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

As in Phase I, BC concentrations were recorded every 5 minutes in Phase II by the duplicate Aethalometers™. The 5-minute BC concentration readings from the two Aethalometers™ for Phase II of the verification test are shown in Figure 6-4a. In Figure 6-4b, these data are plotted against one another to illustrate the correlation between the two monitors. Breaks in the data indicate episodes during which the tape in the Aethalometer™ was advancing, and no data are available. As a result of the high $PM_{2.5}$ levels during Phase II, the filter tape in the Aethalometer™ was advanced much more frequently than in Phase I, resulting in a substantial loss of data.

The vendor has indicated that in its operating parameters setup, the instrument offers the "Tape Saver" option that allows the sample air flow to be diverted from the collecting portion of the filter tape for a fraction of each timebase period. The diversion fraction is controlled dynamically

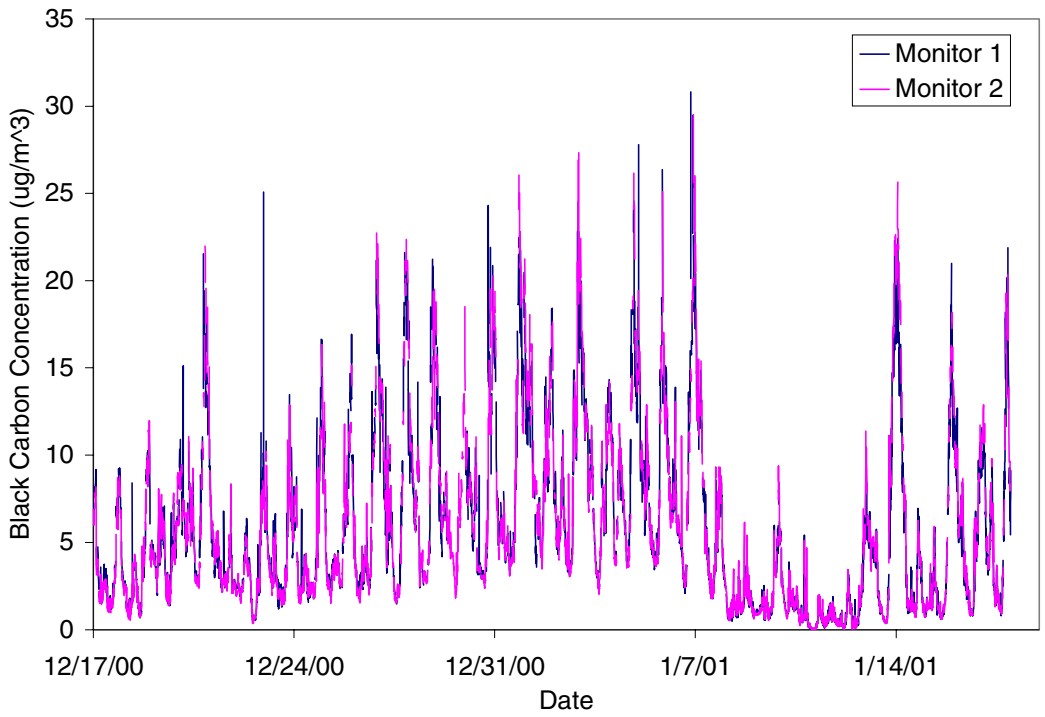

Figure 6-4a. 5-Minute BC Concentrations from Duplicate Aethalometers™ During Phase II

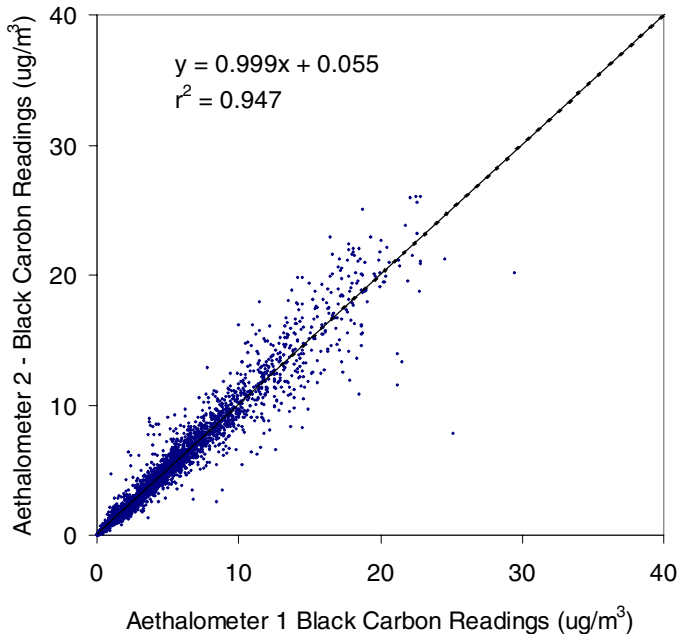

Figure 6-4b. Correlation Plot of 5-Minute BC Concentrations from Duplicate Aethalometers™ During Phase II

by the software according to the BC concentration and varies from 50% to 90% of the timebase period. This results in an extension of filter spot lifetime by a factor of 2 to 10, thereby reducing the frequency of tape advances, the consumption of tape, and the loss of data coverage. This "Tape Saver" feature was not invoked during this study, and these claims were not verified.

The 5-minute data were averaged from midnight to midnight for each day to obtain 24-hour average BC concentrations during Phase II of the verification test. In Figure 6-5a, 24-hour averages for Phase II of the verification test are presented for the two Aethalometers™. A correlation plot of these data is shown in Figure 6-5b.

The results of a linear regression analysis of these data are presented in Table 6-7. The CVs for the 5-minute and the 24-hour average values were also calculated and are shown in Table 6-7.

Table 6-7. Linear Regression and Coefficient of Variation Results for 5-Minute and 24-Hour Average BC Concentrations from Duplicate Aethalometers™ for Phase II

Parameter	5-Minute Data	24-Hour Average Data
Slope (95% CI)	0.999 (0.007)	1.004 (0.027)
Intercept ($\mu g/m^3$) (95% CI)	0.055 (0.038)	-0.052 (0.157)
r^2	0.947	0.995
CV	12.3%	2.7%

The 5-minute data from the duplicate Aethalometers show an r^2 value of 0.947, and a slope that is statistically indistinguishable from unity at 95% confidence [0.999 (0.007)]. The regression results show a statistically significant intercept of 0.055 (0.038) $\mu g/m^3$. The CV for the 5-minute data was 12.3%.

The 24-hour averages for the duplicate monitors show an r^2 value of 0.995 and show a slope that is statistically indistinguishable from unity at 95% confidence [slope = 1.004 (0.027)]. These data show no statistically significant intercept at the 95% confidence level. The CV for the 24-hour averages was 2.7%.

6.2.2 Comparability/Predictability

To compare with the reference measurements, the 5-minute results from the duplicate Aethalometers™ were appropriately averaged to correspond to the five daily sampling periods for the reference sequential filter sampler. Table 6-8 summarizes the concentration of EC during these sampling periods. Figure 6-6a shows the reference measurements and the corresponding averages from the duplicate Aethalometers™ for Phase II of the verification test. These same data are also shown in Figure 6-6b as scatter plots to illustrate the correlation between the results of the duplicate Aethalometers™ and the reference measurements.

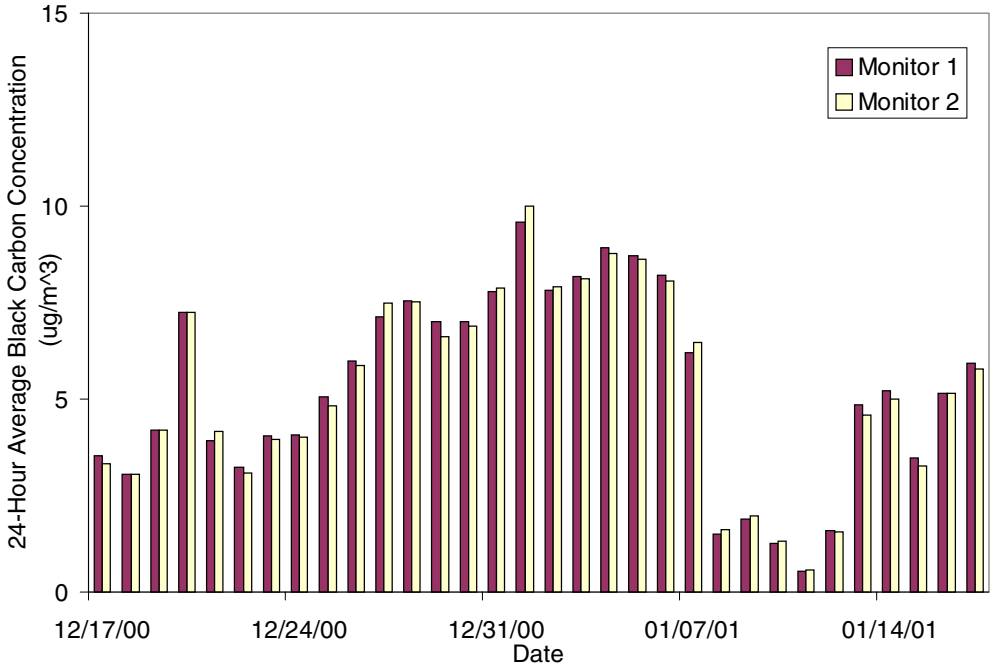

Figure 6-5a. 24-Hour Average BC Concentrations from Duplicate Aethalometers™ During Phase II

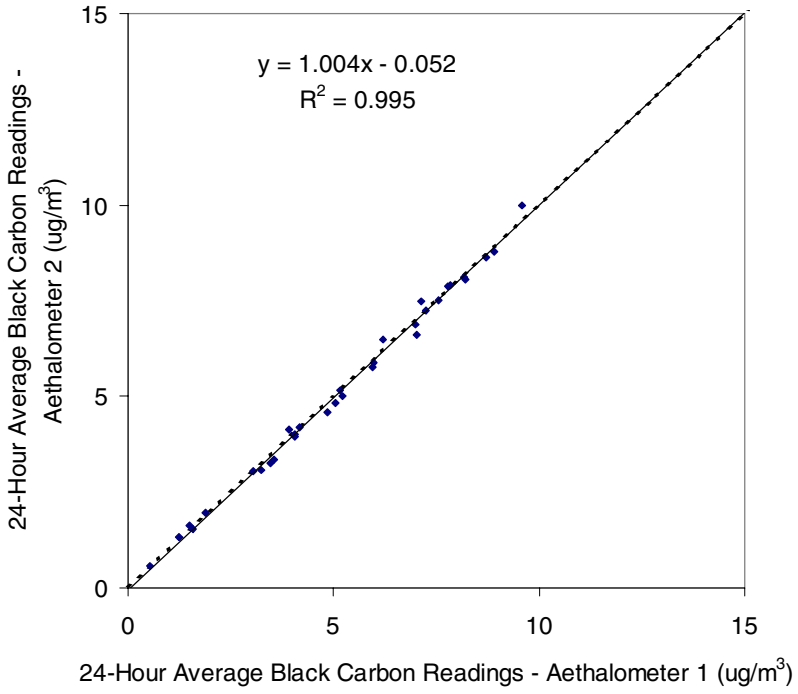

Figure 6-5b. Correlation Plot of 24-Hour Average BC Concentrations from Duplicate Aethalometers™ During Phase II

Table 6-8. Summary of Reference EC Concentrations During Phase II

EC Concentration µg/m³	Sampling Period					
	All[a]	0000-0500	0500-1000	1000-1300	1300-1600	1600-2400
Average	6.10	9.47	5.80	3.34	2.42	9.35
Maximum	22.87	22.87	16.25	8.73	6.68	17.20
Minimum	0.00	0.00	0.12	0.17	0.22	0.80

[a]Summary of all individual samples treated equally, i.e., no time-weighting.

Linear regression analysis of these data was performed independently for each Aethalometer™, and the results are presented in Table 6-9. Regression analyses were also performed separately for each of the sampling periods (i.e, 0000-0500, 0500-1000, 1000-1300, 1300-1600, and 1600-2400). These regression results are also presented in Table 6-9 for the duplicate Aethalometers™.

Table 6-9. Comparability of the Aethalometers™ with EC Reference Measurements for Phase II

Short-Term Sampling Period	Monitor 1			Monitor 2		
	Slope	Intercept (µg/m³)	r^2	Slope	Intercept (µg/m³)	r^2
All	0.711 (0.031)	0.54 (0.25)	0.930	0.735 (0.031)	0.47 (0.25)	0.934
0000-0500	0.719 (0.051)	-0.04 (0.57)	0.967	0.794 (0.061)	-0.44 (0.69)	0.960
0500-1000	0.648 (0.087)	1.07 (0.59)	0.887	0.689 (0.080)	0.91 (0.55)	0.911
1000-1300	0.705 (0.175)	0.78 (0.62)	0.709	0.809 (0.172)	0.62 (0.66)	0.769
1300-1600	0.797 (0.176)	0.25 (0.48)	0.762	0.756 (0.168)	0.32 (0.46)	0.759
1600-2400	0.793 (0.104)	-0.03 (0.109)	0.898	0.764 (0.102)	0.07 (0.07)	0.894

The regression results indicate that both monitors showed a varying degree of correlation with the reference measurements over the different sampling periods. In both cases, the best correlation (i.e., r^2 closest to 1) with the reference measurements occurred during the midnight to 5:00 AM sampling period, and the lowest correlation in the 10:00 AM to 1:00 PM period for Monitor 1 and in the 1:00 PM to 4:00 PM period for Monitor 2. For Monitor 1, the r^2 values ranged from 0.709 to 0.967; and for Monitor 2 the r^2 values ranged from 0.759 to 0.960 for the different sampling periods. Both monitors showed a substantial negative bias relative to the EC reference measurements. For Monitor 1, the regression results including all sampling periods show a slope of 0.711 (0.031), an intercept of 0.54 (0.25) µg/m³, and an r^2 value of 0.930. For Monitor 2, the regression results show a slope of 0.735 (0.031), an intercept of 0.47 (0.25) µg/m³,

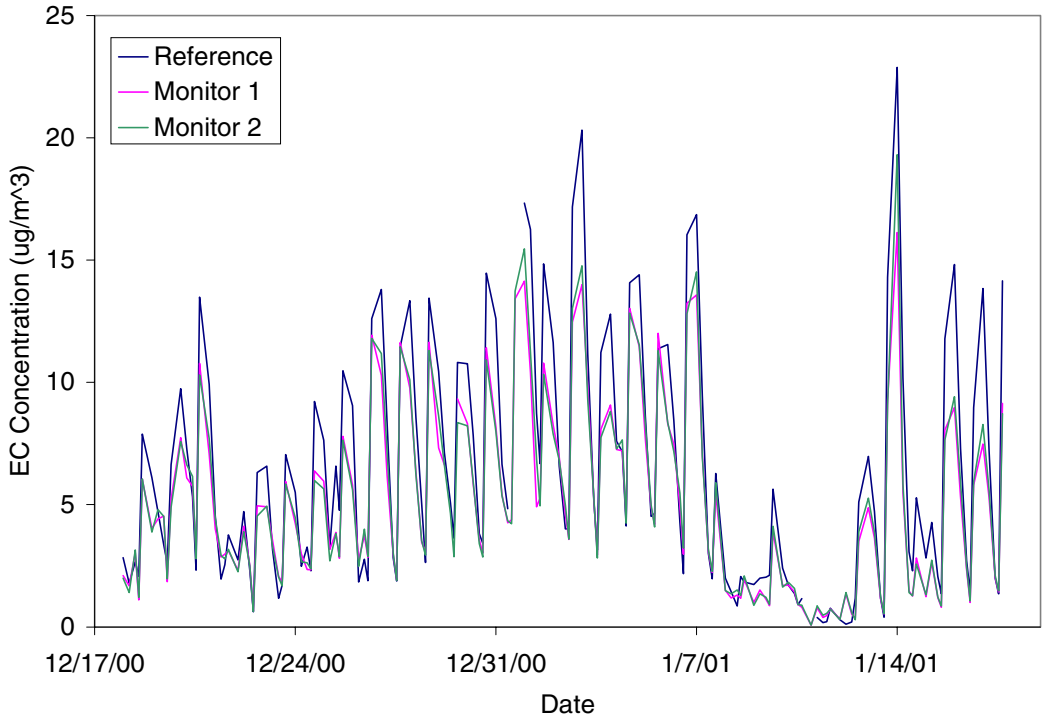

Figure 6-6a. Average BC Concentrations from Duplicate Aethalometers™ and EC Reference Concentrations During Phase II of Verification Testing

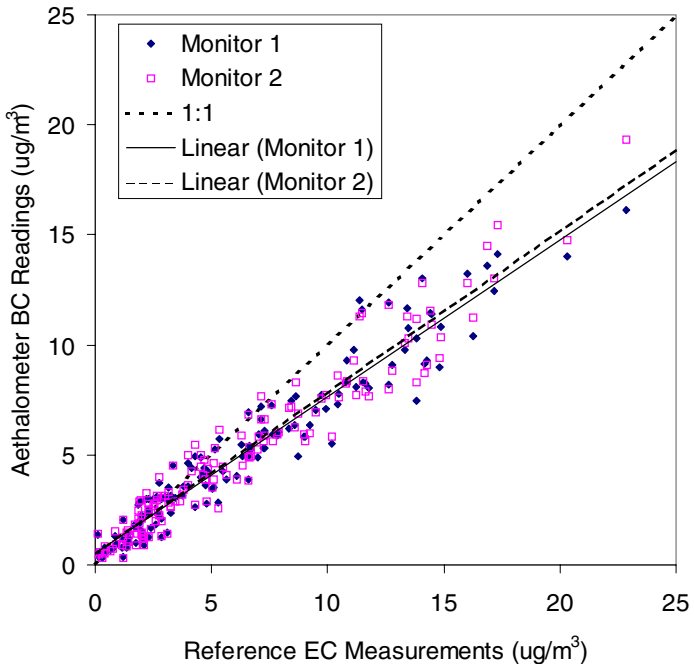

Figure 6-6b. Correlation Plot of Average BC Concentrations from Duplicate Aethalometers™ and EC Reference Concentrations During Phase II of Verification Testing

and an r^2 value of 0.934. The slopes of the regression lines for the individual sampling periods ranged from 0.648 to 0.797 for Monitor 1, and from 0.689 to 0.809 for Monitor 2.

6.2.3 Meteorological Effects

A multivariable model analysis, as described in Section 5.3, was used to determine if the meteorological conditions had an influence on the readings of the Aethalometers™ in Phase II. This analysis involved a backward elimination process to remove from the analysis those parameters showing no statistically significant influence on the results. This model ascribed to wind speed, wind direction, the standard deviation of the wind direction, relative humidity, solar radiation, and barometric pressure an influence on the two Aethalometers™ relative to the reference results at the 90% confidence level. The analysis shows the following relationships:

$$\text{Monitor 1} = 0.600*\text{Ref} + 90.3\ \mu g/m^3 - 1.54*\text{WS} - 0.0197*\text{WD} - 0.185*\text{WDSTD} + 0.0551*\text{RH} + 0.0168*\text{RAD} - 0.112*\text{BP}.$$

and,

$$\text{Monitor 2} = 0.613*\text{Ref} + 90.4\ \mu g/m^3 - 1.50*\text{WS} - 0.0204*\text{WD} - 0.189*\text{WDSTD} + 0.0495*\text{RH} + 0.0146*\text{RAD} - 0.112*\text{BP}$$

where Ref is the reference EC measurement in $\mu g/m^3$, WS is the wind speed in meters per second, WD is the wind direction in degrees, WDSTD is the standard deviation of the wind direction in degrees, RH is the percent relative humidity, RAD is the solar radiation in W/m^2, and BP is the barometric pressure in mmHg.

Substituting the average values for these parameters during Phase II (Section 6.2) into these equations, the average BC concentrations predicted by the multivariable model are:

$$\text{Monitor 1} = 0.600*6.10 + 90.3 - 1.54*1.43 - 0.0197*186 - 0.185*18.7 + 0.0551*75.4 + 0.0168*88.2 - 0.112*756.2$$

$$= 5.6\ \mu g/m^3$$

and,

$$\text{Monitor 2} = 0.613*6.10 + 90.4 - 1.50*1.43 - 0.0204*186 - 0.189*18.7 + 0.0495*75.4 + 0.0146*88.2 - 0.112*756.2$$

$$= 5.0\ \mu g/m^3.$$

Based on the linear regression results (Table 6-9) and the average EC concentrations during Phase II, the predicted average BC readings would be:

$$\text{Monitor 1} = 0.711*6.10 + 0.54$$

$$= 4.9\ \mu g/m^3$$

and

$$\text{Monitor 2} = 0.735*6.10 + 0.47$$

$$= 5.0\ \mu g/m^3$$

For Monitor 1, the multivariable model results differ by about 14% from the simple linear regression result. For Monitor 2, the difference between the multivariable model and the linear regression results is negligible.

6.2.4 Influence of Precursor Gases

As with the meteorological data, a multivariable model analysis was used in Phase II to test for any influence of the measured precursor gases on the readings of the Aethalometers™ relative to the reference measurements. This analysis also involved backward elimination of parameters that were found to have no statistical effect. The model ascribed to both nitric oxide and nitrogen oxides a statistically significant (90% confidence) effect on the readings of the Aethalometer™ monitors. The analysis shows the following relationships:

$$\text{Monitor 1} = 0.442*\text{Ref} - 1.73\ \mu g/m^3 - 0.106*\text{NO} + 0.115*\text{NOx}$$

and

$$\text{Monitor 2} = 0.464*\text{Ref} - 1.70\ \mu g/m^3 - 0.106*\text{NO} + 0.113*\text{NOx}$$

where the concentrations of nitric oxide and nitrogen oxides are in ppb. As with the results from Phase I, these equations illustrate that the effects of these gases on the Aethalometer™ readings are similar in magnitude for the two monitors, and oppose one another.

Using the average values for these parameters during Phase II (Section 6.2), these multivariable equations predict average BC readings of

$$\text{Monitor 1} = 0.442*6.10 - 1.73 - 0.106*61.8 + 0.115*94.4$$

$$= 5.3\ \mu g/m^3$$

and

$$\text{Monitor 2} = 0.464*6.10 - 1.70 - 0.106*61.8 + 0.113*94.4$$

$$= 5.2\ \mu g/m^3.$$

The difference between the multivariable model results and the linear regression results noted in Section 6.2.3 is 8.2% for Monitor 1 and 4.0% for Monitor 2.

6.3 Instrument Reliability/Ease of Use

The only maintenance done on the Aethalometers™ during Phase I was the occasional adjustment of the sample flow rate. During Phase II, the filter tape was replaced in one of the Aethalometers™. The Aethalometers™ ran almost unattended for the duration of each phase. Data disks were replaced in each instrument weekly to capture the data, but no maintenance on either Aethalometer™ was required during either phase. Data capture during Phase I was near 100%. During Phase II, the high $PM_{2.5}$ concentrations resulted in the need to advance the filter tape on a frequent basis. As such, the data capture was approximately 75% during this phase of testing. The Aethalometer™ offers a flow-diversion feature in its operational setup, which is intended to reduce the frequency of tape advance and loss of data.

6.4 Shelter/Power Requirements

The duplicate Aethalometers™ were installed and operated inside an instrument trailer during Phase I of testing and were run on a single 15 A circuit. During Phase II, one monitor was installed in the instrument trailer and the second was installed inside the CARB facility.

6.5 Instrument Cost

The list price for Aethalometers™ varies according to model and options. The price of a basic instrument capable of performing the measurements described in this report is approximately $17,000. Filter tape is the only consumable required for operation of the Aethalometer™. A roll of filter tape is expected to last for at least 60 days of continuous sampling.

Chapter 7
Performance Summary

The Aethalometer™ is a semi-continuous particle monitor designed to provide indications of the ambient particulate black carbon. Duplicate Aethalometers™ were operated on a timebase of 5 minutes for evaluation under field test conditions in two separate phases of this verification test. The results from each phase of this verification test are summarized below.

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

Inter-unit precision was assessed in Phase I for both 5-minute and 24-hour data. Regression analysis showed r^2 values of 0.932 and 0.982, respectively, for the 5-minute data and 24-hour averages from the duplicate Aethalometers™. The slopes of the regression lines were 0.914 (0.005)and 0.963 (0.049), respectively, for the 5-minute data and 24-hour averages. The slope of the 5-minute data was statistically different from unity at 95% confidence. For the 5-minute data, a statistically significant intercept of 0.051 (0.007) $\mu g/m^3$ was observed, and the intercept for the 24-hour data [-0.003 (0.058)]was not significantly different from zero at the 95% confidence level. The calculated CV for the 5-minute data was 17.8%; and, for the 24-hour averages, the CV was 4.2%.

Comparisons of the 24-hour Aethalometers™ BC averages with IMPROVE TOR reference results for EC showed intercepts indistinguishable from zero and slopes of the regression lines of 0.815 (0.280) and 0.791 (0.270), respectively, for Monitor 1 and Monitor 2. The regression results showed r^2 values of 0.590 and 0.593 for Monitor 1 and Monitor 2, respectively.

Multivariable model analysis was used to establish if meteorological conditions influenced the readings of the duplicate Aethalometers™ relative to the EC reference measurements during Phase I. The multivariable model ascribed to wind speed and air temperature a significant effect on one of the Aethalometers™, and to wind direction an effect on the other monitor. The difference between multivariable model results and simple linear regression results was small for one monitor (approximately 2.5%) and substantial for the other (approximately 60%).

Multivariable model analysis also was used to determine whether the concentrations of precursor gases had an effect on the Aethalometer™ readings. The model ascribed to both nitric oxide and total nitrogen oxides a statistically significant (90% confidence) effect on the readings of both Aethalometers™ relative to the EC reference measurements. The effects of these gases were

similar in magnitude and opposing in nature. The multivariable model results were the same as the simple linear regression results.

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

During Phase II, regression analysis showed r^2 values of 0.947 and 0.995, respectively, for the inter-unit comparison of 5-minute and 24-hour average data from the duplicate monitor. The slopes of the regression lines were 0.999 (0.007) and 1.004 (0.027), respectively, for the 5-minute data and 24-hour averages. These slopes were not statistically different from unity at 95% confidence. The intercepts were 0.055 (0.038) and -0.052 (0.157), for 5-minute and hourly data, respectively. The calculated CV for the 5-minute data was 12.3%; and, for the 24-hour averages, the CV was 2.7%.

Comparison of the appropriately averaged data from the Aethalometers™ with EC reference results from all of the sampling periods in Phase II showed slopes of the regression lines of 0.711 (0.031) and 0.735 (0.031), with intercepts of 0.54 (0.25) and 0.47 (0.25), for Monitors 1 and 2, respectively, indicating a bias between the Aethalometer™ BC measurement and the EC reference measurement. The regression results showed r^2 values of 0.930 and 0.934 for Monitor 1 and Monitor 2, respectively. Correlation with the reference measurements was best for both monitors for the period between midnight and 5:00 AM, and lowest for the period from 10:00 AM to 1:00 PM for Monitor 1 and from 1:00 PM to 4:00 PM for Monitor 2.

Multivariable analysis was performed to establish if meteorological conditions influenced the readings of the duplicate Aethalometers™ relative to the EC reference measurements during Phase II. The model ascribed to wind speed, wind direction, standard deviation of wind direction, relative humidity, solar radiation, and barometric pressure an influence on the two Aethalometers™ relative to the reference results at the 90% confidence level. The multivariable model results differ from simple linear regression against the reference results by about 14% for Monitor 1; the difference for Monitor 2 was negligible.

Multivariable analysis also was performed to determine whether the presence of precursor gases had an effect on the Aethalometer™ readings. As with the results from Phase I, this analysis ascribed to both nitric oxide and nitrogen oxides a statistically significant (90% confidence) effect on the readings of both Aethalometers™ relative to the EC reference measurements. The effects of these gases were similar in magnitude and opposing in nature. The multivariable model results differed from the linear regression results by 8.2% for Monitor 1 and 4.0% for Monitor 2.

The Aethalometers™ ran almost unattended for the duration of each phase. Data disks were replaced in each instrument weekly to capture the data, but no maintenance on either Aethalometer™ was required during either phase. Data capture during Phase I was near 100%. During Phase II, the high $PM_{2.5}$ concentrations resulted in the need to advance the filter tape on a frequent basis. As such, the data capture was approximately 75% during this phase of testing.

Chapter 8
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