Environmental Technology Verification Report

RUPPRECHT & PATASHNICK, CO. SERIES 5400 AMBIENT PARTICULATE CARBON MONITOR

Prepared by

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Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

ETV

EPA
U.S. Environmental Protection Agency

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ETV Joint Verification Statement

TECHNOLOGY TYPE: Continuous Ambient Particulate Carbon Monitor

APPLICATION: MEASURING PARTICULATE CARBON IN AMBIENT AIR

TECHNOLOGY NAME: Series 5400 Monitor

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

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

The Advanced Monitoring Systems (AMS) Center, one of six technology centers under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center has recently evaluated the performance of continuous monitors used to measure fine particulate mass and species in ambient air. This verification statement provides a summary of the test results for the Rupprecht & Patashnick, Co. Series 5400 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 Series 5400 reports particulate organic, elemental, and total carbon concentrations (OC, EC, and TC) and was compared with particulate carbon concentrations determined by laboratory thermal/optical reflectance (TOR) analysis of filter-based reference samples. Ambient aerosol carbon levels differed markedly in the two phases of testing, with OC, EC, and TC averages of 4.6, 1.3, and 5.9 $\mu g/m^3$, respectively, in Phase I, and of 19.8, 6.1, and 25.9 $\mu g/m^3$, respectively, 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 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 Series 5400 is an automatic speciation analyzer of suspended particulate matter. It measures the elemental and organic carbon contained in suspended particulate matter at averaging times as short as one hour. Its thermal CO_2 analysis technique is similar to that used in many analytical laboratories to measure carbon particulate concentration. Results from the instrument can be used to compare organic and elemental carbon particulate concentrations (in $\mu g/m^3$) with mass-based measurements such as $PM_{2.5}$, PM_{10} or PM_1 (in $\mu g/m^3$). Ambient air passes through a $PM_{2.5}$, PM_{10}, or PM_1 size-selective inlet before entering the instrument. The Series 5400 contains two cartridges located in temperature-regulated ovens to collect the sampled particulate matter. While one cartridge is being used for particle collection, the instrument performs its thermal CO_2 analysis on the previously collected particulate matter contained in the other collector. The Series 5400 differentiates between organic and elemental carbon particulate matter by oxidizing collected samples at an intermediate temperature and at a high final burn temperature. When operated at a two-hour cycle, the Series 5400 can perform up to three sample oxidations at intermediate temperatures prior to the final burn. With zero and span gas sources attached, the Series 5400 automatically audits and calibrates the CO_2 sensor at user-defined intervals. Sample oxidation during the analysis phase regenerates the Series 5400's exchangeable collection cartridges. The Series 5400 is constructed to be operated automatically and unattended for months at a time between maintenance routines. The Series 5400 makes carbon particulate data available to external devices through analog outputs and a bidirectional RS-232 interface. Data stored internally may be viewed from the monitor's display, or may be downloaded through the RS-232 port directly to a PC or by modem to a remote location. Internal diagnostics notify the user of status conditions that might affect data quality.

VERIFICATION OF PERFORMANCE

Inter-Unit Precision: Linear regression results of the hourly readings of the duplicate Series 5400 monitors indicate r^2 values of 0.94, 0.93, and 0.95, respectively, for OC, EC, and TC in Phase I. The calculated slopes of the regression lines for these data were 1.063 (0.021), 1.037 (0.022), and 1.069 (0.020), respectively where the numbers in parentheses are 95% confidence intervals. Daily 24-hour averages were calculated for OC, EC, and TC and showed similar correlation and agreement results as the hourly data. The regression results for these data indicate r^2 values of 0.97, 0.94, and 0.97, respectively. The calculated slopes of the regression lines for the

24-hour average data were 1.094 (0.081), 1.038 (0.113), and 1.098 (0.088), respectively, for OC, EC, and TC. During Phase II, linear regression results on hourly readings from the duplicate monitors indicate r^2 values of 0.94, 0.92, and 0.86, for OC, EC, and TC, respectively. The calculated slopes of the regression lines for these data were 0.971 (0.019),1.029 (0.024), and 1.074 (0.035), respectively. Daily 24-hour averages were calculated for OC, EC, and TC in Phase II and showed similar correlation and agreement results as the hourly data. The regression results for these data indicate r^2 values of > 0.97, for each carbon fraction. The calculated slopes of the regression lines for these data were 1.027 (0.072), 1.164 (0.083), and 1.090 (0.070), respectively. Without the application of a correction factor to the results of one monitor, a bias of approximately 50% was observed.

Comparability/Predictability: During Phase I, comparison of the 24-hour averages from the Series 5400 monitors to the OC, EC, and TC reference measurements showed a negative bias of the Series 5400 readings. The slopes of the regression lines for each monitor were below 0.4 for all three carbon fractions, and the r^2 values were between 0.43 and 0.52. During Phase II, comparison of the 24-hour averages to the OC, EC, and TC reference measurements again showed a negative bias of the Series 5400 readings. The slopes of the regression lines for each monitor fell between approximately 0.2 and 0.7 for Monitor 1 and 0.2 and 0.9 for Monitor 2 for all three carbon fractions, when all sampling periods were included in the analysis. However, better quantitative agreement between the Series 5400 monitors and the reference measurements was observed for some of the sampling periods relative to others. The r^2 values for the Phase II regression analyses, when all sampling periods are included, were between 0.65 and 0.90.

Meteorological Effects: During Phase I, the multivariable model ascribed to vertical and horizontal wind speed, wind direction, and ambient air temperature at 2 meters and 10 meters a significant effect on Series 5400 readings relative to the reference carbon results at 90% confidence. In general, the combined effect of these parameters was small. For example, the multivariable model predicts an average value of OC during Phase I for one of the monitors which is different from the linear regression model by ~5%. During Phase II, the multivariable model ascribed to wind speed, wind direction, the standard deviation of the wind direction, solar radiation, relative humidity, and barometric pressure a significant effect on readings relative to the reference carbon results at 90% confidence. Again, the combined effects of these parameters were small.

Influence of Precursor Gases: The multivariable model ascribed to ozone, hydrogen sulfide, and nitrogen dioxide a statistical influence on the readings of one or both monitors relative to the reference carbon results during Phase I. During Phase II, the model ascribed to nitric oxide and total nitrogen oxides a statistical influence on the readings of both Series 5400 monitors relative to the reference EC and TC results, and to nitrogen dioxide an influence on the readings of one monitor relative to the OC results at the 90% confidence level. The combined effect of the multiple parameters was typically a few percent, relative to the linear regression of Series 5400 and reference results.

Other Parameters: In general, these monitors required little maintenance and could be operated largely unattended. The monitors require 240 V power and should be installed indoors. Data recovery of approximately 90% was achieved for the two monitors over both phases of testing.

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	

US EPA ARCHIVE DOCUMENT

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Rupprecht & Patashnick, Co. Series 5400 Ambient Particulate Carbon 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

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List of Abbreviations

ADQ	audit of data quality
AMS	Advanced Monitoring Systems
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
IMPROVE	Interagency Monitoring for Protection of Visual Environments
L/min	liters per minute
mm	millimeters
in.	inch
NETL	National Energy Technology Laboratory
N_2	nitrogen
NIST	National Institute of Standards and Technology
NO	nitric acid
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
O_3	ozone
OC	organic carbon
QA/QC	quality assurance/quality control
QMP	quality management plan
R&P	Rupprecht & Patashnick
SFS	sequential filter sampler
TC	total carbon
TSA	technical systems audit
TOR	thermal optical reflectance
µg	microgram

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 Rupprecht and Patashnick (R&P) Series 5400 particulate carbon monitor.

Chapter 2
Technology Description

The following description of the Series 5400 particulate carbon monitor is based on information provided by the vendor.

The Series 5400 monitor is an automatic speciation analyzer of suspended particulate matter. It measures total and organic carbon (and thus elemental carbon by difference) contained in suspended particulate matter at averaging times as short as one hour. Its thermal CO_2 analysis technique is similar to that used in many analytical laboratories to measure particulate carbon concentration. Results from the instrument can be used to compare organic and elemental carbon particulate concentrations (in µg/m³) with mass-based measurements such as $PM_{2.5}$, PM_{10} or PM_1 (in µg/m³). For this test, a conventional PM_{10} head and $PM_{2.5}$ sharp cut cyclone were used for aerosol size selection, with a sample flow rate of 16.7 L/min. The Series 5400 monitor contains two cartridges located in temperature-regulated ovens to collect the sampled particulate matter. While one cartridge is being used for particle collection, the instrument performs its thermal CO_2 analysis on the previously collected particulate matter contained in the other collector. The Series 5400 monitor differentiates between organic and elemental carbon particulate matter by oxidizing collected samples at an intermediate temperature and at a high final burn temperature. When operated at a two-hour cycle, the Series 5400 can perform up to three sample oxidations at inter-mediate temperatures prior to the final burn.

With zero and span gas sources attached, the Series 5400 automatically audits and calibrates the CO_2 sensor at user-defined intervals. Sample oxidation during the analysis phase regenerates the Series 5400 monitor's exchangeable collection cartridges. The Series 5400 monitor is constructed to be operated automatically and unattended for months at a time between maintenance routines. The Series 5400 monitor makes particulate carbon data available to external devices through analog outputs and a bidirectional RS-232 interface. Data

Figure 2-1. Rupprecht & Patashnick, Co. Series 5400 Particulate Carbon Monitor

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stored internally may be viewed from the monitor's display, or may be downloaded through the RS-232 port directly to a personal computer or by modem to a remote location. Internal diagnostics notify the user of status conditions that might affect data quality.

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 Series 5400 monitors were tested in side-by-side operation during each phase of testing. During Phase I, the monitors tested were Serial Number 20237 and Serial Number 20277. During Phase II, the monitors tested were Serial Number 20120 and Serial Number 20277. Collocation of the Series 5400 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

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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, relative to the reference method. 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 Series 5400 determines organic carbon (OC) particulate mass and total carbon (TC) particulate mass. Elemental carbon (EC) is deduced from the difference between TC and OC readings. As such, the measurements from the Series 5400 monitors were compared with results of thermal/optical reflectance (TOR) analysis[4] of collected 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 Analysis

The primary comparisons of the Series 5400 carbon readings were made relative to the TOR method for carbon analysis used in the IMPROVE network.[5] This technique involves the preferential oxidation and detection of OC and elemental carbon EC fractions at different temperatures. 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 Series 5400 monitors that should be noted. Most importantly, the Series 5400 monitors do not use quartz filters, which may absorb vapor phase organics in some circumstances; the TOR method does use quartz filters. In addition, the Series 5400 monitors apply no correction for pyrolysis of organic material on the filter, whereas the TOR method does incorporate such a correction. Differences in sampling conditions (i.e., flow rate) between the reference sampler and the Series 5400 monitors 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 at Consol.

To supplement the 24-hour samples, additional samples for $PM_{2.5}$ mass were collected at the Fresno site over shorter sampling periods (i.e., 3-, 5-, 8-hour) to assess the capabilities of the monitors being tested in indicating short-term $PM_{2.5}$ levels. A medium-volume sequential filter sampling (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 one to five sets of filters at midnight each day. A vacuum pump drew air through the paired filter packs when the valves were open. The flow rate was controlled by maintaining a constant pressure across a valve with a differential pressure regulator.

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

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.

3.3.2 Supplemental Measurements

Various supplemental measurements were used to further establish the performance of the continuous monitors being tested. Meteorological conditions were monitored and recorded continuously throughout each phase of the verification test. These measurements included temperature, relative humidity, wind speed, direction, barometric pressure, and solar radiation. These data were provided to Battelle for Phase I by DOE/NETL and for Phase II by DRI. Likewise, the ambient concentrations of various precursor gases (including ozone, nitrogen oxides, carbon monoxide, sulfur dioxide, and hydrogen sulfide) 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.

3.4 Data Comparisons

The primary means used to verify the performance of the Series 5400 monitors was comparison with the TOR carbon results of samples from the reference samplers. 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, relative to the results of the reference method. 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

The Series 5400 monitors were verified in a test that included duplicate monitors of 13 different fine particle monitoring instruments. With 26 total monitors in the field, it was not possible to operate every monitor in an ideal location relative to reference sampling devices.

During Phase I of testing, the two Series 5400 monitors were installed and operated in a DOE/NETL instrument trailer. The Series 5400 monitors were placed on a counter top, with each monitor below a port through the roof of the trailer. Separate inlet tubes, approximately three meters (10 feet) in length, were installed vertically through the sampling ports and secured on the trailer roof. A PM_{10} head and $PM_{2.5}$ Sharp Cut Cyclone were used with each Series 5400 monitor to provide particle size selection. Data generated by the Series 5400 monitors were logged on the DOE/NETL data logger and provided to the Verification Test Coordinator in electronic format.

During Phase II of testing, the two Series 5400 monitors were installed and operated in the Battelle instrument trailer. The Series 5400 monitors were placed on a counter top, with each monitor directly below a port through the roof of the trailer. Separate inlet tubes, approximately three meters (10 feet) in length, were installed vertically through the sampling ports and secured on the trailer roof. A PM_{10} head and $PM_{2.5}$ Sharp Cut Cyclone were used with each Series 5400 monitor to provide particle size selection. Data generated by the Series 5400 monitors were recorded internally and downloaded daily onto an on-site personal computer.

3.5.1 Phase I

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

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

Most of the DOE/NETL continuous monitoring equipment, including the continuous precursor gas monitors, was located inside the DOE/NETL instrument trailer. A DOE/NETL Andersen RAAS sampler was located outside on a DOE/NETL platform. The Series 5400 monitors were installed inside the DOE/NETL instrument trailer, and a Battelle Andersen RAAS sampler was installed on the Battelle/ETV platform. In this arrangement, the Series 5400 monitor inlets were within 10 m horizontally and 2 m vertically of the inlet of the RAAS sampler. A 10-meter (33-foot) meteorological tower was located approximately 25 meters (65 feet) to the north of the DOE/NETL instrument trailer.

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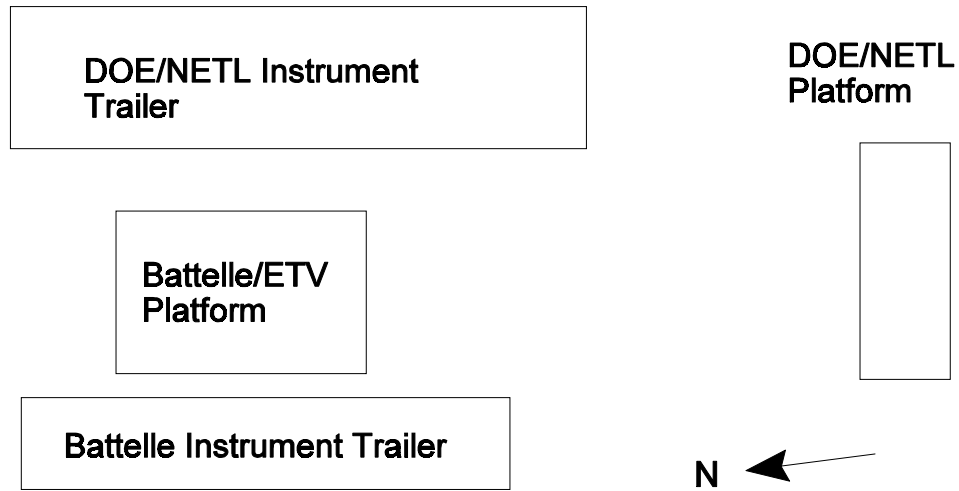
Figure 3-1. Site Layout During Phase I of Verification Testing (not drawn to scale)

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. 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. The Series 5400 monitors were located inside the Battelle trailer with sampling systems similar to those used in Phase I of the verification test. In this arrangement, the inlets of the Series 5400 monitors were within about 40 m horizontally and 7 to 8 meters vertically of the inlet of the reference sampler.

Battelle Trailer

BGI FRM Samplers

Roof of CARB Site

CARB Samplers

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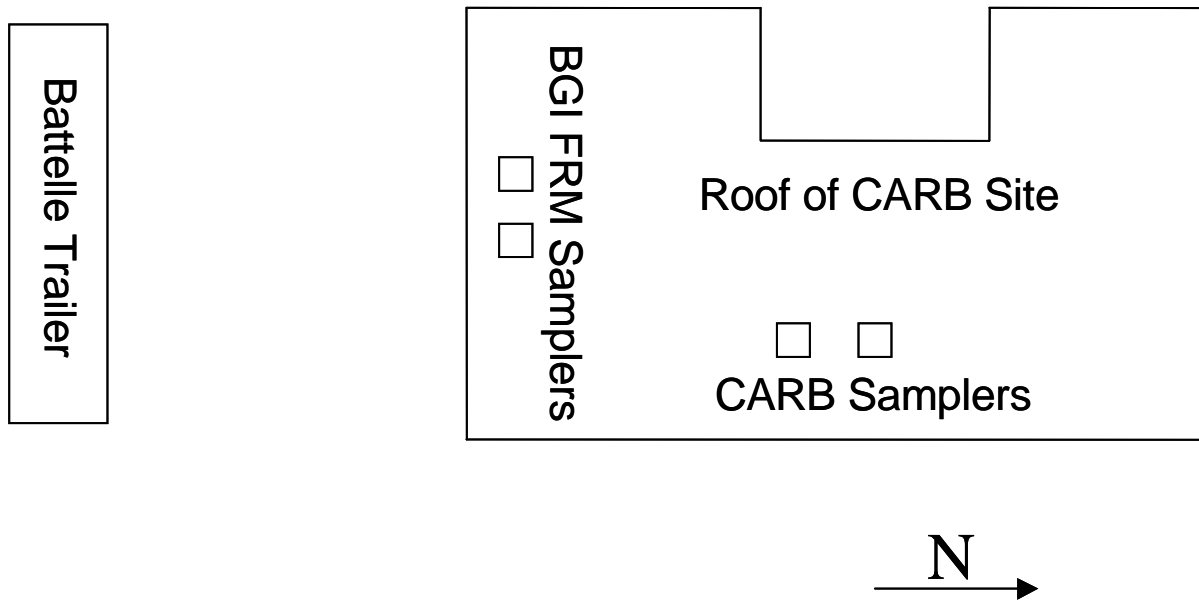
Figure 3-2. Site Layout During Phase II of Verification Testing (not drawn to scale)

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 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 Series 5400 monitors were validated by a representative of R&P and reviewed by the Verification Test Coordinator before being used in statistical calculations. Data were checked for error flags and not used if flagged for power or instrument failure.

4.2 Deviations from the Test/QA Plan

The following deviation from the test/QA plan related to verification of the Series 5400 monitors was documented and approved by the AMS Center Manager. This deviation had no deleterious effect on the verification data.

■ The distance between the reference sampler and the monitors 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.

Prior to shipment to the field for Phase I of the verification test, the Andersen RAAS sampler was calibrated in a laboratory setting at Battelle's facilities in Columbus, Ohio. This procedure included calibration of the flow meters, filter and ambient temperature sensors, and barometric pressure sensor. The calibration and the subsequent verification of these sensors are described below. Calibration of the sequential filter sampler was maintained by DRI as part of its ongoing monitoring effort.

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).

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 Instruments Inc. dry gas meter (identification number 103652, calibrated March 30, 2000). The flow rate was checked prior to testing on July 30, 2000 and again after testing 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.

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.

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

4.4.1 Phase I

To establish the precision of the carbon reference method, the Battelle Andersen RAAS sampler was collocated with the 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 were within four meters of one another. A series of three samples were collected from each of the two samplers, before and again after Phase I. This total of six collocated samples was analyzed by DRI. For OC at concentrations of 3.5 to 5.8 $\mu g/m^3$, the percent difference between collocated samples ranged from 2.4% to 61%, and showed median agreement of 13%. For EC at concentrations of 1.0 to 2.0 $\mu g/m^3$, the differences ranged from 6% to 41% and agreed within 23% as a median value. The TC results, at concentrations of 4.7 to 7.8 $\mu g/m^3$, showed percent differences that ranged from 0% to 48% and agreed within 15% as a median value. The source of the observed differences was not investigated.

4.4.2 Phase II

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. Linear regression analysis of the organic carbon results show a slope of 0.68 (0.18); intercept of 4.22 (2.53) $\mu g/m^3$; and correlation coefficient (r) of 0.63, where the values in parentheses are the standard error. The regression results for the elemental carbon show a slope of 0.58 (0.12); intercept of 1.75 (0.68); and correlation coefficient of 0.72.

4.5 Field Blanks

At least 10% of the samples collected throughout Phase I of the verification test were field blanks. These blanks showed OC mass ranging from 5.5 $\mu g/filter$ to 7.1 $\mu g/filter$, with an average value of 6.2 $\mu g/filter$. None of these blanks showed any EC mass on the filter above the detection limit of 0.8 $\mu g/filter$. TC is determined from the sum of OC and EC. As such, the TC results are identical to the OC blanks, since no EC blank mass was observed. Assuming a sample volume of 11 m^3 (i.e., 24 hours at 8 L/min), the blank concentrations for OC would account for 0.5 to 0.65 $\mu g/m^3$, or approximately 20% of the lowest 24-hour reference OC concentration during Phase I. The EC 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. The TC blank concentrations would not exceed 20% of the lowest observed 24-hour reference measurement. Phase I carbon reference measurements are not corrected for field blanks.

At least 10% of the samples collected throughout Phase II of the verification test were field blanks. These blanks showed an OC mass ranging from 7.9 µg/filter to 20.5 µg/filter, with an average value of 13.4 µg/filter. None of these blanks showed any EC mass on the filter above the detection limit of 0.9 µg/filter. TC is determined from the sum of OC and EC. As such, the TC results are identical to the OC blanks since no EC blank mass was observed. The OC mass of the reference samples ranged from 17.1 µg/filter to 572 µg/filter, with an average of 134 µg/filter. For EC, the sample mass ranged from nondetectable up to 158 µg/filter and averaged 38.6 µg/filter. For TC, the sample mass ranged from 17.8 to 719 µg/filter, with an average of 173 µg/filter. In each case the average blank mass could be significant for some samples but, on average, accounted for 10% or less of the reference sample mass. 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, volume sampled, 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, sample flow rate, and average temperature and pressure readings.

4.6.2 Series 5400 Monitors

Data from each of the Series 5400 monitors were recorded in an internal memory buffer every 10 minutes throughout each phase of the verification test. For each day, the data were stored in tabular format, which included hourly readings for OC and TC, along with a variety of instrumental parameters. EC values reported here were calculated by the vendor from the difference between TC and OC. The recorded data were downloaded directly onto the DOE/NETL data logger (Phase I) or an on-site personal computer and saved as text files (Phase II). These files were imported into a spreadsheet for analysis, and copies of the data were stored by the Verification Test Coordinator on a floppy disk, as well as on a computer hard drive.

4.7 Assessments and Audits

4.7.1 Technical Systems Audit

Phase I—Pittsburgh

The technical systems audit (TSA) ensures that the verification tests are conducted according to the test/QA plan[1] and that all activities associated with the tests are in compliance with the ETV pilot QMP.[3] The Battelle Quality Manager conducted an internal TSA on August 3, 2000, at the Pittsburgh test site. All findings noted during this TSA were documented and submitted to the Verification Test Coordinator for correction. The corrections were documented by the Verification Test Coordinator and reviewed by Battelle's Quality Manager, Verification Testing Leader, and AMS Center Manager. None of the findings adversely affected the quality or outcome of this phase of the verification test. All corrective actions were completed to the satisfaction of the Battelle Quality Manager. The records concerning the 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 Series 5400. 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 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 Series 5400 monitors.

Chapter 5
Statistical Methods

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

5.1 Inter-Unit Precision

The inter-unit precision of the continuous 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 Series 5400 monitors were paired, and the behavior of their differences was used to assess precision. The following coefficient of variation (CV) was calculated and is reported for the carbon concentration measurements of the duplicate monitors. 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 continuous monitors and the carbon reference measurements was assessed for the Series 5400 monitors. The relationship between the two was assessed from a linear regression of the data using the carbon reference results as the independent variable and the Series 5400 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 carbon reference measurement; C_i is the average of the Series 5400 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 appropriate number of Series 5400 hourly measurements from each monitor (i.e., 3, 5, 8, or 24) is used as the quantity that is most comparable to the corresponding reference carbon measurements.

Comparability is expressed in terms of bias between the Series 5400 monitor and the carbon 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 carbon reference measurements and the Series 5400 monitor. 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 Series 5400 carbon measurements is simply equivalent to the carbon 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 Series 5400 measurements is almost entirely explained by the variability in the carbon reference measurements.

Quantities reported include r^2, intercept, and slope with 95% CIs for the intercept and slope. Comparability to the reference method was determined independently for each of the duplicate Series 5400 monitors 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 relatonship between the readings of the Series 5400 monitors and the carbon reference measurements was evaluated by using meteorological data such as temperature and humidity as parameters in multivariable analyses. 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 reference time period, γ_j is the associated slope parameters, 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 duplicate Series 5400 monitors 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. 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	0.0397
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$_2$S (ppb)	NO (ppb)	NO$_2$ (ppb)	NO$_x$ (ppb)	O$_3$ (ppb)
Average	6.9	1.5	3.1	10.1	13.0	24
Max	12.8	2.9	10.4	17.4	27.4	51
Min	2.7	-0.6	0.14	5.3	5.3	5

6.1.1 Inter-Unit Precision

Both organic carbon (OC) and total carbon (TC) concentrations were measured and recorded hourly throughout Phase I by duplicate Series 5400 monitors. The difference between these hourly readings was calculated by the vendor and taken as the EC concentration. Figures 6-1a, b, and c, show the hourly OC, EC and TC data, respectively, for the duplicate monitors recorded during Phase I of verification testing. Breaks in the data indicate periods during which no data are available owing to instrument failure or power outages. These figures show that the readings of the two Series 5400 monitors were closely matched for OC, EC, and TC throughout Phase I of the verification. Figures 6-2a, b, and c are scatter plots of these same data that illustrate the correlation between the two monitors in measuring these carbon fractions. These data were analyzed by linear regression; the results of this analysis are shown by the regression lines plotted in Figures 6-2a, b, and c, and are presented in Table 6-3. The CV for these values was also determined according to Section 5.1, and the calculated CV is shown in Table 6-3.

Table 6-3. Linear Regression and Coefficient of Variation Results for Hourly OC, EC, and TC Concentrations from Duplicate Series 5400 Monitors During Phase I

Parameter	OC	EC	TC
Slope (95% CI)	1.063 (0.021)	1.037 (0.022)	1.069 (0.020)
Intercept ($\mu g/m^3$) (95% CI)	-0.141 (0.041)	0.099 (0.018)	-0.077 (0.054)
r^2	0.943	0.934	0.951
CV	12.0%	27.0%	17.1%

The hourly data from the duplicate monitors show r^2 values of 0.93 or greater for all three carbon fractions. The calculated CV for the hourly data is 12.0% for OC, 27.0% for EC, and 17.1% for TC. The regression slopes indicate that a bias of 7% or less existed between the two monitors, with Monitor 2 generally reading higher than Monitor 1 (i.e., all three slopes in Table 6-3 are statistically greater than 1.0). The regression results for the hourly data in Table 6-3 show intercepts that are all within 0.15 $\mu g/m^3$ of zero, but statistically significant at the 95% confidence level.
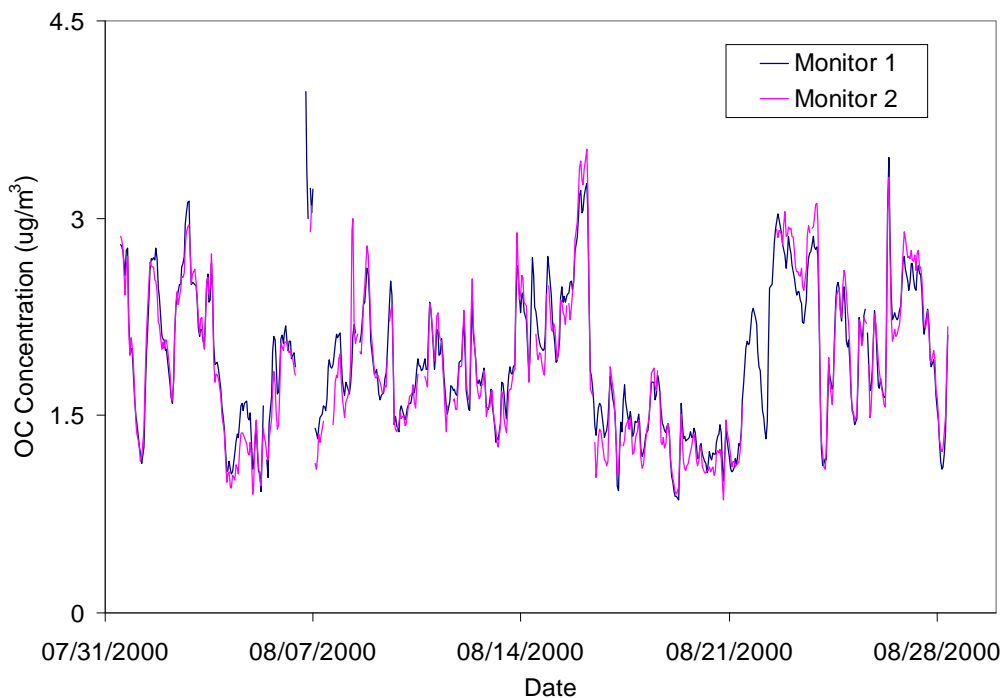
Figure 6-1a. Hourly OC Concentrations from Duplicate Series 5400 Monitors During Phase I
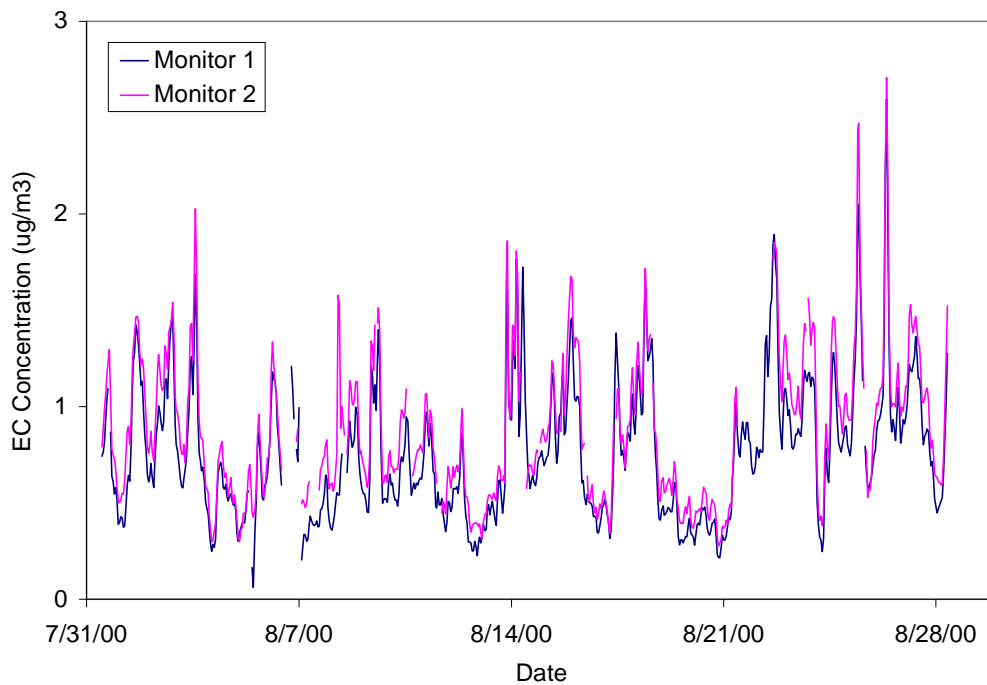
Figure 6-1b. Hourly EC Concentrations from Duplicate Series 5400 Monitors During Phase I

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Figure 6-1c. Hourly TC Concentrations from Duplicate Series 5400 Monitors During Phase I

y = 1.063x - 0.141
r^2 = 0.943

Figure 6-2a. Correlation Plot of Hourly OC Concentrations from Duplicate Series 5400 Monitors During Phase I
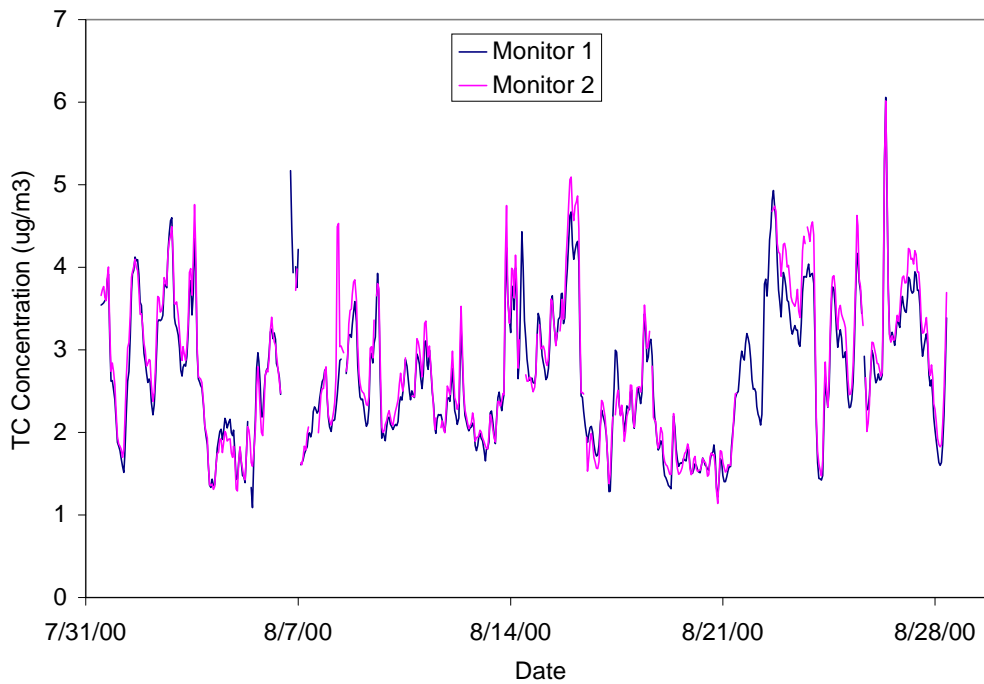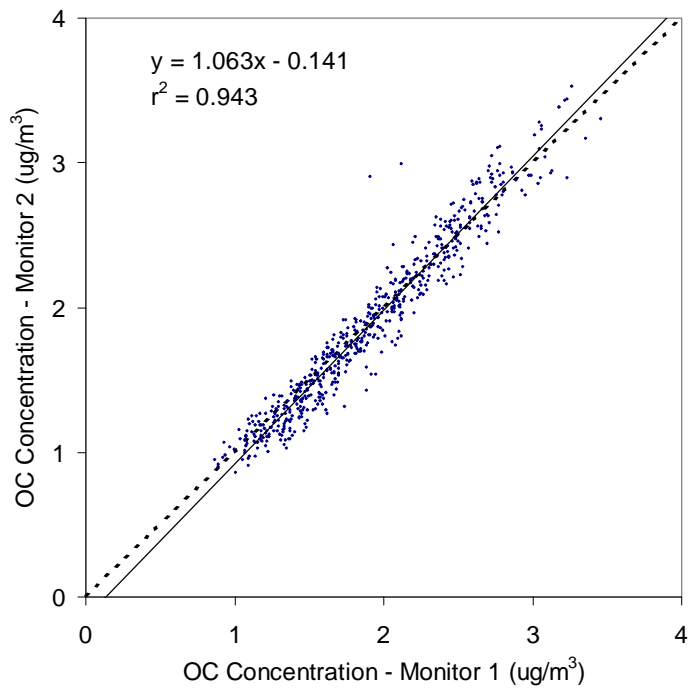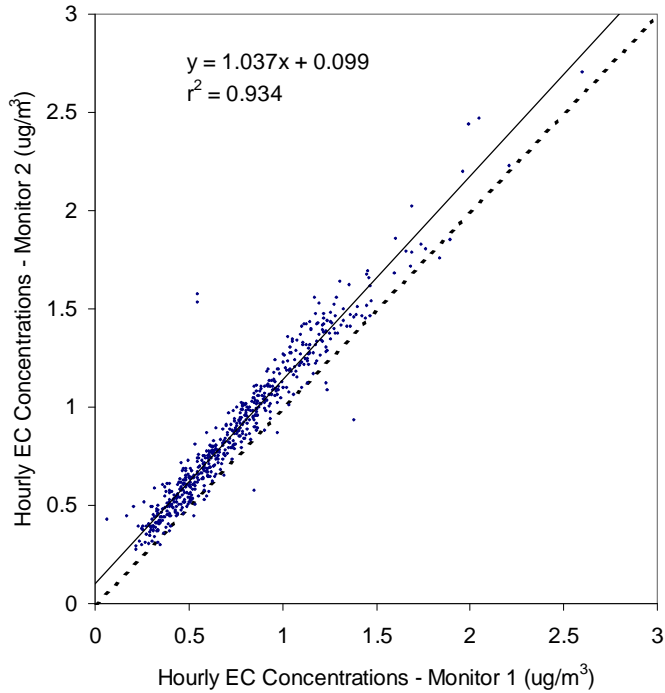
Figure 6-2b. Correlation Plot of Hourly EC Concentrations from Duplicate Series 5400 Monitor During Phase I
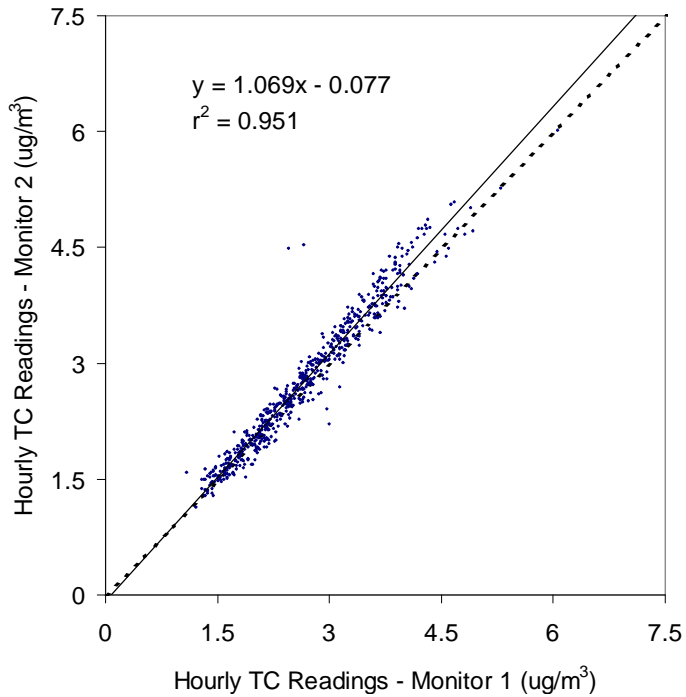

Figure 6-2c. Correlation Plot of Hourly TC Concentrations from Duplicate Series 5400 Monitors During Phase I

For comparison with the 24-hour carbon reference measurements, the hourly data were averaged from noon to noon for each day to correspond with the 24-hour sampling periods used in Phase I of the verification test. In Figures 6-3a, b and c, the noon-to-noon averages for Phase I of the verification test are presented for the two Series 5400 monitors. Correlation plots of these data are shown in Figures 6-4a, b, and c, and the results of a linear regression analysis of these data are presented in Table 6-4. The CV for these noon-to-noon average values was also calculated and is shown in Table 6-4.

Table 6-4. Linear Regression and Coefficient of Variation Results for 24-Hour Average OC, EC, and TC Concentrations from Duplicate Series 5400 Monitors During Phase I

Parameter	OC	EC	TC
Slope (95% CI)	1.094 (0.081)	1.038 (0.113)	1.098 (0.088)
Intercept (μg/m^3) (95% CI)	-0.20 (0.16)	0.10 (0.09)	-0.15 (0.24)
r^2	0.970	0.937	0.965
CV	3.6%	13.0%	4.3%

For the 24-hour average carbon concentration results, the regression results indicate r^2 values of 0.93 or greater for all three carbon fractions. The calculated CV for the 24-hour averages is 3.6% for OC, 13.0% for EC, and 4.3% for TC. The slopes of the correlation plots are all slightly greater than 1.0, but only the OC and TC slopes are significantly different from 1.0. Small but statistically significant intercepts were observed for both OC and EC (95% confidence). No statistically significant intercept was observed for TC, at 95% confidence.

6.1.2 Comparability/Predictability

In Figures 6-5a, b, and c, the noon-to-noon averages of the Series 5400 measurements are shown for the OC, EC, and TC fractions, respectively, along with the respective carbon reference measurements for Phase I of the verification test. These same data are shown in Figures 6-6a, b, and c as scatter plots to illustrate the correlation between the Series 5400 monitors and the reference method. The data for each of the different carbon fractions were analyzed by linear regression according to Section 5.2 to establish the comparability of each of the Series 5400 monitors and the carbon reference measurements. The calculated slope, intercept, and r^2 value of the regression analyses are presented in Table 6-5 for each monitor.
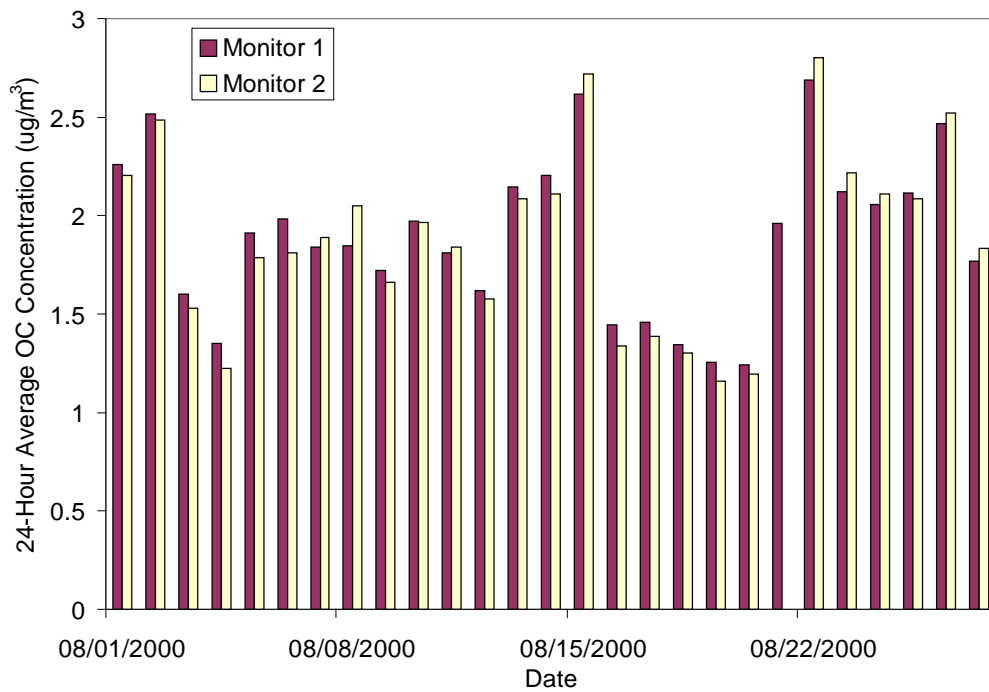
Figure 6-3a. 24-Hour Average OC Concentrations from Duplicate Series 5400 Monitors During Phase I
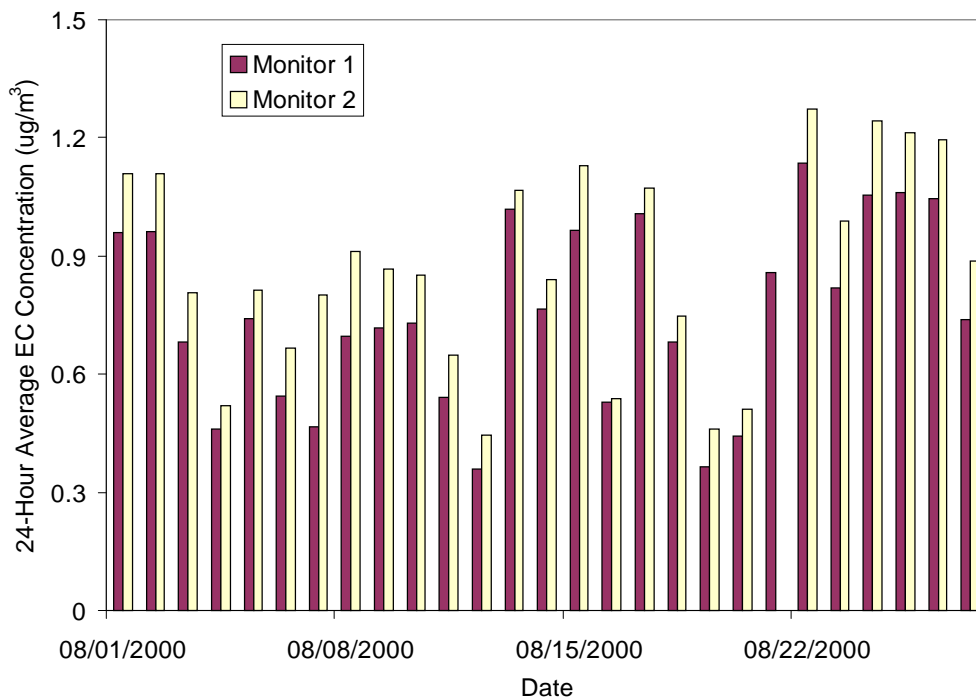
Figure 6-3b. 24-Hour Average EC Concentrations from Duplicate Series 5400 Monitors During Phase I
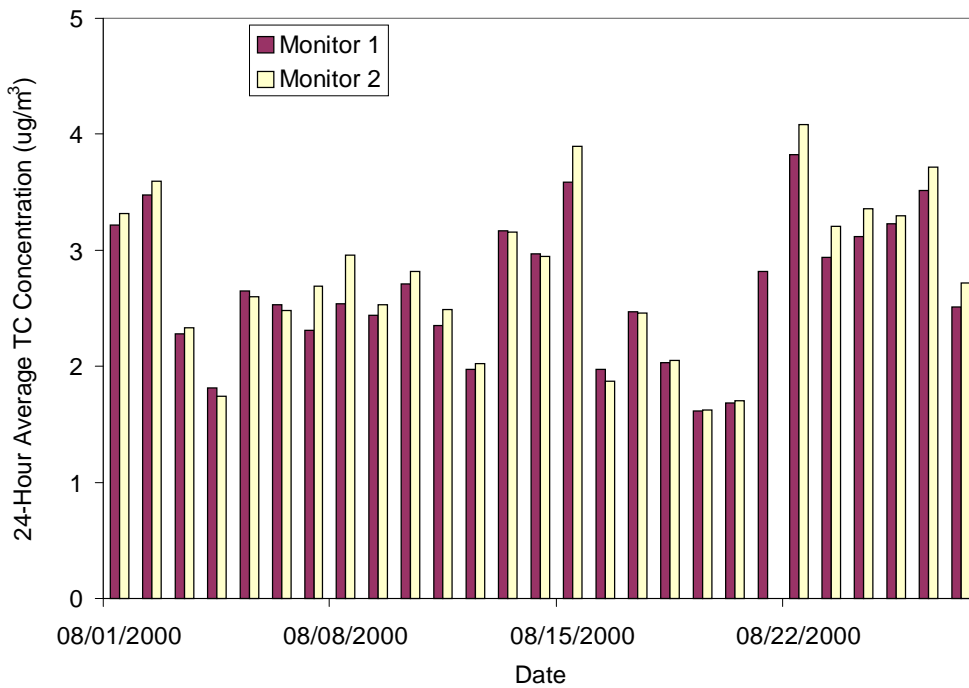
Figure 6-3c. 24-Hour Average TC Concentrations from Duplicate Series 5400 Monitors During Phase I
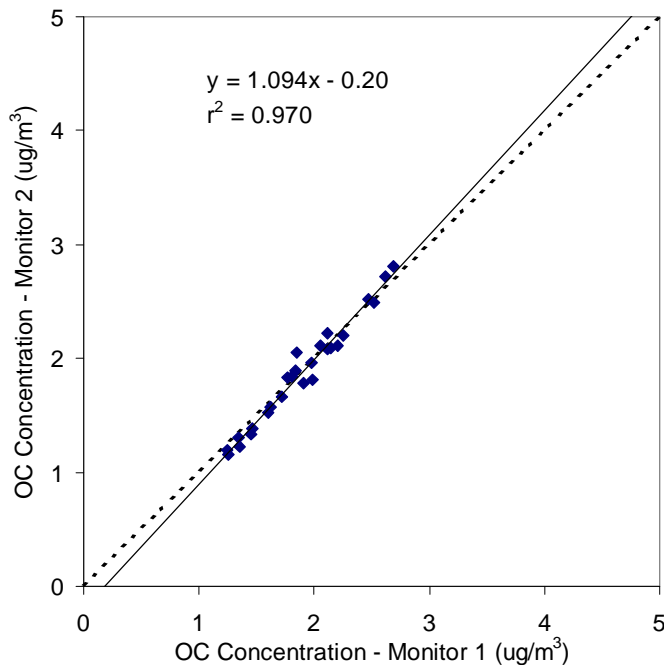
Figure 6-4a. Correlation Plot of 24-Hour Average OC Concentrations from Duplicate Series 5400 Monitors During Phase I
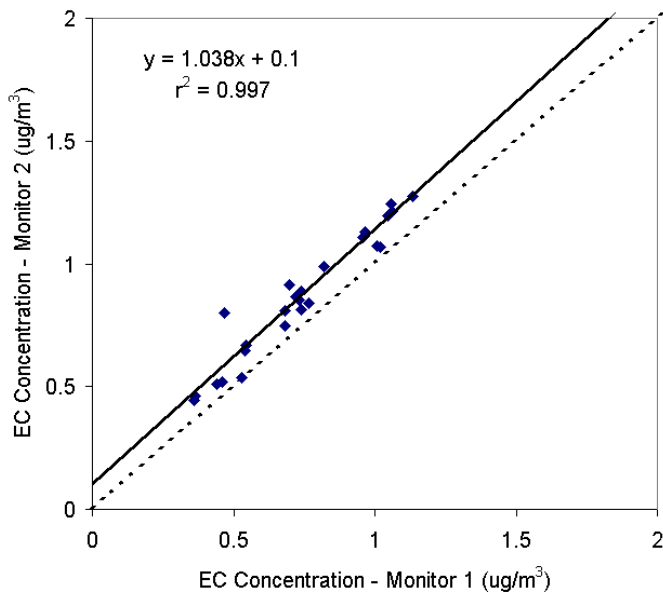
Figure 6-4b. Correlation Plot of 24-Hour Average EC Concentrations from Duplicate Series 5400 Monitors During Phase I
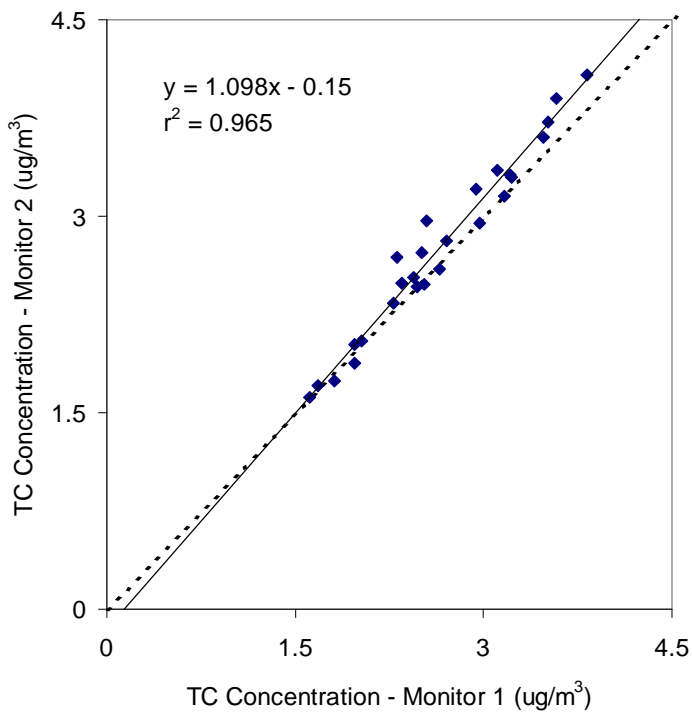
Figure 6-4c. Correlation Plot of 24-Hour TC Concentrations from Duplicate Series 5400 Monitors During Phase I
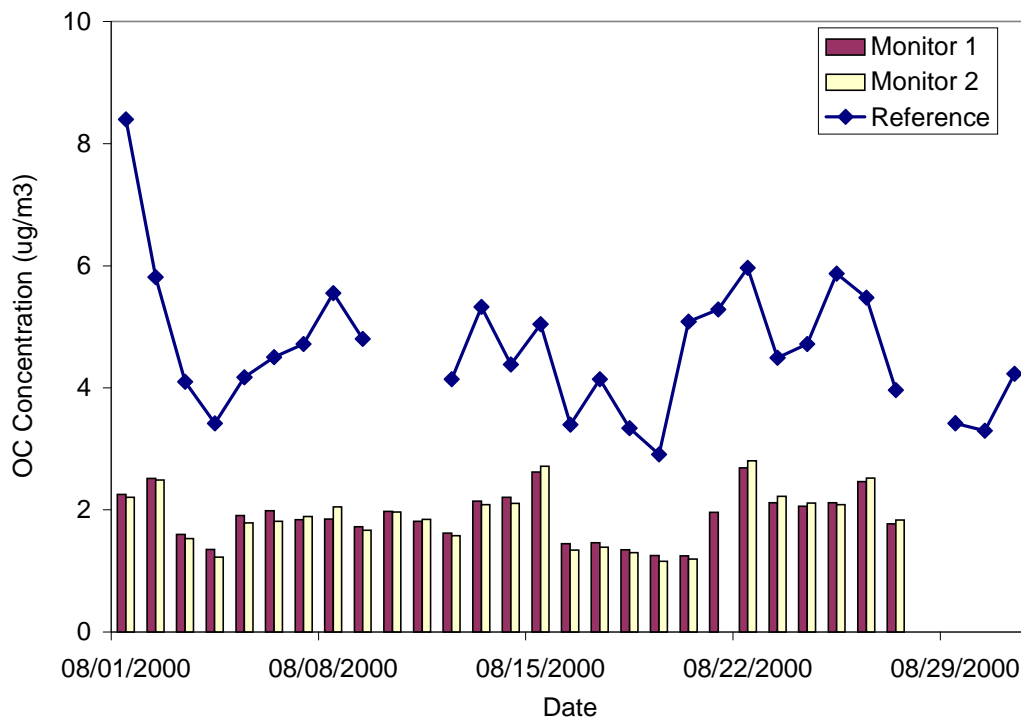
Figure 6-5a. Daily OC Reference Concentrations and 24-Hour Averages from Duplicate Series 5400 Monitors During Phase I
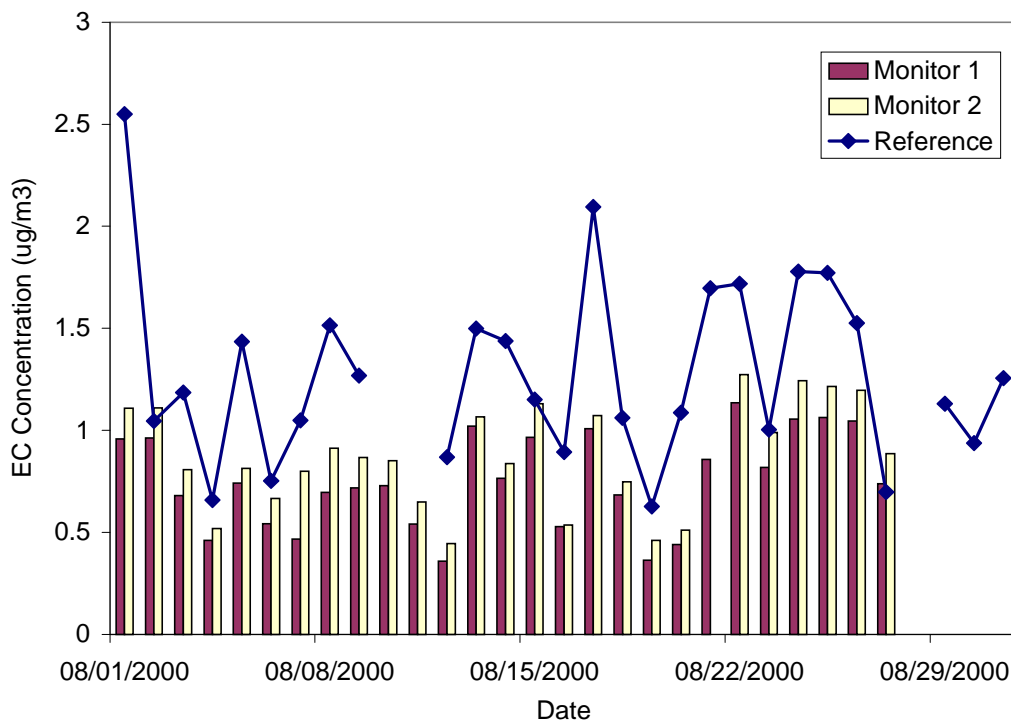
Figure 6-5b. Daily EC Reference Concentrations and 24-Hour Averages from Duplicate Series 5400 Monitors During Phase I
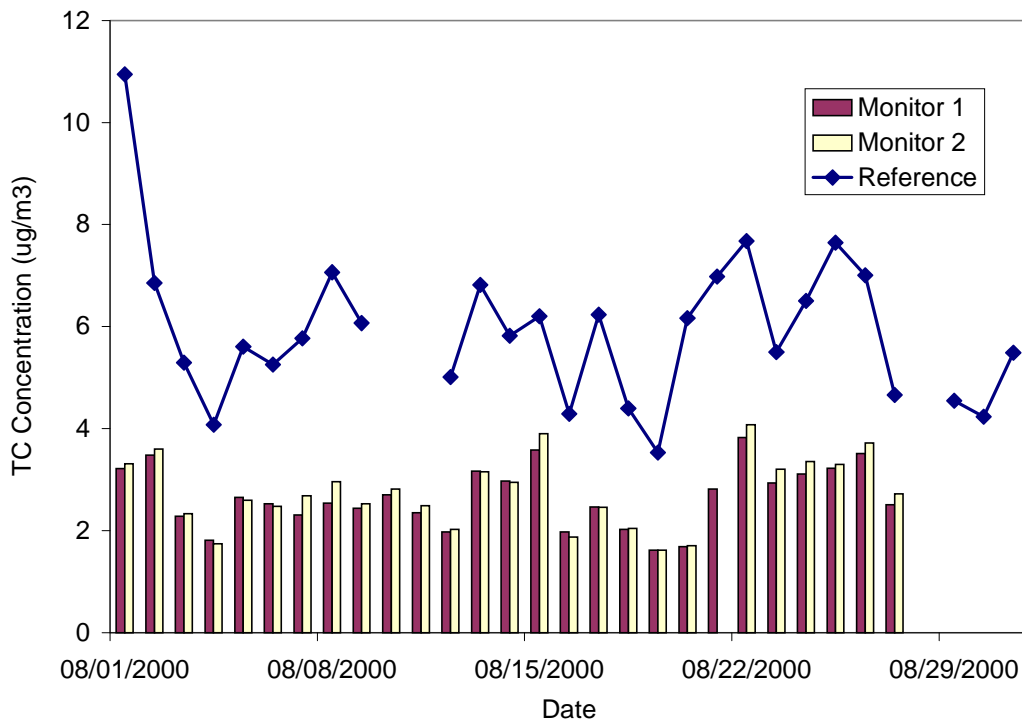
Figure 6-5c. Daily TC Reference Concentrations and 24-Hour Averages from Duplicate Series 5400 Monitors During Phase I
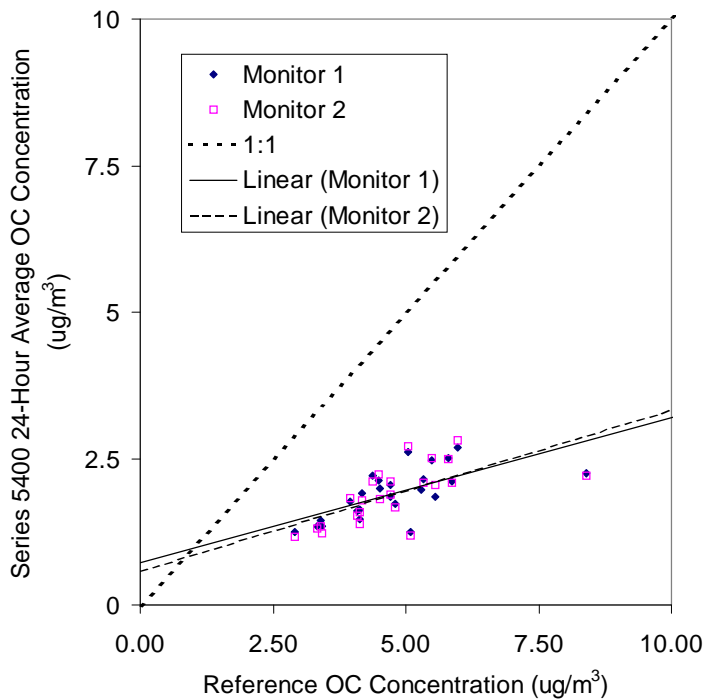
Figure 6-6a. Correlation Plot of 24-Hour Average OC Concentrations from Duplicate Series 5400 Monitors and OC Reference Results During Phase I
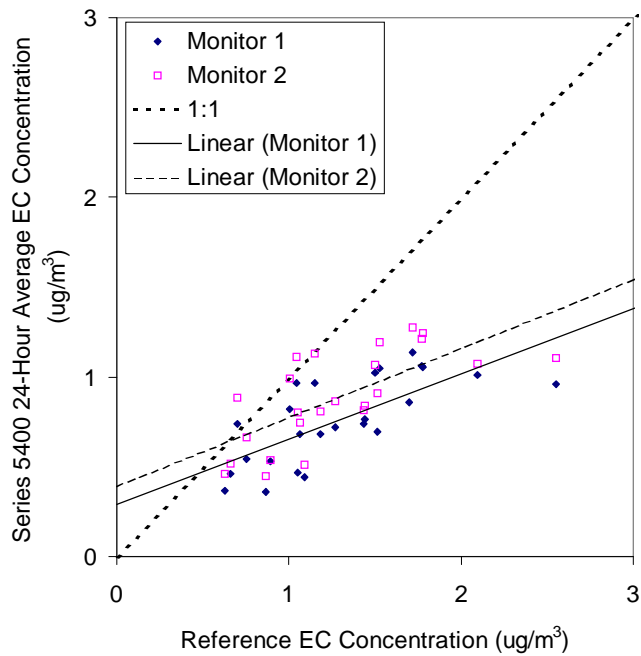
Figure 6-6b. Correlation Plot of 24-Hour Average EC Concentrations from Duplicate Series 5400 Monitors and EC Reference Results During Phase I
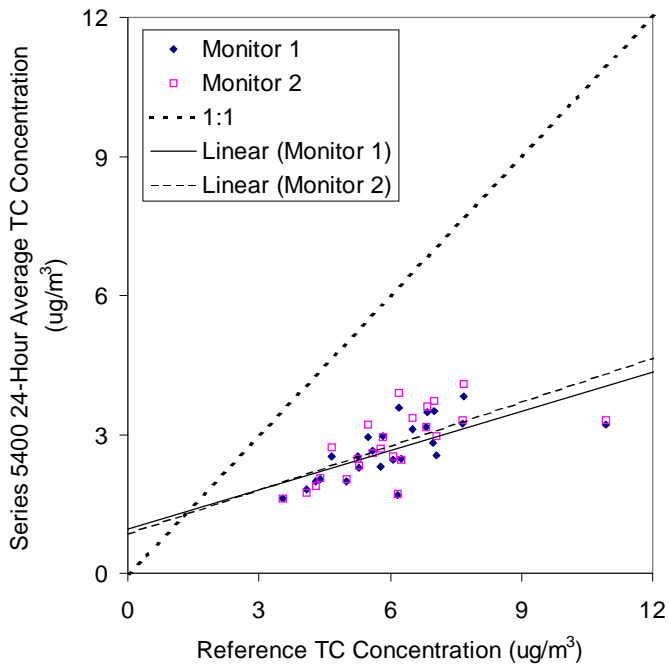
Figure 6-6c. Correlation Plot of 24-Hour Average TC Concentrations from Duplicate Series 5400 Monitors and TC Reference Results During Phase I

Table 6-5. Comparability of the Series 5400 Monitors with the Carbon Reference Results During Phase I

Regression Parameter	OC		EC		TC	
	Monitor 1	Monitor 2	Monitor 1	Monitor 2	Monitor 1	Monitor 2
Slope (95% CI)	0.247 (0.122)	0.275 (0.141)	0.363 (0.152)	0.384 (0.175)	0.282 (0.132)	0.315 (0.153)
Intercept ($\mu g/m^3$) (95% CI)	0.73 (0.60)	0.58 (0.69)	0.29 (0.21)	0.39 (0.24)	0.96 (0.81)	0.87 (0.95)
r^2	0.431	0.428	0.514	0.486	0.461	0.452

For all three carbon fractions, the correlation between the two Series 5400 monitors and the TOR carbon reference analyses shows r^2 values between 0.43 and 0.52. The slopes of the regression lines for both monitors are below 0.4 for each of three carbon fractions, indicating substantial negative biases relative to the reference method. For Monitor 1, all intercepts were statistically significant at 95% confidence; for Monitor 2, only the EC results showed a statistically significant intercept (95% confidence).

6.1.3 Meteorological Effects

A multivariable model analysis, as described in Section 5.3, was used to determine if the readings of the Series 5400 monitor could be accounted for by the meteorological conditions. 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 horizontal wind speed (WS) and the ambient air temperature at 10 meters (T10) an influence on both monitors relative to the reference results in determining both OC and TC. The model results for EC show a statistical dependence on the wind direction (WD) and vertical wind speed (VWS) for both monitors. Additionally, the model indicated that the air temperature at 2 meters (T2) and the horizontal wind speed (WS) influenced the results of Monitor 2. Table 6-6 summarizes the results of this analysis. This table shows the model estimates of the coefficients for each indi-cated variable that relate the readings of each duplicate monitor to the appropriate reference measurements (Ref.). Except for the intercept (Int.), which is a constant, the relationships are linear.

As shown in Table 6-5, about half of the variance in 24-hour Series 5400 results could be explained by linear regression with the reference data (i.e., r^2 values were 0.43 to 0.52). The multivariable model ascribes the unexplained variance to meteorological parameters, but does not imply cause and effect or rely upon physical principles in doing so. The magnitude of the inferred effects can be examined by comparing predicted Series 5400 readings from the multivariable analysis to those from the simple linear regression. For example, the results in

Table 6-6 indicate the following relationship for the determination of organic carbon by Monitor 1:

Monitor 1 = 0.148*Ref - 1.79 - 0.249*WS + 0.0570*T10

Substituting the average values for these parameters from Phase I (Table 6-1) into this equation, an average value of 1.92 µg/m^3 is predicted:

Monitor 1 = 0.148*4.6 - 1.79 - 0.249*3.35 + 0.0570*68.0

$$= 1.93 \, \mu g/m^3$$

Using the linear regression results presented in Table 6-5, an average value of 1.84 µg/m^3 is predicted:

Monitor 1 = 0.247*4.5 + 0.73

$$= 1.84 \, \mu g/m^3$$

Thus, a difference of approximately 5% results from the multivariable analysis relative to the linear regression analysis. In general, the multivariable equations indicate only small effects on Series 5400 readings relative to the reference results.

Table 6-6. Summary of Meteorological Effects on Duplicate Series 5400 Monitors During Phase I of Verification Testing

		Ref.	Int. (µg/m^3)	WS (mph)	T10 (°F)	WD (degrees)	VWS (mph)	T2 (°F)
OC	Monitor 1	0.148	-1.79	-0.249	0.0570	--[a]	--	--
	Monitor 2	0.150	-2.55	-0.300	0.0705	--	--	--
EC	Monitor 1	0.291	0.095	--	--	6.18E-5	-1.01	--
	Monitor 2	0.274	-0.5450	-0.0837	--	6.60E-5	-1.25	0.0174
TC	Monitor 1	0.174	-2.27	-0.398	0.078	--	--	--
	Monitor 2	0.176	-3.63	-0.477	0.104	--	--	--

[a] No statistical significance at 90% confidence.

6.1.4 Influence of Precursor Gases

As with the meteorological data, a multivariable model was used to establish any statistical relationships between the measured precursor gases and the readings of the Series 5400 monitors 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 ozone an influence on the results in most cases, and indicated that both hydrogen sulfide and nitrogen

dioxide had an effect on one of the monitors relative to the EC results. Table 6-7 summarizes the results of this analysis.

Table 6-7. Summary of Precursor Gas Influences on Duplicate Series 5400 Monitors During Phase I of Verification Testing

		Ref.	Int. ($\mu g/m^3$)	O_3 (ppb)	H_2S (ppb)	NO_2 (ppb)
OC	Monitor 1	0.142	0.915	0.0242	–[a]	--
	Monitor 2	0.209	0.413	0.0207	--	--
EC	Monitor 1	0.248	-0.203	0.009	0.131	0.0253
TC	Monitor 1	0.172	1.38	0.028	--	--

[a] No statistical significance at 90% confidence.

An analogous evaluation to that in Section 6.1.3 can be done to assess the magnitude of the implied precursor gas effects. For example, from Table 6-7, the multivariable model indicates the following relationship for OC from Monitor 1:

Monitor 1 = 0.142*Ref + 0.915 + 0.0242*O_3

Substituting the average values for these parameters from Phase I (Section 6.1) into this equation, the multivariable model predicts an average OC value of

Monitor 1 = 0.142*4.5 + 0.915 + 0.0242*24

$= 2.13 \mu g/m^3$

and the linear regression results (Table 6-5) predict a value of 1.84 $\mu g/m^3$, as described in Section 6.1.3.

Thus, the multivariable model results in a difference of 157% relative to the linear regression.

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. Sulfate accounted for only about 2% of the daily $PM_{2.5}$ mass. Both nitrate and sulfate were deter-mined by ion chromatography, and carbon was determined by the IMPROVE TOR method.

Table 6-8 summarizes the meteorological conditions during Phase II, and Table 6-9 summarizes the observed concentrations of the measured precursor gases during this period.

Table 6-8. Summary of Daily Values for the Measured Meteorological Parameters During Phase II of Verification Testing

	Wind Speed (mps)	Wind Direction (Degrees)	Change in Wind Direction (Degrees)	Air Temp. (C)	RH (%)	Solar Radiation (W/m^2)	Press. (mmHg)
Average	1.43	186	34.2	8.3	75.4	88.2	756.2
Max	4.18	260	48.8	12.8	92.0	123.5	761.7
Min	0.91	116	21.3	4.6	51.6	17.1	747.3

Table 6-9. 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

The hourly OC, EC, and TC mass concentration readings from the two Series 5400 monitors for Phase II of the verification test are shown in Figures 6-7a, b, and c, respectively. (Note: The results from Monitor 1 have been multiplied by a correction factor of 0.505 to account for an apparent offset in the collection temperature setting of the monitor. This correction factor was empirically determined by a representative of R&P. The need for this factor was identified by virtue of the operation of duplicate Series 5400 monitors in this test). These figures show close agreement in the temporal patterns of the OC, EC, and TC indicated by the two Series 5400 monitors throughout Phase II. The strong diurnal pattern in particulate matter at this site is evident in these figures, with peak values occurring around midnight and in the early morning hours. In Figures 6-8a, b, and c, these same data are plotted against one another to illustrate the correlation between the two monitors. These data were analyzed by linear regression, and the results of this analysis are presented in Table 6-10. The coefficient of variation (CV) for these values was also determined according to Section 5.1, and the calculated CV is shown in Table 6-10.

Figure 6-7a. Hourly OC Concentrations from Duplicate Series 5400 Monitors During Phase II

Figure 6-7b. Hourly EC Concentrations from Duplicate Series 5400 Monitors During Phase II

Figure 6-7c. Hourly TC Concentrations from Duplicate Series 5400 Monitors During Phase II

Figure 6-8a. Correlation Plot of Hourly OC Concentrations from Series 5400 Monitors During Phase II

Figure 6-8b. Correlation Plot of Hourly EC Concentrations from Series 5400 Monitors During Phase II

Figure 6-8c. Correlation Plot of Hourly TC Concentrations from Series 5400 Monitors During Phase II

Table 6-10. Linear Regression and Coefficient of Variation Results for Hourly OC, EC, and TC Concentrations from Duplicate Series 5400 Monitors During Phase II

Parameter	OC	EC	TC
Slope (95% CI)	0.971 (0.019)	1.029 (0.024)	1.074 (0.035)
Intercept ($\mu g/m^3$) (95% CI)	1.00 (0.17)	1.88 (0.35)	1.09 (0.20)
r^2	0.944	0.922	0.858
CV	32.9%	64.7%	42.1%

The regression slopes for these data are all near, but statistically different from unity, after the correction factor is applied. Without the correction factor, a bias of ~50% between the two monitors was observed. The r^2 values are 0.858 or greater. The regression results show statistically significant intercepts of between 1 and 2 $\mu g/m^3$ for the three carbon fractions. The CV values for the corrected values range from about 33 to 65%.

The hourly data were also averaged from midnight to midnight to provide 24-hour averages for the OC, EC, and TC concentrations. These 24-hour averages are shown in Figures 6-9a, b, and c, respectively. Figures 6-10a, b, and c show these same data as scatter plots to show the correlation between the duplicate monitors. The results of a linear regression analysis of these data are presented in Table 6-11. The coefficient of variation for these noon-to-noon average values was also calculated and is shown in Table 6-11.

Table 6-11. Linear Regression and Coefficient of Variation Results for 24-Hour OC, EC, and TC Concentrations from Duplicate Series 5400 Monitors During Phase II

Parameter	OC	EC	TC
Slope (95% CI)	1.027 (0.072)	1.164 (0.083)	1.090 (0.070)
Intercept ($\mu g/m^3$) (95% CI)	0.53 (0.53)	0.66 (0.38)	1.09 (0.83)
r^2	0.972	0.971	0.976
CV	12.1%	27.1%	17.1%

The 24-hour results for all three carbon fractions show r^2 values of 0.97 or greater. The slope of the regression line for OC is not statistically different from unity at 95% confidence, whereas the regression slopes for EC and TC do show a statistical difference from unity. The intercepts of the regression lines are approximately 1 $\mu g/m^3$ or less for the three fractions.
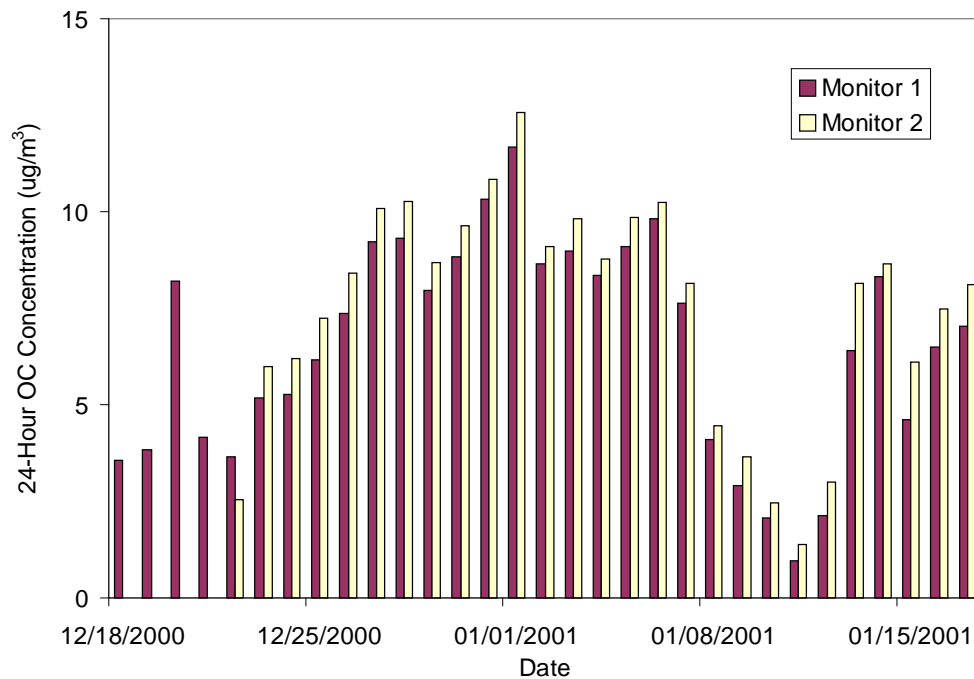
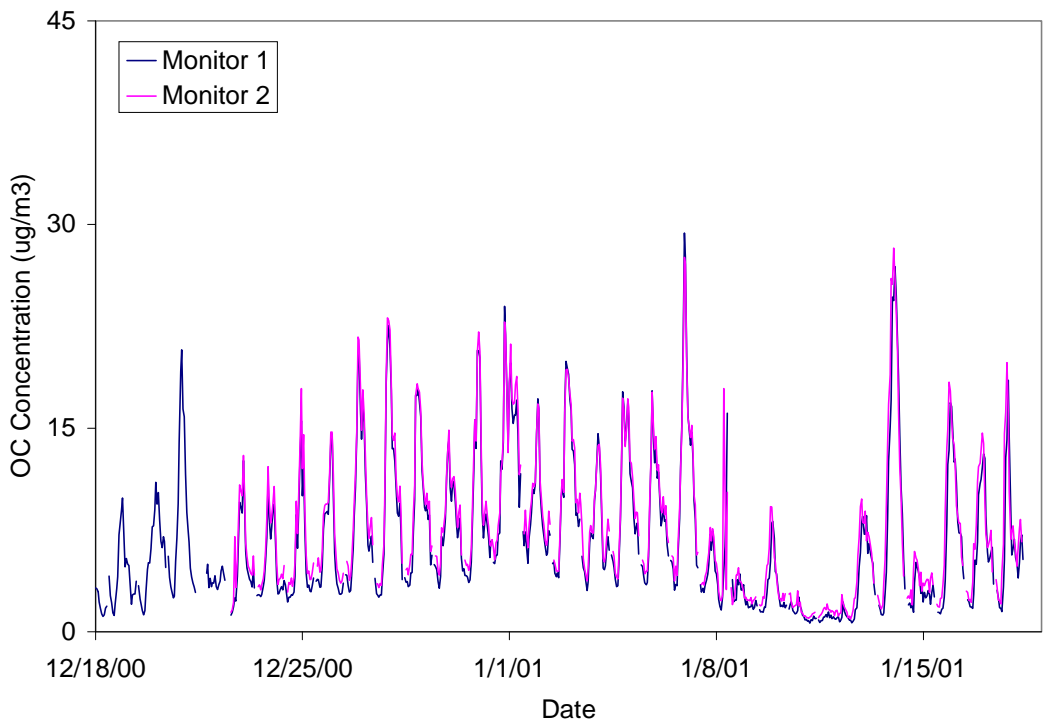**Figure 6-9a. 24-Hour OC Average Concentrations from Duplicate Series 5400 Monitors During Phase II**
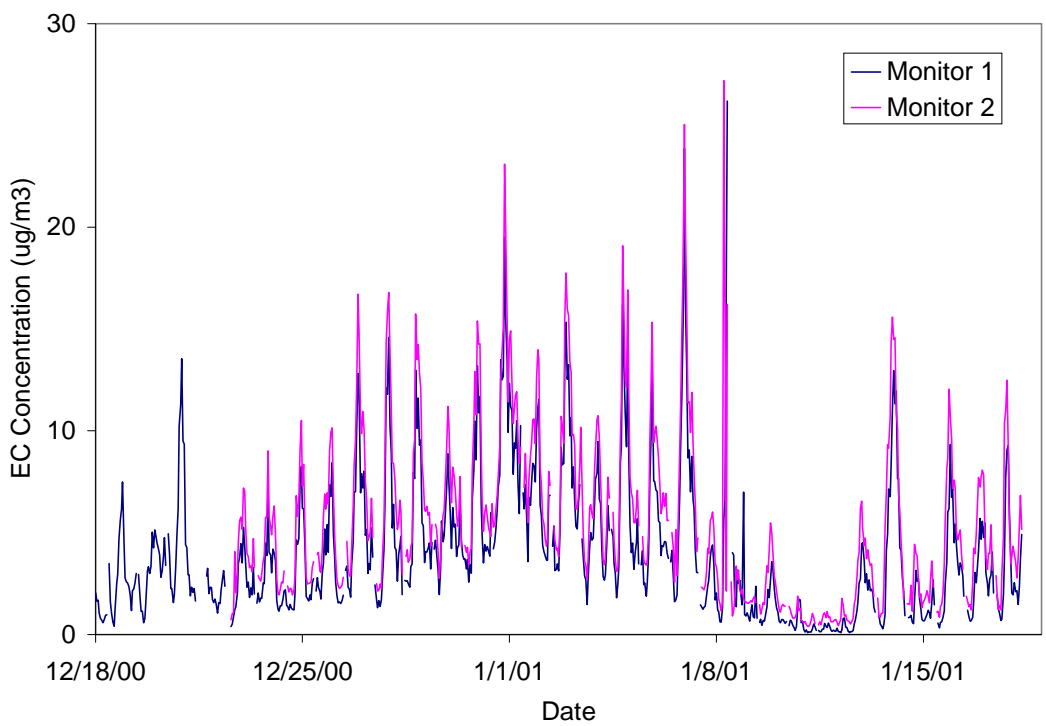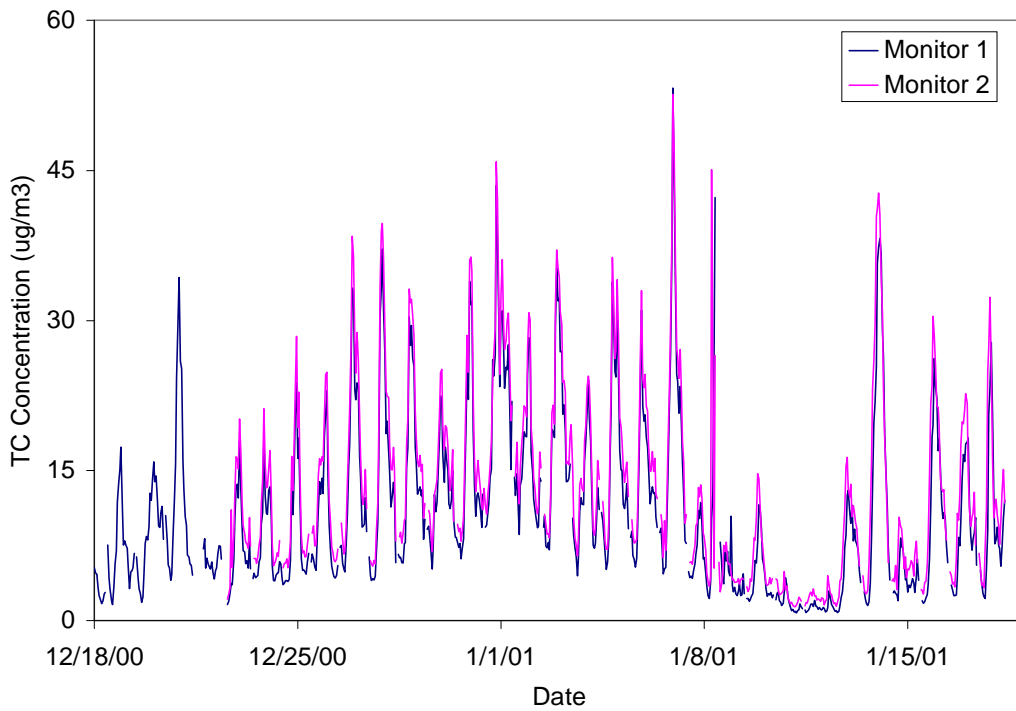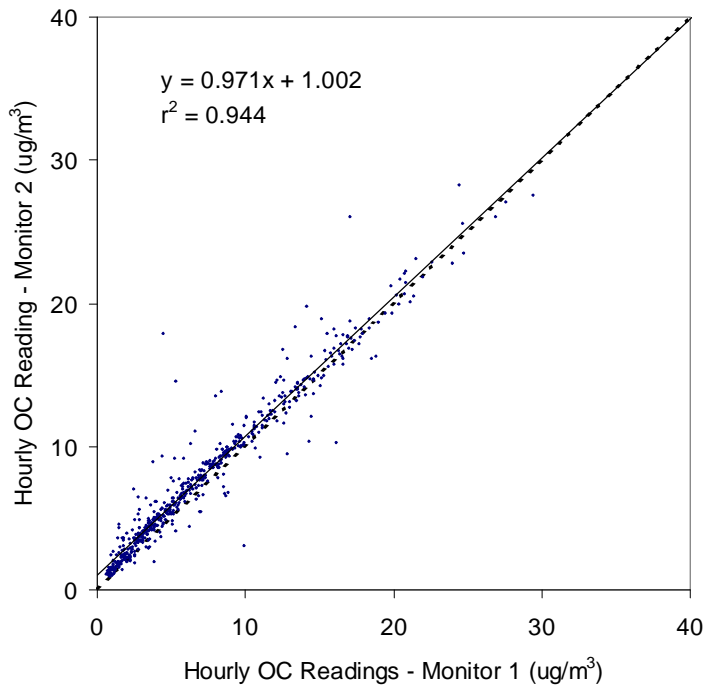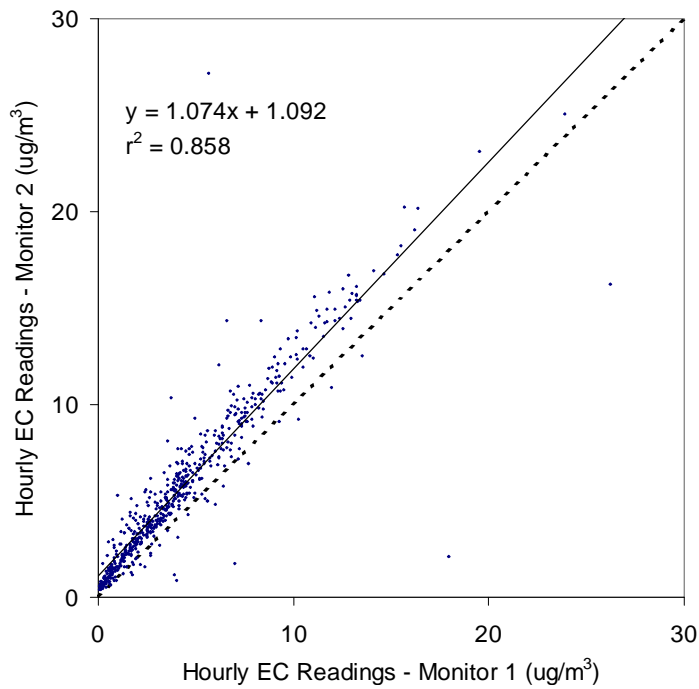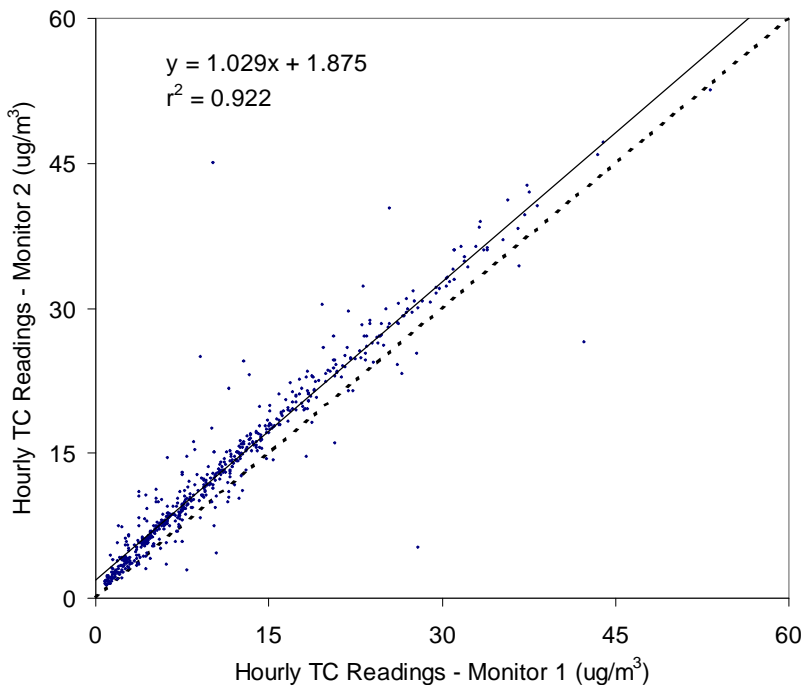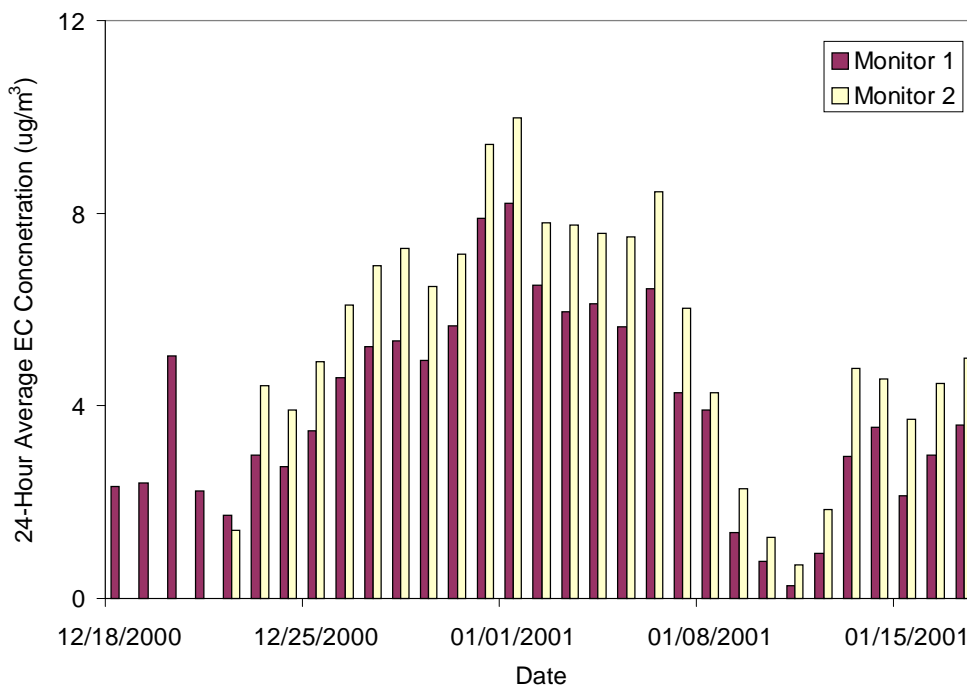

Figure 6-9b. 24-Hour EC Average Concentrations from Duplicate Series 5400 Monitors During Phase II

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Figure 6-9c. 24-Hour TC Average Concentrations from Duplicate Series 5400 Monitors During Phase II

Figure 6-10a. Correlation Plot of 24-Hour Average OC Concentrations from Duplicate Series 5400 Monitors During Phase II

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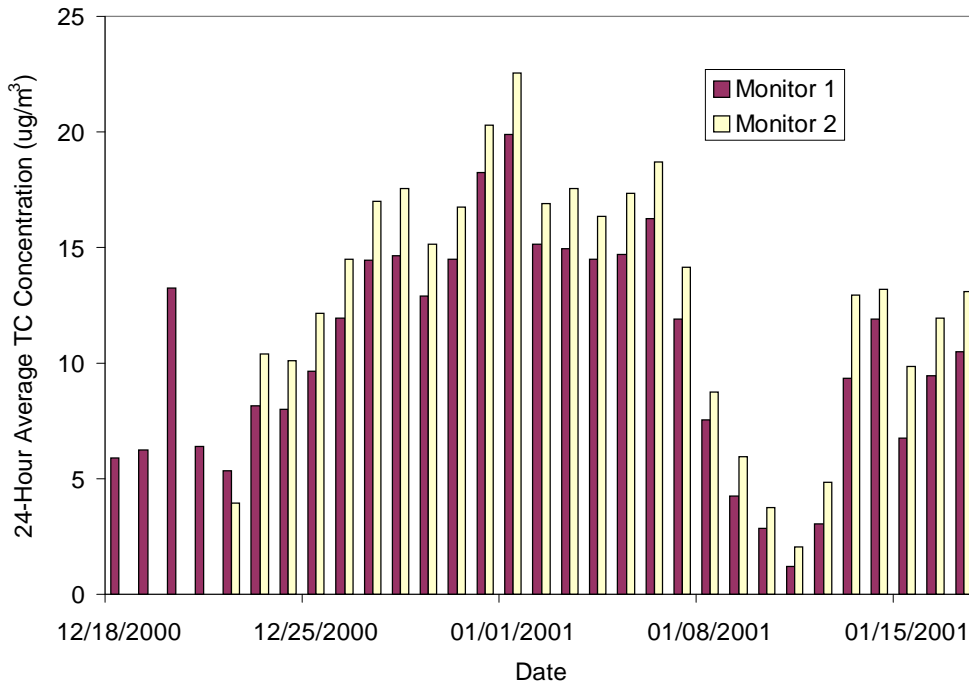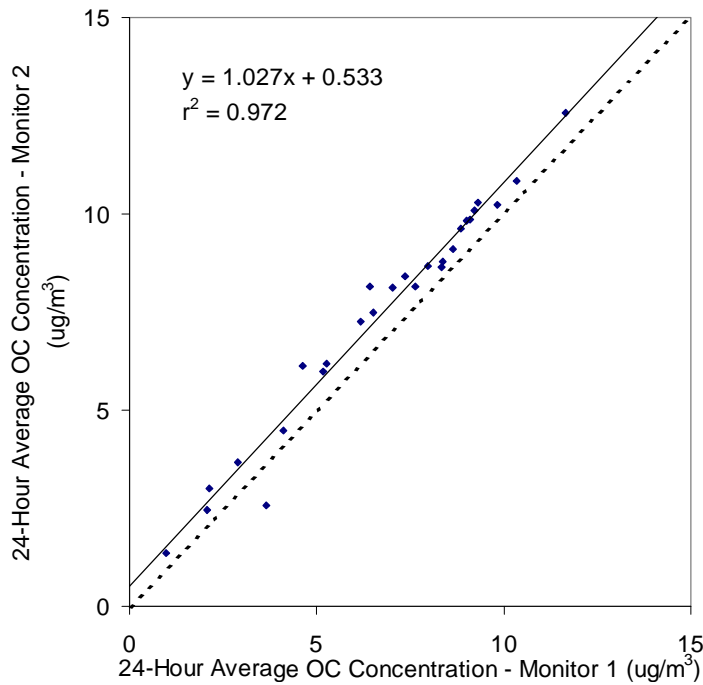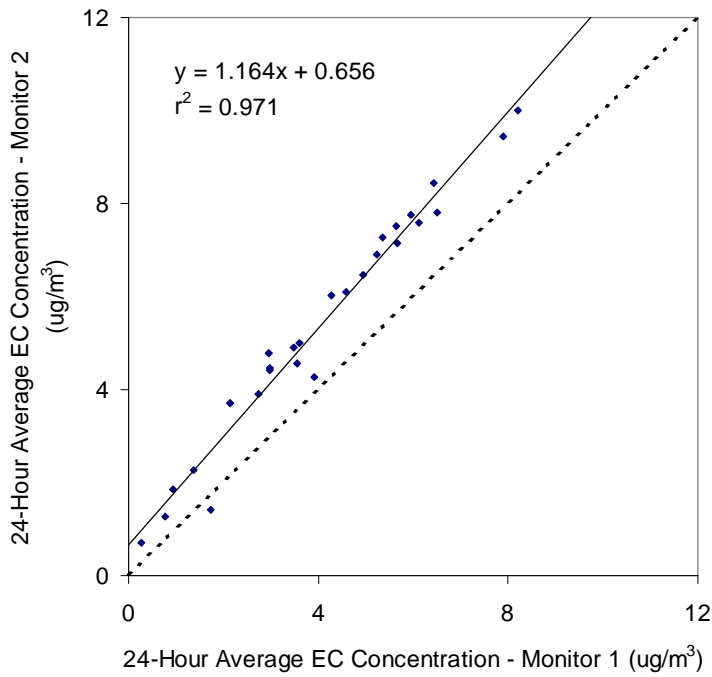**Figure 6-10b. Correlation Plot of 24-Hour Average EC Concentrations from Duplicate Series 5400 Monitors During Phase II**
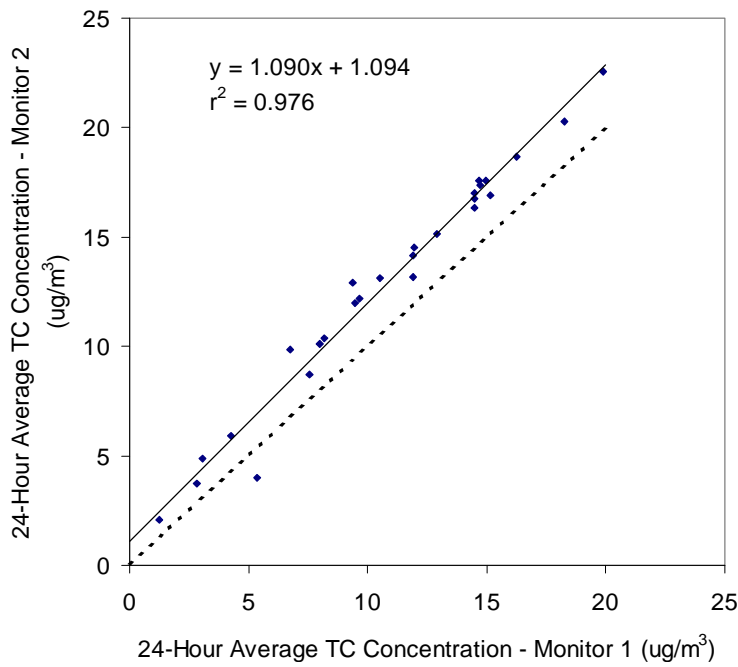
Figure 6-10c. Correlation Plot of 24-Hour Average TC Concentrations from Duplicate Series 5400 Monitors During Phase II

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6.2.2 Comparability/Predictability

To compare with the short-term reference measurements, the hourly results from the duplicate Series 5400 monitors were appropriately averaged to correspond to the five daily sampling periods for the reference sequential filter sampler. Tables 6-12a, b, and c summarize the concentrations of OC, EC, and TC during Phase II, respectively. Figures 6-11a, b, and c show the reference measurements and the corresponding averages from the duplicate Series 5400 monitors for Phase II of the verification test. These same data are also shown in Figures 6-12a, b, and c as scatter plots to illustrate the correlation between the results of the duplicate Series 5400 monitors and the carbon reference measurements.

Table 6-12a Summary of OC Concentrations During Phase II

OC Concentration µg/m³	Sampling Period					
	All	**0000-0500**	**0500-1000**	**1000-1300**	**1300-1600**	**1600-2400**
Average	19.84	29.96	17.19	12.79	10.35	28.64
Maximum	70.55	70.55	45.16	32.34	27.23	61.00
Minimum	0.64	0.85	0.64	1.87	1.08	2.10

Table 6-12b Summary of EC Concentrations During Phase II

EC Concentration µg/m³	Sampling Period					
	All	**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

Table 6-12c Summary of TC Concentrations During Phase II

TC Concentration µg/m³	Sampling Period					
	All	0000-0500	0500-1000	1000-1300	1300-1600	1600-2400
Average	25.93	39.42	22.98	16.10	12.74	37.97
Maximum	93.41	93.41	61.40	41.05	33.88	77.00
Minimum	0.75	0.84	0.75	2.02	1.28	2.80

Figure 6-11a. OC Concentrations from Reference Samples and Duplicate Series 5400 Monitors During Phase II

Figure 6-11b. EC Concentrations from Reference Samples and Duplicate Series 5400 Monitors During Phase II
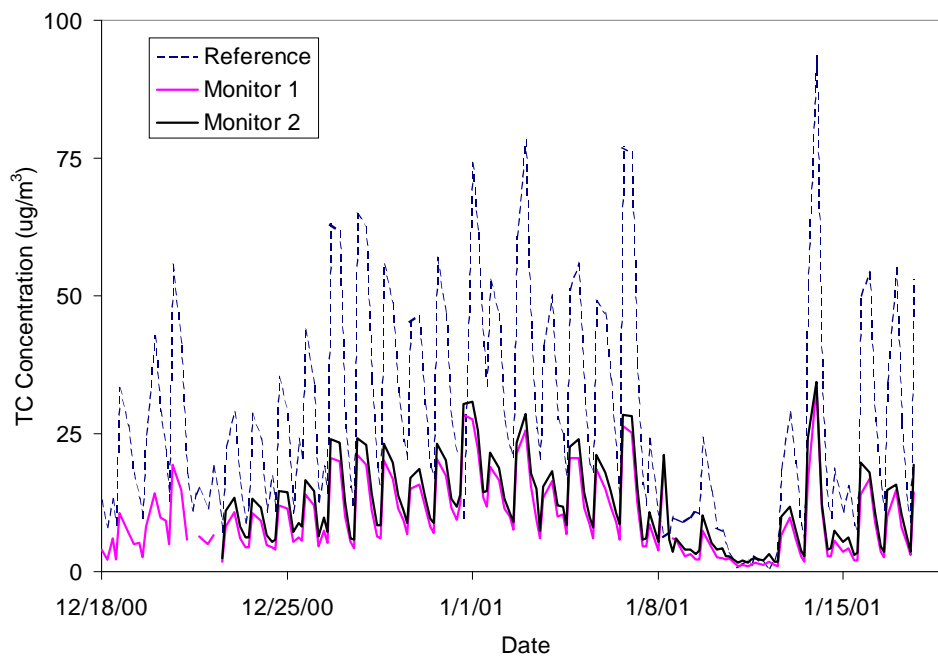
Figure 6-11c. TC Concentrations from Reference Samples and Duplicate Series 5400 Monitors During Phase II

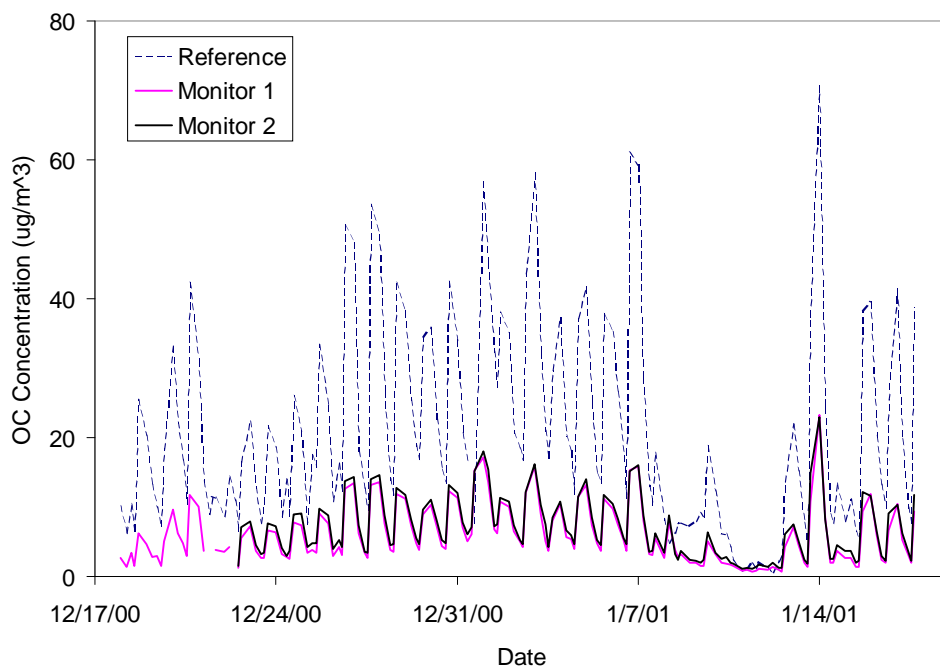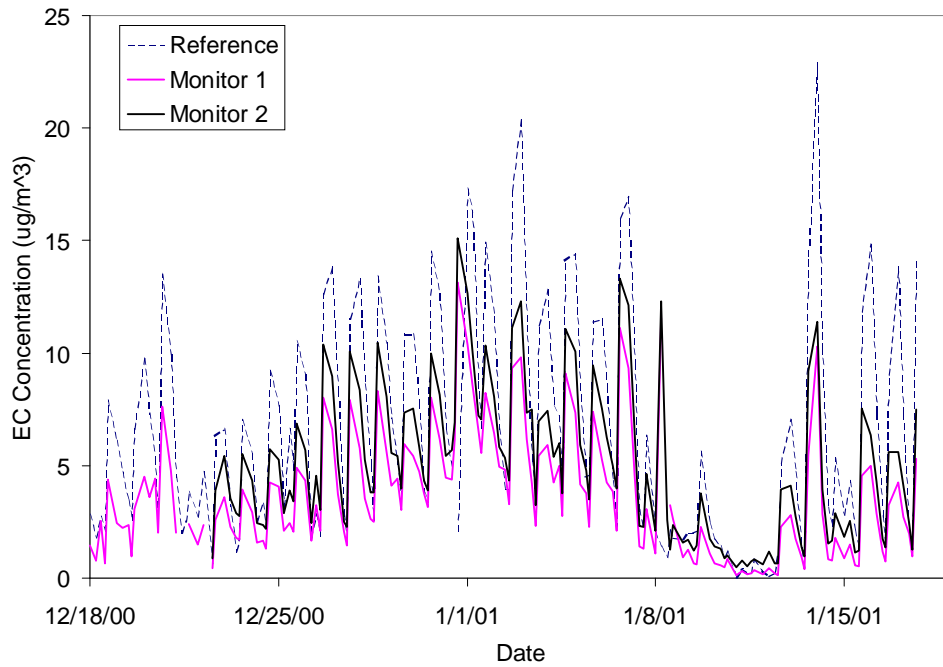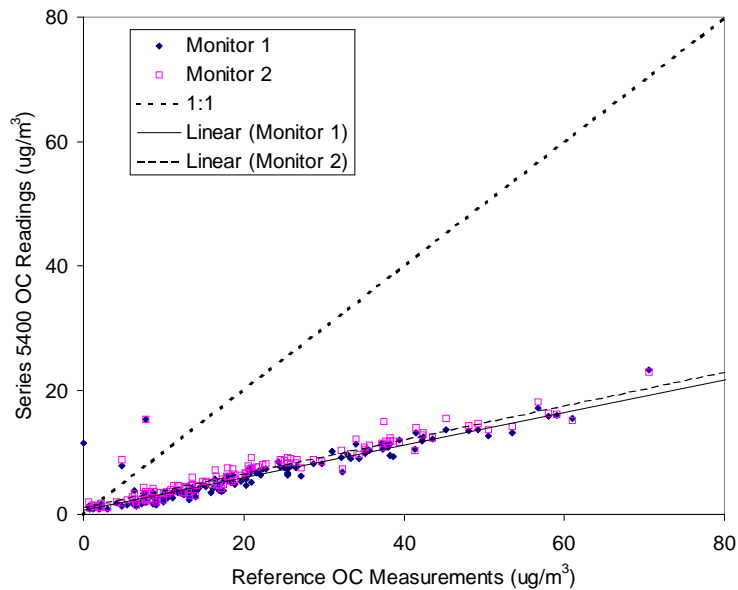**Figure 6-12a. Correlation Plot of Reference OC Measurements and Average OC Concentrations from Duplicate Series 5400 Monitors During Phase II**
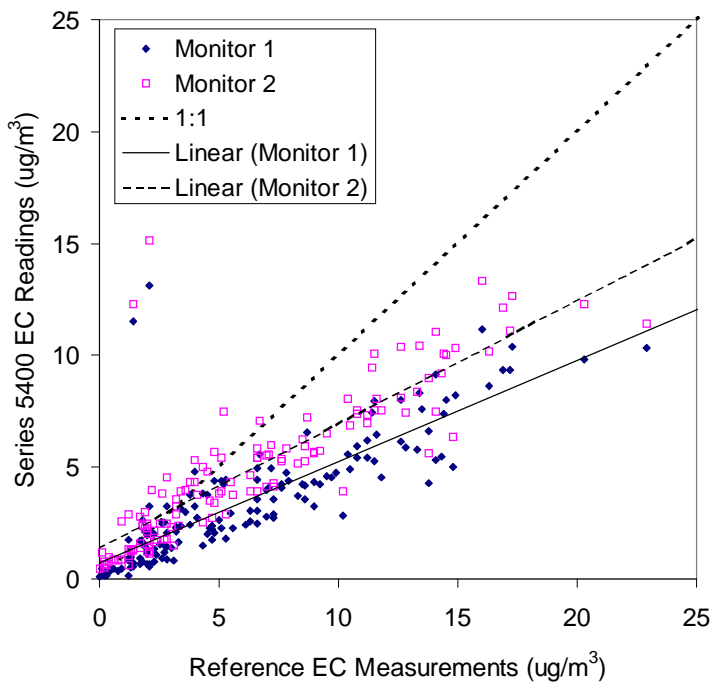
Figure 6-12b. Correlation Plot of Reference EC Measurements and Average EC Concentrations from Duplicate Series 5400 Monitors During Phase II
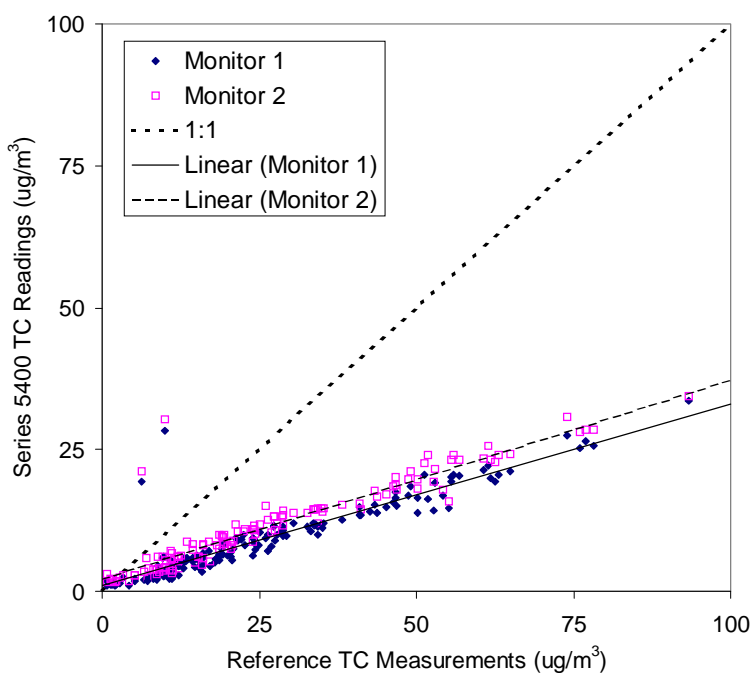
Figure 6-12c. Correlation Plot of Reference TC Measurements and Average TC Concentrations from Duplicate Series 5400 Monitors During Phase II

Linear regression analysis of these data was performed independently for each Series 5400 monitor, and the results are presented in Tables 6-13, 6-14, and 6-15. 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 these tables for the duplicate Series 5400 monitors.

Table 6-13. Comparability of the Series 5400 Monitors with OC Reference Results During Phase II

Reference Method Sampling Period	Monitor 1			Monitor 2		
	Slope	Intercept ($\mu g/m^3$)	r^2	Slope	Intercept ($\mu g/m^3$)	r^2
All	0.270 (0.016)	0.45 (0.39)	0.886	0.273 (0.018)	1.16 (0.45)	0.879
0000 - 0500	0.287 (0.019)	0.32 (0.66)	0.971	0.280 (0.024)	1.14 (0.87)	0.961
0500 - 1000	0.260 (0.048)	0.90 (0.94)	0.812	0.268 (0.055)	1.74 (1.12)	0.811
1000 -1300	0.217 (0.043)	0.69 (0.61)	0.801	0.241 (0.050)	0.91 (0.73)	0.804
1300 -1600	0.217(0.033)	0.47 (0.38)	0.872	0.250 (0.043)	0.81 (0.51)	0.856
1600 -2400	0.208 (0.055)	2.45 (1.81)	0.669	0.205 (0.060)	3.66 (2.00)	0.663

Table 6-14. Comparability of the Series 5400 Monitors with EC Reference Results During Phase II

Reference Method Sampling Period	Monitor 1			Monitor 2		
	Slope	Intercept (µg/m³)	r²	Slope	Intercept (µg/m³)	r²
All	0.453 (0.053)	0.73 (0.42)	0.659	0.556 (0.062)	1.39 (0.50)	0.709
0000 - 0500	0.476 (0.051)	0.02 (0.57)	0.926	0.556 (0.082)	0.84 (0.97)	0.890
0500 - 1000	0.473 (0.078)	0.21 (0.54)	0.846	0.545 (0.089)	0.98 (0.65)	0.874
1000 -1300	0.713 (0.180)	0.08 (0.73)	0.719	0.820 (0.230)	0.57 (0.93)	0.703
1300 -1600	0.715 (0.187)	-0.03 (0.52)	0.695	0.893 (0.197)	0.37 (0.56)	0.785
1600 -2400	0.427 (0.193)	1.39 (2.02)	0.413	0.527 (0.229)	2.26 (2.44)	0.473

Table 6-15. Comparability of the Series 5400 Monitors with TC Reference Results During Phase II

Reference Method Sampling Period	Monitor 1			Monitor 2		
	Slope	Intercept (µg/m³)	r²	Slope	Intercept (µg/m³)	r²
All	0.321 (0.023)	0.96 (0.74)	0.840	0.349 (0.026)	2.28 (0.87)	0.846
0000 - 0500	0.335 (0.021)	0.23 (0.95)	0.974	0.351 (0.029)	1.80 (1.42)	0.963
0500 - 1000	0.289 (0.088)	2.02 (2.34)	0.607	0.312 (0.101)	3.74 (2.79)	0.628
1000 -1300	0.365 (0.063)	-0.02 (1.18)	0.843	0.407 (0.084)	0.68 (1.58)	0.812
1300 -1600	0.341 (0.055)	0.08 (0.78)	0.857	0.409 (0.063)	0.68 (0.92)	0.882
1600 -2400	0.267 (0.086)	3.62 (3.67)	0.582	0.291 (0.095)	5.68 (4.16)	0.612

The data show that the agreement between the duplicate Series 5400 monitors differs for OC, EC, and TC. For OC, the overall regression results indicate a negative bias relative to the Series 5400 monitors (slope = 0.270 for Monitor 1 and slope = 0.273 for Monitor 2). The regression results for TC show somewhat higher values for the slopes [slope = 0.321 (0.023) for Monitor 1 and 0.349 (0.026) for Monitor 2). For EC, the slopes were 0.453 (0.053) for Monitor 1 and 0.556 (0.062) for Monitor 2, showing better agreement with the reference measurements than the other two carbon fractions. These regression results also indicate that the correlation between the Series 5400 monitors and the OC, EC, and TC reference measurements was best between midnight and 5:00 am during Phase II, i.e., during the time period of peak aerosol carbon levels.

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 Series 5400 monitor. This analysis involved a backward elimination process to remove from the analysis those parameters showing no statistically significant influence on the results. The model results for EC ascribe a statistical dependence on wind speed (WS), wind direction (WD), and the variability in wind direction (WDSD) for both monitors. Additionally, the solar radiation (RAD), relative humidity (RH), and barometric pressure (BP) show a statistical effect on at least one set of readings. Table 6-16 summarizes the results of this analysis. This table shows the model estimates of the coefficients for each indicated variable that relate the readings of each duplicate monitor to the appropriate reference measurements (Ref.). Except for the intercept (Int.), which is a constant, the relationships are linear.

Table 6-16. Summary of Meteorological Effects on Duplicate Series 5400 Monitors During Phase II of Verification Testing.

		Ref.	Int. ($\mu g/m^3$)	WS (mps)	WD (degrees)	WDSD (degrees)	RAD (W/m^2)	RH (%)	BP (mmHg)
OC	Monitor 1	0.224	6.82	-0.903	–[a]	-0.127	-0.0176	--	--
	Monitor 2	0.190	7.45	-1.44	-0.012	-0.224	--	0.0562	--
EC	Monitor 1	0.350	8.54	-1.02	-0.014	-0.163	--	--	--
	Monitor 2	0.373	12.5	-1.55	-.0178	-0.229	--	--	--
TC	Monitor 1	0.279	231	-2.77	-0.0251	-0.372	--	0.121	-0.293
	Monitor 2	0.235	21.7	-2.78	-0.0254	-0.390	--	--	--

[a] No statistical significance at 90% confidence.

The multivariable model ascribes unexplained variance to the meteorological parameters. The magnitude of the inferred effects can be examined by comparing predicted Series 5400 readings from the multivariable analysis to those from the simple linear regression. For example, using the parameter coefficients in Table 6-16 and the average values for these parameters during Phase II (Table 6-8), the average value for OC for Monitor 1 would be:

$$Monitor\ 1 = 0.224*Ref + 6.82 - 0.903*WS - 0.127*WDSD - 0.0176*RAD$$

$$= 0.224*19.84 + 6.82 - 0.903*1.43 - 0.127*18.7 - 0.0176*88.2$$

$$= 6.05\ \mu g/m^3$$

Using the linear regression parameters from Table 6-13, the average value for OC for Monitor 1 is

Monitor 1 = 0.270*19.84 + 0.45

$= 5.81 \ \mu g/m^3$

Thus, the multivariable model results in a difference of approximately 4% relative to the linear regression.

6.2.4 Influence of Precursor Gases

As with the meteorological data, a multivariable analysis was performed to establish any statistical relationships between the measured precursor gases and the readings of the Series 5400 monitors relative to the reference measurements. This analysis also involved backward elimination of parameters that were found have no statistical effect. The model ascribed to nitric oxide and nitrogen oxides an effect on the EC and TC results, and to nitrogen dioxide an effect on one of the monitors relative to the OC reference results, at 90% confidence. Table 6-17 summarizes the results of this analysis.

Table 6-17. Summary of Precursor Gas Influences on Duplicate Series 5400 Monitors During Phase II of Verification Testing

		Ref. $(\mu g/m^3)$	Int. (ppb)	NO (ppb)	NO_2 (ppb)	NO_x (ppb)
OC	Monitor 1	0.196	0.076	--[a]	0.0662	--
EC	Monitor 1	0.289	-1.62	-0.142	--	0.131
	Monitor 2	0.386	-1.29	-0.149	--	0.138
TC	Monitor 1	0.234	-1.59	-0.211	--	0.194
	Monitor 2	0.282	-0.212	-0.185	--	0.170

[a] No statistical significance at 90% confidence.

An analogous evaluation to that in Section 6.2.4 can be done to assess the magnitude of the implied precursor gas effects. For example, from Table 6-17, the multivariable model indicates the following relationship for OC from Monitor 1:

Monitor 1 = 0.196*Ref + 0.076 + 0.0662*NO_2

Substituting the average values for these parameters from Phase II into this equation, the model predicts an average OC value of

$$\text{Monitor } 1 = 0.196 * 19.84 + 0.076 + 0.0662 * 32.6$$

$$= 6.12 \, \mu g/m^3$$

and, as shown in Section 6.2.3, the linear regression results predict a value of 5.81 $\mu g/m^3$. Thus, the multivariable model results in a difference of approximately 5% relative to the linear regression.

6.3 Instrument Reliability/Ease of Use

During Phase I, the heater in one of the Series 5400 monitors was replaced. No other maintenance was required during Phase I. Data recovery of approximately 90% was achieved for Monitor 1, and recovery of approximately 85% was achieved for Monitor 2.

During Phase II, Monitor 1 achieved 94% data recovery, and Monitor 2 achieved 93%. No maintenance was performed on either monitor during Phase II.

Instrument installation could be performed in a day depending upon the facilities available. After installation, the instruments can be operated largely unattended.

6.4 Shelter/Power Requirements

The Series 5400 monitors were installed and operated inside an instrument trailer during each phase of testing. During Phase I, the monitors were installed in the DOE/NETL instrument trailer, and during Phase II, the monitors were installed in the Battelle instrument trailer. The monitors require a 240V AC source. Consequently, boost transformers (approximately $300 each) were required for Phase II to boost the 110 V AC line voltage to achieve the recommended voltage. An appropriate power source was already available at the DOE/NETL facility.

6.5 Instrument Cost

The cost of the Series 5400 monitor is subject to change and may be different for domestic and international markets. As such, no pricing data were provided by the vendor for this report.

Chapter 7
Performance Summary

The Series 5400 monitor is a semi-continuous particle monitor designed to provide hourly indications of the ambient particulate carbon concentration. Duplicate Series 5400 monitors were evaluated under field test conditions in two separate phases of this verification test. The duplicate monitors were operated side by side and were installed with a $PM_{2.5}$ cyclone to provide size selection of the aerosol. The results from each phase of this verification test are summarized below.

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

Linear regression results of the hourly measurements from the duplicate Series 5400 monitors in Phase I indicate r^2 values of 0.94, 0.93, and 0.95, respectively, for OC, EC, and TC. The calculated regression lines for these data had slopes of 1.063 (0.021), 1.037 (0.022), and 1.069 (0.020), and intercepts of -0.14 (0.04) $\mu g/m^3$, 0.10 (0.02) $\mu g/m^3$, and -0.08 (0.05) $\mu g/m^3$ for OC, EC, and TC, respectively. Daily 24-hour averages were calculated for OC, EC, and TC and showed similar correlation and agreement results as the hourly data. The regression results for these data indicate r^2 values of 0.97, 0.94, and 0.97; slopes of 1.094 (0.081), 1.038 (0.113), and 1.098 (0.088); and intercepts of -0.20 (0.16) $\mu g/m^3$, 0.10 (0.09) $\mu g/m^3$, and -0.15 (0.24) $\mu g/m^3$, for OC, EC, and TC, respectively.

Comparison of the 24-hour averages to the OC, EC, and TC reference measurements showed a negative bias of the Series 5400 readings. The slopes of the regression lines for each monitor relative to the reference data were below 0.4 for all three carbon fractions, and the r^2 values were between 0.43 and 0.52.

Multivariable model analysis ascribed to vertical and horizontal wind speed, wind direction, and ambient air temperature at 2 meters and 10 meters significant effects on Series 5400 readings relative to the reference carbon results at 90% confidence. The multivariable model results typically differ from the linear regression with reference data by only a few percent, under average Phase I conditions.

Multivariable model analysis ascribed to ozone, hydrogen sulfide, and nitrogen dioxide a statistical influence on the readings of one or both monitors relative to the reference carbon results. The multivariable model results typically differ by only a few percent from the linear regression with reference data, under average Phase I conditions.

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

Linear regression results of the hourly measurements from the duplicate Series 5400 monitors during Phase II indicate r^2 values of 0.94, 0.92, and 0.86, for OC, EC, and TC, respectively. After application of a correction factor to the results of one of the monitors, the calculated slopes of the regression lines for these data were 0.971 (0.019), 1.029 (0.024), and 1.074 (0.035), respectively. Daily 24-hour averages were calculated for OC, EC, and TC and showed similar correlation and agreement results as the hourly data. The regression results for these data indicate r^2 values of > 0.97, for each case. The calculated slopes of the regression lines for these data were 1.027 (0.072), 1.164 (0.083), and 1.090 (0.070), for OC, EC, and TC, respectively. Without this correction factor, a bias of ~50% was observed.

Comparison of the 24-hour averages to the OC, EC, and TC reference measurements showed a substantial negative bias of the Series 5400 readings. The slopes of the regression lines for each monitor fell between approximately 0.2 and 0.7 for Monitor 1, and 0.2 and 0.29 for Monitor 2, for all three carbon fractions, when all sampling periods were included in the analysis. However, better quantitative agreement between the Series 5400 monitors and the reference measurements was observed for some of the sampling periods relative to others. The r^2 values for regression analyses, when all sampling periods, were between 0.65 and 0.90.

Multivariable model analysis ascribed to wind speed, wind direction, the change in wind direction, solar radiation, relative humidity, and barometric pressure a significant influence on Series 5400 readings relative to the reference carbon measurements, at the 90% confidence level. The multivariable model results typically differ by only a few percent from the linear regression with reference data, under average Phase II conditions.

Multivariable model analysis ascribed to nitric acid and nitrogen dioxide a statistical influence on the readings of both Series 5400 monitors relative to the reference EC and TC results. Also, the model found nitrogen dioxide to have an effect on the readings of one monitor relative to the OC reference measurements at the 90% confidence level. The multivariable model results typically differ by only a few percent from the linear regression with reference data, under average Phase II conditions.

7.3 Other Parameters

The duplicate Series 5400 monitors required little maintenance during either phase of testing, with the exception of the replacement of a heater in one unit during Phase I. Overall, the monitors achieved approximately 90% data recovery combined in the two phases.

Chapter 8
References

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