August 2001

Environmental Technology Verification Report

RUPPRECHT & PATASHNICK, CO. SERIES 8400N AMBIENT PARTICULATE NITRATE MONITOR

Prepared by

Battelle
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Battelle

Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

. . . Putting Technology To Work

ETV Joint Verification Statement

TECHNOLOGY TYPE: **Continuous Ambient Particulate Nitrate Monitor**

APPLICATION: **MEASURING PARTICULATE NITRATE CONCENTRATIONS IN AMBIENT AIR**

TECHNOLOGY NAME: **Series 8400N Particulate Nitrate Monitor**

COMPANY: **Rupprecht & Patashnick, Co.**

ADDRESS: **25 Albany Circle**
Albany, NY 12203
PHONE: 518-452-0065
FAX: 518-452-0067
WEB SITE: **http://www.rpco.com**
E-MAIL: **info@rpco.com**

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

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

The Advanced Monitoring Systems (AMS) Center, one of six technology centers under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center has recently evaluated the performance of continuous monitors used to measure fine particulate mass and species in ambient air. This verification statement provides a summary of the test results for the Rupprecht & Patashnick, Co. Series 8400N particulate 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 8400N reports measurement results in terms of particulate nitrate concentration in $\mu g/m^3$ and, therefore, was compared with ion chromatographic nitrate determinations on collected particulate matter samples. The ambient nitrate concentrations differed markedly in the two phases, ranging from about 0.5 to 3.5 $\mu g/m^3$, averaging 1.2 $\mu g/m^3$ in Phase I, and ranging from about 0.5 to 65 $\mu g/m^3$, averaging 17 $\mu g/m^3$, in Phase II. Additionally, comparisons with a variety of supplemental measurements were made to establish specific performance characteristics.

Quality assurance (QA) oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a data quality audit of 10% of the test data, and an internal technical systems audit for Phase I and Phase II. EPA QA staff conducted an external technical systems audit during Phase II.

TECHNOLOGY DESCRIPTION

The Series 8400N consists of a weather-protection inlet and transport tubing, pulse generator, microprocessor-based control system, user interface, nitrogen oxides detector, sample pump, and gas cylinder. Built-in software and hardware automatically calibrate and verify zero and span. Bidirectional RS-232 communication provides the capability for remote data interchange and internal data storage. A stream of ambient air containing particulate matter enters the sample inlet line beneath a rain cap mounted above the roof of the air quality monitoring station. A sheath flow surrounds the sample line, and then enters the sample processing section of the pulse generator after being filtered. The sheath air flow is designed to keep the sample stream and inside of the instrument as close as possible to the ambient air temperature. A $PM_{2.5}$ sharp cut cyclone removes the larger particles from the sample stream. A bypass flow, which shortens the residence time of the sample stream in the sampling section, passes through a critical orifice. An activated charcoal denuder removes acidic gases that would otherwise interfere with the measurement of the ambient particulate nitrate concentration.The Series 8400N uses a flash volatilization technique to measure the concentration of particulate nitrate contained in $PM_{2.5}$. To achieve high collection efficiencies even for very small secondary aerosols, a humidifier moistens the sample stream and causes the hygroscopic nitrate particles to grow. The remaining part of the sample stream forms a jet as it passes through a critical orifice. Particles collect on an impactor/flashing strip during the sample collection phase (eight minutes by default). The sample and bypass flows then combine and exit from the instrument on their way to an external pump. Flash volatilization of the collected particulate matter in a nitrogen atmosphere occurs at approximately 350°C through the resistive heating of the metal impactor/flashing strip, which creates a pulse of oxides of nitrogen that is quantified by the chemiluminescent reaction with excess ozone. The Series 8400N computes a new data point every 10 minutes, with a resolution of the reported values of $\pm 0.2\ \mu g/m^3$.

VERIFICATION OF PERFORMANCE

Inter-Unit Precision: For the hourly average data from Phase I, the linear regression analysis showed a slope of 0.827 (0.029), an intercept of 0.007 (0.019) $\mu g/m^3$, and an r^2 value of 0.905, where the numbers in parentheses are 95% confidence intervals. The regression results of the 24-hour average data show a slope of 0.802 (0.190), an intercept of 0.008 (0.097) $\mu g/m^3$, and an r^2 value of 0.843. In both cases, a statistically significant bias (95% confidence) between the two monitors was indicated, with Monitor 1 reading higher than Monitor 2. During Phase II, with nitrate concentrations about 10 times higher than in Phase I, the regression results of the hourly average data from the duplicate monitors showed a slope of 1.052 (0.025), an intercept of 0.02 (0.43), and an r^2 value of 0.907. For the 24-hour average data, the regression results showed a slope of 1.089 (0.067), an intercept of -0.42 (1.08) µg/m^3, and an r^2 value of 0.975. In both cases the slope of the regression line is statistically different from unity and the intercept is statistically indistinguishable from zero.

Comparability/Predictability: For Phase I, the 24-hour average results of the duplicate Series 8400N monitors were compared by linear regression to the reference measurements of denuded filter samples analyzed by ion chromatography. The regression results for Monitor 1 during Phase I show a slope of 0.30 (0.20), an intercept of 0.21 (0.25) µg/m^3, and an r^2 value of 0.315, when one apparent outlying reference data point was removed from the analysis. For Monitor 2, the regression results show a slope of 0.37 (0.15), an intercept of 0.02 (0.17) µg/m^3, and an r^2 value of 0.770. During Phase II, with much higher ambient nitrate levels, nitrate reference samples were collected on a 5-per-day schedule. The regression results, including all the reference data, show a slope of 0.600 (0.041), an intercept of 3.18 (0.94) µg/m^3, and an r^2 value of 0.855 for Monitor 1. For Monitor 2, the regression results show a slope of 0.625 (0.054), an intercept of 3.42 (1.22) µg/m^3, and an r^2 value of 0.774. These results indicate a statistical bias relative to the reference measurement for both monitors. For the various sampling periods, the slopes of the regression lines ranged from 0.537 to 0.914 for Monitor 1 and from 0.561 to 1.087 for Monitor 2. The best agreement with the reference measurements was seen during the night time and early morning sampling periods (i.e., 0000-0500, and 0500-1000) and the worst agreement during the mid-day sampling periods (i.e., 1000-1300 and 1300-1600).

Meteorological Effects: The multivariable model of Phase I data provided no conclusive results about the effect of meteorological conditions on the readings of the Series 8400N monitors. Multivariable analysis of Phase II data indicated that, for one monitor, wind speed, relative humidity, and barometric pressure had a significant effect and, for the other monitor, only ambient temperature had a significant effect. However, the effects totaled 5% or less relative to the regression of monitor results against reference data alone.

Influence of Precursor Gases: The multivariable model ascribed to nitric oxide and sulfur dioxide a statistically significant (90% confidence) influence on the readings of the Series 8400N monitors relative to the nitrate reference measurements in Phase I. However, the overall effects of these two gases were small and opposing, amounting to less than 10% difference relative to the regression of monitor results against reference data alone. In Phase II, none of the measured precursor gases had a statistically significant influence on either

Other Parameters: During Phase I, maintenance included replacement of purge and calibration gas cylinders at a greater frequency than expected due to leaks in valves in the Series 8400N monitors. Flash strips were also replaced several times. As a result of the frequent maintenance, data recovery was 80% for one monitor and 44% for the other monitor. In Phase II, less frequent maintenance was required. Data recovery was 91% for one monitor and 100% for the other monitor.

Gabor J. Kovacs Date
Vice President
Environmental Sector
Battelle

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

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Rupprecht & Patashnick, Co.
Series 8400N Ambient Particulate Nitrate Monitor

by

Kenneth Cowen
Thomas Kelly
Basil Coutant
Karen Riggs

Battelle
Columbus, Ohio 43201

Notice

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

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. In particular we would like to thank the staff at the Department of Energy's National Energy Technology Laboratory, including Richard Anderson, Don Martello, and Curt White, for their assistance in conducting Phase I of the verification test reported here. We would like to thank the California Air Resources Board for its assistance in conducting Phase II of verification testing. We would like to acknowledge the efforts of ETV stakeholders for their assistance in planning this verification test and for reviewing the test/QA plan and the verification reports. Specifically, we would like to acknowledge Judith Chow of Desert Research Institute, Jeff Cook of the California Air Resources Board, Tim Hanley of EPA, and Rudy Eden of the South Coast Air Quality Management District. We also would like to thank Tim Hanley of EPA for the loan of a BGI FRM sampler for Phase II.

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List of Abbreviations

ADQ	audit of data quality
AMS	Advanced Monitoring Systems
CARB	California Air Resources Board
CI	confidence interval
CO	carbon monoxide
CV	coefficient of variation
DOE	U.S. Department of Energy
DRI	Desert Research Institute
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FRM	federal reference method
H_2S	hydrogen sulfide
IC	ion chromatography
IMPROVE	Interagency Monitoring for Protection of Visual Environments
in.	inch
mm	millimeters
mps	meters per second
L/min	liters per minute
NETL	National Energy Technology Laboratory
N_2	nitrogen
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO_2	nitrogen dioxide
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
QMP	quality management plan
R&P	Rupprecht & Patashnick
SFS	sequential filter sampler
TOR	thermal optical reflectance
TSA	technical systems audit
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 Pataschnick (R&P) Series 8400N particulate nitrate monitor.

Chapter 2
Technology Description

The following description of the Series 8400N particulate nitrate monitor is based on information provided by the vendor.

The Series 8400N consists of a weather-protection inlet and transport tubing, pulse generator, microprocessor-based control system, user interface, nitrogen oxides detector, sample pump, and gas cylinder. Built-in software and hardware automatically calibrate and verify zero and span. Bidirectional RS-232 communication provides the capability for remote data interchange and internal data storage.

A stream of ambient air (16.7 L/min) containing particulate matter enters the sample inlet line beneath a rain cap mounted above the roof of the air quality monitoring station. A sheath flow surrounds the sample line, and then enters the sample processing section of the pulse generator after being filtered. The sheath air flow is designed to keep the sample stream and inside of the instrument as close as possible to the ambient air temperature. A $PM_{2.5}$ sharp cut cyclone removes the larger particles from the sample stream. A bypass flow, which shortens the residence time of the sample stream in the sampling section, passes through a critical orifice. An activated charcoal denuder removes acidic gases that would otherwise interfere with the measurement of the ambient particulate nitrate concentration.

Figure 2-1. Rupprecht & Patashnick, Co. Series 8400N Particulate Nitrate Monitor

The Series 8400N uses a flash volatilization technique to measure the concentration of particulate nitrate contained in $PM_{2.5}$. To achieve high collection efficiencies even for very small secondary aerosols, a humidifier moistens the sample stream and causes the hygroscopic nitrate particles to grow. The remaining part of the sample stream forms a jet as it passes through a critical orifice. Particles collect on an impactor/flashing strip during the sample collection phase (eight minutes by default). The sample and bypass flows then combine and exit from the instrument on their way to an external pump. Flash volatilization of the collected particulate matter in a nitrogen atmosphere occurs at approximately 350°C through the resistive heating of the metal impactor/flashing strip, which creates a pulse of oxides of nitrogen that is quantified by the chemiluminescent reaction with excess ozone. The Series 8400N computes a new data point every 10 minutes, with a resolution of the reported values of ±0.2 µg/m^3.

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 8400N monitors were tested in side-by-side operation during each phase of testing. Collocation of the Series 8400N monitors with reference systems for time-integrated sampling of fine particulate mass and chemical speciation provided the basis for assessing the degree of agreement and/or correlation between the continuous and reference methods. Each test site was equipped with continuous monitors to record meteorological conditions and the concentration of key precursor gases (ozone, nitrogen oxides, sulfur dioxide, etc.). The data from the meteorological and gas monitors were used to assess the influence of these parameters on the performance of the fine particle monitors being tested. Statistical calculations, as described in Chapter 5, were used to establish each of these performance characteristics.

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

3.3 Reference Method and Supplemental Measurements

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

The Series 8400N reports measurement results in terms of particulate nitrate concentration. As such the measurements from the Series 8400N were compared with results of ion chromatography (IC) analysis of collected particulate matter samples. Additionally, comparisons with a variety of supplemental measurements were made to establish specific performance characteristics. Descriptions of the reference method and supplemental measurements used during the verification test are given below.

3.3.1 Nitrate Reference Method

The primary comparisons of the Series 8400N nitrate readings were made relative to IC results for particulate nitrate. This technique involves collection of particulate matter samples using any of a variety of air samplers and subsequent digestion and analysis of the collected sample.(4)

During Phase I, all nitrate reference samples were collected using an Andersen RAAS $PM_{2.5}$ speciation sampler. Samples were collected daily (i.e., over 24-hour periods) at a normal flow rate of 7.3 L/min on nylon filters downstream of a magnesium oxide-coated compound annular denuder. The samples were collected and analyzed by Consol Energy, of Library, PA, under subcontract to Battelle.

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

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

Collocated samples were collected during Phase I to establish the precision of the reference method. Precision estimates for Phase II, are based on previously reported results. A discussion of the collocated sampling is presented in Section 4.4 of this report.

3.3.2 Supplemental Measurements

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

3.4 Data Comparisons

The primary means used to verify the performance of the Series 8400N monitors was comparison with the IC nitrate 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. The comparisons were based on statistical calculations as described in Section 5 of this report.

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

3.5 Site Layout/Instrument Installation

In each phase of testing, the two Series 8400N monitors were installed and operated indoors. The Series 8400N monitors were placed on a counter top, with each monitor below a port through the roof of the trailer. Separate 3" polyvinyl chloride (PVC) tubes were installed in the sampling ports and extended to approximately 1.5 meters above the roof of the trailer. These PVC tubes were secured to the roof of the trailer using wire guidelines, and a rain cap was positioned on the top of each. Separate flexible sampling lines were run from the monitors to the inside of the rain caps for sampling of the outside air. Particle size selection for the Series 8400N monitors was achieved using internal cyclones in each of the monitors. Data generated by the Series 8400N monitors were logged 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 8400N monitors were installed inside the Battelle trailer, and a Battelle Andersen RAAS sampler was installed on the Battelle/ETV platform. A vertical separation of approximately 2 to 3 meters and a horizontal

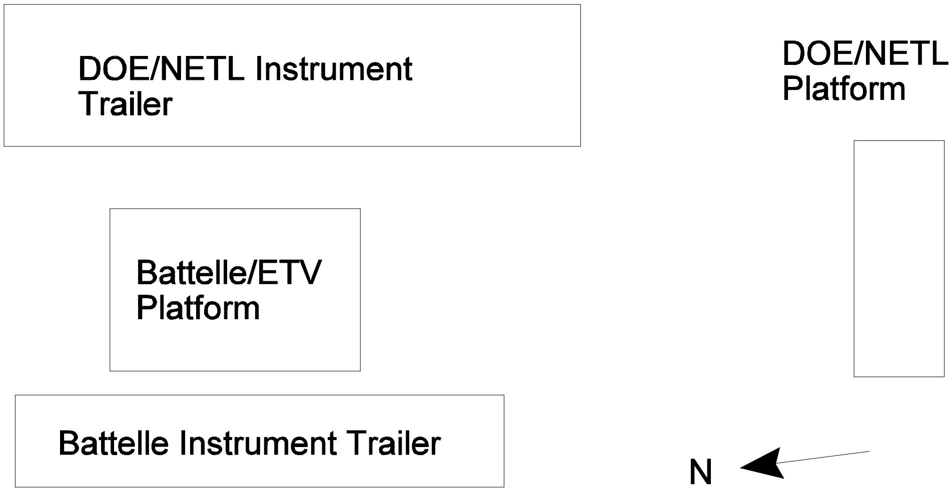

Figure 3-1. Site Layout During Phase I of Verification Testing (not drawn to scale)

separation of approximately 3 meters existed between the inlets of the Series 8400N monitors and the Battelle Andersen 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.

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 3 miles north of the center of Fresno. The 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 Series 8400N monitors and the continuous gas monitors were located inside the CARB office space and sampled through a port in the roof of the building. The sequential filter sampler was located near the center of the rooftop. The Battelle trailer used during Phase I of this verification test also was used during Phase II. For Phase II, the Battelle trailer was located in the parking lot adjacent to the building in which the CARB site is located and housed the majority of the other continuous monitors tested in this verification test. A difference in elevation of approximately 1 meter and horizontal separation of approximately 5 meters existed between the inlets of the SFS and the Series 8400N monitors.

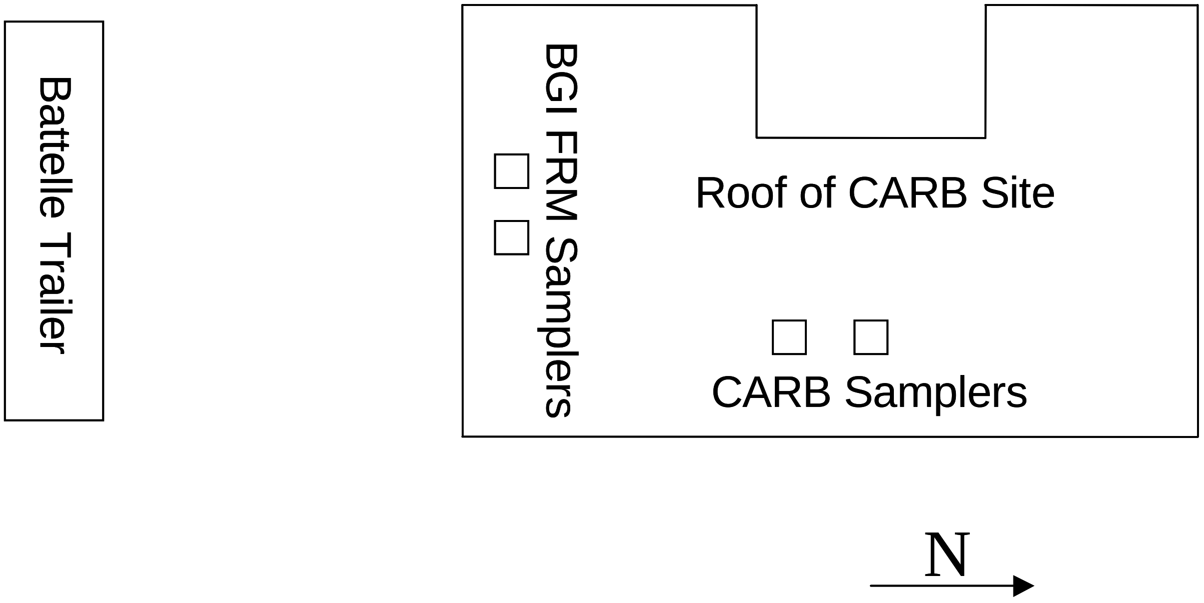

Figure 3-2. Site Layout During Phase II of Verification Testing (not drawn to scale)

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 8400N 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

No deviations related to verification of the Series 8400N monitor occurred.

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. In Phase II, calibration of the sequential filter sampler was maintained by DRI as part of their ongoing monitoring efforts.

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

4.4 Collocated Sampling

4.4.1 Phase I

To establish the precision of the nitrate reference method, the 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 five samples were collected from each of the two samplers during periods before and after Phase I. These collocated samples were analyzed by Consol. The measured nitrate concentration for these samples ranged from 0.5 to 2.5 µg/m^3. On average, these collocated samples showed relative agreement with one another (i.e., difference divided by mean) of 18.2%. The observed differences ranged from 57% for the lowest concentration sample to 2% for the highest concentration sample.

4.4.2 Phase II

Precision estimates for the SFS sampler used in Phase II are based on previously reported results of a study(2) performed in Bakersfield, CA. In that study, collocated SFSs identical to those used in this verification test were used to collect a series of 24 3-hour nitrate samples, at particulate nitrate levels similar to those observed in Phase II. For non-volatilized nitrate, the regression results of these samples showed a slope of 1.00 (0.09), an intercept of 0.39 (0.41) µg/m^3, and an r value of 0.92 (r^2 = 0.85), where the values in parentheses are standard errors. The average difference of the sample pairs was -0.44 µg/m^3 with a standard deviation of 3.10 µg/m^3. For volatilized nitrate, which comprised a small fraction of the reference nitrate values, the regression results showed a slope of 0.56 (0.15), an intercept of 0.30 (0.34) µg/m^3, and an r value of 0.62 (r^2 = 0.38). The average difference for these sample pairs was 0.14 µg/m^3 with a standard deviation of 1.73 µg/m^3.

4.5 Field Blanks

Ten percent of the reference samples that were collected with the Andersen RAAS sampler in Phase I of the verification test were field blanks. These blanks showed nitrate mass per filter ranging from 1.8 to 3.2 µg. Assuming a sample volume of 11 m^3, these blank values account for 0.16 to 0.29 µg/m^3 of the total observed nitrate concentration. Nitrate reference concentrations for Phase I were not blank corrected. Also, at least 10% of the reference nitrate samples collected with the sequential filter sampler during Phase II were field blanks. These samples were analyzed by IC at DRI. These blank samples showed nitrate mass that ranged from nondetectable (<0.5 µg/filter) to 4.08 µg/filter, with fewer than 50% of the samples showing detectable amounts of nitrate. Since the duration of sampling periods varied, the sample volume was not consistent from period to period. However, for the shortest sampling period, the nominal volume sampled was 3.6 m^3. Assuming this volume, the blank values ranged up to approximately 1.1 µg/m^3 nitrate. These blank values were incorporated into a DRI database of blank results, that was used to calculate a running average nitrate blank value. Nitrate reference concentrations for Phase II were then blank corrected by DRI, using that running average.

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 8400N Nitrate Monitors

Data from each of the Series 8400N 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 with 10-minute values reported along with a variety of instrumental parameters. The recorded data were downloaded directly onto an on-site personal computer and saved as text files. 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 and the Consol laboratory facilities. All findings noted during this TSA were documented and submitted to the Verification Test Coordinator for correction. The corrections were documented by the Verification Test Coordinator and reviewed by Battelle's Quality Manager, Verification Testing Leader, and AMS Center Manager. None of the findings adversely affected the quality or outcome of this phase of the verification test. All corrective actions were completed to the satisfaction of the Battelle Quality Manager. The records concerning this TSA are permanently stored with the Battelle Quality Manager.

Phase II—Fresno

An internal TSA was conducted by the Battelle Quality Manager on January 9, 2001, at the Fresno test site. An external TSA was also conducted concurrently by EPA quality staff, Ms. Elizabeth Betz and Ms. Elizabeth Hunike. All findings noted during these TSAs were documented and submitted to the Verification Test Coordinator for corrective action. None of the findings adversely affected the quality or outcome of this phase of the verification test for the Series 8400N. All corrective actions were completed to the satisfaction of the Battelle Quality Manager and the EPA.

4.7.2 Performance Evaluation Audit

The reference sampler provided by Battelle for this verification test was audited during Phase I to ensure that it was operating properly. During Phase I of the verification test, the flow rate of the 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 nitrate channel was within the ±4% acceptance criterion with respect to the internal flow meter.

The ambient and filter temperature sensors 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.

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

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 8400N monitor.

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 8400N 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 nitrate 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 nitrate reference measurements was assessed for the Series 8400N monitors, since these monitors yield measurements with the same units of measure as the nitrate reference method. The relationship between the two was assessed from a linear regression of the data using the nitrate reference results as the independent variable and the Series 8400N monitor results as the dependent variable as follows:

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

where R_i is the i^{th} nitrate reference measurement;, C_i is the average of the Series 8400N measurements over the same time period as the i^{th} 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 Series 8400N 10-minute measurements over the time period of the corresponding reference sample is used because this is the quantity that is most comparable to the reference sampler measurements.

Comparability is expressed in terms of bias between the Series 8400N monitor and the nitrate 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 nitrate reference measurements and the Series 8400N 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 8400N nitrate measurements is simply equivalent to the nitrate 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 8400N measurements is almost entirely explained by the variability in the nitrate reference measurements.

Quantities reported include r^2, intercept, and slope, with estimates of 95% confidence intervals (CIs) for the intercept and slope. Comparability to the reference method was determined independently for each of the duplicate Series 8400N 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 correlation between the Series 8400N monitors and the nitrate reference measurements was evaluated, by using meteorological data such as temperature and humidity as parameters in multivariable analyses of the reference/monitor comparison data. The same evaluation was 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 8400N 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 results 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 $\mu g/m^3$ to 36.2 $\mu g/m^3$, with an average daily concentration of 18.4 $\mu g/m^3$. Typically, the $PM_{2.5}$ composition was dominated by sulfate and carbon species. On average, the measured sulfate concentration, determined by ion chromatography, accounted for approximately 47% of the daily $PM_{2.5}$ mass. Total carbon, as measured by the IMPROVE thermal optical reflectance (TOR) method, accounted for approximately 38% of the $PM_{2.5}$ mass, with elemental carbon contributing approximately 22% and organic carbon contributing approximately 77% of the total carbon. Additionally, nitrate contributed about 8.3% of the daily $PM_{2.5}$ concentration.

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

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

	Wind Speed (mph)	**Vertical Wind Speed (mph)**	**Wind Direction (degrees)**	**Air Temp. @ 10 m (C)**	**Air Temp. @ 2 m (C)**	**RH (%)**	**Solar Radiation (W/m^2)**	**Press. (mbar)**	**Total Precip. (in.)**
Average	3.35	0.09	196	20.0	16.6	89.4	162.8	979.7	0.0014
Max.	6.45	0.29	298	24.1	22.5	95.8	246.1	986.7	0.0297
Min	1.88	-0.03	106	14.6	12.1	80.2	47.9	974.5	0.0000

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

	SO_2 (ppb)	**H_2S (ppb)**	**NO (ppb)**	**NO_2 (ppb)**	**NO_x (ppb)**	**O_3 (ppb)**
Average	6.9	1.5	3.1	10.1	13.0	24
Max	12.8	2.9	10.4	17.4	27.4	51
Min	2.7	-0.6	0.14	5.3	5.3	5

6.1.1 *Inter-Unit Precision*

Ambient particulate nitrate concentrations were measured and recorded every 10 minutes throughout Phase I by duplicate Series 8400N monitors. These data were averaged to obtain hourly averages for nitrate concentration. Figure 6-1a shows the hourly nitrate averages for the duplicate monitors recorded during Phase I of verification testing. The ambient nitrate levels in Phase I were low, usually below 1 μg/m^3, with peak daily values up to approximately 3 μg/m^3. Figure 6-1a shows close agreement between the two Series 8400N monitors when both were operating. Breaks in the data indicate periods during which no data are available because of instrument failure or power outages. Figure 6-1b is a scatter plot of these same data that illustrates the correlation between the two monitors in measuring particulate nitrate concentration.

For comparison with the 24-hour nitrate reference measurements, the hourly data were averaged from noon to noon for each day to correspond with the 24-hour sampling periods used in Phase I of the verification test. In Figure 6-2a, the noon-to-noon averages for Phase I of the verification test are presented for the two Series 8400N monitors. A correlation plot of the simultaneous data from both monitors is shown in Figure 6-2b.

These data were analyzed by linear regression, and the results of this analysis are presented in Table 6-3. The CV 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 and 24-Hour Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase I

Parameter	Hourly	24-Hour
Slope (95% CI)	0.827 (0.029)	0.802 (0.190)
Intercept (μg/m^3) (95% CI)	0.007 (0.019)	0.008 (0.097)
r^2	0.905	0.843
CV	37.8%	41.7%

The regression results for the hourly average data from the duplicate monitors indicate a bias between the two monitors, with Monitor 1 reading higher in general than Monitor 2 [slope = 0.827 (0.029)]. The intercept of the regression line is 0.007 (0.019) and is not statistically different from zero. For the 24-hour average nitrate concentrations, the regression results also indicate a similar bias between the two monitors [slope = 0.802 (0.190)]. As with the hourly data, the intercept is not significantly different from zero. The regression results show an r^2 value of 0.843 for the 24-hour data, with slightly better correlation ($r^2 = 0.905$) for the hourly data. The CV value for the 24-hour data is also somewhat higher than the hourly data. These results are undoubtedly affected by the low nitrate concentrations present in Phase I. For example, all the 24-hour reference nitrate values in Figure 6-2b are 1.1 μg/m^3 or less.

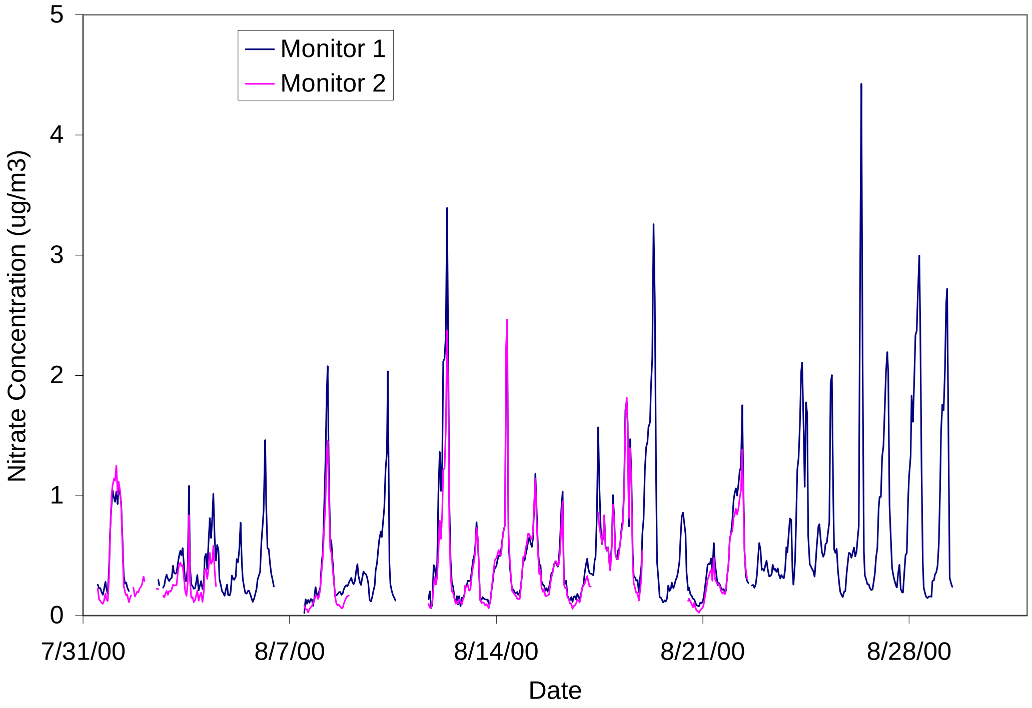

Figure 6-1a. Hourly Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase I of Verification Testing

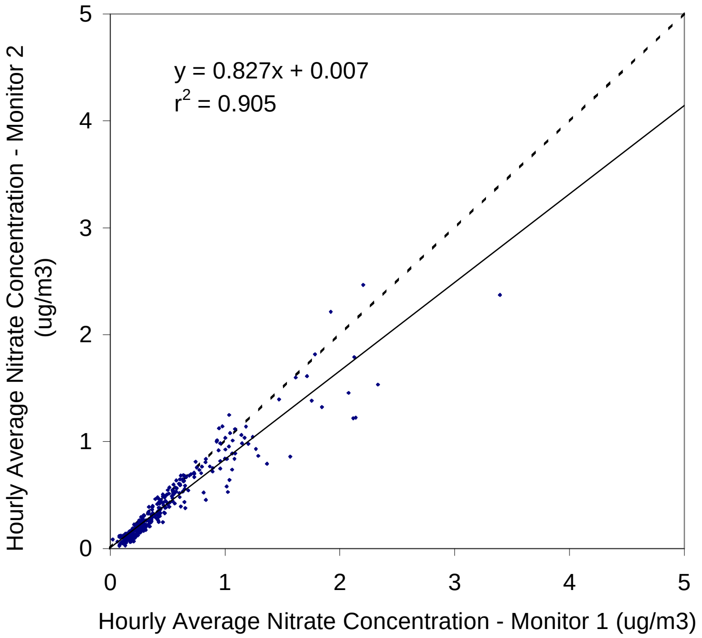

Figure 6-1b. Correlation Plot of Hourly Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase I of Verification Testing

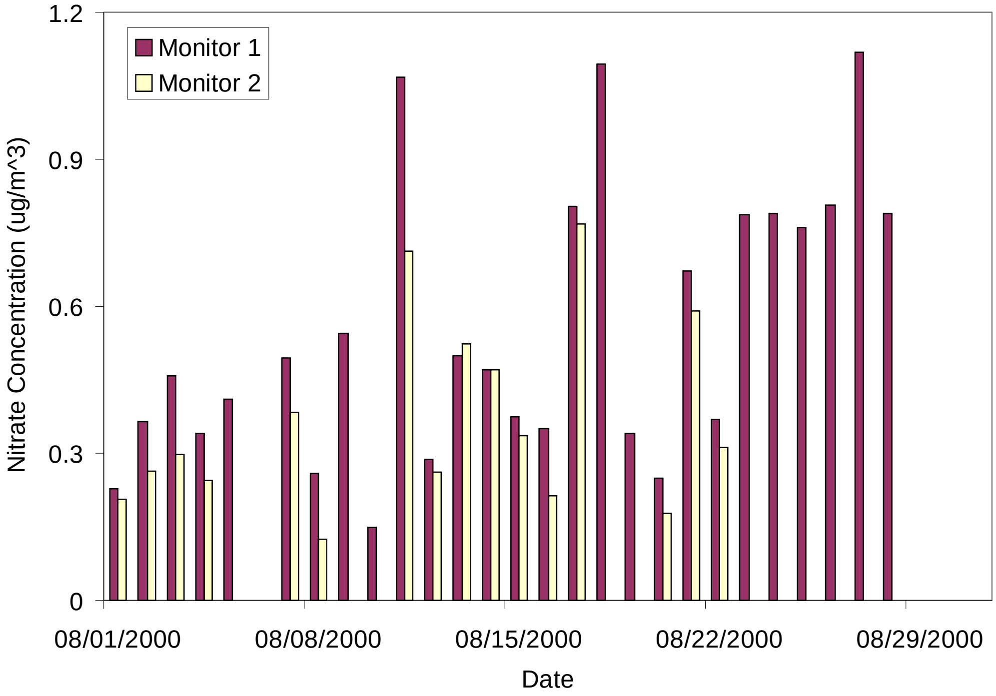

Figure 6-2a. 24-Hour Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase I of Verification Testing

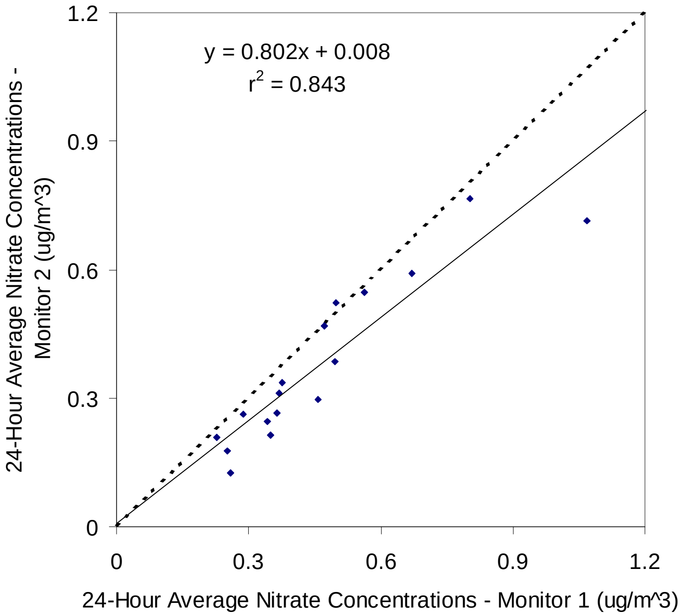

Figure 6-2b. Correlation Plot of 24-Hour Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase I of Verification Testing

6.1.2 Comparability/Predictability

In Figure 6-3a, the noon-to-noon averages of the Series 8400N nitrate measurements are shown, along with the nitrate reference measurements. These same data are shown in Figure 6-3b as a scatter plot to illustrate the correlation between the Series 8400N monitors and the reference measurements. These data were analyzed by linear regression according to Section 5.2 to establish the comparability of each of the Series 8400N monitors and the reference sampler. The calculated slope, intercept, and r^2 value of the regression analyses are presented in Table 6-4 for each monitor.

In Figure 6-3a, the nitrate readings from both Series 8400N monitors are always lower than the corresponding reference results. However, the nitrate reference measurement on August 14, 2000, is an apparent outlier because it is approximately twice the magnitude of the next greatest value and does not match the temporal pattern observed with the $PM_{2.5}$ mass values. As such the regression analyses were performed both with and without that data point. The two sets of results are presented in Table 6-4.

Table 6-4. Comparability of the Series 8400N Monitors with the Nitrate Reference Method During Phase I

	With Outlier		**Without Outlier**	
Regression Parameter	**Monitor 1**	**Monitor 2**	**Monitor 1**	**Monitor 2**
Slope (95% CI)	0.136 (0.158)	0.122 (0.130)	0.300 (0.199)	0.372 (0.153)
Intercept (µg/m^3) (95% CI)	0.38 (0.22)	0.26 (0.19)	0.21 (0.25)	0.02 (0.17)
r^2	0.127	0.304	0.315	0.770

Table 6-4 shows that, in Phase I, both monitors exhibited a substantial negative bias relative to the reference method. Even with the August 14 data point removed, the regression slopes relative to the reference method are less than 0.4, and the r^2 values are only 0.32 and 0.77. It should be noted that the nitrate reference concentrations have not been blank corrected. As noted in Section 4.5, nitrate concentrations of field blanks for the reference method ranged from 0.2 to 0.3 µg/m^3. The negative bias seen here may be reduced if the reference measurements were corrected for field blank levels.

6.1.3 Meteorological Effects

A multivariable model, as described in Section 5.3, was used to determine if the readings of the Series 8400N monitors were affected by meteorological conditions. However, no conclusive relationship could be determined because of the weak correlation between the Series 8400N monitors and the reference measurement.

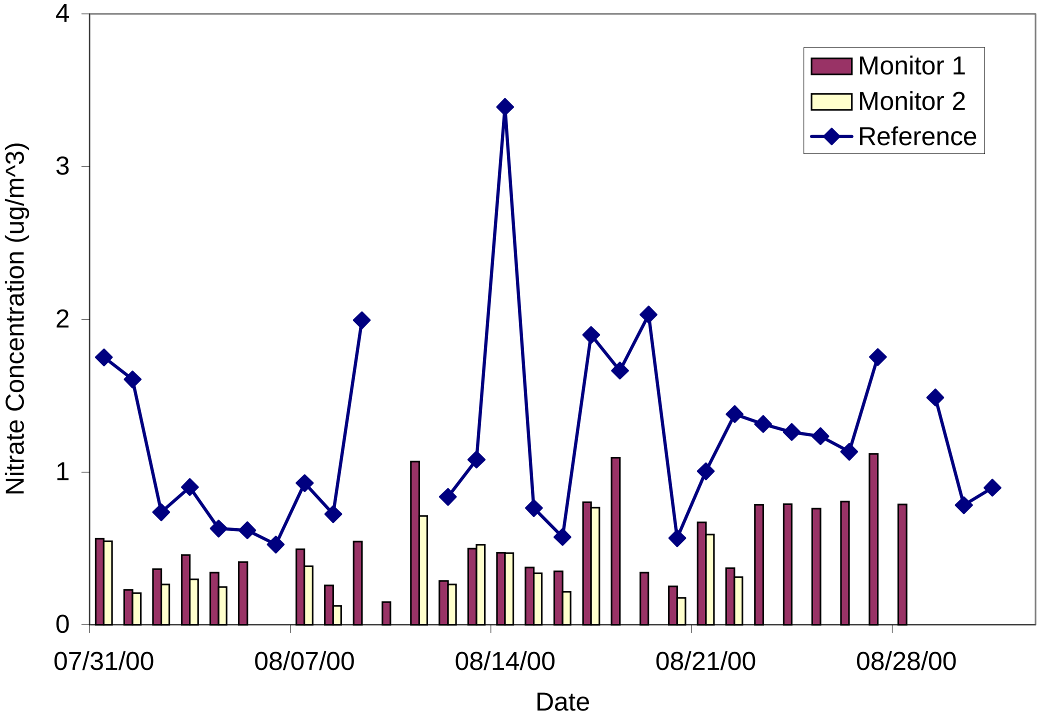

Figure 6-3a. Nitrate Reference Concentrations and 24-Hour Averages from Duplicate Series 8400N Monitors During Phase I of Verification Testing

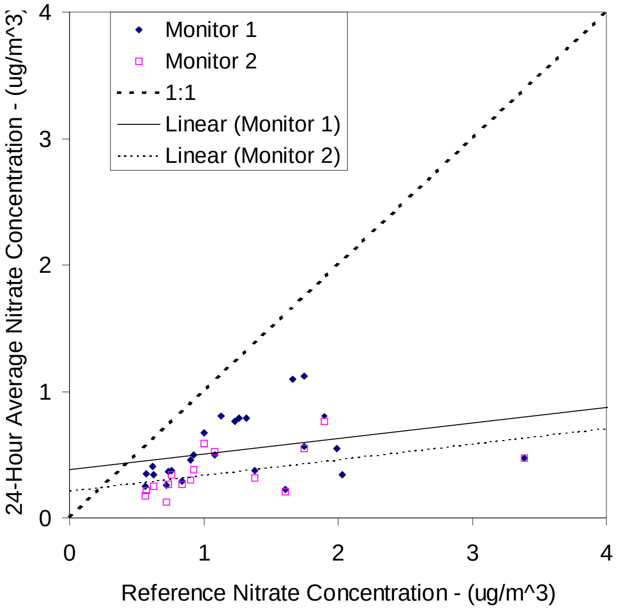

Figure 6-3b. Correlation Plot of 24-Hour Average Nitrate Concentrations from Duplicate Series 8400N Monitors and Nitrate Reference Concentrations During Phase I of Verification Testing

6.1.4 Influence of Precursor Gases

A multivariable model analysis was used to determine if precursor gas concentrations had a significant effect on the readings of the Series 8400N monitors relative to the reference measurements. Using daily average data, the model ascribed to both nitric oxide and sulfur dioxide a statistically significant influence on the readings of both monitors relative to the nitrate reference results, at the 90% confidence level. This analysis included the outlying data point identified in Section 6.1.2. The analysis shows the following relationships:

$$\text{Monitor 1} = 0.192*\text{Ref} + 0.467\ \mu g/m^3 + 0.0392*\text{NO} - 0.0375*\text{SO}_2$$

and,

$$\text{Monitor 2} = 0.167*\text{Ref} + 0.243\ \mu g/m^3 + 0.0362*\text{NO} - 0.0264*\text{SO}_2$$

where Ref is the nitrate reference measurement in $\mu g/m^3$, and the concentrations of nitric oxide and sulfur dioxide are in ppb. The relationships for Monitors 1 and 2 are quite similar, with nitric oxide and sulfur dioxide apparently exerting small and opposing effects on monitor response.

The magnitude of the apparent effects can be examined, relative to the linear regression results shown in Table 6-4. For example, using the average values for the nitrate concentration, NO, and SO_2, during Phase I (Section 6.1), the above equations would predict average nitrate values of:

$$\text{Monitor 1} = 0.192*1.2 + 0.467 + 0.0392*3.1 - 0.0375*6.9$$

$$= 0.56\ \mu g/m^3$$

and

$$\text{Monitor 2} = 0.167*1.2 + 0.243 + 0.0362*3.1 - 0.0264*6.9$$

$$= 0.37\ \mu g/m^3$$

The linear regression parameters (with the outlier included) from Table 6-4 would predict values of

$$\text{Monitor 1} = 0.136*1.2 + 0.38$$

$$= 0.54\ \mu g/m^3$$

and

$$\text{Monitor 2} = 0.122*1.2 + 0.26$$

$$= 0.41\ \mu g/m^3.$$

In both cases, the multivariable results differ little from the linear regression results, i.e., by 3.7% for Monitor 1 and by -9.8% for Monitor 2.

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

During Phase II, daily 24-hour $PM_{2.5}$ concentrations averaged 74 µg/m^3 and ranged from 4.9 µg/m^3 to 146 µg/m^3. A strong diurnal pattern was observed in the $PM_{2.5}$ concentration, with the peak levels occurring near midnight. However, the nitrate concentration shows a contrasting diurnal pattern with the peak levels occurring near mid day. Particle composition was dominated by nitrate and carbon. On average, nitrate and carbon comprised 22% and 40% of the overall daily $PM_{2.5}$ concentration, respectively. Overall, ambient nitrate levels in Phase II were about a factor of 10 higher than in Phase I. Sulfate accounted for only about 2% of the daily $PM_{2.5}$ mass in Phase II. Both nitrate and sulfate were determined by ion chromatography, and carbon was determined by the IMPROVE TOR method.

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

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

	Wind Speed (mps)	Wind Direction (Degrees)	Change in Wind Direction (Degrees)	Air Temp. (C)	RH (%)	Solar Radiation (W/m^2)	Press. (mm Hg)
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 6-6. Summary of Daily Values for the Measured Precursor Gas Concentrations During Phase II of Verification Testing

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

6.2.1 Inter-Unit Precision

As in Phase I, nitrate concentrations were measured and recorded every 10 minutes throughout Phase II by duplicate Series 8400N monitors. These data were averaged to obtain hourly averages for nitrate concentration. Figure 6-4a shows the hourly nitrate averages for the duplicate monitors recorded during Phase II of the verification testing. Breaks in the data indicate periods during which no data are available because of instrument failure or power outages. Figure 6-4a shows that the two monitors indicated very similar temporal patterns in ambient nitrate concentrations. Figure 6-4b is a scatter plot of these same data that illustrates the correlation between the two monitors in measuring particulate nitrate concentration.

The hourly data were also averaged from midnight to midnight to obtain 24-hour averages for the nitrate concentration during Phase II of the verification test. In Figure 6-5a, these 24-hour averages are presented. A correlation plot of these data is shown in Figure 6-5b.

These data were analyzed by linear regression, and the results of this analysis are presented in Table 6-7. The CV for these values was also determined according to Section 5.1, and the calculated CV is shown in Table 6-7.

The regression slopes for both hourly [slope = 1.052 (0.025)] and 24-hour data [slope = 1.089 (0.067)] indicate a statistically significant bias of less than 10% between the two monitors, with Monitor 2 reading higher than Monitor 1. However, neither intercept is significantly different from zero, and both r^2 values exceed 0.9. The inter-unit slopes and CV values in Phase II (Table 6-7) in particular are better than those found in Phase I (Table 6-3), probably as a result of the much higher nitrate concentrations present in Phase II.

Table 6-7. Linear Regression and Coefficient of Variation Results for Hourly and 24-Hour Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase II

Parameter	Hourly	24-Hour
Slope (95% CI)	1.052 (0.025)	1.089 (0.067)
Intercept (µg/m^3) (95% CI)	0.02 (0.43)	-0.42 (1.08)
r^2	0.907	0.975
CV	13.8%	8.8%

6.2.2 Comparability/Predictability

To compare with the reference samples, the hourly results from the duplicate Series 8400N monitors were appropriately averaged to correspond to the five daily sampling periods for the reference sampler. Table 6-8 summarizes the nitrate concentrations during these sampling periods. Figure 6-6a shows the reference measurements and the corresponding averages from the duplicate Series 8400N monitors for Phase II of the verification test. These same data are also shown in Figure 6-6b as a scatter plot to illustrate the correlation between the results of the duplicate Series 8400N monitors and the reference measurements.

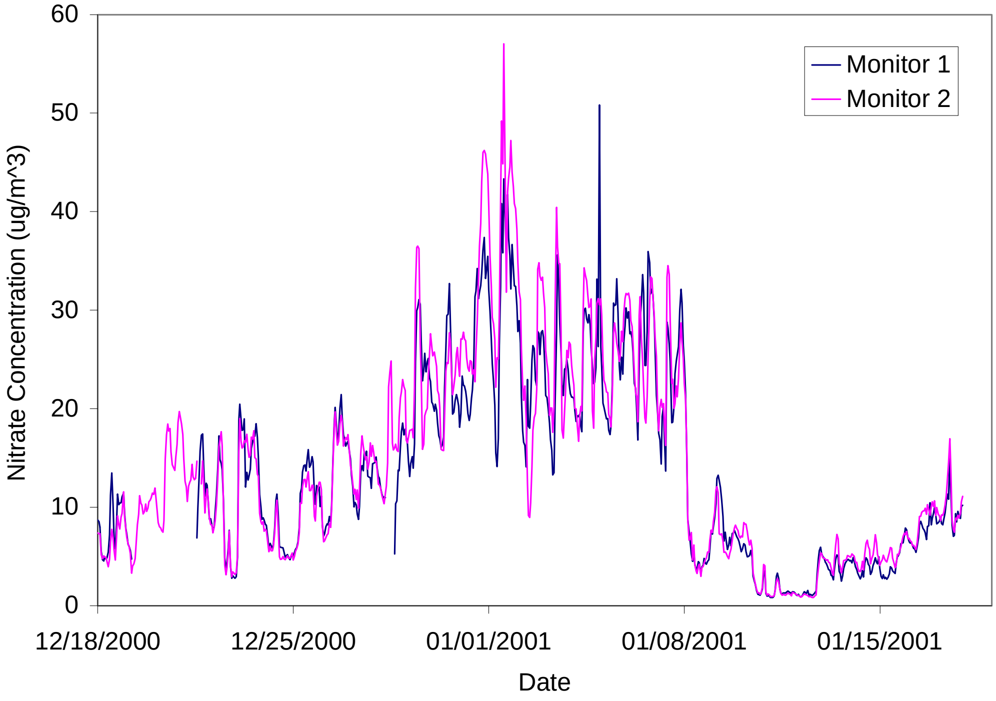

Figure 6-4a. Hourly Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase II of Verification Testing

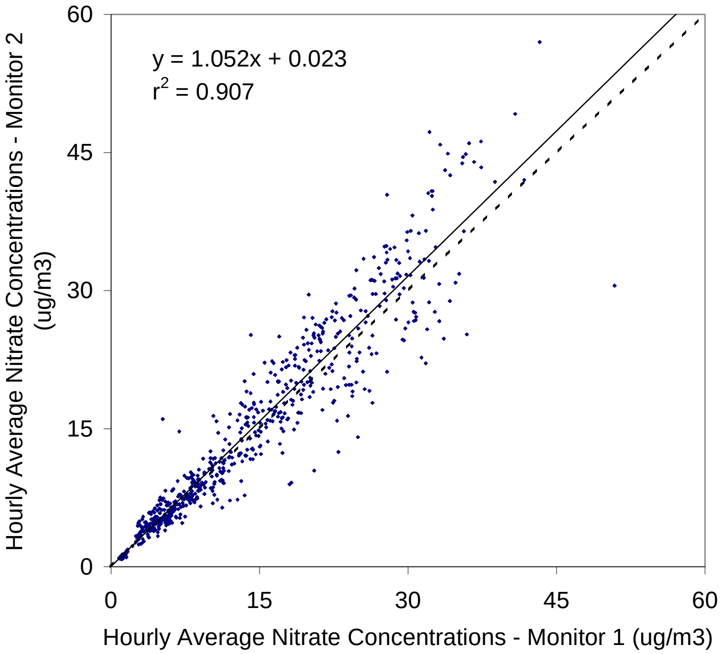

Figure 6-4b. Correlation Plot of Hourly Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase II of Verification Testing

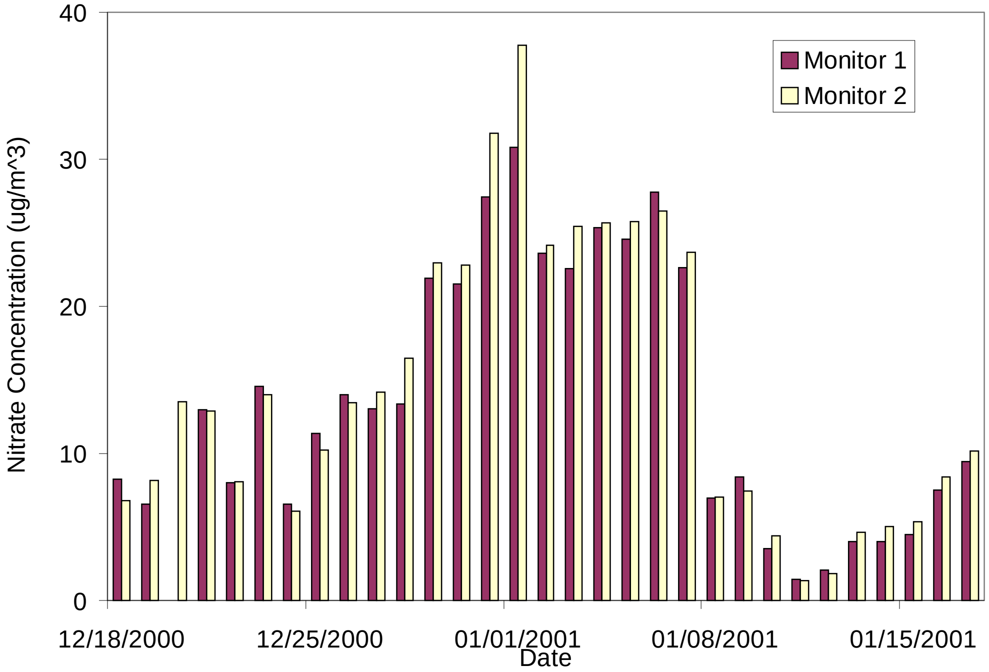

Figure 6-5a. 24-Hour Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase II of Verification Testing

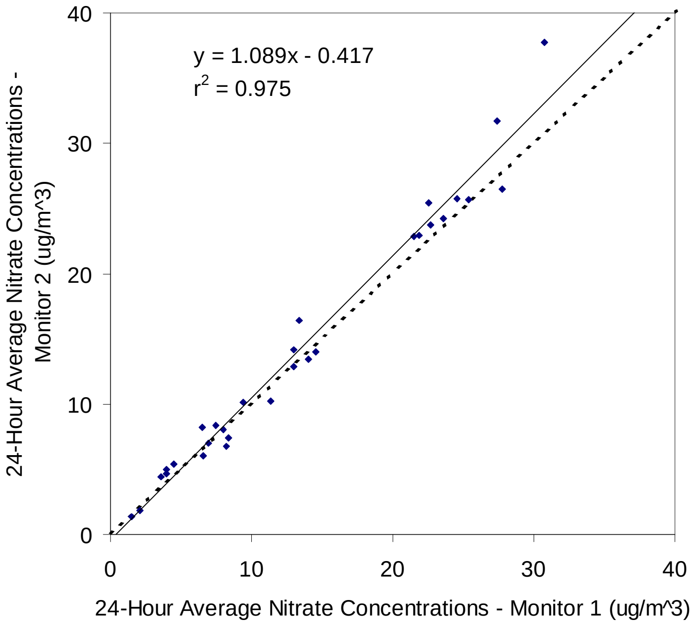

Figure 6-5b. Correlation Plot of 24-Hour Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase II of Verification Testing

Linear regression analysis of these data was performed independently for each Series 8400N monitor, and the results are presented in Table 6-9. Regression analyses were also performed separately for each of the sampling periods (i.e, 0000-0500, 0500-1000, 1000-1300, 1300-1600, and 1600-2400). These regression results are also presented in Table 6-9 for the duplicate Series 8400N monitors.

Table 6-8. Summary of Reference Nitrate Results in Phase II of Verification Testing

Nitrate Concentration ($\mu g/m^3$)	Sampling Period					
	All[a]	0000-0500	0500-1000	1000-1300	1300-1600	1600-2400
Average	17.39	13.02	12.65	23.71	19.97	17.97
Maximum	65.84	28.09	27.89	62.46	65.84	48.37
Minimum	0.47	0.47	0.86	0.58	0.57	0.56

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

Table 6-9. Comparability of the Series 8400N Monitors with the Nitrate Reference Method in 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	0.600 (0.041)	3.18 (0.94)	0.855	0.625 (0.054)	3.42 (1.22)	0.774
0000 - 0500	0.914 (0.097)	0.69 (1.50)	0.933	1.087 (0.117)	-0.34 (1.81)	0.925
0500 - 1000	0.725 (0.088)	1.97 (1.30)	0.917	0.867 (0.095)	1.19 (1.43)	0.923
1000 -1300	0.537 (0.067)	2.61 (2.05)	0.908	0.561 (0.112)	2.93 (3.37)	0.782
1300 -1600	0.600 (0.841)	1.98 (2.24)	0.892	0.573 (0.070)	2.28 (1.83)	0.909
1600 -2400	0.688 (0.116)	2.72 (2.40)	0.851	0.734 (0.154)	2.51 (3.47)	0.774

Table 6-9 shows that when all the sampling periods are considered together, the correlation between the duplicate Series 8400N monitors and the nitrate reference measurements gives $r^2 = 0.855$ for Monitor 1 and $r^2 = 0.774$ for Monitor 2. The regression results, including all the reference data, show slopes of 0.600 (0.041) for Monitor 1 and 0.625 (0.054) for Monitor 2, indicating a significant negative bias relative to the reference measurements. Inspection of Figure 6-6a shows that absolute differences between the reference and Series 8400N data were

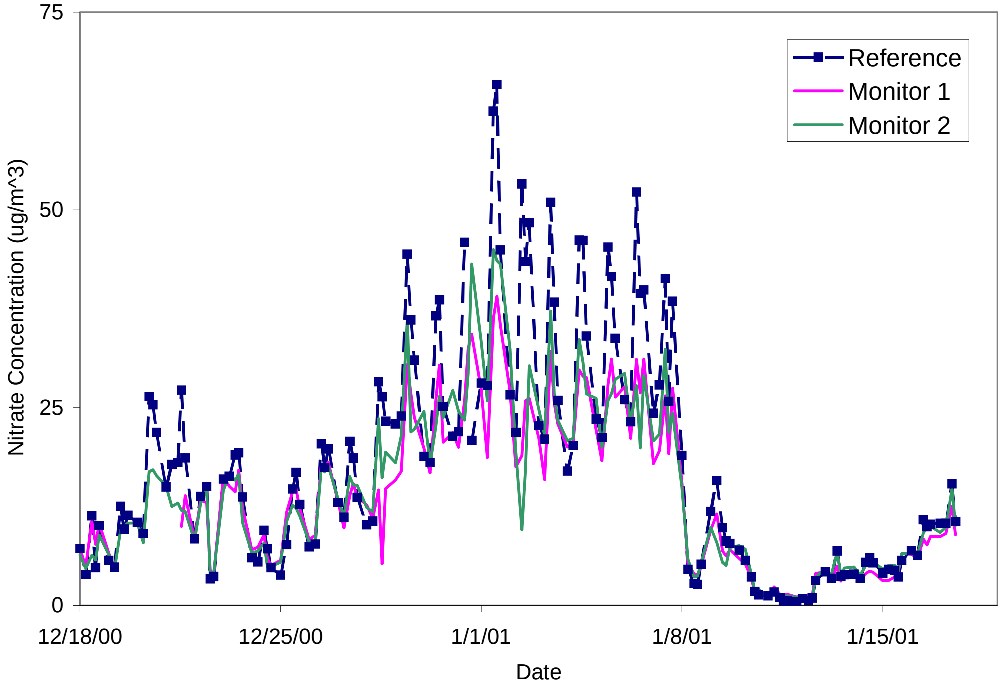

Figure 6-6a. Nitrate Concentrations from Reference Samples and Duplicate Series 8400N Monitors During Phase II of Verification Testing

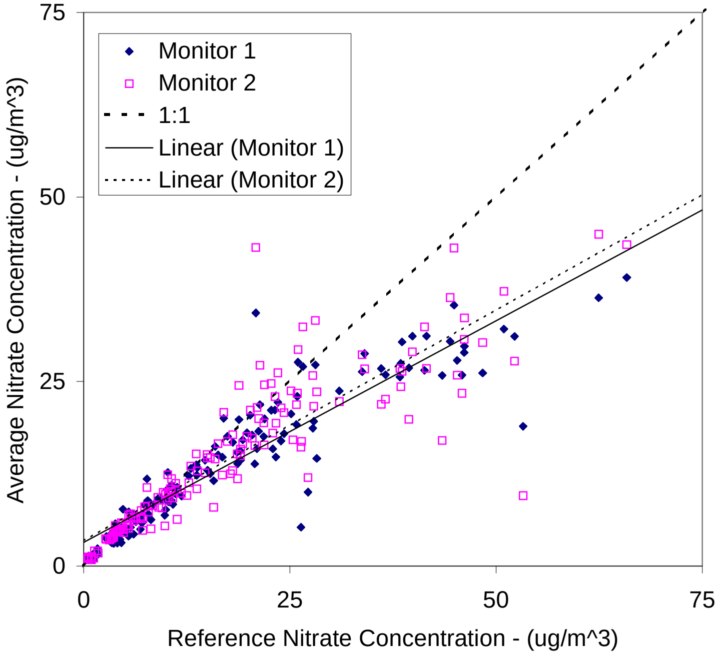

Figure 6-6b. Correlation Plot of Reference Samples and Average Nitrate Concentrations from Duplicate Series 8400N Monitors During Phase II of Verification Testing

largest when the nitrate concentrations were highest, which occurred during the mid-day sampling periods. This observation is confirmed when the five daily sampling periods are considered separately (Table 6-9). For the various sampling periods, the slopes of the regression lines vary from 0.537 to 0.914 for Monitor 1 and from 0.561 to 1.087 for Monitor 2. For both monitors, the lowest slopes relative to the reference measurements were during the mid-day sampling periods (i.e., 1000-1300 and 1300-1600).

6.2.3 Meteorological Effects

As with Phase I, a multivariable model analysis was used to determine if the meteorological conditions had an influence on the readings of the Series 8400N monitors in Phase II. This analysis involved a backward elimination process to remove from the analysis those parameters showing no statistically significant influence on the results. This analysis showed the following relationships:

$$\text{Monitor 1} = 0.715{*}\text{Ref} + 271.5 - \mu\text{g/m}^3 - 2.33{*}\text{WS} + 0.120{*}\text{RH} - 0.364{*}\text{BP}$$

and

$$\text{Monitor 2} = 0.780{*}\text{Ref} + 6.09\ \mu\text{g/m}^3 - 0.593{*}\text{T}$$

where Ref is the reference nitrate measurement in $\mu g/m^3$, WS is the average wind speed in meters per second (mps), RH is the average relative humidity in percent, BP is the barometric pressure in mm Hg, and T is the ambient air temperature in °C. Thus, the multivariable model ascribed significant effects to meteorological factors that were different for the two monitors, with Monitor 1 showing wind speed and barometric pressure effects that oppose the apparent effect of relative humidity and Monitor 2 showing only an effect of temperature.

Again, the magnitude of the apparent effects can be examined, in this case relative to the linear regression results shown in Table 6-9. For example, substituting the average values for each of the parameters from Phase II (Table 6-5) into these equations, the predicted average nitrate values would be:

$$\text{Monitor 1} = 0.715{*}16.6 + 271.5 - 2.33{*}1.43 + 0.120{*}75.4 - 0.364{*}756.2$$

$$= 13.8\ \mu\text{g/m}^3$$

and

$$\text{Monitor 2} = 0.780{*}16.6 + 6.09 - 0.593{*}8.3$$

$$= 14.1\ \mu\text{g/m}^3.$$

The overall linear regression equations (Table 6-9) predict average nitrate values of

$$\text{Monitor 1} = 0.600*16.6 + 3.18$$

$$= 13.1\ \mu g/m^3$$

and

$$\text{Monitor 2} = 0.625*16.6 + 3.42\ \mu g/m^3$$

$$= 13.8\ \mu g/m^3.$$

In both cases, the multivariable results differ little from the linear regression results, i.e., by 5.3% for Monitor 1 and by 2.2% for Monitor 2.

6.2.4 Influence of Precursor Gases

A multivariable analysis was performed to establish any statistical relationships between the measured precursor gases and the readings of the Series 8400N monitors relative to the reference measurements. This analysis also involved backward elimination of parameters that were found to have no statistical effect. The results of this analysis were that none of measured gases had a statistically significant influence on the readings of either monitor relative to the reference measurements at a 90% confidence level.

6.3 Instrument Reliability/Ease of Use

During Phase I of the verification test, several routine maintenance procedures were performed on the Series 8400N monitors. The Series 8400N monitors use high-purity nitrogen (99.99%) as a purge gas and 1 ppm nitrogen dioxide in nitrogen as a calibration gas. The purge gas cylinder was replaced several times during Phase I, and the calibration gas cylinder was replaced once. The frequency of cylinder replacement was greater than expected because of leaks in one or more of the valves in the Series 8400N monitors. These leaks were repaired by a representative of R&P approximately halfway through Phase I. Additionally, several times during Phase I, the flash strips used for the flash volatilization of nitrate were replaced in each of the monitors. Data recovery during Phase I was 80% for Monitor 1 and 44% for Monitor 2.

During Phase II, the only maintenance required for the Series 8400N monitors involved replacement of the gas cylinders. Data recovery during Phase II was 91% for Monitor 1 and 100% for Monitor 2.

6.4 Shelter/Power Requirements

The Series 8400N monitors were installed and operated inside the Battelle instrument trailer during Phase I of testing. During Phase II, the duplicate Series 8400N monitors were installed and operated in the CARB facility. It is recommended by the vendor that these monitors be operated indoors. Each monitor was run on a single 15A circuit.

6.5 Instrument Cost

The cost of the Series 8400N 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 8400N monitor is a semi-continuous particle monitor designed to provide indications of the ambient particulate nitrate concentration on a 10-minute time scale. Duplicate Series 8400N monitors were evaluated under field test conditions in two separate phases of this verification test, with widely different particulate nitrate levels. In Phase I, reference 24-hour nitrate values ranged from 0.5 to about 3.5 μg/m^3, averaging 1.2 μg/m^3. In Phase II, the corresponding range and average were 0.5 to 65 μg/m^3, and 17 μg/m^3, respectively. The duplicate monitors were operated side by side and were installed with internal $PM_{2.5}$ cyclones to provide size selection of the aerosol. The 10-minute readings of the Series 8400N monitors were averaged to one hour or longer time periods to facilitate comparisons between units and with reference results. The results from each phase of this verification test are summarized below.

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

Inter-unit precision was assessed using one-hour and 24-hour averaging of the Series 8400N data. The linear regression analysis of the hourly data from Phase I showed a slope of 0.827 (0.029), an intercept of 0.007 (0.019) μg/m^3, and an r^2 value of 0.905. The regression results of the 24-hour average data show a slope of 0.802 (0.190), an intercept of 0.008 (0.097) μg/m^3, and an r^2 value of 0.843. In both cases, a significant bias between the two monitors was indicated, with Monitor 1 reading higher than Monitor 2.

The 24-hour average results of the duplicate Series 8400N monitors from Phase I were compared to the 24-hour reference measurements by linear regression. The regression results for Monitor 1 show a slope of 0.30 (0.20), an intercept of 0.21 (0.25) μg/m^3, and an r^2 value of 0.315, when one apparent outlying reference data point was removed from the analysis. For Monitor 2, the regression results show a slope of 0.37 (0.15), an intercept of 0.02 (0.17) μg/m^3, and an r^2 value of 0.770.

Multivariable analysis provided no conclusive results about the influence of meteorological conditions on the readings of the Series 8400N monitors.

The multivariable analysis model ascribed to nitric oxide and sulfur dioxide a statistically significant (90% confidence) influence on the readings of the Series 8400N monitors relative to the nitrate reference results. The apparent effects of these two gases were small and opposing, with the result that their impact was less than 10%, relative to the linear regression results.

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

During Phase II of verification testing, with nitrate concentrations about 10 times higher than in Phase I, the inter-unit regression results of the hourly data showed a slope of 1.052 (0.025), an intercept of 0.02 (0.43), and an r^2 value of 0.907. For the 24-hour data, the regression results showed a slope of 1.089 (0.067), an intercept of -0.42 (1.08) $\mu g/m^3$, and an r^2 value of 0.975. These results indicate a bias of less than 10% between the two monitors, with Monitor 2 reading slightly higher than Monitor 1.

Comparisons to the nitrate reference samples showed regression results including all the reference data with a slope of 0.600 (0.041), an intercept of 3.18 (0.94) $\mu g/m^3$, and an r^2 value of 0.855 for Monitor 1. For Monitor 2, the regression results show a slope of 0.625 (0.054), an intercept of 3.42 (1.22) $\mu g/m^3$, and an r^2 value of 0.774. For both monitors, these results indicate a significant bias relative to the reference measurements. For the various sampling periods, the slopes of the regression lines ranged from 0.537 to 0.914 for Monitor 1 and from 0.561 to 1.087 for Monitor 2. The best agreement with the reference measurements was seen during the night-time and early morning sampling periods (i.e., 0000-0500 and 0500-1000), and the worst agreement during the mid-day sampling periods (1000-1300 and 1300-1600), when nitrate levels were highest.

Multivariable analysis showed different results in terms of the influence of meteorological parameters on the duplicate monitors. For one monitor, the wind speed, relative humidity, and barometric pressure had a statistical effect; and, for the other monitor, only ambient temperature had a statistical effect on the readings relative to the reference measurements. The apparent effects were small, i.e., 5% difference or less relative to the simple linear regression results. None of the measured precursor gases had a statistically significant influence on the readings of either monitor at a 90% confidence level.

Chapter 8
References

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

2. *Project Overview: 1995 Integrated Monitoring Study Design, Operations, Measurements, and Post-Field Activities*, Report No.: 026.22-98.2., California Air Resources Board, July 1999.

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

4. *Particulate Matter ($PM_{2.5}$) Speciation Guidance*, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 7, 1999.