

**DEVELOPMENT OF FINE PARTICULATE EMISSION FACTORS AND
SPECIATION PROFILES FOR OIL- AND GAS-FIRED COMBUSTION
SYSTEMS**

**TOPICAL REPORT: TEST RESULTS FOR A COMBINED CYCLE POWER PLANT
WITH OXIDATION CATALYST AND SCR AT SITE ECHO**



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**TOPICAL REPORT: TEST RESULTS FOR A COMBINED CYCLE POWER PLANT
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Prepared by:

Glenn C. England, Stephanie Wien, Thomas P. McGrath and David Hernandez
GE Energy and Environmental Research Corporation
18 Mason
Irvine, CA 92618

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This report presents test results obtained on one source measured at two nominal operating conditions with different sources of emissions using an experimental dilution measurement technique. The test results are not necessarily representative of the emissions from the source category, or the typical operation of the specific source tested, and should be interpreted as preliminary measurements from the specific source at the measured operating conditions. Also, the test results should be qualified by carefully considering the limited number of tests, background levels and other data quality issues detailed in this report.

Although the report includes preliminary emission factors generated from these test results, it must be recognized that these emission factors were developed using the experimental dilution measurement technique, not regulatory approved test methods. Emission factors developed with the regulatory approved test methods may be substantially different for specific pollutants. Thus, GE Energy does not support or recommend the use of these emission factors for regulatory purposes, permitting or commercial use. The data in this report may be useful for future refinement and validation of the experimental dilution method for specific applications so that it may be applied in future tests to develop more robust emission factors.

The dilution sampling and ambient air methods used in this test to characterize stack emissions were previously applied on stationary combustion sources for research purposes. They are not currently approved by any regulatory agency for demonstrating compliance with existing regulatory limits or standards. Further tests are needed to properly validate these methods for stationary combustion sources, especially for extremely low pollutant concentrations characteristic of gas-fired sources.

The emission factors developed from this test are source-specific for the time and conditions of this test (see table below); therefore, they do not necessarily represent emission factors for typical operation of this specific source or the general population of similar sources. The emission factors are not representative of combustion turbines, combined cycle plants, or duct burners. These emission factors are considered for information only in support of the dilution test method for measurement of fine particulate matter, and the test methods described herein continue to be in the developmental phase. No conclusions may be drawn from use of the dilution test method for pollutants other than fine particulate matter.

SITE ECHO OPERATING CONDITIONS ^(a)

	Hi-Run 1	Hi-Run 2	Hi-Run 3	Hi-Run 4	Lo-Run 1	Lo Run 2	Lo-Run 3
GT (Load) (%)	100	98	100	100	59	59	59
Duct Burner	OFF	OFF	OFF	OFF	OFF	OFF	OFF
SCR	ON	ON	ON	ON	ON	ON	ON
Oxidation Catalyst	ON	ON	ON	ON	ON	ON	ON

(a) Values are based on average megawatt values calculated over the 6-hour test run period.

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GE ENERGY AND ENVIRONMENTAL RESEARCH CORPORATION

PROJECT TEAM MEMBERS

Glenn England, Project Manager
Stephanie Wien, Project Engineer
Dr. Oliver M.C. Chang, Project Engineer
Thomas P. McGrath, Senior Engineer
Prof. Judith Chow, Desert Research Institute
Prof. John Watson, Desert Research Institute
Prof. Barbara Zielinska, Desert Research Institute
Prof. Lynn Hildemann, Stanford University
Prof. Philip Hopke, Clarkson University
Prof. Glen Cass, Georgia Institute of Technology

AD HOC COMMITTEE MEMBERS

Dr. Karl Loos, Shell Global Solutions (US) Inc.
Prof. James Schauer, University of Wisconsin-Madison
Dr. Praveen Amar, NESCAUM
Thomas Logan, U.S. EPA
Ron Myers, U.S. EPA
Karen Magliano, California Air Resources Board

PROJECT SPONSORS

Kathy Stirling, U.S. Department of Energy National Energy Technology Laboratory
Marla Mueller, California Energy Commission
Dr. Paul Drayton, Gas Research Institute
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FOREWORD

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM_{2.5}). PM_{2.5} in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and/or incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. These deficiencies in the current methods can have significant impacts on regulatory decision-making. The current program was jointly funded by the U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) to provide improved measurement methods and reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM_{2.5} concentrations. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source apportionment and source receptor analysis for PM_{2.5} NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

The goals of this program were to:

- Develop improved dilution sampling technology and test methods for PM_{2.5} mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.
- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source-receptor and source apportionment analysis;
- Identify and characterize PM_{2.5} precursor compound emissions that can be used in source-receptor and source apportionment analysis.

This report is part of a series of progress, topical and final reports presenting the findings of the program.

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EXECUTIVE SUMMARY

BACKGROUND

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (μm)—referred to as PM_{2.5}. PM_{2.5} in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. Primary aerosol includes both filterable particles that are solid or liquid aerosols at stack temperature plus those that form as the stack gases cool through mixing and dilution processes in the plume downwind of the source. These deficiencies in the current methods can have significant impacts on regulatory decision-making. PM_{2.5} measurement issues were extensively reviewed by the American Petroleum Institute (England et al., 1998), and it was concluded that dilution sampling techniques are more appropriate for obtaining a representative particulate matter sample from combustion systems for determining PM_{2.5} emission rate and chemical speciation. Dilution sampling is intended to collect primary aerosols including those that condense and/or react to form solid or liquid aerosols as the exhaust plume mixes with ambient air and cools to near-ambient temperature immediately after the stack discharge. These techniques have been widely used in recent research studies. For example, Hildemann et al. (1994) and McDonald et al. (1998) used filtered ambient air to dilute the stack gas sample followed by 80-90 seconds residence time to allow aerosol formation and growth to stabilize prior to sample collection and analysis. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source-receptor and source apportionment analysis for PM_{2.5} NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

The overall goals of this program were to:

- Develop improved dilution sampling technology and test methods for PM_{2.5} mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.
- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source-receptor and source apportionment analyses.
- Identify and characterize PM_{2.5} precursor compound emissions that can be used in source-receptor and source apportionment analyses.

This report is part of a series of progress, topical and final reports presenting the findings of the research program. The research program includes field tests at several different types of gas- and oil-fired combustion sources, pilot-scale tests to help develop an improved measurement technology and methods, and technology transfer activities designed to disseminate results and incorporate scientific peer review into project plans and results. The reports present results and identify issues, procedures, methods and results that can be useful for future studies.

TEST PROGRAM

Particulate emission measurements were performed using an innovative dilution sampling protocol on a supplementary-fired natural gas combined cycle power plant (NGCC-SF) employing a heavy-duty gas turbine, heat recovery steam generator (HRSG), steam turbine and post-combustion emission controls. The gas turbine is equipped with a lean premix combustion system for oxides of nitrogen (NO_x) emissions control. The HRSG is equipped with natural gas-fired duct burners for additional steam production (although these were off during all tests), an oxidation catalyst for reduction of carbon monoxide emissions followed by a selective catalytic reduction system for reduction of NO_x emissions. Particulate and particulate precursor emission measurements were made at the stack downstream of the HRSG and emissions controls systems. Thus, the results do not represent emissions from the gas turbine alone. Separate tests were conducted at full load and at low load conditions. The flue gas temperature at the stack measurement location averaged approximately 219 degrees Fahrenheit (°F) at full load and 206 °F at low load during the tests.

The dilution sampler used in these tests follows the well-characterized Hildemann et al. (1989) design. The sampler simulates the cooling and dilution processes that occur in the plume immediately downwind of a combustion source, so that organic compounds and other substances that condense and/or react under ambient conditions will be collected as particulate matter. The stack gas sample was extracted and diluted continuously with filtered ambient air in the sampler prior to sample collection. Generally accepted ambient air sample collection and analysis protocols and methods for PM_{2.5} mass and chemical speciation were used after the sample was diluted. It should be noted that whereas dilution sampling is widely accepted for demonstrating compliance with mobile source particulate emission standards and for stationary source receptor and source apportionment analysis, it is not currently accepted by regulatory agencies for demonstrating compliance with stationary source particles with aerodynamic diameter smaller than 10 µm—referred to as PM₁₀—emission standards or permit limits. Widely accepted, standardized procedures for stationary source dilution sampling do not currently exist. Concurrent measurements also were made using a newly developed dilution sampler based on the Hildemann concept but with faster mixing, shorter residence time and lower sample flow rate. The new sampler design, intended to be more practical for routine stationary source stack emissions sampling, was developed in a separate task of this program. The concurrent tests provide a preliminary assessment of the new sampler performance compared to the benchmark Hildemann design.

Seven six-hour test runs were performed at the stack on separate, consecutive days with duct burners off. Full load runs were conducted at 98 to 100 percent of rated capacity; low load tests were performed at 59 percent of rated capacity, with duct burners off during all tests. Although the process operating conditions were steady during the tests, the results may not represent any particular or typical operating condition at this facility, but rather are the average of the operating conditions during the test. Because the results are based on a single test of a single unit, the emission factors may not be representative of the full population of similar plants and may best be used in conjunction with similar test results from other units to develop more robust, reliable emission factors.

FINDINGS

The main findings of this test are:

- The majority of elements and organic compounds were detected at levels comparable to the ambient air or background levels in the dilution system, and/or were near the minimum detection limits of the test methods. This indicates that the levels of these substances measured in the stack samples are not distinguishable from the ambient air or measurement background levels¹. These findings strongly indicate the need for further development and validation of the dilution apparatus and method for measuring the extremely low concentrations of such substances that may be present in the stack emissions from gas-fired combustion sources.
- Particulate mass emissions from this NGCC-SF (including post-combustion emission controls) are extremely low, qualitatively consistent with levels expected for gaseous fuel combustion based on published emission factors and other independent tests. The low particulate and related pollutant concentrations in the exhaust from the plant contribute to moderate uncertainties in most of the emission factors derived from these test results.
- The average source-specific PM_{2.5} mass emission factor obtained using dilution sampling is 0.00013 pounds of pollutant per million British thermal units of gas fired (lb/MMBtu), which is approximately 1/50 of the published AP-42 particulate matter emission factor for similar sources. The test result is consistent with other tests of stationary gas-fired sources using dilution methods. Previous tests suggest the difference is largely due to measurement artifacts associated with the published emission factors (conversion of gaseous sulfur dioxide to solid sulfate residue in the iced impinger method, excessive condensation of vapors that would not occur under ambient conditions) and other limitations (inadequate sensitivity of the hot filter method) of the hot filter/iced impinger methods. Therefore, dilution sampling results are considered the most representative of actual PM_{2.5} emissions during this test.
- Tests performed with dilution sampling at high load and low load show that the difference in PM_{2.5} concentrations is small, within the uncertainty of the average result (± 41 percent, or ± 0.00006 milligrams per dry standard cubic meter, at the 95 percent confidence level).
- Tests performed comparing a new dilution sampler design to an established benchmark design showed agreement within the uncertainty bounds of the results. The estimated accuracy of the new dilution sampler design is 19 percent and estimated precision is 27 percent compared to the benchmark design.
- Organic and elemental carbon comprise approximately 71 and 1.8 percent of the average reconstructed PM_{2.5} mass, respectively, as measured using the dilution sampler. However, it is likely that the organic carbon results are biased high due to an organic adsorption artifact on the quartz fiber filters used for sample collection, which is more pronounced for clean sources such as gas combustion. Back-up filter results indicate that

¹ Note that this method was previously used to measure such pollutants at Site Bravo. At Site Bravo, a dilution sampler blank was not collected and analyzed; however, the measured stack concentrations of these substances at Site Echo and Site Bravo are similar. Further, many of the substances measured in the stack at site Bravo are indistinguishable from the ambient and field blanks collected at the site. Therefore, the levels measured in the stack samples at site Bravo for elemental and organic compounds may also be due to measurement background.

59 to 136 percent of the measured organic carbon may be due to this artifact. Further research is needed to improve the reliability of organic carbon measurements.

- Sulfate, chloride, nitrate, ammonium and soluble sodium account for approximately 25 percent of the reconstructed PM_{2.5} mass. Sulfate alone accounts for approximately 11 percent of the total PM_{2.5} mass.
- The reconstructed PM_{2.5} mass based on the sum of all measured chemical species is 2.5 times higher than the measured PM_{2.5} mass. The difference lends further support to the likelihood of a positive bias in the organic carbon measurement due to measurement artifacts.
- Emission factors for secondary particle precursors are low and qualitatively consistent with published emission factors for gaseous fuel combustion, other literature, and previous plant test results.
- Additional tests on other similar sources are recommended to corroborate the results and findings from this test and verify dilution sampling method performance. The results of this test provide a plausible upper bound for the measured emissions.
- Exploratory measurements using a commercial laser photometer to measure real-time PM_{2.5} trends in the diluted sample and ambient air were made to determine if the technique could be used to optimize the filter mass loadings in the dilution sampler and to determine if any correlation between ambient PM_{2.5} and stack PM_{2.5} trends could be established. Results were equivocal because large swings in the stack laser photometer response could not be related to stack PM_{2.5} or any other measurements. Further evaluation of the technique is needed to assess whether it can be useful in this type of application.
- Further refinement and testing of the dilution sampling equipment and procedures is needed to minimize procedural errors and improve knowledge of method precision and accuracy.

The data in this report were developed using an experimental dilution test method applied to one source operating under two nominal conditions with different sources of emissions that are not necessarily representative of the source category or the typical operation of the specific source tested. Accordingly, GE Energy does not recommend using any emissions factors contained herein for any regulatory and/or commercial applications. The data in this report may be useful for future refinement and validation of the experimental dilution method for specific applications so that it may be applied in future tests to develop more robust emission factors.

1. PROJECT DESCRIPTION

PROJECT OVERVIEW

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (μm) referred to as PM_{2.5}. PM_{2.5} in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. Primary aerosol includes both filterable particles that are solid or liquid aerosols at stack temperature plus those that form as the stack gases cool through mixing and dilution processes in the plume downwind of the source. These deficiencies in the current methods can have significant impacts on regulatory decision-making. PM_{2.5} measurement issues were extensively reviewed by the American Petroleum Institute (API) (England et al., 1998), and it was concluded that dilution sampling techniques are more appropriate for obtaining a representative particulate matter sample from combustion systems for determining PM_{2.5} emission rate and chemical speciation. Dilution sampling is intended to collect aerosols including those that condense and/or react upon cooling and dilution in the ambient air to form solid or liquid aerosols immediately after discharge from the stack. These techniques have been widely used in recent research studies. For example, Hildemann et al. (1994) and McDonald et al. (1998) used filtered ambient air to dilute the stack gas sample followed by 80-90 seconds residence time to allow aerosol formation and growth to stabilize prior to sample collection and analysis. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source-receptor and source apportionment analysis for PM_{2.5} NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

Dilution sampling was used to collect particulate emissions data from a supplementary-fired natural gas combined cycle power plant (NGCC-SF) at Site Echo from May 9 to May 21, 2003. The combined cycle process included a heavy-duty gas turbine and heat recovery steam generator (HRSG) equipped with duct burners for supplementary heat input, oxidation catalyst for carbon monoxide (CO) emission reduction, and selective catalytic reduction (SCR) for NO_x emission reduction. The U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the API jointly funded the tests. This research program is designed to provide reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM_{2.5} concentrations.

The goals of this research program were to:

- Develop improved dilution sampling technology and test methods for PM_{2.5} mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.
- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source-receptor and source apportionment analyses.
- Identify and characterize PM_{2.5} precursor compound emissions that can be used in source-receptor and source apportionment analyses.

PROJECT OBJECTIVES

The overall goals of this test were to compare results obtained using two different dilution sampler designs and to characterize speciated PM_{2.5} and precursor emissions from an NGCC-SF. The specific test objectives were to:

- Compare PM_{2.5} measurements using two dilution sampler designs: the original Desert Research Institute (DRI) design based on Hildemann et al. (1989); and a new design based on the same concept (dilution + mixing + aging) but with lower residence time and a different geometric configuration intended to make the equipment more portable and practical for routine emission testing;

- Provide an extensive set of speciated primary fine particle emissions data for a NGCC-SF equipped with a supplementary fired HRSG, oxidation catalyst, and SCR that can be used in source receptor, source apportionment and other analyses;
- Compare PM_{2.5} mass measured at base load with duct burners off and at reduced load with duct burners off;
- Develop emission factors and speciation profiles for organic aerosols and PM_{2.5} mass for use in source receptor and source apportionment analysis;
- Characterize sulfate (SO₄⁻), nitrate (NO₃⁻), ammonium (NH₄⁺), inorganic elements, elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media in the dilution sampler;
- Characterize key secondary particle precursors in stack gas samples: volatile organic compounds (VOC) with carbon number of 7 and above, sulfur dioxide (SO₂); oxides of nitrogen (NO_x), and ammonia (NH₃) using ambient air methods with the dilution sampler;
- Characterize selected hazardous air pollutants (e.g., benzene, toluene, xylenes and formaldehyde) using ambient air methods with the dilution sampler;
- Quantify semivolatile organic compound (SVOC) species that contribute to organic particle constituents (for PM_{2.5} source apportionment);
- Compare emission factors based on the test results with emission factors currently available in the open literature; and
- Identify issues associated with particulate measurement from sources with relatively dilute exhaust streams.

TEST OVERVIEW

The scope of testing is summarized in Table 1-1. Two different dilution samplers, designated Alpha and Beta, were used for measurements. These samplers are described in Section 3. The emissions testing included simultaneous collection and analysis of both source level (undiluted) and diluted stack gas samples. All stack gas samples were collected from the stack of the unit downstream of all combustion processes and emission controls. The samples were analyzed for the compounds listed in Table 1-2. Process data and fuel gas samples were collected during the tests to document operating conditions.

Table 1-1. Test Matrix for Site Echo.

Sampling Location	No. of Test Runs (Total)	Sample Type/ Parameter	Sampling/ Test Method	Equipment	Sample Run Time (min)	Analytical Method/ Principle
Unit Stack	7 (4 at base load; 3 at low load)	Flue Gas/ PM2.5 (mass, OC/EC, elements, ions)	DS (Filter packs)	Alpha and Beta dilution samplers	360	Gravimetry, TOR, XRF, IC
		Flue Gas/ SO ₂	DS (K ₂ CO ₃ filter pack)	Alpha and Beta dilution samplers	360	IC
		Flue Gas/ NH ₃	DS (citric acid filter pack)	Alpha and Beta dilution samplers	360	Colorimetry
		Flue Gas/ NH ₃	BAAQMD ST-1B	Iced impinger train	240	IC
		Flue Gas/ aldehydes	DS (DNPH cartridges)	Alpha dilution sampler	360	HPLC
		Flue Gas/ VOC	DS (Canister)	Alpha dilution sampler	360	GCFID
		Flue Gas/ SVOC	DS (TIGF/ PUF/ XAD)	Alpha dilution sampler	360	GCMS
		Flue Gas/ Velocity, Flowrate	EPA Method 1, 2 (40CFR60 Appendix A)	Pitot tube	10*	Water Manometer
		Flue Gas/ Moisture	EPA Method 4 (40CFR60 Appendix A)	Iced impinger train	240	Gravimetric
		Flue Gas/ O ₂ , CO ₂ , CO, NO _x	40CFR60 Appendix B	Continuous monitors	360	Paramagnetism, NDIR, Electrochemical cell, Chemiluminescence
Ambient Air (Combustion inlet)	1	Ambient/ PM2.5 (mass, OC/EC, elements, ions)	DS (Filter packs)	Samplers	360	Gravimetry, TOR, XRF, IC
		Ambient/ VOC	DS (Canister)	Samplers	360	GCFID
		Ambient/ SO ₂	DS (K ₂ CO ₃ filter pack)	Samplers	360	IC
		Ambient/ NH ₃	DS (citric acid filter pack)	Samplers	360	IC
		Ambient/ aldehydes	DS (DNPH cartridges)	Samplers	360	HPLC
		Ambient/ SVOC	DS (TIGF/ PUF/ XAD)	Samplers	360	GCMS
Natural Gas Header	4 (2 at high load, 2 at low load)	C1-C6 hydrocarbons, Gross Btu, Sulfur Species	Silica coated canisters	Grab	GC-FID, FPD	

* Velocity measured pre- and post-dilution sampler operation
 DNPH: dinitrophenylhydrazine
 DS: dilution sampler
 GCMS: gas chromatography/ mass spectrometry
 HPLC: high performance liquid chromatography
 IC: ion chromatography
 ICP-MS: inductively coupled plasma-mass spectrometry
 FPD: flame photometric detector

NDIR: Non-Dispersive Infrared Spectroscopy
 PUF: polyurethane foam
 TIGF: Teflon impregnated glass fiber filter
 TOR: thermal-optical reflectance
 XRD: x-ray diffraction
 XRF: x-ray fluorescence
 FID: flame ionization detector

Table 1-2. Summary of Analytical Targets (Site Echo).

Table 1-2. Summary of Analytical Targets.

Parameters	In-Stack		Dilution Sampler									
	Impingers	Gases	Quartz Filter	TIGF/PUF /XAD-4	TMF	SS Cans	DNPH	K ₂ CO ₃ Filter	Citric acid Filter	Gases	Dust Trak	Fuel
PM2.5 mass					A,B						A	
Sulfate			A,B									
Chloride			A,B									
Ammonium			A,B									
Nitrate			A,B									
Elements					A,B							
Organic carbon			A,B									
Elemental carbon			A,B									
Semivolatile organic compounds				A								
Volatile organic compounds						A						
Carbonyls							A					
Ammonia (gaseous)	X								A,B			
NO _x		X										
SO ₂								A				
CO		X										
O ₂		X										
CO ₂		X										
Moisture or relative humidity	X									A,B		
Velocity		X										
Temperature		X								A,B		
C1-C6 Hydrocarbons												X
Sulfur Species												X
Gross (higher) heating value												X

SS Cans = stainless steel evacuated canisters

DNPH: dinitrophenylhydrazine

TMF = Teflon[®] membrane filter

TIGF = Teflon[®]-impregnated glass fiber filter

A = Alpha dilution sampler

B = Beta dilution sampler

Source Level (Undiluted Exhaust Gas) Samples

Direct extractive integrated sampling for NH₃ was performed using a traditional wet impingement method.

Diluted Exhaust Gas Samples

Dilution sampling was used to characterize PM2.5 including aerosols formed in the near-field plume. The dilution sampler extracted a raw stack gas sample stream from the stack into a mixing chamber, where it was diluted approximately 30:1 with ambient air purified by passing through a high efficiency particulate air (HEPA) filter and activated carbon. Because PM2.5 behaves aerodynamically almost like a gas at typical stack conditions, the samples were extracted anisokinetically from a single sampling point. A slipstream of the mixed and diluted sample was conveyed to a residence time chamber where it resided for approximately 70 seconds

in the Alpha sampler and 10 seconds in the Beta sampler to allow time for low-concentration aerosols, especially organics, to condense and grow. The diluted and aged sample then passed through cyclone separators sized to remove particles larger than 2.5 μm , after which samples were collected on various media:

- High-purity quartz fiber filters (QFFs) for ions and carbon speciation;
- Teflon[®] membrane (TMF) for PM_{2.5} mass and elements;
- Potassium carbonate (K₂CO₃)-impregnated cellulose fiber for SO₂;
- Citric acid-impregnated cellulose fiber for NH₃;
- Organic sample media (Alpha sampler only):
 - Teflon[®]-impregnated glass fiber (TIGF) filters for particle phase SVOCs;
 - Polyurethane foam (PUF)/Amberlite[®] sorbent resin (XAD-4[™])/PUF cartridge to collect gas phase SVOCs;
 - Stainless steel canisters to capture VOCs with a carbon number greater than two; and
 - Dinitrophenylhydrazine (DNPH)-coated silica gel cartridges to capture carbonyls (aldehydes).

Emissions measurements using the two dilution samplers were performed simultaneously. Four runs at base load (100 percent of base load) with duct burners off and three runs at reduced load (59 percent of base load) with duct burners off were collected over six hours on seven separate test days. An ambient air sample was collected to establish background concentrations of measured substances. The same sampling and analysis procedures used for the dilution sampler were applied for collecting ambient air samples.

Process Samples

Several natural gas samples were collected over the course of the test series and analyzed for specific gravity, heating value, sulfur (S) content and hydrocarbon speciation.

KEY PERSONNEL

GE Energy and Environmental Research Corporation (GE EER) had primary responsibility for the test program. Key personnel and managers involved in the tests were:

- Glenn England (GE EER) – Program Manager (949) 859-8851 ext. 136
- Stephanie Wien (GE EER) – Project Engineer
- Bob Zimperman (GE Mostardi-Platt Associates) – Field Team Leader
- Neal Conroy (GE Mostardi-Platt Associates) – Dilution Tunnel Sampling Leader
- Aaron McGushion (GE EER) – Project Engineer
- Judith Chow, John Watson, and Barbara Zielinska (DRI) – Consulting and Laboratory Analysis
- Karl Loos (Shell Global Solutions (US) Inc.) – API Work Group Chairman
- Karin Ritter (API) – API Project Officer
- Paul Drayton (GRI) – GRI Project Manager
- Marla Mueller (CEC) – CEC Project Manager
- Kathy Stirling (DOE/NETL) – DOE Contracting Officer’s Representative
- Barry Liebowitz (NYSERDA) – NYSERDA Project Manager

2. PROCESS DESCRIPTION

The host facility for this test cogenerates both process steam for a nearby manufacturing facility and electricity for sale to the grid. The facility is rated for a base load power output of 512 megawatt (MW). It can produce a peak-load power output of 554 MW (at ambient temperature of 90 degrees Fahrenheit (°F)). The plant employs two heavy-duty gas turbines and one steam turbine in a combined cycle arrangement. The hot exhaust gases from each gas turbine pass through a separate HRSG before venting to the atmosphere via the stack (Figure 2-1). The HRSG is equipped with supplementary firing for additional steam production and post-combustion emission control equipment. The unit fired natural gas during these tests. The stack is equipped with continuous emissions monitors for CO, molecular oxygen (O₂) and NO_x.

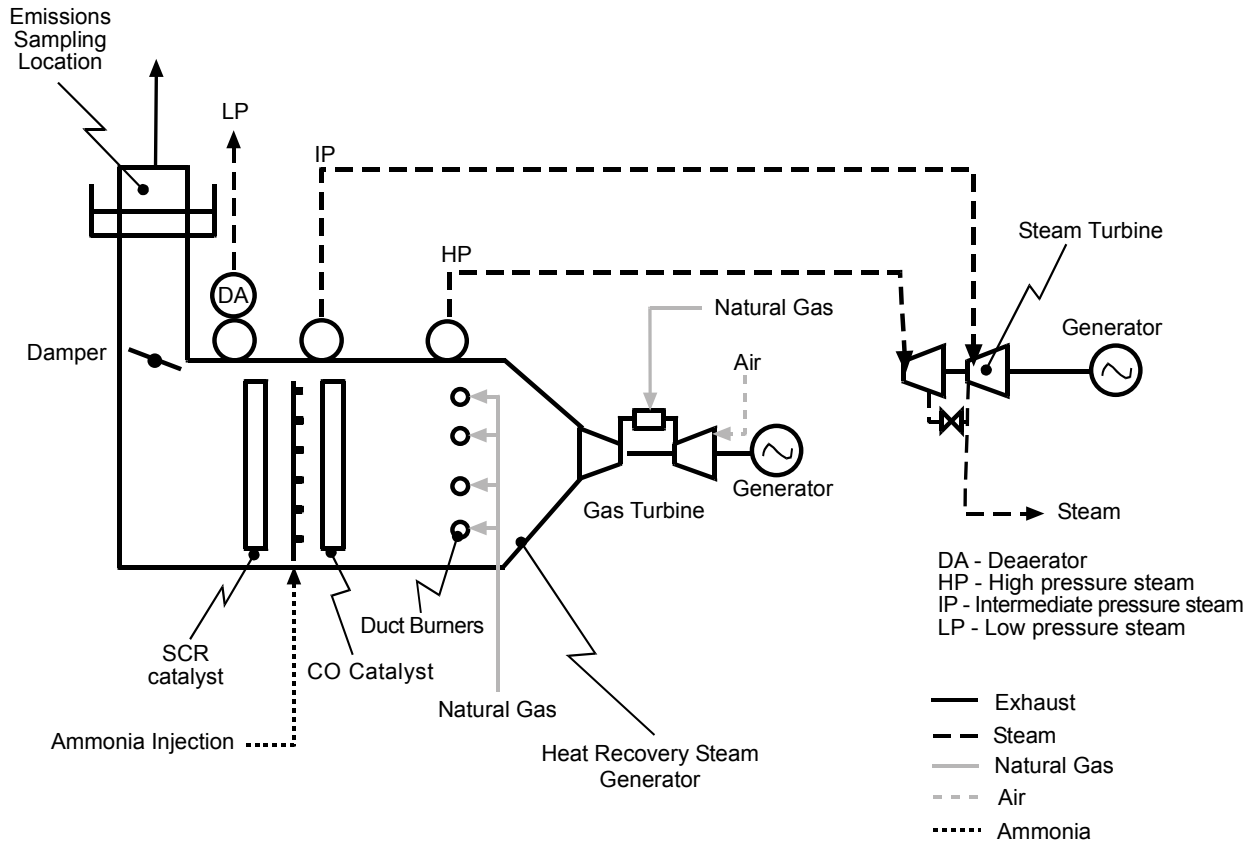


Figure 2-1. Site Echo Process Overview.

Pollution Control Equipment Description

The unit is equipped with a lean premix combustion system for NO_x emissions control over the normal operating load range. The lean premix combustion system achieves low NO_x and CO emissions by staging the fuel and air addition to achieve initial combustion under premixed, fuel-lean conditions. The remaining fuel is added downstream of the premix zone.

In addition to the lean premix combustion system, the unit has post-combustion air pollution control equipment. The HRSG is fitted with an oxidation catalyst for reduction of CO emissions followed by a SCR system for reduction of NO_x emissions. The SCR reagent, NH₃, is injected through a grid just upstream of the SCR catalyst.

SAMPLING LOCATIONS

Flue Gas Sampling Locations

The exhaust gases vent to atmosphere through a vertical, cylindrical stack that is 139 feet tall (Figure 2-2). Emissions sampling was conducted at the stack, downstream of all the pollution control equipment, which has an inside diameter of 19.5 feet (234 inches). The stack sampling location is accessed from a single circular (360 degrees) platform that is approximately 3 feet wide. The platform is approximately 140 feet above the ground and is accessed by stairs to the top of the HRSG, followed by ladders for the final 50 feet to the platform. There are seven sample ports accessible from the sampling platform. Four six-inch diameter flanged sample ports are positioned at 90 degrees to each other. The western sample port is blocked by the access ladder and considered unusable for these tests. These sample ports are located approximately 6 feet above the sampling platform. There are also three four-inch sample ports offset by 45 degrees from the six-inch ports and located at 90 degrees to each other; the ports are flanged and located 4 feet above the platform. All ports are at least 50 feet (2.5 stack diameters) downstream from the HRSG duct and 24 feet (1.2 diameters) upstream from the top of the stack, exceeding the minimum EPA Method 1 requirements for upstream and downstream disturbances. Absence of cyclonic flow and stratification was established from previous testing at this unit. A preliminary velocity check was performed prior to the tests to determine the point of average velocity. Sampling was performed with the probes located near a point of average velocity through their respective ports.

A single ambient air sample was collected adjacent to and at the same elevation as the combustion air filter inlet for the NGCC-SF.

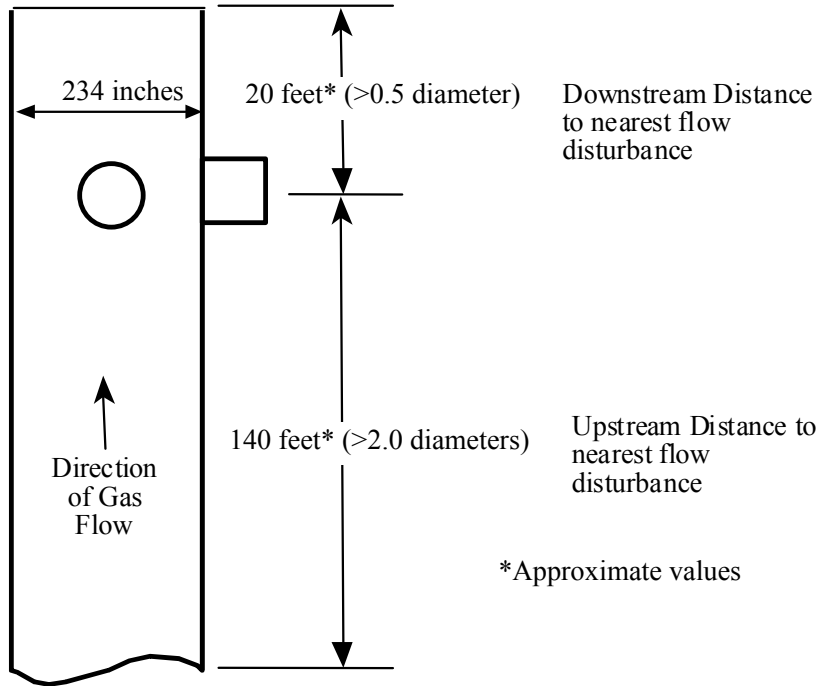


Figure 2-2. Stack sample location.

3. TEST PROCEDURES

An overview of the sampling and analysis procedures is given in Table 3-1. Figure 3-1 shows the testing chronology for the dilution sampler and in-stack methods. The time of day for the start and finish of each measurement run is shown on the figure. For example, Run 1 began at 10:40 hours and finished at 16:40 hours on Monday, May 12. The Alpha and Beta dilution samplers were tested concurrently. All samples were collected at points of average flow through their respective ports to allow for comparability of results, since it is assumed that the fine particulate will follow the gas streamlines and hence be as well-mixed as the gases. A sample run time of six hours was chosen as the longest practical sampling time in a single test day, so that sufficient material would be collected to exceed detection limits.

STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

An S-type Pitot tube (EPA Method 2) was used to determine the average stack gas velocity and volumetric flow rate. Stack gas molecular weight was calculated in accordance with EPA Method 3. Moisture content of the sample was determined based on weight gain in the impingers of the NH₃ sampling train according to EPA Method 4. A full velocity traverse of the stack was performed before and after each test to determine total stack gas flow rate.

UNDILUTED EXHAUST GAS TEST METHODS

O₂, Carbon Dioxide, CO, and NO_x

Major gases and pollutant concentrations in the stack sample were monitored using the plant's continuous emission monitoring system (CEMS), which is operated in accordance with 40 CFR 60 Appendix B, and with a portable electrochemical cell analyzer. The portable electrochemical cell analyzer measured O₂, carbon dioxide (CO₂), CO and NO_x, while the plant CEMS measured only O₂, CO and NO_x. Where duplicate measurements existed, the plant CEMS results were used for final data reduction and the portable analyzer results were used for a quality assurance (QA) check.

Table 3-1. Summary of Test Procedures (Site Echo).

Sampling Location/Type	Parameter	Sampling Method	Analytical Method	Reference	Dilution Sampler Alpha	Dilution Sampler Beta
Stack/Stack Gas	Velocity, Temperature and Flow Rate	S-type Pitot tube and thermocouple traverse	Manometer, digital thermocouple readout	U.S. EPA Method 2	--	--
	Moisture	Iced impingers	Gravimetry	U.S. EPA Method 4	--	--
	O ₂ , CO and NO _x	Portable gas analyzer and plant continuous emission monitors	Electrochemical cells; paramagnetism; NDIR; chemiluminescence	U.S. EPA Method 3A (40CFR60, App. A); U.S. EPA PS2 (40CFR60 App.B)	--	--
	NH ₃	Iced impingers with 0.1N HCl absorbing solution	ISE	BAAQMD Method ST-1B (BAAQMD, 1982)	--	--
Stack/Diluted Stack Gas	PM2.5 mass	Dilution sampler and ringed Teflon membrane filter	Gravimetry	U.S. EPA, 1999a	X	X
	PM2.5 elements	Dilution sampler and ringed Teflon membrane filter	XRF	U.S. EPA, 1999d	X	X
	PM2.5 cations/anions (SO ₄ ⁻ , Cl ⁻ , SO ₃ ⁻ , NH ₄ ⁺ , soluble Na, soluble K)	Dilution sampler and quartz fiber filter	IC	U.S. EPA, 1999a	X	X
	PM2.5 OC and EC	Dilution sampler and quartz fiber filter	TOR	SOP 2-204.6 (DRI, 2000)	X	X
	SO ₂	Dilution sampler and K ₂ CO ₃ -impregnated cellulose fiber	IC	Johnson and Atkins, 1975	X	--
	NH ₃	Dilution tunnel and citric acid-impregnated cellulose fiber	IC	Chow and Watson, 1998	X	--
	Carbonyls	Dilution sampler and DNPH-coated silica gel cartridges	HPLC	U.S. EPA Method TO-11A (U.S. EPA, 1999c)	X	--
	VOC	Dilution Sampler and Stainless steel canisters	GC with FID and ECD	U.S. EPA Method TO-15 (U.S. EPA, 1999b)	X	--
	SVOC	Dilution tunnel and TIGF/ PUF/ XAD pack	Electron impact GC with MSD and FTIR (selective ion detection)	SOP 2-750.2 (DRI, 2003)	X	--
Ground/ Ambient Air	PM2.5 mass	Ringed Teflon membrane filter	Gravimetry	U.S. EPA, 1999a	--	--
	PM2.5 elements	Ringed Teflon membrane filter	XRF	U.S. EPA, 1999d	--	--
	PM2.5 cations/anions (SO ₄ ⁻ , Cl ⁻ , SO ₃ ⁻ , NH ₄ ⁺ , soluble Na, soluble K)	Quartz fiber filter	IC	U.S. EPA, 1999a	--	--
	PM2.5 OC and EC	Quartz fiber filter	TOR	SOP 2-204.6 (DRI, 2000)	--	--
	SO ₂	K ₂ CO ₃ -impregnated cellulose fiber filter	IC	Johnson and Atkins, 1975	--	--
	NH ₃	Citric acid-impregnated cellulose fiber filter	IC	Chow and Watson, 1998	--	--
	Carbonyls	DNPH-coated silica gel cartridges	HPLC	U.S. EPA Method TO-11A (U.S. EPA, 1999c)	--	--
	VOC	Stainless steel canisters	GC with FID and ECD	U.S. EPA Method TO-15 (U.S. EPA, 1999b)	--	--
SVOC	TIGF/ PUF/ XAD pack	Electron impact GC with MSD and FTIR (selective ion detection)	SOP 2-750.2 (DRI, 2003)	--	--	

DNPH: dinitrophenylhydrazine

GCMS: gas chromatography/ mass spectrometry

HPLC: high performance liquid chromatography

IC: ion chromatography

ICP-MS: inductively coupled plasma-mass spectrometry

ISE: ion selective electrode

PUF: polyurethane foam

TIGF: Teflon impregnated glass fiber filter

TOR: thermal-optical reflectance

XAFS: x-ray absorption fine structure spectroscopy

XRD: x-ray diffraction

XRF: x-ray fluorescence

	Time	HRSG Exhaust Stack				Dilution Sampler Blank
		Velocity	CEM	Dilution Samplers	BAAQMD ST-1B: Ammonia	Dilution Samplers
09-May-03 Fri.	10:00					Dilution Sampler Blank 1
	11:00					11:00
	12:00					
	13:00					
	14:00					
	15:00					
	16:00					
	17:00					17:00
12-May-03 Mon.	9:00	9:03 - 9:11	Run 1 High	Run 1 High		
	10:00		10:40	10:40		
	11:00				Run 1 High	
	12:00				11:50	
	13:00					
	14:00					
	15:00					
	16:00	16:00 - 16:15	16:40	16:40	15:50	
17:00						
13-May-03 Tues.	12:00	12:03 - 12:13	Run 2 High	Run 2 High	Run 2 High	
	13:00		13:05	13:05	13:15	
	14:00					
	15:00					
	16:00					
	17:00				17:15	
	18:00	18:42 - 18:50				
	19:00		19:05	19:05		
20:00						
14-May-03 Wed.	13:00	9:55 - 10:11	Run 3 High	Run 3 High	Run 3 High	
	14:00		14:10	14:10	14:30	
	15:00					
	16:00					
	17:00					
	18:00				18:30	
	19:00					
	20:00	19:58 - 20:08	20:10	20:10		
21:00						
15-May-03 Thur.	11:00		Run 4 High	Run 4 High	Run 4 High	
	12:00	12:01 - 12:08	12:30	12:30	12:30	
	13:00					
	14:00					
	15:00					
	16:00				16:30	
	17:00					
	18:00	(a)	18:17	18:17		
19:00						

(a) Velocity traverse stopped due to change in load conditions

Figure 3-1. Testing Chronology for Site Echo

	Time	HRSO Exhaust Stack				Dilution Sampler Blank	Ambient Sample	Field Blank	Field Blank
		Velocity	CEM	Dilution Samplers	BAAQMD ST-1B: Ammonia	Dilution Samplers	Dilution Sampling Media	Dilution Sampling Media	BAAQMD ST-1B
17-May-03 Sat.	5:00		Run 1 Low	Run 1 Low	Run 1 Low				
	6:00	6:07 - 6:24	6:00	6:00	6:00				
	7:00								
	8:00								
	9:00								
	10:00				10:00				
	11:00								
	12:00	11:31 - 11:45	12:00	12:00					
13:00									
18-May-03 Sun.	4:00		Run 2 Low	Run 2 Low	Run 2 Low				
	5:00	5:40 - 6:09	5:45	5:45	5:45				
	6:00								
	7:00								
	8:00								
	9:00				9:45				
	10:00								
	11:00	11:31 - 11:42	11:45	11:45					
12:00									
19-May-03 Mon.	5:00		Run 3 Low	Run 3 Low	Run 3 Low				
	6:00	6:06 - 6:25	6:05	6:05	6:05				
	7:00								
	8:00								
	9:00								
	10:00				10:05				
	11:00								
	12:00	11:44 - 11:55	12:05	12:05					
13:00									
20-May-03 Tue.	7:00					Dilution Sampler Blank 2			Field Blank
	8:00					8:55			8:40
	9:00								
	10:00								
	11:00								
	12:00								
	13:00								
	14:00					14:55			
15:00							Field Blank		
16:00							16:00		
21-May-03 Wed.	8:00						Ambient Air		
	9:00						9:50		
	10:00								
	11:00								
	12:00								
	13:00								
	14:00								
	15:00						15:50		
16:00									

Dilution Sampling Media Trip Blank collected on 27-May-03.

Figure 3-1 (continued). Testing Chronology for Site Echo.

NH₃

Concentrations of NH₃ were measured using Bay Area Air Quality Management District Method ST-1B (BAAQMD, 1982). In this method, a gas sample is withdrawn from the stack through a glass probe and collected in a Greenburg-Smith impinger train (Figure 3-2). A quartz wool plug is placed in the sample nozzle to filter large particles (some small ammonium salt particles may penetrate the filter, and subsequently collected in the impingers to be counted as NH₃ gas). The sampling train consists of four impingers connected in series. The first and second impingers contain 0.1 normal (N) hydrochloric acid (HCl), the third impinger is empty, and the fourth impinger contains a weighed amount of silica gel. NH₃ in the sampled gas is collected in the impingers and in rinses of the sample probe and connecting glassware. Sampling was performed for six hours at a constant rate of 0.5 cubic feet per minute (cfm). The recovery of the sampling train was performed on-site to reduce the probability of sample loss during shipment. During this recovery, all the impinger catches and glassware rinses were collected into a single bottle. A field blank (FB) was also submitted for analysis. NH₃ content was determined by ion selective electrode analysis.

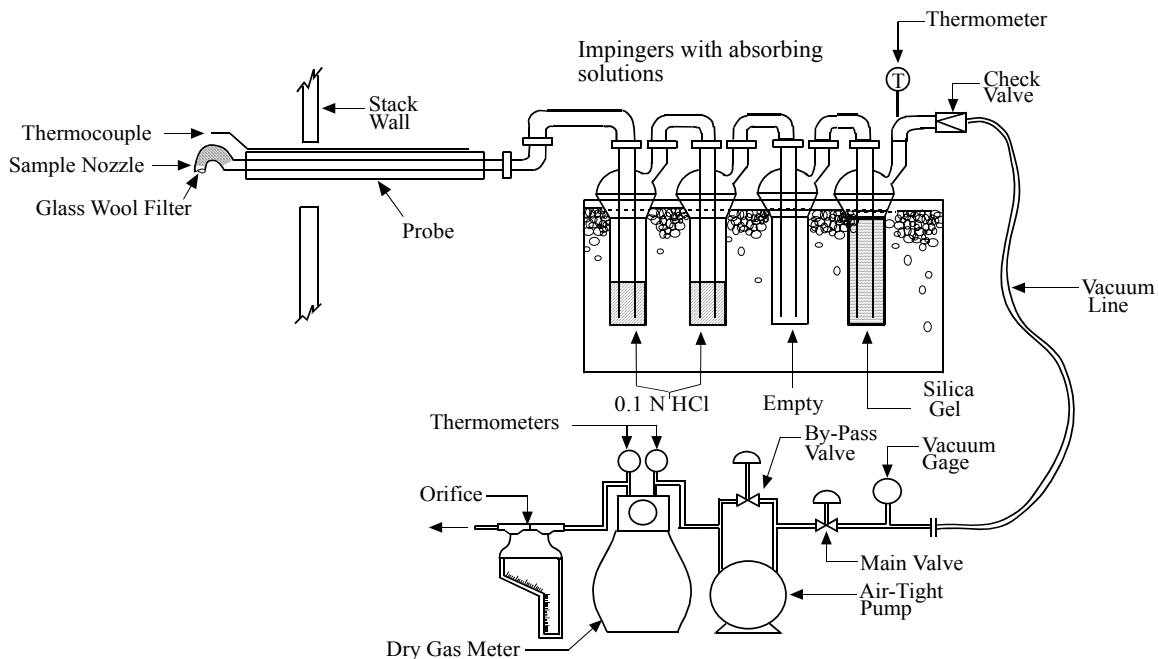


Figure 3-2. NH₃ Collection Train for BAAQMD Method ST-1B.

DILUTED SAMPLING METHOD

PM_{2.5} mass and chemical speciation in the stack gas were determined using a dilution sampling method. Two separate sampler designs were sampled simultaneously to allow comparison of a new compact design (Beta Sampler) with an existing benchmark design (Alpha Sampler).

Alpha Sampler

PM_{2.5} mass and chemical speciation in the stack gas was determined using a dilution sampler (Figure 3-3). A heated stainless steel probe with a buttonhook nozzle was used to withdraw the stack gas sample at a rate of approximately 25 liters per minute (L/min). The sample was transported from the probe through a heated copper line into the dilution sampler. The sample was mixed in the sampler with purified ambient air under turbulent flow conditions to cool and dilute the sample to near-ambient conditions. The ambient air used for dilution was purified using a HEPA filter to remove particulate matter (PM) and an activated carbon bed to remove gaseous organic compounds. The temperature and relative humidity (RH) of the dilution air were measured but not controlled. After passing through a tube length equal to 10 diameters, approximately 50 percent of the diluted sample was withdrawn into a large chamber, where the sample aged for approximately 70 seconds to allow low-concentration aerosols (especially organic aerosols) to fully form. The aged sample was withdrawn from the residence time chamber through three cyclone separators to remove particles larger than 2.5 µm into a sample manifold that distributed the sample to the sample collection media.

Prior to testing, the entire assembly was cleaned with DI water followed by acetone to remove surface contamination. After the acetone rinse, the assembly was wrapped with heating blankets and heated to a temperature of 150 degrees Celsius (°C) for at least two hours while flowing purified air through the system at 8 L/min to remove any trace organic residues. Prior to commencing the first test run, a leak check was performed by closing the dilution air valve and plugging the sample inlet and the Hi-Vol fan bypass, and drawing a slight negative pressure in the aging chamber typical of that during testing (-1 to -2 inches of water) while monitoring flow through one of the low range mass flow meters. The maximum allowable leak rate was established at 2.0 percent of the total flow rate through the system (336 L/min), or less than 6.7 L/min. Leak rates achieved during these tests were typically less than 0.5 percent.

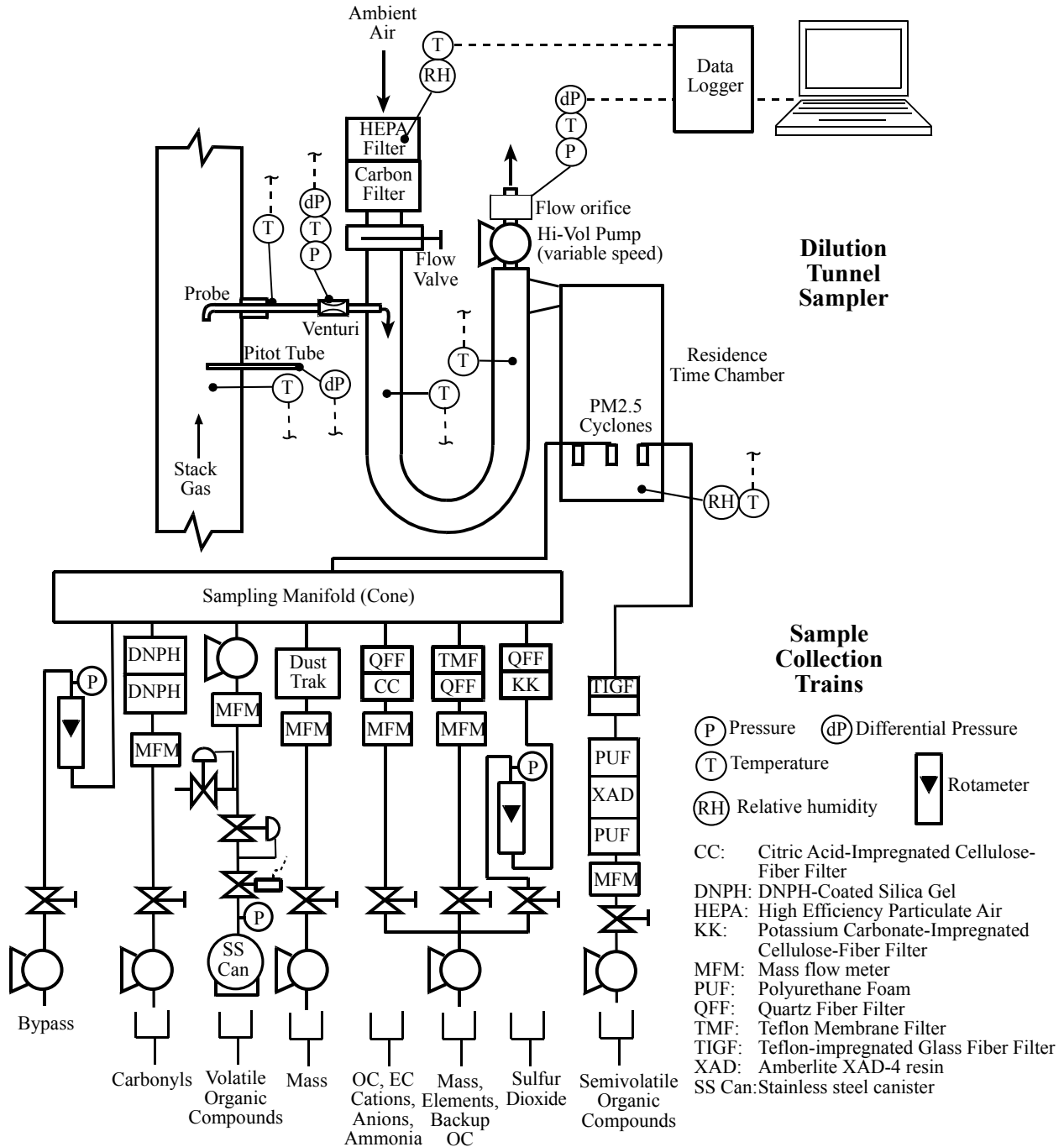


Figure 3-3. Dilution Sampler System – Alpha Sampler (Site Echo).

The sample flow rate through the probe was monitored using a heated (150 °C) venturi flow meter. The venturi velocity head was measured continuously during the test using a pressure transducer and gas temperature at the venturi inlet was measured with a thermocouple. An S-type Pitot tube with electronic pressure transducer and thermocouple were used to monitor the velocity in the stack. The thermocouples and pressure transducers were connected to a laptop computer data acquisition system. The dilution airflow and backpressure were adjusted to maintain the target dilution ratio and sample flow rates. Total sampling time for each test run was 6 hours.

The nominal target dilution ratio based on work by Hildemann et al. (1989) was 30:1 (dilution air:exhaust). This prior work suggests that mixing between the sample and the dilution air in the tunnel section begins to degrade when the dilution ratio is less than approximately 20:1, which sets one of the minimum operating limits for this dilution sampler design. Anticipating extremely low concentrations for most of the target pollutants, an intermediate dilution ratio was chosen to allow detection of as many target substances as possible within a practical sample run time. Actual dilution ratio ranged from 31 to 32 during the stack runs, which resulted in average diluted sample temperatures of 21 to 37 °C (70 to 99 °F) (Table 3-1). Diluted sample temperatures are within 12 °C of the ambient air temperature. An RH sensor in the residence time chamber malfunctioned during the test. Calculated RH of the diluted sample based on measured ambient air RH, dilution ratio, measured stack gas moisture content and sample temperature ranged from 12 to 49 percent. Aerosol growth due to deliquescence and hygroscopic absorption is expected to be negligible below an RH of approximately 70 percent (Seinfeld and Pandis, 1998). Since the RH of the fully diluted sample was well below 70 percent for all tests, aerosol growth due to moisture in the sample is assumed negligible even though the RH of the dilution air slightly exceeded 70 percent in two of the runs.

At the end of each test run, the probe, nozzle, sample venturi, and connecting sample line (Alpha sampler only) were quantitatively rinsed with acetone to recover any deposited particulate matter. A single acetone reagent blank (from the primary reagent container) was collected for the test campaign.

Two dilution system blanks (DSBs) were also collected using the dilution sampler. Filtered dilution air was drawn into the module without sample gas flow for a sampling period of 6 hours. For both the ambient air sample and the dilution sampler system blanks, the same sampling media were used as described below and in Figure 3-2. Table 3-2 lists the sample gas conditions and flow rates for the Alpha Sampler dilution samples.

Table 3-2. Dilution Sampler Operating Conditions – Alpha Sampler (Site Echo).

Parameter	Units	09-May-03 Alpha-DSB1	12-May-03 Alpha-Hi-R1	13-May-03 Alpha-Hi-R2	14-May-03 Alpha-Hi-R3	15-May-03 Alpha-Hi-R4	17-May-03 Alpha-Lo-R1	18-May-03 Alpha-Lo-R2	19-May-03 Alpha-Lo-R3	20-May-03 Alpha-DSB2	21-May-03 Alpha-Ambient
Ambient Air Temp.	°C	18.2	25.6	24.0	19.7	18.8	17.1	17.8	22.7	27.8	29.4
Ambient RH	%	74.5	71.4	47.3	51.6	47.8	58.4	53.8	45.6	62.0	30.9
Dilution Chamber Temp.	°C	27.5	37.4	35.3	22.1	21.1	25.0	27.3	32.2	42.5	NA
Dilution Chamber RH	%	44.6	39.4	28.8	53.6	50.0	41.9	36.0	30.8	28.0	NA
Stack Sample Flow Rate (standard T,P)	L/min	NA	25.0	25.8	26.1	25.6	25.0	25.5	25.3	NA	NA
Stack Sample Flow Rate (dry, standard T,P)	L/min	NA	15.7	16.1	16.3	16.0	16.1	16.4	16.2	NA	NA
Hi-Vol Fan Flow Rate (actual)	L/min	126	227	252	249	233	236	246	237	237	NA
Dilution Ratio (actual)	L/L	NA	30.7	31.1	31.3	31.2	31.7	31.4	30.9	NA	NA
Dilution Ratio (dry)	L/L	NA	32.7	33.6	33.9	33.7	33.8	33.5	33.0	NA	NA
TMF/QFF Flow Rate - mass, elements, backup OC (dry, standard T,P)	L/min	37.1	36.8	37.1	37.2	37.2	37.2	37.2	37.1	36.9	37.2
QFF/CCF Flow Rate - ions, OC/EC, NH3 (dry, standard T,P)	L/min	37.1	36.8	37.1	37.2	37.2	37.2	37.2	37.1	36.9	37.2
QFF/KKF Flow Rate - SO2 (dry, standard T,P)	L/min	36.7	35.4	36.1	37.0	37.1	36.8	36.9	36.8	36.5	37.2
Canister Flow Rate (estimated, dry, standard T,P)	L/min	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
PUF/XAD/PUF - SVOC (dry, standard T,P)	L/min	111	110	111	111	112	112	112	111	111	112
DNPH Flow Rate - Carbonyls (dry, standard T,P)	L/min	0.40	0.39	0.39	0.39	0.39	0.40	0.40	0.40	0.39	0.38
DustTrak Flow Rate - PM (dry, standard T,P)	L/min	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Bypass Flow Rate (dry, standard T,P)	L/min	108	104	105	108	108	108	102	107	104	0

DSB = dilution sampler blank; Ambient = ambient air sample

Beta Sampler

Figure 3-4 shows a schematic arrangement for the Beta sampler. This dilution sampler differed from the Alpha design in the following ways:

- The heated sample line between the probe and venturi was removed;
- The mixing section was shortened by using a multiple parallel jet mixing design to achieve faster mixing between the sampler and dilution air; and
- The residence time was shortened to approximately 10 seconds, thereby eliminating the large residence time chamber.
- The sample path through the dilution sampler is linear rather than convoluted.

Table 3-3 lists the sample gas conditions and flow rates for the Beta Sampler dilution samples. As with the Alpha sampler, the temperature and RH of the dilution air were measured but not controlled. Further details of the Beta Sampler are given elsewhere (Chang and England, 2004).

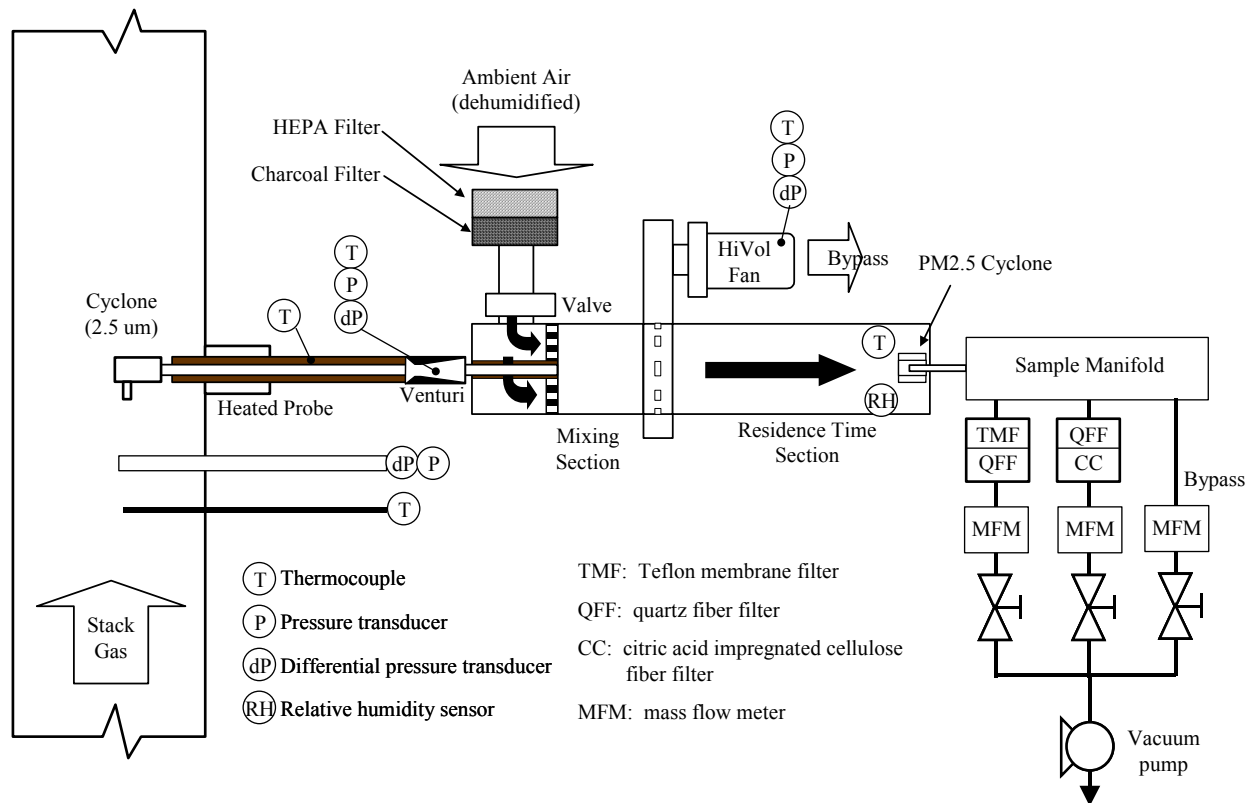


Figure 3-4. Schematic of Beta (EER) Dilution Sampler.

Table 3-3. Dilution Sampler Operating Conditions – Beta Sampler (Site Echo).

Parameter	Units	09-May-03 Beta-DSB1	12-May-03 Beta-Hi-R1	13-May-03 Beta-Hi-R2	14-May-03 Beta-Hi-R3	15-May-03 Beta-Hi-R4	17-May-03 Beta-Lo-R1	18-May-03 Beta-Lo-R2	19-May-03 Beta-Lo-R3	20-May-03 Beta-DSB2
Ambient Air Temp.	°C	18.2	25.6	24.0	19.7	18.8	17.1	17.8	22.7	27.8
Ambient RH	%	74.5	71.4	47.3	51.6	47.8	58.4	53.8	45.6	62.0
Dilution Chamber Temp.	°C	28.7	38.9	36.3	31.1	30.0	27.7	29.1	35.2	38.6
Dilution Chamber RH	%	39.7	38.3	30.5	32.8	32.5	36.5	33.5	27.0	34.1
Stack Sample Flow Rate (standard T,P)	L/min	NA	26.7	27.1	28.1	26.4	26.2	28.0	27.0	NA
Stack Sample Flow Rate (dry, standard T,P)	L/min	NA	16.8	16.8	17.6	16.6	16.8	18.0	17.2	NA
Hi-Vol Fan Flow Rate (actual)	L/min	391	291	250	412	290	401	410	439	378
Dilution Ratio (actual)	L/L	NA	19.4	17.3	24.6	20.1	26.1	24.7	26.6	NA
Dilution Ratio (dry)	L/L	NA	20.7	18.7	26.6	21.7	27.9	26.3	28.6	NA
TMF/QFF Flow Rate - mass, elements, backup OC (dry, standard T,P)	L/min	37.1	36.7	37.0	37.2	37.2	37.2	37.2	37.1	36.8
QFF/CCF Flow Rate - ions, OC/EC, NH3 (dry, standard T,P)	L/min	37.2	36.7	37.0	37.2	37.2	37.2	37.2	37.1	36.8
TMF Flow Rate - mass (dry, standard T,P)	L/min	33.4	32.4	32.7	33.1	33.2	33.6	33.5	33.2	32.6

DSB = dilution sampler blank; Ambient = ambient air sample

PM2.5 Mass

Samples for PM2.5 mass measurements were collected on a 47-millimeter (mm) diameter polymethylpentane ringed, 2.0 µm pore size, TMF (Gelman No. RPJ047) placed in a Teflon[®] filter holder. The filter packs were equipped with quick release connectors to ensure that no handling of the filters was required in the field. The flow rate through the filter was monitored during sampling by a mass flow meter at a sampling rate of approximately 37 L/min. Weighing was performed on a Cahn 31 electro-microbalance with ±1 microgram (µg) sensitivity. These samples were collected with the Alpha and Beta samplers simultaneously. Two TMFs were used with the Beta sampler to obtain a partial assessment of method precision by comparing the mass results from two simultaneously samples filters.

In addition to the filter mass, the probe, heated line and venturi were recovered after each test run using acetone, then the rinses were dried and weighed. To minimize contamination of organic samples, the probe heated line and venturi were rinsed with water following the acetone rinse.

Elements

Sample collected on the TMF was analyzed by energy dispersive x-ray fluorescence (ED-XRF) analysis for the following 40 elements: aluminum (Al), silver (Ag), arsenic (As), gold (Au), barium (Ba), bromine (Br), calcium (Ca), cadmium (Cd), chlorine (Cl), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium (Ga), mercury (Hg), indium (In), potassium (K), lanthanum (La), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), palladium (Pd), rubidium (Rb), S, antimony (Sb), selenium (Se), silicon (Si), tin (Sn), strontium (Sr), titanium (Ti), thallium (Tl), uranium (U), vanadium (V), yttrium (Y), zinc (Zn), and zirconium (Zr). Mg and Na results are considered semiquantitative because of analytical technique limitations. These samples were collected with the Alpha and Beta samplers simultaneously.

A KeveX Corporation Model 700/8000 ED-XRF analyzer with a side-window, liquid-cooled, 60 kiloelectron volts (keV), 3.3 milliamp rhodium anode x-ray tube and secondary fluorescers was used. The silicon detector had an active area of 30 square mm, with a system resolution better than 165 electron volts (eV). The analysis was controlled, spectra were acquired, and elemental concentrations were calculated by software on a microcomputer, which was interfaced to the analyzer. Five separate x-ray fluorescence (XRF) analyses were conducted on each sample to optimize the detection limits for the specified elements. The filters were removed from their petri slides and placed with their deposit sides downward into polycarbonate filter cassettes. A polycarbonate retainer ring kept the filter flat against the bottom of the cassette. The cassettes were loaded into a carousel in the x-ray chamber. The sample chamber was evacuated to 10^{-3} Torr. A computer program controlled the positioning of the samples and the excitation conditions. Complete analysis at five excitation conditions required approximately 5 hours for each sample.

SO₄⁼, NO₃⁻, and Cl⁻

Samples for determining water-soluble Cl⁻, NO₃⁻, and SO₄⁼ were collected on QFFs. The flow rate through the filter was monitored during sampling by a mass flow meter at a sample flow rate of approximately 37 L/min. These samples were collected simultaneously with the Alpha and Beta samplers.

Each QFF was cut in half, and one filter half was placed in a polystyrene extraction vial with 15 milliliter (mL) of distilled deionized (DI) water. The extraction vials were capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material. After extraction, these solutions were stored under refrigeration prior to analysis. Cl⁻, NO₃⁻, and SO₄⁼ were measured with a Dionex 2020i ion chromatograph (IC). Approximately 2 mL of the filter extract was injected into the ion chromatograph.

OC and EC

Forty-seven mm QFFs were used to collect samples for determination of OC and EC mass. The filters were heated in air for at least three hours at approximately 900 °C prior to use. The flow rate through the filter was monitored during sampling by a mass flow controller at a sample flow rate of approximately 37 L/min. These samples were collected with the Alpha and Beta samplers simultaneously. A ½-inch diameter punch was taken from each QFF for analysis.

The thermal/optical reflectance (TOR) method was used to determine OC and EC on the QFFs. The TOR method is based on the principle that different types of carbon-containing particles are converted to gases under different temperature and oxidation conditions. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments; 2) converting these compounds to CO₂ by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO₂); 3) reduction of CO₂ to methane (CH₄) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantification of CH₄ equivalents by a flame ionization detector (FID).

Monochromatic (laser) light reflected from the filter is continuously monitored by a photodetector throughout the analysis cycle. During the initial portion of the thermal cycle in an He atmosphere, a negative change in reflectance occurs which is assumed to be proportional to the degree of pyrolytic conversion of carbon that takes place during OC analysis. During the final part of the thermal cycle, oxygen is introduced, and the reflectance increases rapidly as the light-absorbing carbon burns off the filter. The carbon measured after the reflectance attains the value it had at the beginning of the analysis cycle is defined as EC. The specific cycle employed in these tests was developed for the Interagency Monitoring of Protected Visual Environments (IMPROVE) program (DRI, 2000).

VOC

An integrated sample was collected in a canister using a pump and flow control device to maintain a constant sample flow rate into the canister over the entire sampling period. Canisters were used in order to quantify VOCs with a carbon number of two or more. The flow rate used is a function of the final sample pressure and the specified sampling period, for our purposes, 0.017 L/min. Because the raw sample had already been diluted and cooled before introduction into the canister and the canisters were stored at temperatures above the dew point of the sample, liquid formation in the canisters was not a concern. These samples were collected with the Alpha sampler only.

For analysis, a known volume of gaseous sample was passed through a cryogenically cooled trap, cooled with liquid argon, cryogenically trapping out carbon number of two (C_2) and heavier VOC without trapping methane. The trap containing the condensed VOC was warmed with hot water and its contents injected into a gas chromatograph (GC) capillary column where separation of the VOC takes place. Detection of the hydrocarbons and oxygenated hydrocarbons was by FID while detection of the halogenated compounds was by electron capture detection (ECD). The resultant peaks were quantified and recorded by an electronic integrator and by the chromatographic data system.

SVOCs

SVOCs were collected using a filter followed by an adsorbent cartridge. The media used for collecting SVOCs are as follows:

- Pallflex (Putnam, CT) T60A20 102-mm TIGF filters;
- PUF sheets, purchased from E.R. Carpenter Company, Inc. (Richmond, VA) and cut into 2-inch diameter plugs;
- XAD-4™ resin (20-60 mesh) purchased from Aldrich Chemical Company, Inc.

The sample is transferred from the dilution sampler residence time chamber through a ½-inch copper manifold leading to a momentum diffuser chamber. The diffuser chamber is followed by the cartridge holder and is connected to a vacuum pump through a needle valve. The flow through the sampler was monitored during the test by a mass flow meter at a sample flow rate of approximately 113 L/min. These samples were collected with the Alpha sampler only.

The samples were isotopically spiked, extracted in dichloromethane, and concentrated prior to analysis. Sample extracts were analyzed by the electron impact (EI) gas chromatography/mass spectrometric (GC/MS) technique, using a Hewlett-Packard 5890 GC equipped with a model 7673A Automatic Sampler and interfaced to a model 5970B Mass Selective Detector (MSD). To assist in the unique identification of individual compounds, selected samples were analyzed by combined gas chromatography/Fourier transform infrared/mass spectrometry (GC/IRD/MSD) technique, i.e., using the Fourier transform infrared detector to aid mass spectrometric identification. Quantification of polycyclic aromatic hydrocarbons (PAH), and other compounds of interest, was obtained by multiple ion detection (MID).

Carbonyls (Aldehydes and Ketones)

Carbonyls in the diluted sample were collected by drawing the sample through a cartridge impregnated with acidified DNPH, following principles outlined in EPA Method TO-11A (U.S. EPA, 1999c). The resulting products (hydrazones) in the cartridge were measured in the laboratory using high performance liquid chromatography (HPLC) to determine the levels of the carbonyl compounds originally present in sample gas. Typically, C₁-C₆ carbonyl compounds, including benzaldehyde, are measured effectively by this technique. The flow rate used for this sample was approximately 0.4 L/min. These samples were collected with the Alpha sampler only.

SO₂

Filter packs containing a QFF followed by a K₂CO₃-impregnated cellulose-fiber filter were used to collect SO₂ gas downstream of the dilution sampler. The flow rate through the filter was monitored during sampling by a mass flow meter at a sample flow rate of approximately 37 L/min. The filters were extracted with hydrogen peroxide and then analyzed using IC. These samples were collected with the Alpha and Beta samplers simultaneously

NH₃

Filter packs containing a QFF followed by a citric acid impregnated cellulose-fiber filter were used to collect NH₃ gas downstream of the dilution sampler. The flow rate through the filter was monitored during sampling by a mass flow meter at a target sample flow rate of approximately 37 L/min. These filters were extracted with DI water and then analyzed using automated colorimetry. These samples were collected with the Alpha and Beta samplers simultaneously.

Continuous PM_{2.5} Mass Concentration

Aerosol concentration was measured instrumentally using a laser photometer (Thermo Scientific Incorporated (TSI) DustTrak, Model 8250). Two laser photometers were used during the tests. One was attached to the Alpha dilution sampler in parallel with the filter packs, while the other was located near the combustion air inlet to the NGCC-SF. These instruments provided real-time indicators of aerosol concentrations in the size range of approximately 0.1 to 2.5 micrometers (µm). These measurements were intended primarily for trend analysis rather than absolute measurements, since the instruments could not be calibrated for the specific aerosol characteristics of this test. By comparing the measurements in the ambient air inlet and diluted exhaust sample, the influence of varying ambient air aerosol concentrations on stack emissions may be determined.

Light scattering is the basic principle of operation. An aerosol sample is continuously drawn through a greased impactor to remove particles larger than 2.5 µm, then into the sensing chamber (Figure 3-5). One section of the aerosol stream is illuminated with a small beam of laser light. Particles in the aerosol stream scatter light in all directions. A lens at 90° to both the aerosol stream and laser beam collects some of the scattered light and focuses it onto a photodetector. The detection circuitry converts the light into a voltage. This voltage is proportional to the

amount of light scattered which is, in-turn, proportional to the volume concentration of the aerosol. Based on the wavelength of the laser (780 nanometers, nm) and the sensitivity of the photodiode, the minimum particle size that can be measured is approximately 0.1 μm . The actual response depends on the aerosol size distribution, physical properties and optical properties. Each laser photometer was factory calibrated against a gravimetric reference using the respirable fraction of standard International Organization for Standardization (ISO) 12103-1, A1 test dust (Arizona Test Dust). This test dust has a wide size distribution covering the entire size range of the laser photometer and is representative of a wide variety of ambient aerosols. The wide range of particle sizes averages the effect of particle size dependence on the measured signal. However, the accuracy of the reading depends on the actual physical and optical properties of the aerosol being measured.

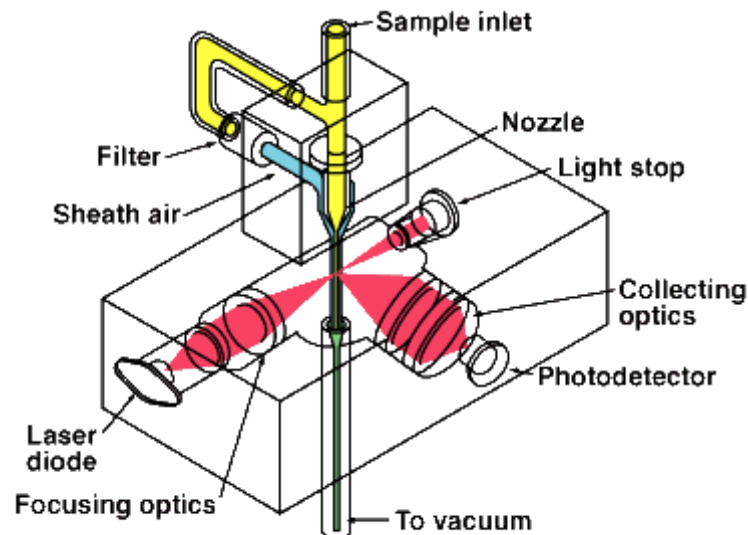


Figure 3-5. Laser Photometer (TSI DustTrak, Model 8250).

A ¼-inch Tygon[®] sample line approximately four feet in length was used to connect the laser photometer to the Alpha dilution sampler. Tygon[®] is reported to have good particle transmission characteristics. The port to which the Tygon[®] line was attached was grounded through the sample manifold legs, but with the line itself being nonconductive there may be potential for some particle losses due to electrostatic charge. The instrument near the combustion air inlet sampled directly from the ambient air. The instruments were warmed up for at least 30 minutes prior to use. Prior to testing, a filter was temporarily attached to each sample inlet to verify the

instrument zero. Sampling rate was 1.7 L/min. Instrument response during each test was recorded using the internal data logger and later transferred to a computer for data reduction. The visible display of the instrument at the Alpha sampler also was recorded manually at approximately 30-minute intervals for quality assurance purposes.

4. TEST RESULTS

All stack emission results are presented in units of milligrams (mg) per dry standard cubic meter (mg/dscm) and pounds per hour (lb/hr). Concentrations are corrected to a standard temperature of 68°F (20°C) and a standard pressure of 29.92 inches (760 mm) of mercury unless otherwise indicated. See the conversion factors presented in Appendix B to convert to Système Internationale (SI) units. Substances that were not detected in any of the four test runs generally are not listed on the tables. Where shown, undetected data are flagged “ND”, treated as zeroes in sums, and excluded from average calculations. Data with one or more, but not all, constituents less than the detection limit are flagged with a “<” symbol to indicate an upper estimate of the true emission. This treatment of detection limits was used, rather than using one-half of the minimum detection limit in sums and averages, to make the results less ambiguous when used in source apportionment analysis. In the tables that follow, results that were detected in only one or two test runs are shaded, which indicates they may be useful in combination with results from other tests but are not considered reliable for quantitative analysis based on this test alone.

The approximate in-stack minimum detection limits (MDL) achieved for all measured substances are given in Table 4-1a-d. These detection limits are calculated from the analytical detection limits, an average sample volume and an average dilution ratio. Lower quantification limits (LQL), which provide an indication of the minimum concentrations that can be distinguished from the background based on FB results, are discussed elsewhere (England, 2004).

PROCESS OPERATING CONDITIONS

Table 4-2 summarizes the plant operating conditions during testing. The NGCC-SF operated at 98 to 100 percent of rated load, an average of 169 MW, during the high load test series. During the reduced load test series, the unit operated at approximately 59 percent of base load for each of the three test runs. The duct burners were not in service during any of the tests. The average conditions are not considered representative of any particular or typical operating condition for this plant, but rather are simply the average of the operating conditions during the test.

Table 4-1. Approximate In-Stack Detection Limits Achieved for NGCC-SF Tests (Site Echo)

Alpha Tunnel: High Load			
Substance	Dilution mg/dscm	Substance	Dilution mg/dscm
PM2.5 mass	2.5E-3	Pb	2.3E-5
Ag	9.0E-5	Pd	8.1E-5
Al	7.5E-5	Rb	7.2E-6
As	1.2E-5	S	3.6E-5
Au	2.3E-5	Sb	1.3E-4
Ba	3.9E-4	Se	9.3E-6
Br	7.5E-6	Si	4.2E-5
Ca	3.3E-5	Sn	1.3E-4
Cd	9.0E-5	Sr	8.4E-6
Cl	7.8E-5	Ti	2.2E-5
Co	6.6E-6	Tl	1.9E-5
Cr	1.4E-5	U	1.8E-5
Cu	8.1E-6	V	1.9E-5
Fe	1.1E-5	Y	9.9E-6
Ga	1.4E-5	Zn	8.1E-6
Hg	1.9E-5	Zr	1.3E-5
In	1.0E-4	SO4=	3.8E-3
K	4.5E-5	NO3-	3.8E-3
La	4.8E-4	NH4+	3.8E-3
Mg	0.0E+0	Cl-	3.8E-3
Mn	1.2E-5	OC	2.8E-2
Mo	2.0E-5	EC	6.5E-3
Na	0.0E+0	SO2 (Dilution Tunnel)	2.6E-3
Ni	6.6E-6	NH3 (Dilution Tunnel)	1.0E-3
P	4.2E-5	NH3 (BAAQMD ST-1B)	1.5E-3

Alpha Tunnel: Low Load			
Substance	Dilution mg/dscm	Substance	Dilution mg/dscm
PM2.5 mass	3.4E-3	Pb	3.1E-5
Ag	1.2E-4	Pd	1.1E-4
Al	1.0E-4	Rb	9.7E-6
As	1.6E-5	S	4.8E-5
Au	3.1E-5	Sb	1.8E-4
Ba	5.2E-4	Se	1.2E-5
Br	1.0E-5	Si	5.6E-5
Ca	4.4E-5	Sn	1.8E-4
Cd	1.2E-4	Sr	1.1E-5
Cl	1.0E-4	Ti	2.9E-5
Co	8.9E-6	Tl	2.5E-5
Cr	1.9E-5	U	2.4E-5
Cu	1.1E-5	V	2.5E-5
Fe	1.5E-5	Y	1.3E-5
Ga	1.9E-5	Zn	1.1E-5
Hg	2.6E-5	Zr	1.7E-5
In	1.4E-4	SO4=	5.1E-3
K	6.0E-5	NO3-	5.1E-3
La	6.4E-4	NH4+	5.1E-3
Mg	0.0E+0	Cl-	5.1E-3
Mn	1.6E-5	OC	3.8E-2
Mo	2.7E-5	EC	8.8E-3
Na	0.0E+0	SO2 (Dilution Tunnel)	3.4E-3
Ni	8.9E-6	NH3 (Dilution Tunnel)	1.4E-3
P	5.6E-5	NH3 (BAAQMD ST-1B)	1.5E-3

Beta Tunnel: High Load			
Substance	Dilution mg/dscm	Substance	Dilution mg/dscm
PM2.5 mass	1.7E-3	Pb	1.5E-5
Ag	6.1E-5	Pd	5.5E-5
Al	5.0E-5	Rb	4.8E-6
As	7.9E-6	S	2.4E-5
Au	1.6E-5	Sb	9.1E-5
Ba	2.6E-4	Se	6.3E-6
Br	5.0E-6	Si	2.8E-5
Ca	2.2E-5	Sn	8.9E-5
Cd	6.1E-5	Sr	5.7E-6
Cl	5.3E-5	Ti	1.5E-5
Co	4.4E-6	Tl	1.3E-5
Cr	9.7E-6	U	1.2E-5
Cu	5.5E-6	V	1.3E-5
Fe	7.7E-6	Y	6.7E-6
Ga	9.7E-6	Zn	5.5E-6
Hg	1.3E-5	Zr	8.5E-6
In	6.9E-5	SO4=	2.6E-3
K	3.0E-5	NO3-	2.6E-3
La	3.2E-4	NH4+	2.6E-3
Mg	0.0E+0	Cl-	2.6E-3
Mn	8.1E-6	OC	1.9E-2
Mo	1.4E-5	EC	4.4E-3
Na	0.0E+0	SO2 (Dilution Tunnel)	1.7E-3
Ni	4.4E-6	NH3 (Dilution Tunnel)	6.8E-4
P	2.8E-5	NH3 (BAAQMD ST-1B)	1.5E-3

Beta Tunnel: Low Load			
Substance	Dilution mg/dscm	Substance	Dilution mg/dscm
PM2.5 mass	2.8E-3	Pb	2.6E-5
Ag	1.0E-4	Pd	9.1E-5
Al	8.4E-5	Rb	8.1E-6
As	1.3E-5	S	4.0E-5
Au	2.6E-5	Sb	1.5E-4
Ba	4.4E-4	Se	1.0E-5
Br	8.4E-6	Si	4.7E-5
Ca	3.7E-5	Sn	1.5E-4
Cd	1.0E-4	Sr	9.4E-6
Cl	8.7E-5	Ti	2.5E-5
Co	7.4E-6	Tl	2.1E-5
Cr	1.6E-5	U	2.0E-5
Cu	9.1E-6	V	2.1E-5
Fe	1.3E-5	Y	1.1E-5
Ga	1.6E-5	Zn	9.1E-6
Hg	2.2E-5	Zr	1.4E-5
In	1.1E-4	SO4=	4.2E-3
K	5.0E-5	NO3-	4.2E-3
La	5.4E-4	NH4+	4.2E-3
Mg	0.0E+0	Cl-	4.2E-3
Mn	1.3E-5	OC	3.2E-2
Mo	2.3E-5	EC	7.3E-3
Na	0.0E+0	SO2 (Dilution Tunnel)	2.8E-3
Ni	7.4E-6	NH3 (Dilution Tunnel)	1.1E-3
P	4.7E-5	NH3 (BAAQMD ST-1B)	1.5E-3

Table 4-2. Process Operating Conditions (Site Echo)².

Parameter	Units	HI - Run 1	HI - Run 2	HI - Run 3*	HI - Run 4	Average - High Load	RSD - High Load	LO - Run 1	LO - Run 2	LO - Run 3	Average - Low Load	RSD - Low Load
		12-May-03	13-May-03	14-May-03	15-May-03			17-May-03	18-May-03	19-May-03		
Date	dd-mmm-yy											
Start time	hh:mm	10:40	13:05	14:10	12:30			6:00	5:45	6:05		
End time	hh:mm	16:40	19:05	20:10	18:17			12:00	11:45	12:05		
NGCC-SF fuel flow rate	lb/sec.	21.3	20.8	--	20.8	21.0	1%	15.3	14.9	15.1	15.1	1%
Generator electrical output	MW	170	166	169	170	169	1%	100	100	100	100	0.0%
Ambient air temperature	°F	75.2	79.0	--	68.9	74.4	7%	65.9	67.4	72.3	68.5	5%
Ambient relative humidity	%	58	70	--	71	67	11%	42	30	35	36	17%
Gas turbine exit gas temperature	°F	1,130	1,136	--	1,131	1,132	0%	1,174	1,174	1,176	1,175	0.1%
Barometric pressure	in. Hg	29.63	29.55	--	29.69	29.62	0.2%	29.66	29.77	29.75	29.72	0.2%
Compressor inlet air pressure	psia	14.6	14.5	--	14.6	14.5	0.2%	14.6	14.6	14.6	14.6	0.2%
Compressor inlet air temperature	°F	58.0	64.4	--	57.4	59.9	7%	68.7	68.7	73.9	70.4	4%
Compressor air discharge pressure	psig	213	208	--	212	211	1%	149	149	149	149	0.1%
Compressor air discharge temperature	°F	704	728	--	726	719	2%	659	663	707	676	4%
Inlet air humidity	lb H ₂ O/lb air	0.0060	0.0093	--	0.0072	0.0075	22%	0.0065	0.0049	0.006	0.0058	15%
Oxidation catalyst gas temperature	°F	847	843	--	838	843	1%	817	813	811	814	0.4%
Ammonia feed rate	lb/hr	80	71	--	77	76	6%	58	62	59	60	3%
Stack gas NO _x Concentration (dry, 15% O ₂)	ppmv	1.8	2.1	--	2.0	2.0	8%	2.0	2.1	2.0	2.0	3%
Stack gas CO Concentration (dry, 15% O ₂)	ppmv	0.045	0.150	--	0.150	0.115	53%	-0.032	-0.074	-0.046	-0.051	-42%
Stack gas O ₂ Concentration (dry)	%v	13.58	13.50	13.50	13.61	13.55	0%	13.80	13.90	13.87	13.86	0.4%
Gross heat input	MMBtu/hr	1,766	1,747	1,772	1,804	1,772	1%	1,262	1,262	1,262	1,262	0.0%
Combustion reference temperature	°F	--	--	--	2,411	2,411	n/a	2,277	2,277	2,275	2,276	0.1%

RSD - relative standard deviation

*Plant data pending for this test condition. MW shown is average of Runs 1, 2 and 4. O₂ from portable analyzer. Gross heat input estimated from measured stack gas flow rate, O₂ and average F factor from Runs 1, 2 and 4.

The average gross heat input to the NGCC-SF during the tests was obtained from the plant process data system, which automatically calculates the value from the measured fuel flow rate and continuous on-site natural gas analysis. The average gross heat input was used to convert in-stack emission rates (lb/hr) to emission factors pounds of pollutant per million British thermal units of gas fired (lb/MMBtu), which are presented in Section 5. Analyses of four samples of the natural gas (one sample for each of the test days) indicate total S levels ranging from 0.254 to 0.403 grains per 100 standard (0 °C) cubic feet (gr/100 scf) (sum of all S species expressed as elemental S) (Table 4-3). Most of the S is present in the fuel as methyl mercaptan (added as an odorant) and thiophane. Applying the gross Btu content measured in the four samples to the measured fuel flow rates reported by the plant process data, the calculated gross heat inputs compare very well (within 2 percent) with the value reported by the process data system in Table 4-2.

² Plant data for high load Run 3 is currently being retrieved. Based on measured stack gas flow rate, O₂, temperature and moisture content, operating conditions for Run 3 and the other high load runs are estimated to be the same. Table 4-2 will be updated upon receipt of final data.

Table 4-3. Natural Gas Analysis Results (Site Echo).

Test Condition	Units	Results					
	--	Run 3 High	Run 4 High	Run 2 Low	Run 3 Low	Average	RSD (%)
Non-Hydrocarbon Gases							
Nitrogen	% v/v	1.05	1.2	3.93	3.76	2.49	63
Carbon Dioxide	% v/v	0.84	0.89	0.78	0.83	0.84	5
Hydrocarbons							
Methane	% v/v	91.4	90.3	88.1	88.3	89.5	2
Ethane	% v/v	5.33	5.79	5.31	5.24	5.42	5
Propane	% v/v	1.07	1.34	1.37	1.35	1.28	11
i-Butane	% v/v	0.114	0.148	0.158	0.151	0.143	14
n-Butane	% v/v	0.146	0.189	0.208	0.202	0.186	15
i-Pentane	% v/v	0.031	0.042	0.049	0.046	0.042	19
n-Pentane	% v/v	0.023	0.031	0.037	0.036	0.032	20
Hexane +	% v/v	0.0318	0.0431	0.0514	0.0452	0.0429	19
Hydrogen Sulfide	% v/v	ND	0.00002	ND	ND	< 0.00002	n/a
Calculated Elemental Composition							
Carbon	% w/w	73.37	73.26	70.23	70.33	71.80	2
Hydrogen	% w/w	23.44	23.26	22.31	22.36	22.84	3
Nitrogen	% w/w	1.67	1.89	6.08	5.84	3.87	62
Oxygen	% w/w	1.52	1.59	1.38	1.47	1.49	6
Heat of Combustion % Physical Properties							
Lower Heating Value (dry)	Btu/scf	955.3	963.2	937.5	937.1	948.3	1
Higher Heating Value (dry)	Btu/scf	1058.6	1067	1038.5	1038.1	1,050.6	1
Specific Gravity	--	0.6093	0.6171	0.6262	0.6249	0.6194	1
Wobbe Index	--	1356.2	1358.3	1312.4	1313.2	1335.03	2
Extended Hydrocarbon Analysis by GC-FID							
Cycloalkanes							
Cyclopentane	% v/v	0.002	0.0028	0.0033	0.0029	0.0028	20
Methylcyclopentane	% v/v	0.0027	0.0037	0.0056	0.0047	0.0042	30
Cyclohexane	% v/v	0.0036	0.0048	0.0061	0.0052	0.0049	21
Methylcyclohexane	% v/v	0.0024	0.0029	0.0044	0.0036	0.0033	26
Aromatics							
Benzene	% v/v	0.0011	0.0015	0.0015	0.0015	0.0014	14
Toluene	% v/v	0.0011	0.0013	0.0015	0.0015	0.00135	14
Ethylbenzene	% v/v	0.0001	0.0001	0.0001	0.0001	0.0001	0
m,p-Xylene	% v/v	0.0002	0.0002	0.0002	0.0002	0.0002	0
o-Xylene	% v/v	0.0001	0.0001	0.0001	0.0001	0.0001	0
c3 Benzenes	% v/v	ND	ND	ND	0.0001	< 0.0001	n/a
Paraffins							
Hexanes	% v/v	0.0133	0.0191	0.0199	0.018	0.01758	17
Heptanes	% v/v	0.0035	0.0046	0.0057	0.0049	0.00468	19
2,2,4-Trimethylpentane	% v/v	0.0002	0.0002	0.0003	0.0002	0.00023	22
Octanes	% v/v	0.0011	0.0013	0.0019	0.0015	0.00145	24
Nonanes	% v/v	0.0004	0.0005	ND	0.0007	< 0.00053	29

* At 60 °F and 14.696 psia; ** At 0 °C and 14.696 psia

*** Detection limit is 0.1 ppmv for hydrogen sulfide and 0.05 ppmv for all other compounds.

~ below standard detection limit; value shown for information only; < Below detection limit in some runs; n/a - not applicable

ND - Not Detected; RSD = relative standard deviation

Table 4-3 (continued). Natural Gas Analysis Results (Site Echo).

Test Condition	Units	Results					
	--	Run 3 High	Run 4 High	Run 2 Low	Run 3 Low	Average	RSD (%)
Trace Sulfur Species (ASTM D6228-98)***							
Hydrogen Sulfide	ppmv	ND	0.19	~ 0.06	~ 0.06	< 0.10	73
Methyl Mercaptan	ppmv	ND	1.57	1.45	1.72	< 1.58	9
Ethyl Mercaptan	ppmv	ND	0.28	0.22	0.2	< 0.23	18
i-Propyl Mercaptan	ppmv	ND	0.08	0.07	0.06	< 0.07	14
t-Butyl Mercaptan	ppmv	0.05	1.27	1.08	1.12	0.88	64
Dimethyl Disulfide	ppmv	0.12	ND	ND	~ 0.02	< 0.07	101
Methyl Ethyl Disulfide	ppmv	0.06	ND	ND	ND	< 0.06	n/a
Methyl i-Propyl Disulfide	ppmv	~ 0.02	ND	ND	ND	< 0.02	n/a
Methyl t-Butyl Disulfide	ppmv	0.83	ND	ND	ND	< 0.83	n/a
Di-i-Propyl Disulfide	ppmv	0.22	ND	ND	ND	< 0.22	n/a
i-Propyl t-Butyl Disulfide	ppmv	0.03	ND	ND	ND	< 0.03	n/a
Dimethyl Trisulfide	ppmv	~ 0.01	ND	ND	0.04	< 0.03	85
Diethyl Trisulfide	ppmv	0.19	0.02	ND	ND	< 0.11	114
Di-t-Butyl Trisulfide	ppmv	0.35	ND	ND	ND	< 0.35	n/a
Benzothiophene	ppmv	0.11	ND	ND	ND	< 0.11	n/a
Thiophane	ppmv	2.02	1.48	1.18	1.54	1.56	22
Unidentified Sulfur (as monosulfides)	ppmv	0.05	ND	ND	0.13	< 0.09	63
Total Sulfur	ppmv	6.44	4.93	4.06	4.99	5.11	19
Total Sulfur (as S)**	gr/100 scf	0.403	0.308	0.254	0.312	0.319	19
Total Sulfur (calculated, as SO ₄)	lb/MMBtu	1.5E-03	1.2E-03	9.9E-04	1.2E-03	1.2E-03	19

* At 60 °F and 14.696 psia; ** At 0 °C and 14.696 psia

*** Detection limit is 0.1 ppmv for hydrogen sulfide and 0.05 ppmv for all other compounds.

~ below standard detection limit; value shown for information only; < Below detection limit in some runs; n/a - not applicable
 ND - Not Detected; RSD = relative standard deviation

PRELIMINARY TEST RESULTS

Preliminary tests were conducted to establish a single point in the stack for sample collection for each dilution sampler. Full stack velocity traverses were performed with a Pitot probe before and after each test run, providing velocity profiles that were used to correct the average velocity measured at the Alpha sampling point during each test run to the average stack velocity for flow rate calculations. The repeatability of the velocity profile from run to run was very good.

STACK GAS CONDITIONS AND FLOW RATE

A summary of the stack conditions during testing is presented in Table 4-4. Stack gas temperature during the tests ranged from 205 to 228 °F.

Table 4-4. Average Stack Conditions (Site Echo).

Parameter	Units	Run 1 High	Run 2 High	Run 3 High	Run 4 High	Run 1 Low	Run 2 Low	Run 3 Low
Date		12-May-03	13-May-03	14-May-03	15-May-03	17-May-03	18-May-03	19-May-03
Stack Temperature	°F	228	221	222	206	205	206	206
Moisture	%v	8.3	8.8	8.6	8.3	7.4	7.4	7.6
Velocity	ft/s	62	62	62	61	45	45	45
	m/s	18.8	18.9	18.8	18.6	13.7	13.7	13.7
Flow Rate	acfm	1,104,000	1,109,000	1,104,000	1,096,000	806,000	808,000	808,000
	dscfm	778,000	769,000	773,000	795,000	591,000	591,000	590,000
	dscmm	22,000	21,800	21,900	22,500	16,700	16,700	16,700

DILUTION SAMPLER RESULTS

Particulate Mass

PM2.5 mass measurements using the dilution samplers include both solid aerosols that are directly emitted and those that condense under simulated stack plume conditions. The dilution sampler determines only the PM2.5 fraction of PM emissions. Particles in the stack with an aerodynamic diameter larger than 2.5 µm and those that grow larger than 2.5 µm in the dilution sampler are excluded. For gas combustion, it is reasonable to assume that PM2.5 accounts for most or all of the emitted particulate matter during normal operation.

All the TMF net weights from the Alpha sampler are positive, ranging from 39 to 54 µg. These weights are well above the analytical uncertainty of 6.4 µg. Two DSBs were taken for both samplers during the field campaign: a pre-test DSB at the beginning prior to collecting the first (high load) stack sample; and a post-test DSB following the last (low load) stack sample. Three DSB net filter weights for both the Alpha and Beta samplers ranged from 7 to 18 µg (average 12 µg), while the net filter weight for the post-test DSB for the Alpha sampler was abnormally high (33 µg). The post-test DSB may include both measurement background plus any cross-run contamination of the sampler. The fact that the Alpha sampler post-test DSB is roughly three times higher than the other three DSB results may indicate random contamination. The pre-test DSB PM2.5 mass result for the Alpha sampler, which is considered the most representative of measurement background for the high load runs, is 22 to 30 percent of the PM2.5 masses measured with the Alpha sampler in the high load stack samples. PM2.5 concentration measured with the Alpha sampler at high load averages 0.11 mg/dscm and the run results are fairly tightly grouped, with a relative standard deviation (RSD) of 15 percent (Table 4-5a). Because the data are tightly grouped, the 95 percent confidence lower bound of the average high load stack PM2.5

mass is greater than the pre-test DSB. This suggests the stack and pre-test DSB are significantly different at this confidence level.

At low load, the average stack PM2.5 mass concentration using the Alpha sampler is lower (0.068 mg/dscm) with a RSD of 29 percent (Table 4-5c). At low load, the 95 percent confidence lower bound of the average stack PM2.5 mass result is less than the post-test DSB result, indicating the results are not significantly above the DSB at this confidence level. However, because of the unusually high post-test DSB result, this may be a conservative assessment of the true difference between sample and background.

Table 4-5. PM2.5 Mass Concentrations (Site Echo).
(a) Alpha Sampler, High Load

Units		Results							
Run Number	-	Alpha-Hi-R1 ⁽ⁱ⁾	Alpha-Hi-R2 ⁽ⁱ⁾	Alpha-Hi-R3 ⁽ⁱ⁾	Alpha-Hi-R4	Average	RSD (%)	Ambient	MDL
Date	-	11-May-03	12-May-03	13-May-03	14-May-03			21-May-03	(1)
PM2.5	mg/dscm	1.0E-1	1.4E-1	1.2E-1	9.9E-2	1.1E-1	15	1.5E-2	2.5E-3
	lb/hr	3.0E-1	3.9E-1	3.5E-1	2.9E-1	3.3E-1	14	n/a	n/a

(b) Beta Sampler - High load

Units		Results							
Run Number	-	Beta-Hi-R1	Beta-Hi-R2	Beta-Hi-R3	Beta-Hi-R4	Average	RSD (%)		MDL
Date	-	11-May-03	12-May-03	13-May-03	14-May-03				(1)
PM2.5 (T1 Filter)	mg/dscm	6.0E-2	7.8E-2	1.8E-2	6.7E-2	5.6E-2 a	47		1.7E-3
	lb/hr	1.7E-1	2.3E-1	5.3E-2	2.0E-1	1.6E-1	47		n/a
PM2.5 (T2 Filter)	mg/dscm	5.1E-2	5.2E-2	4.3E-2	5.0E-2	4.9E-2	9		1.7E-3
	lb/hr	1.5E-1	1.5E-1	1.2E-1	1.5E-1	1.4E-1	9		n/a

(c) Alpha Sampler - Low Load

Units		Results							
Run Number	-	Alpha-Lo-R1	Alpha-Lo-R2	Alpha-Lo-R3	-	Average	RSD (%)		MDL
Date	-	16-May-03	17-May-03	18-May-03	-				(1)
PM2.5	mg/dscm	8.7E-2	6.9E-2	4.8E-2	-	6.8E-2 a	29		3.4E-3
	lb/hr	1.9E-1	1.5E-1	1.1E-1	-	1.5E-1	29		n/a

(d) Beta Sampler - Low Load

Units		Results							
Run Number	-	Beta-Lo-R1	Beta-Lo-R2	Beta-Lo-R3		Average	RSD (%)		MDL
Date	-	16-May-03	17-May-03	18-May-03					(1)
PM2.5 (T1 Filter)	mg/dscm	5.8E-2	4.7E-2	8.3E-2		6.2E-2	30		2.8E-3
	lb/hr	1.3E-1	1.0E-1	1.8E-1		1.4E-1	30		n/a
PM2.5 (T2 Filter)	mg/dscm	2.1E-2	3.4E-2	4.4E-2		3.3E-2 a b	34		2.8E-3
	lb/hr	4.7E-2	7.5E-2	9.7E-2		7.3E-2	34		n/a

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the Field Blank concentration.

⁽ⁱ⁾ High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

High winds on the stack during the tests caused significant local static air pressure fluctuations around the stack, which interfered with the bypass (Hi-Vol) fan flow measurements on the Alpha sampler during high load condition Runs 1 to 3. The bypass fan provides one of the primary measurements for determining the dilution air flow rate, and hence the dilution ratio. The bypass fan contains an orifice and an internal pressure tap. By monitoring the pressure differential across the orifice, the flow can be calculated from calibration data. The orifice discharges directly to the open surroundings. A differential pressure transducer is used to measure the orifice pressure differential. In the equipment configuration supplied by DRI, the transducer was located in a small box located a few feet away from the dilution sampler, with a single length of tubing to connect one port of the transducer to the upstream orifice tap on the bypass fan. The other port on the transducer was open to atmosphere. Because of the gusty high winds, static pressure varied with both time and location around the outside of the stack, causing the transducer reading to exhibit large random fluctuations. The wind interference was corrected for the remaining tests by running a length of tubing from the static pressure tap on the transducer to a point directly adjacent to the bypass fan and placing a temporary wind shield around the assembly. During subsequent laboratory tests, it was shown that this configuration did not significantly affect the flow calibration of the bypass fan orifice. It is likely that the average bypass flow for Runs 1 to 3 is valid, since the period of the fluctuations (milliseconds to seconds) was typically much less than the total run duration (six hours) and the fluctuations should average out. However, this problem possibly introduced a small degree of bias in the measured bypass fan flow rate which affects the calculated dilution ratio and hence in-stack PM_{2.5} mass concentration. The Alpha sampler results for Runs 1 to 3 are slightly higher compared to Run 4 (Table 4-5), indicating the possibility of a positive bias on the order of 20 percent due to the flow interference.

PM_{2.5} mass results from the Beta dilution sampler TMFs are similar in magnitude but somewhat lower (on average 27 percent) compared to those from the Alpha dilution sampler. TMF net weights ranged from 9 to 54 μg , with middle range of weights falling between 25 and 39 μg (25th to 75th percentile). All but one of the weights (9 μg) is well above the analytical uncertainty of 6.4 μg . Samples were collected on two TMFs in parallel (designated T1 and T2) to gain a preliminary assessment of measurement precision. The PM_{2.5} concentration measured with the

Beta sampler at high load averages 0.056 and 0.049 mg/dscm for filters T1 and T2, respectively (Table 4-5b). The run results are very tightly grouped for the T2 filters, with a RSD of 9 percent, whereas the T1 filters have a somewhat high standard deviation of 47 percent, driven by the single low value for Run 3. At low load, the average concentrations are slightly lower - 0.062 and 0.033 mg/dscm with a RSD of 30 and 34 percent for filters T1 and T2, respectively (Table 4-5d). A paired sample t-test of the T1 and T2 filter results for high load and low load cases separately shows the difference in mean results is not significant at the 95 percent confidence level. Compared to the other high load runs, the Beta sampler results for Run 3 are slightly lower. A review of the test results showed no reason to exclude Run 3 as an outlier, however it remains a potential anomaly. It should be noted that the sample flow rate for T2 was measured using far less accurate type of flow meter (Dwyer RateMaster, ± 5 percent accuracy at typical reading) than was used for the T1 filter (TSI, Inc. thermal mass flow, ± 0.25 percent accuracy at typical reading). In addition, an error in placement of the pressure gage near the rotameter probably magnified the potential error. Much of the observed difference between the T1 and T2 results may be due to this difference; therefore, the T2 filter results are not considered reliable.

The Beta sampler mean PM_{2.5} mass concentrations for the high load tests are approximately one-half of the corresponding Alpha sampler average, while the low load results are in good agreement (Table 4-5). The difference in the high load results is probably influenced by the flow measurement interference discussed earlier. If high load Runs 1 to 3 are excluded, the comparison between the two samplers is much more favorable. A paired sample t-test of the high and low load results shows no significant difference between the samplers at the 95 percent confidence level, regardless of whether high load Runs 1, 2 and 3 are included, implying the bias is not significant. An F-test shows the variances of the two samplers are similar; hence, method precision for the two designs also is similar. No reason, other than the wind interference problem that occurred with the Alpha sampler during high load tests, was found to explain why the apparent bias is relatively large for the high load tests and nearly indistinguishable for low load tests. The results suggest that the Beta sampler results may be biased low compared to the Alpha sampler, although any bias was too small to discern above the variability in the results. See Section 7 for further discussion of these issues.

Exploratory measurements using a commercial laser photometer to measure real-time PM_{2.5} trends in the diluted sample and ambient air were made to determine if the technique could be used to optimize the filter mass loadings in the dilution sampler and to determine if any correlation between ambient PM_{2.5} and stack PM_{2.5} trends could be established. Measurements were made concurrently at the combustion air inlet and in the diluted sample from the Alpha sampler. No significant correlation was found between the two measurements for any of the test runs (Figures 4-1 and 4-2). Large variations in the laser photometer response can be seen in the stack samples, while response of the instrument at the ambient location is relatively constant. The average laser photometer response during each test run does not agree well with the filter results, although the difference is not significant at the 95 percent confidence level considering the variation in the laser photometer response. The apparent difference between the laser photometer and the filter results may indicate that the aerosol properties in the stack samples are significantly different from those of the calibration aerosol (see Section 3). The Alpha sampler laser photometer trends show some similarities from run to run. High load Runs 2, 3 and 4 show a decrease in concentration after about 1-2 hours, while all the low load runs show an increase in concentration throughout the runs. There are no other readings (dilution sampler flows, temperatures, RH, etc.) that seem to correlate with these trends. The exponential character of the low load trends seems to suggest a mixing or deposition (e.g., in the Tygon[®] sample line) related phenomenon in the measurement system. The trends are surprising given the relatively steady conditions indicated by other readings. Further assessment of the technique based on these results is needed to determine the usefulness of this measurement technique in this application.

One developmental aspect of the dilution sampling protocol is recovery of deposits on the surfaces of the sampler upstream of the filters. Hildemann (1989) demonstrated that losses of monodisperse ammonium fluorescein particles between 1.3 and 6.2 μm occur mainly in the probe and venturi. Approximately 5 to 20 percent of particles smaller than 2.5 μm were deposited in the sample inlet line and sample venturi. Losses in the tunnel section and aging chamber account for less than 1.5 to 3 percent of all particles from 1.3 to 6.2 μm . Therefore, quantitative recovery in this test focused on the probe nozzle, probe, inlet line (Alpha sampler only) and sample venturi. These sections were rinsed with acetone following each test

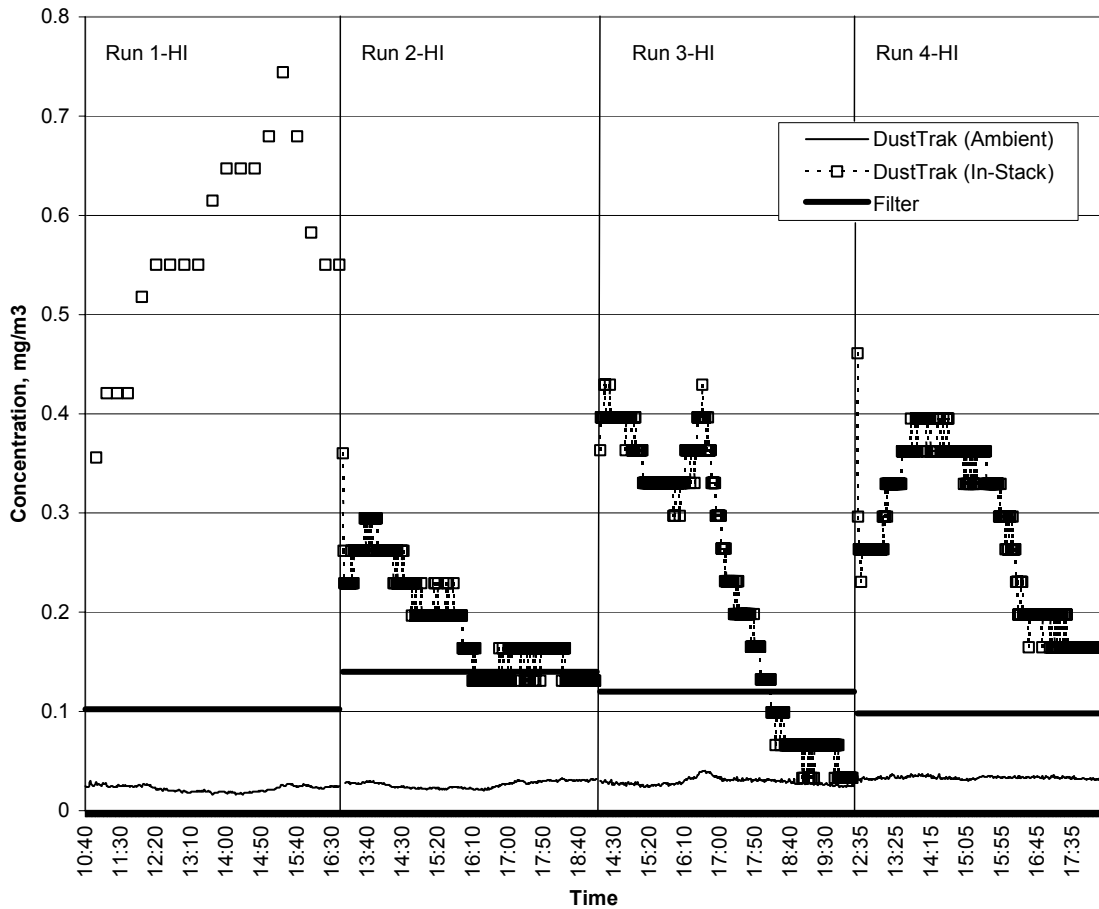


Figure 4-1. Ambient and In-Stack Laser Photometer Trends – High Load (Site Echo).

run, following similar procedures given in EPA Method 5 (40CFR60, App. A). This produced three rinse samples for the Alpha sampler (probe/nozzle, sample line, sample venturi) and two rinse samples for the Beta sampler (probe/nozzle, sample venturi). A single acetone reagent blank (from the reagent bottle) was collected for the test campaign. Due to the low concentration of PM in gas combustion products, the volume of the reagent blank was made larger than normal (500 mL) to obtain better analytical resolution. An acetone recovery blank (from the wash bottle) inadvertently was not collected. Therefore, results from previous tests were used as an indication of probable acetone recovery blank levels. In general, the levels found in the probe rinses (Table 4-6) are significant compared to the TMF results. For example, the average total mass found in the high load Alpha sampler rinses (corrected for reagent blank) is 0.40 mg/dscm,

compared to an average TMF result of 0.11 mg/dscm. This is strongly inconsistent with Hildemann's earlier results.

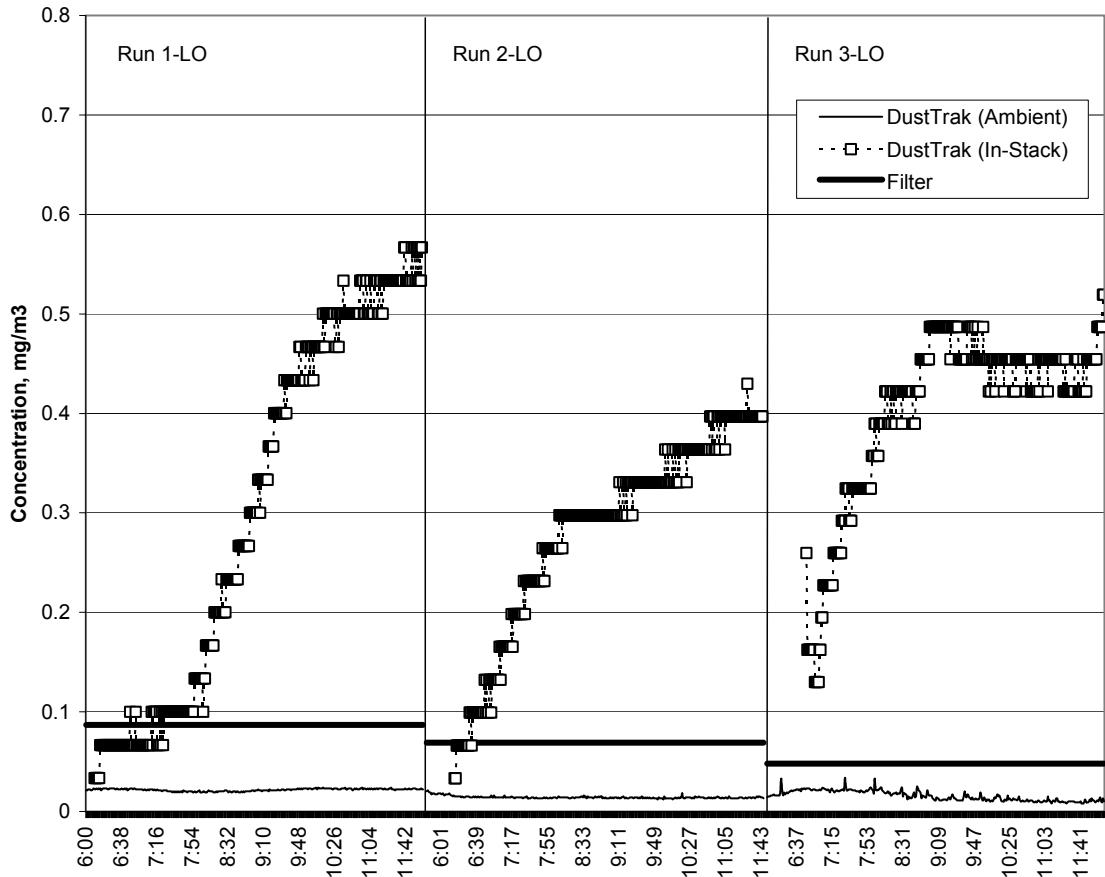


Figure 4-2. Ambient and In-Stack Laser Photometer Trends – Low Load (Site Echo).

Examining the acetone reagent blank (from the reagent bottle) results adds further insight. The acetone reagent blank represents 36 to 330 percent (average 100 percent) of the TMF results, and 2 to 204 percent (average 31 percent) of the probe rinse results. Although an acetone recovery blank (from the field wash bottle) inadvertently was not obtained, typical results from other tests (also shown on Table 4-6) suggest it is expected to be even more significant, accounting for an equivalent in-stack concentration of 0.53 mg/dscm for this test. It should be noted that these blank levels are very low, far below the upper limit of ≤ 0.001 weight percent (10 ppm) residue

Table 4-6. Dilution Sampler Probe, Nozzle, Sample Line and Venturi Rinse Results (Site Echo).

	Units	Alpha-HI-1 (1)	Alpha-HI-2 (1)	Alpha-HI-3 (1)	Alpha-HI-4	Alpha-LO-1	Alpha-LO-2	Alpha-LO-3	Beta-HI-1	Beta-HI-2	Beta-HI-3	Beta-HI-4	Beta-LO-1	Beta-LO-2	Beta-LO-3
Rinse mass - probe & nozzle	mg	7.4	2.4	6.1	0.6	1.2	0.3	0.6	7.1	6.8	6.9	2.2	2.2	2.8	3.5
Rinse volume - probe & nozzle	mL	122	128	164	138	52.0	163	123	76.0	94.0	176	178	73.0	161	111
Rinse mass - sample line	mg	6.8	5.3	3.5	5.3	1.6	3.8	0.6	na	na	na	na	na	na	na
Rinse volume - sample line	mL	133	129	162	123	121	198	164	na	na	na	na	na	na	na
Rinse mass - venturi	mg	0.1	1.4	1.4	0.1	-	1.9	0.1	0.3	0.2	5.6	2.2	0.4	0.1	(1)
Rinse volume - venturi	mL	103	97.0	158	127	69.0	139	121	63.0	46.0	68.0	71.0	29.0	25.0	(1)
Rinse Mass (total, corrected for RB)	mg	13.7	8.5	10.2	5.4	2.4	5.2	0.6	7.2	6.8	12.1	4.0	2.4	2.6	3.3
Rinse Mass (total, corrected for RB, in-stack equivalent)	mg/dscm	0.59	0.36	0.42	0.23	0.14	0.29	0.04	0.29	0.27	0.47	0.16	0.13	0.13	0.17
Reagent blank mass	mg	0.8													
Reagent blank volume	mL	497													
Reagent blank (in-stack equivalent)	mg/dscm	0.10	0.10	0.13	0.11	0.07	0.07	0.07	0.04	0.04	0.06	0.07	0.03	0.05	0.03
Recovery blank mass (typical) (2)	mg	0.4													
Recovery blank volume (typical) (2)	mL	50													
Recovery blank (in-stack equivalent)	mg/dscm	0.50	0.47	0.64	0.53	0.33	0.67	0.55	0.18	0.18	0.30	0.33	0.13	0.23	0.14

(1) Sample container was broken on-site.

(2) A recovery (wash bottle) blank was not collected. Typical results from other tests are shown.

RB=reagent blank

(1) High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

specified for acetone reagent in EPA Method 5 (equivalent to approximately 3.9 mg for the volume of the reagent blank in this test) and typical reagent manufacturer's specifications for ACS grade (10 ppm) or HPLC-UV grade (5 ppm). Further, based on an EPA study that showed a standard deviation of 0.36 mg for 22 sample train blanks performed in the laboratory using glass probes (Shigehara, 1996), approximately 70 percent of the rinse results are below the LQL (ten times standard deviation or 3.6 mg) of the acetone rinse procedure.

It is clear from these considerations that the acetone rinse results may be dominated by background levels or analytical limitations, and therefore may not be representative of actual particle deposits in the sampler. Therefore, the rinse results are not added to the TMF results for determining total PM_{2.5} mass. These results indicate that the acetone rinse procedure does not have the required sensitivity for these low concentrations. An improved method of recovering deposits from the probe, sample line and venturi is needed for gas combustion sources.

However, based on Hildemann's earlier results, these deposits are expected to account for less than 20 percent of the total PM_{2.5}. Further tests are needed to assess particle losses at these low concentrations.

A single ambient air sample was collected at the end of the field campaign. The average PM_{2.5} mass concentration in the ambient sample is 0.15 mg/dscm. The 2001 annual average PM_{2.5} concentration, obtained from a nearby ambient air monitoring station, was 0.019 mg/dscm, comparable to the ambient sample taken on-site.

SO₄⁼, NO₃⁻, Cl⁻, NH₄⁺ and Soluble Sodium (Na⁺) Ions

QFFs were analyzed for SO₄⁼, Cl⁻, NO₃⁻, NH₄⁺ and Na⁺ ions. Of these, SO₄⁼ and NH₄⁺ are the highest with average concentrations of approximately 0.031 and 0.018 mg/dscm, respectively, in the Alpha sampler at high load (Table 4-7). SO₄⁼ concentration is approximately one-fourth of the PM_{2.5} mass concentration (Alpha sampler). Cl⁻ concentrations are generally not significantly above the DSB, FB or trip blank (TB). Soluble Na, Cl⁻, and NO₃⁻ concentrations in the stack are not significantly greater than in the ambient air in 3 out of 4 cases. Comparing the Alpha sampler results for high versus low load (Table 4-8), the results generally are not significantly different using a 2-sample t-test.

The Beta sampler ion results are on average two-thirds of the Alpha sampler results, indicating the possibility of a low bias in the Beta sampler results. The differences between Alpha and Beta results are generally significant at the 95 percent confidence level, based on paired sample t-tests. It should be noted that the paired and 2-sample t-tests did not include sampling bias, which contributes to total uncertainty. Taking this into account reduces the significance of the differences. The Alpha sampler flow interference problem (discussed earlier) may have introduced a positive bias in the Alpha sampler results for Runs 1, 2 and 3, which may account for some of the observed differences.

The QFFs used for these measurements have the potential for a positive SO₄⁼ bias due to their high surface area providing the potential for adsorptive artifacts. The average SO₄⁼ is approximately one third the expected value based on the elemental S content on the TMF (see later discussion). Although agreement is normally expected to be much better than this, it indicates that positive bias due to SO₂ adsorption is probably not significant. The discrepancy between elemental S and SO₄⁼ measurements indicates a possible low bias in the SO₄⁼ measurement or a high bias in the elemental S measurement.

Table 4-7. Particulate SO₄⁼, NO₃⁻, Cl⁻, NH₄⁺ and Soluble Na Concentrations – High Load (Site Echo).

(a) Alpha Sampler - High Load

Parameter	Units	Value							
		Alpha-Hi-R1 (i)	Alpha-Hi-R2 (i)	Alpha-Hi-R3 (i)	Alpha-Hi-R4	Average	RSD (%)	Ambient 21-May-03	MDL (1)
Run Number	-	12-May-03	13-May-03	14-May-03	15-May-03				
Date	-								
Sulfate	mg/dscm	2.3E-2	4.0E-2	3.6E-2	2.6E-2	3.1E-2	25	1.3E-3	3.8E-3
	lb/hr	6.8E-2	1.1E-1	1.0E-1	7.8E-2	9.1E-2	24	n/a	
Nitrate	mg/dscm	3.8E-3	4.1E-3	4.2E-3	5.3E-3	4.3E-3	15	6.8E-4	3.8E-3
	lb/hr	1.1E-2	1.2E-2	1.2E-2	1.6E-2	1.3E-2	17	n/a	
Chloride	mg/dscm	4.9E-3	7.7E-3	9.0E-3	9.6E-3	7.8E-3 a b c	27	2.2E-4	3.8E-3
	lb/hr	1.4E-2	2.2E-2	2.6E-2	2.9E-2	2.3E-2	28	n/a	
Ammonium	mg/dscm	1.4E-2	2.3E-2	2.0E-2	1.6E-2	1.8E-2	21	8.0E-4	3.8E-3
	lb/hr	4.2E-2	6.6E-2	5.9E-2	4.8E-2	5.4E-2	20	n/a	
Soluble Na	mg/dscm	1.8E-3	2.4E-3	3.5E-3	4.0E-3	2.9E-3 a	34	4.1E-4	3.8E-4
	lb/hr	5.3E-3	6.8E-3	1.0E-2	1.2E-2	8.5E-3	35	n/a	

(b) Beta Sampler - High Load

Parameter	Units	Value							
		Beta-Hi-R1	Beta-Hi-R2	Beta-Hi-R3	Beta-Hi-R4	Average	RSD (%)		MDL (1)
Run Number	-	12-May-03	13-May-03	14-May-03	15-May-03				
Date	-								
Sulfate	mg/dscm	1.6E-2	2.2E-2	2.4E-2	2.1E-2	2.1E-2	17		2.6E-3
	lb/hr	4.6E-2	6.4E-2	7.0E-2	6.3E-2	6.1E-2	17		
Nitrate	mg/dscm	3.7E-3	3.3E-3	3.5E-3	4.2E-3	3.7E-3 a	11		2.6E-3
	lb/hr	1.1E-2	9.5E-3	1.0E-2	1.3E-2	1.1E-2	12		
Chloride	mg/dscm	6.0E-3	3.2E-3	ND	ND	< 4.6E-3 b c d	44		2.6E-3
	lb/hr	1.8E-2	9.2E-3	ND	ND	< 1.3E-2	45		
Ammonium	mg/dscm	1.1E-2	1.3E-2	1.1E-2	8.7E-3	1.1E-2	17		2.6E-3
	lb/hr	3.2E-2	3.9E-2	3.2E-2	2.6E-2	3.2E-2	16		
Soluble Na	mg/dscm	1.5E-3	1.4E-3	2.3E-3	2.5E-3	1.9E-3	29		2.6E-4
	lb/hr	4.4E-3	4.0E-3	6.7E-3	7.6E-3	5.7E-3	30		

Shading indicates substance was not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the Field Blank concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Trip Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

(i) High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

Particulate Carbon

OC and EC were measured on QFFs from the dilution sampler as a measurement of particulate carbon emissions including the organic compounds that condense under ambient conditions. OC concentration ranges from 0.053 to 0.22 mg/dscm (Table 4-9). The average OC concentration (0.13 mg/dscm) is greater the PM_{2.5} mass concentration (0.076 mg/dscm) including all runs (except PM_{2.5} mass from the Beta sampler T2 filters). While these concentrations are generally well above the MDL and the ambient air concentration, they are not significantly greater than the DSB and in at least one case are not significantly greater than in the

Table 4-8. Particulate SO₄⁼, NO₃⁻, Cl⁻, NH₄⁺ and Soluble Na Concentrations – Low Load (Site Echo).

(a) Alpha Sampler - Low Load

Parameter	Units	Value							
		Alpha-Lo-R1	Alpha-Lo-R2	Alpha-Lo-R3	-	Average	RSD (%)		MDL (1)
Run Number	-				-				
Date	-	17-May-03	18-May-03	19-May-03	-				
Sulfate	mg/dscm	1.7E-2	2.1E-2	2.2E-2		2.0E-2	14		5.1E-3
	lb/hr	3.7E-2	4.6E-2	4.8E-2		4.4E-2	14		
Nitrate	mg/dscm	4.4E-3	ND	ND		< 4.4E-3 e	n/a		5.1E-3
	lb/hr	9.7E-3	ND	ND		< 9.7E-3	n/a		
Chloride	mg/dscm	8.3E-3	8.9E-3	6.0E-3		7.8E-3 a b c	20		5.1E-3
	lb/hr	1.8E-2	2.0E-2	1.3E-2		1.7E-2	20		
Ammonium	mg/dscm	1.1E-2	1.3E-2	1.4E-2		1.3E-2	13		5.1E-3
	lb/hr	2.4E-2	3.0E-2	3.0E-2		2.8E-2	13		
Soluble Na	mg/dscm	3.4E-3	1.4E-3	1.5E-3		2.1E-3 a b c d	54		5.1E-4
	lb/hr	7.5E-3	3.1E-3	3.3E-3		4.6E-3	54		

(b) Beta Sampler - Low Load

Parameter	Units	Value							
		Beta-Lo-R1	Beta-Lo-R2	Beta-Lo-R3	-	Average	RSD (%)		MDL (1)
Run Number	-				-				
Date	-	17-May-03	18-May-03	19-May-03	-				
Sulfate	mg/dscm	1.1E-2	1.2E-2	1.2E-2		1.2E-2	6		4.2E-3
	lb/hr	2.4E-2	2.7E-2	2.7E-2		2.6E-2	6		
Nitrate	mg/dscm	3.6E-3	ND	4.3E-3		< 4.0E-3 a	13		4.2E-3
	lb/hr	8.0E-3	ND	9.5E-3		< 8.8E-3	13		
Chloride	mg/dscm	1.1E-2	9.1E-3	9.2E-3		9.7E-3 a b c	10		4.2E-3
	lb/hr	2.4E-2	2.0E-2	2.0E-2		2.1E-2	10		
Ammonium	mg/dscm	7.9E-3	8.9E-3	8.9E-3		8.5E-3	7		4.2E-3
	lb/hr	1.7E-2	2.0E-2	2.0E-2		1.9E-2	7		
Soluble Na	mg/dscm	2.8E-3	1.1E-3	1.6E-3		1.9E-3 a c d	47		4.2E-4
	lb/hr	6.3E-3	2.5E-3	3.5E-3		4.1E-3	47		

Shading indicates substance was not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the Field Blank concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Trip Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

FB or the TB. OC accounts for essentially all of the total particulate carbon. EC was detected in only one-third of the samples, generally at levels close to the MDL. The differences between Alpha and Beta samplers, and the differences between high load and low load, are generally not significant at the 95 percent confidence level based on paired and 2-sample t-tests

Table 4-9. Primary OC/EC Concentrations (Site Echo).

(a) Alpha Sampler - High Load

Parameter	Units	Value							
		Alpha-Hi-R1 (i) 12-May-03	Alpha-Hi-R2 (i) 13-May-03	Alpha-Hi-R3 (i) 14-May-03	Alpha-Hi-R4 15-May-03	Average	RSD (%)	Ambient 21-May-03	MDL (1)
Run Number	-								
Date	-								
Organic Carbon (OC) **	mg/dscm	2.2E-1	1.6E-1	1.6E-1	2.0E-1	1.8E-1 a	17	1.1E-2	2.8E-2
	lb/hr	6.4E-1	4.6E-1	4.5E-1	5.9E-1	5.4E-1	18	n/a	
Elemental Carbon (EC)	mg/dscm	1.2E-2	ND	ND	ND	< 1.2E-2 e	n/a	2.9E-3	6.5E-3
	lb/hr	3.6E-2	ND	ND	ND	< 3.6E-2	n/a	n/a	
Total Carbon (TC)*	mg/dscm	2.3E-1	< 1.6E-1	< 1.6E-1	< 2.0E-1	< 1.9E-1	19	1.4E-2	6.5E-3
	lb/hr	6.8E-1	4.6E-1	4.5E-1	5.9E-1	5.5E-1	20	n/a	
Backup Filter OC ***	mg/dscm	1.7E-1	1.5E-1	1.7E-1	1.8E-1	1.7E-1 a c	7	7.0E-3	2.8E-2
	lb/hr	4.9E-1	4.4E-1	4.8E-1	5.4E-1	4.9E-1	8	n/a	

(b) Beta Sampler - High Load

Parameter	Units	Value							
		Beta-Hi-R1 12-May-03	Beta-Hi-R2 13-May-03	Beta-Hi-R3 14-May-03	Beta-Hi-R4 15-May-03	Average	RSD (%)		MDL (1)
Run Number	-								
Date	-								
Organic Carbon (OC) **	mg/dscm	1.4E-1	1.0E-1	9.3E-2	5.3E-2	9.7E-2 a b c	37		1.9E-2
	lb/hr	4.1E-1	3.0E-1	2.7E-1	1.6E-1	2.8E-1	36		
Elemental Carbon (EC)	mg/dscm	4.7E-3	3.9E-3	9.1E-3	ND	< 5.9E-3 a d	47		4.4E-3
	lb/hr	1.4E-2	1.1E-2	2.6E-2	ND	< 1.7E-2	47		
Total Carbon (TC)*	mg/dscm	1.4E-1	1.1E-1	1.0E-1	< 5.3E-2	< 1.0E-1	37		4.4E-3
	lb/hr	4.2E-1	3.1E-1	3.0E-1	1.6E-1	3.0E-1	36		
Backup Filter OC ***	mg/dscm	8.3E-2	8.9E-2	8.7E-2	7.2E-2	8.3E-2 a b c	8		1.9E-2
	lb/hr	2.4E-1	2.6E-1	2.5E-1	2.1E-1	2.4E-1	6		

(c) Alpha Sampler - Low Load

Parameter	Units	Value							
		Alpha-Lo-R1 17-May-03	Alpha-Lo-R2 18-May-03	Alpha-Lo-R3 19-May-03	-	Average	RSD (%)		MDL (1)
Run Number	-								
Date	-								
Organic Carbon (OC) **	mg/dscm	1.4E-1	1.6E-1	1.3E-1		1.4E-1 a	11		3.8E-2
	lb/hr	3.1E-1	3.5E-1	2.8E-1		3.1E-1	11		
Elemental Carbon (EC)	mg/dscm	ND	ND	1.1E-2		< 1.1E-2 e	n/a		8.8E-3
	lb/hr	ND	ND	2.5E-2		< 2.5E-2	n/a		
Total Carbon (TC)*	mg/dscm	< 1.4E-1	< 1.6E-1	1.4E-1		< 1.5E-1	7		8.8E-3
	lb/hr	3.1E-1	3.5E-1	3.1E-1		3.2E-1	7		
Backup Filter OC ***	mg/dscm	1.3E-1	1.5E-1	1.4E-1		1.4E-1 a b c	7		3.8E-2
	lb/hr	2.8E-1	3.2E-1	3.2E-1		3.1E-1	7		

(d) Beta Sampler - Low Load

Parameter	Units	Value							
		Beta-Lo-R1 17-May-03	Beta-Lo-R2 18-May-03	Beta-Lo-R3 19-May-03	-	Average	RSD (%)		MDL (1)
Run Number	-								
Date	-								
Organic Carbon (OC) **	mg/dscm	9.2E-2	1.0E-1	1.2E-1		1.0E-1 a b	12		3.2E-2
	lb/hr	2.0E-1	2.2E-1	2.6E-1		2.3E-1	12		
Elemental Carbon (EC)	mg/dscm	ND	ND	ND		< ND e	n/a		7.3E-3
	lb/hr	ND	ND	ND		< ND	n/a		
Total Carbon (TC)*	mg/dscm	< 9.2E-2	< 1.0E-1	< 1.2E-1		< 1.0E-1	12		7.3E-3
	lb/hr	2.0E-1	2.2E-1	2.6E-1		2.3E-1	12		
Backup Filter OC ***	mg/dscm	1.2E-1	1.1E-1	1.3E-1		1.2E-1 a b c	7		3.2E-2
	lb/hr	2.6E-1	2.5E-1	2.8E-1		2.6E-1	7		

Shading indicates substance was not detected in at least 3 valid test runs.

* TC = OC + EC; TC Average is average of TC runs, not OC Average + EC Average; TC MDL is lesser of OC MDL and EC MDL.

** OC measurements are subject to a potential positive bias from adsorption of VOC species. See also footnote *** and Sections 6 & 7.

*** OC measured on a "backup" quartz fiber filter placed downstream of Teflon membrane filter. Refer to Sections 6 & 7 for further discussion.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

The QFFs used for OC/EC analysis have the potential for positive OC bias due to adsorption of VOCs on the media and the collected sample. A backup QFF placed directly behind the TMF was used to evaluate the potential magnitude of the absorptive bias on the clean media. The average OC concentrations on the backup filter and on the primary filter are essentially the same. Therefore, the magnitude of any bias in the OC result is potentially significant, and may be on the same magnitude as the measured value. Some individual VOCs were present in the sample at concentrations similar to OC and the sum of measured VOCs is several times higher than OC, indicating a significant potential source of VOC. Supporting the likelihood of a positive bias is the fact that the reconstructed PM_{2.5} mass (dominated by OC) is nearly twice the measured PM_{2.5}. The OC artifact is the subject of ongoing studies (Turpin et al., 1991, 1994, 2000; Kirshstetter et al., 2001), and because the artifact is not well understood, it is the current convention not to subtract the backup OC from the primary result. However, the similarity of the primary and backup OC results indicates the need for caution when using these results.

Particulate Carbon Speciation

SVOCs were measured to determine the extent to which OC measured on the QFF could be speciated, and to identify specific particulate organic compounds that could serve as markers for source apportionment. The analytical protocol was optimized for detection of PAH, therefore most other SVOCs were not quantified. SVOCs were determined on the combined TIGF/PUF/XAD-4TM/PUF cartridge used with the dilution sampler. This method determines both particulate and vapor phase SVOCs together, but it is assumed that all SVOCs eventually will condense to particulate phase in the atmosphere. For high load conditions, only seven substances were detected in three or more test runs (Table 4-10). Only anthrone, B-trimethylnaphthalene, F-trimethylnaphthalene and E-trimethylnaphthalene were detected at concentrations more than 5 times the MDL (concentrations less 5 times the MDL are not considered significant). Of the seven SVOCs detected in three or more the high load runs, none were detected at concentrations significantly higher than the DSB, FB, TB and/or ambient air sample, and hence these are considered indistinguishable from the background of the measurement methods. Of the remaining 22 SVOCs that were detected in fewer than three high load test runs, 14 have concentrations that are less than 5 times the MDL hence these are not considered significant.

Seven of the eight remaining substances were detected in only one test run, therefore results for these are not considered reliable indicators of actual emissions.

Table 4-10. Primary Particulate Carbon Species Concentrations – High Load (Site Echo).

Parameter	Value							
	mg/dscm					%	mg/dscm	
Units	Alpha-Hi-R1 (i)	Alpha-Hi-R2 (i)	Alpha-Hi-R3 (i)	Alpha-Hi-R4	Average	RSD	Ambient	MDL
Run Number Date	12-May-03	13-May-03	14-May-03	15-May-03			21-May-03	
2-Methylbiphenyl	8.0E-4	1.1E-3	1.7E-3	1.8E-3	1.4E-3 a b c	35	5.6E-5	2.8E-4
3-Methylbiphenyl	6.2E-4	7.1E-4	8.7E-4	8.4E-4	7.6E-4 b c	15	2.2E-5	4.0E-4
1+2-ethylnaphthalene	4.0E-4	2.9E-4	5.6E-4	ND	< 4.1E-4 a b c	33	1.5E-5	2.3E-4
Anthrone	9.1E-6	1.3E-5	1.3E-4	ND	< 4.9E-5 a b	135	ND	1.8E-6
B-trimethylnaphthalene	6.7E-5	2.9E-5	9.3E-6	8.4E-6	2.9E-5 c d	96	4.4E-6	1.8E-6
F-trimethylnaphthalene	3.7E-5	1.0E-5	ND	3.4E-6	< 1.7E-5 a c d	106	1.7E-6	1.7E-6
E-trimethylnaphthalene	4.6E-5	1.2E-5	5.9E-6	4.2E-6	1.7E-5 a c d	115	2.4E-6	1.8E-6
4-Methylbiphenyl	7.5E-4	ND	ND	ND	< 7.5E-4 e	n/a	ND	3.4E-5
D-dimethylphenanthrene	ND	ND	6.6E-4	ND	< 6.6E-4 e	n/a	ND	5.3E-5
1,3+1,6+1,7-dimethylnaphthalene	5.4E-4	ND	ND	ND	< 5.4E-4 e	n/a	3.6E-5	4.1E-4
Biphenyl	ND	3.4E-4	ND	ND	< 3.4E-4 e	n/a	ND	1.2E-4
B-methylphenanthrene	ND	ND	2.4E-4	ND	< 2.4E-4 e	n/a	ND	2.0E-5
2,3,5+1-trimethylnaphthalene	4.7E-5	3.5E-4	ND	ND	< 2.0E-4 a d	108	2.3E-6	5.3E-6
2,6+2,7-dimethylnaphthalene	2.0E-4	ND	ND	ND	< 2.0E-4 e	n/a	1.4E-5	1.9E-4
2-methylnaphthalene	1.8E-4	ND	ND	ND	< 1.8E-4 e	n/a	3.3E-5	1.1E-4
1,4,5-trimethylnaphthalene	1.7E-4	ND	ND	ND	< 1.7E-4 e	n/a	ND	1.7E-4
1,2-dimethylnaphthalene	ND	ND	1.6E-4	ND	< 1.6E-4 e	n/a	4.6E-6	1.2E-4
1-methylnaphthalene	1.8E-4	ND	1.1E-4	ND	< 1.4E-4 a b c d	34	2.1E-5	6.8E-5
Benzo(a)pyrene	ND	ND	9.1E-5	ND	< 9.1E-5 e	n/a	ND	1.1E-5
Anthracene	ND	ND	6.3E-5	ND	< 6.3E-5 e	n/a	ND	0.0E+0
C-trimethylnaphthalene	8.9E-5	2.5E-5	ND	ND	< 5.7E-5 a d	79	4.0E-6	1.4E-5
Fluoranthene	ND	ND	4.3E-5	ND	< 4.3E-5 e	n/a	ND	3.6E-6
Chrysene	ND	ND	ND	4.0E-5	< 4.0E-5 e	n/a	ND	3.6E-6
Benz(a)anthracene	ND	ND	ND	2.9E-5	< 2.9E-5 e	n/a	ND	1.1E-5
J-trimethylnaphthalene	2.4E-5	ND	1.9E-5	ND	< 2.2E-5	15	1.0E-6	1.4E-5
7-methylbenzo(a)pyrene	ND	ND	1.8E-5	ND	< 1.8E-5 e	n/a	ND	1.2E-5
Benzonaphthothiophene	ND	ND	ND	8.4E-6	< 8.4E-6 e	n/a	1.7E-7	3.6E-6
2-methylphenanthrene	5.8E-6	ND	ND	ND	< 5.8E-6 e	n/a	8.2E-7	3.6E-6
D-MePy/MeFl	5.8E-6	ND	ND	ND	< 5.8E-6 e	n/a	ND	1.8E-6

Shading indicates substance was not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the Field Blank concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Trip Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

(i) High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

No SVOCs were detected in all three low load runs (Table 4-11). Of the remaining 14 SVOCs that were detected in fewer than three of the low load runs, 11 did not have concentrations more than 5 times the MDL.

In summary, it was not possible to quantify actual particulate carbon species concentrations with high confidence because of the extremely low concentrations of SVOCs present in the exhaust. The sum of all the SVOCs that were detected in all runs accounts for approximately 3 percent of the OC measured on the QFF (after applying a factor of 1.08 to account for the average carbon weight in the detected SVOCs). This highlights the difficulty of quantifying SVOCs at such low concentrations, and may be a further indication of a positive bias in the OC measurement.

Table 4-11. Primary Particulate Carbon Species Concentrations – Low Load (Site Echo).

Parameter	Value						
	mg/dscm				%	mg/dscm	
Units							
Run Number	Alpha-Lo-R1	Alpha-Lo-R2	Alpha-Lo-R3	Average	RSD	Alpha-Ambient	MDL
Date	17-May-03	18-May-03	19-May-03			21-May-03	
2-Methylbiphenyl	2.2E-3	7.8E-4	ND	< 1.5E-3 a b c d	67	5.6E-5	2.9E-4
3-Methylbiphenyl	9.1E-4	ND	ND	< 9.1E-4 e	n/a	2.2E-5	4.1E-4
Biphenyl	ND	ND	5.5E-4	< 5.5E-4 e	n/a	ND	1.2E-4
1+2-ethylnaphthalene	ND	ND	3.5E-4	< 3.5E-4 e	n/a	1.5E-5	2.3E-4
Benzo(c)phenanthrene	ND	1.6E-4	ND	< 1.6E-4 e	n/a	ND	2.0E-5
2,3,5+I-trimethylnaphthalene	ND	3.4E-5	2.2E-4	< 1.3E-4 a d	104	2.3E-6	5.4E-6
Benz(a)anthracene	ND	4.7E-5	ND	< 4.7E-5 e	n/a	ND	1.1E-5
E-dimethylphenanthrene	ND	3.6E-5	ND	< 3.6E-5 e	n/a	ND	2.7E-5
Benzo(a)pyrene	ND	3.5E-5	ND	< 3.5E-5 e	n/a	ND	1.1E-5
Anthrone	2.6E-6	1.4E-5	ND	< 8.5E-6 a b	98	ND	1.8E-6
Benzonaphthothiophene	ND	6.8E-6	ND	< 6.8E-6 e	n/a	1.7E-7	3.6E-6
E-trimethylnaphthalene	9.4E-6	ND	3.3E-6	< 6.4E-6 a c d	67	2.4E-6	1.8E-6
F-trimethylnaphthalene	6.0E-6	ND	ND	< 6.0E-6 e	n/a	1.7E-6	1.7E-6
B-trimethylnaphthalene	9.4E-6	2.6E-6	ND	< 6.0E-6 a c d	81	4.4E-6	1.8E-6

Shading indicates substance was not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the Field Blank concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Trip Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Particulate Carbon Precursors

Only the reactions of VOCs with carbon numbers higher than seven are considered important in formation of secondary organic aerosols (Grosjean and Seinfeld, 1989), because the products from those having fewer than seven carbon atoms are too volatile to form aerosols under atmospheric conditions.

Evacuated stainless steel canisters were used to collect samples for VOC analysis (Table 4-12). 37 VOCs with carbon number of 8 and higher were detected at extremely low concentrations in all three high load test runs, but only 5 of these were detected at concentrations significantly

Table 4-12. Particulate Carbon Precursor Concentrations – High Load (Site Echo).

Parameter	Value							
	mg/dscm					(%)	mg/dscm	
Units								
Run Number	Alpha-Hi-R1 (i)	Alpha-Hi-R2 (i)	Alpha-Hi-R3 (i)	Alpha-Hi-R4	Stack Average	RSD	Ambient	MDL
Date	12-May-03	13-May-03	14-May-03	15-May-03			21-May-03	(1)
Particulate Carbon Precursors (VOC with Carbon Number 8 or greater)								
alpha-pinene	7.1E-2	3.4E-2	2.6E-2	1.9E-2	3.8E-2 a	61	7.4E-4	3.7E-4
2,2,5-trimethylhexane	5.1E-2	2.9E-2	2.2E-2	1.9E-2	3.0E-2 a	49	7.9E-4	3.7E-4
Limonene	7.2E-2	4.1E-3	3.8E-3	7.5E-4	2.0E-2 a d	171	2.1E-5	3.7E-4
beta-pinene	3.0E-2	1.5E-2	1.2E-2	1.4E-2	1.8E-2 a	46	3.1E-4	3.7E-4
m- & p-xylene	2.4E-2	1.9E-2	1.8E-2	4.1E-3	1.6E-2 a	52	6.7E-4	3.7E-4
1,2,3-trimethylbenzene	3.3E-2	1.5E-3	4.9E-3	1.9E-2	1.4E-2 a d	98	4.3E-4	3.7E-4
3-methyloctane	1.6E-2	1.2E-2	6.0E-3	4.5E-3	9.7E-3 a	55	3.5E-4	3.7E-4
3-methylheptane	3.7E-4	3.8E-4	2.8E-2	1.5E-3	7.5E-3 a d	180	6.2E-5	3.7E-4
Nonanal	7.0E-3	9.4E-3	3.0E-3	9.0E-3	7.1E-3	41	1.1E-4	3.7E-4
2,3,5-trimethylhexane	9.9E-3	8.6E-3	1.9E-3	7.9E-3	7.1E-3 a	50	5.2E-5	3.7E-4
Isopropyltoluene	1.3E-2	ND	5.7E-3	1.5E-3	< 6.7E-3 a	86	ND	3.7E-4
o-xylene	9.9E-3	6.0E-3	6.4E-3	1.9E-3	6.0E-3 a	54	2.9E-4	3.7E-4
3,6-dimethyloctane	5.5E-3	6.8E-3	6.4E-3	4.5E-3	5.8E-3	17	8.3E-5	3.7E-4
2,5-dimethylhexane	1.1E-2	ND	4.9E-3	7.5E-4	< 5.5E-3 a d	93	1.6E-4	3.7E-4
Ethylbenzene	8.1E-3	6.8E-3	5.3E-3	1.5E-3	5.4E-3 a	52	2.5E-4	3.7E-4
2,3-dimethylhexane	5.1E-3	8.6E-3	5.3E-3	2.3E-3	5.3E-3 a	49	6.2E-5	3.7E-4
m-ethyltoluene	5.9E-3	1.9E-3	6.8E-3	ND	< 4.8E-3 a	54	8.3E-5	3.7E-4
1,4-diethylbenzene	4.0E-3	6.0E-3	3.4E-3	5.3E-3	4.7E-3	25	1.3E-4	3.7E-4
o-ethyltoluene	1.1E-2	2.6E-3	3.0E-3	1.9E-3	4.5E-3 a d	90	1.1E-4	3.7E-4
2-methyloctane	4.8E-3	3.8E-3	4.5E-3	ND	< 4.3E-3 a	12	1.7E-4	3.7E-4
1,2,4-trimethylbenzene	6.2E-3	4.1E-3	3.8E-3	2.3E-3	4.1E-3	40	9.3E-5	3.7E-4
2,3-trimethylpentane	4.4E-3	3.0E-3	3.0E-3	2.6E-3	3.3E-3	24	2.4E-4	3.7E-4
2,2,4-trimethylpentane	5.5E-3	3.0E-3	2.3E-3	1.9E-3	3.2E-3 a	51	5.2E-4	3.7E-4
p-ethyltoluene	4.0E-3	3.0E-3	3.0E-3	1.5E-3	2.9E-3 a	36	1.3E-4	3.7E-4
2,4-dimethylhexane	2.2E-3	3.4E-3	ND	1.5E-3	< 2.4E-3 a	40	1.6E-4	3.7E-4
Octanal	3.3E-3	ND	2.6E-3	3.8E-4	< 2.1E-3 a	73	ND	3.7E-4
n-decane	2.2E-3	3.0E-3	ND	3.8E-4	< 1.9E-3 a d	72	5.2E-5	3.7E-4
Nonene-1	2.9E-3	7.5E-4	1.1E-3	7.5E-4	1.4E-3 a	75	9.3E-5	3.7E-4
n-octane	1.8E-3	7.5E-4	1.9E-3	7.5E-4	1.3E-3 a	49	2.0E-4	3.7E-4
n-undecane	7.3E-4	1.9E-3	ND	1.1E-3	< 1.2E-3 a	47	2.1E-5	3.7E-4
Styrene + heptanal	1.5E-3	1.5E-3	7.6E-4	ND	< 1.2E-3 a	34	3.1E-5	3.7E-4
Octene-1	1.5E-3	1.9E-3	1.1E-3	3.8E-4	1.2E-3 a	52	5.2E-5	3.7E-4
3-ethylpentane	2.2E-3	7.5E-4	7.6E-4	1.1E-3	1.2E-3 a	57	9.3E-5	3.7E-4
4-methylheptane	1.8E-3	3.8E-4	3.8E-4	1.9E-3	1.1E-3 a	77	3.1E-5	3.7E-4

Shading indicates substances not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

(i) High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

Table 4-12 (continued). Particulate Carbon Precursor Concentrations – High Load (Site Echo).

Parameter	Value							
	mg/dscm					(%)	mg/dscm	
Units								
Run Number	Alpha-Hi-R1 (i)	Alpha-Hi-R2 (i)	Alpha-Hi-R3 (i)	Alpha-Hi-R4	Stack Average	RSD	Ambient	MDL
Date	12-May-03	13-May-03	14-May-03	15-May-03			21-May-03	(1)
Particulate Carbon Precursors (VOC with Carbon Number 8 or greater)								
n-propylbenzene	3.7E-4	7.5E-4	1.1E-3	1.1E-3	8.4E-4 a	43	3.1E-5	3.7E-4
Isopropylcyclohexane	3.7E-4	1.5E-3	7.6E-4	3.8E-4	7.5E-4 a	71	3.1E-5	3.7E-4
Isobutylbenzene	7.3E-4	1.1E-3	ND	3.8E-4	< 7.5E-4 a	50	ND	3.7E-4
Indan	1.1E-2	ND	ND	ND	< 1.1E-2 e	n/a	ND	3.7E-4
Naphthalene	6.6E-3	ND	ND	ND	< 6.6E-3 e	n/a	ND	3.7E-4
1,2-diethylbenzene	ND	ND	8.3E-3	7.5E-4	< 4.5E-3	118	ND	3.7E-4
4,4-dimethylheptane	1.8E-3	ND	ND	ND	< 1.8E-3 e	n/a	3.1E-5	3.7E-4
1,1-dimethylcyclohexane	1.8E-3	ND	ND	1.5E-3	< 1.7E-3 a	14	3.1E-5	3.7E-4
Isopropylbenzene	1.8E-3	ND	ND	3.8E-4	< 1.1E-3 a	d 93	3.1E-5	3.7E-4
2,5-dimethylheptane	3.7E-4	ND	ND	1.1E-3	< 7.5E-4	d 72	1.0E-5	3.7E-4
1,2,3,5-tetramethylbenzene	7.3E-4	ND	ND	ND	< 7.3E-4 e	n/a	1.0E-5	3.7E-4
1,2,4,5-tetramethylbenzene	7.3E-4	ND	ND	ND	< 7.3E-4 e	n/a	ND	3.7E-4
1,3-diethylbenzene	ND	ND	7.6E-4	3.8E-4	< 5.7E-4	d 47	1.0E-5	3.7E-4
2,6-dimethylheptane	7.3E-4	ND	ND	3.8E-4	< 5.5E-4 a	d 45	5.2E-5	3.7E-4
Indene	ND	ND	3.8E-4	ND	< 3.8E-4 e	n/a	3.1E-5	3.7E-4
n-dodecane	ND	ND	ND	3.8E-4	< 3.8E-4 e	n/a	2.1E-5	3.7E-4
3,3-dimethylheptane	3.7E-4	ND	ND	3.8E-4	< 3.7E-4	2	3.1E-5	3.7E-4
n-nonane	3.7E-4	ND	ND	3.8E-4	< 3.7E-4	2	3.1E-5	3.7E-4
2-methylheptane	3.7E-4	3.8E-4	ND	ND	< 3.7E-4	2	2.1E-5	3.7E-4
1,3,5-trimethylbenzene	3.7E-4	ND	ND	ND	< 3.7E-4 e	n/a	4.1E-5	3.7E-4

Shading indicates substances not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

(i) High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

greater than the DSB and/or the ambient air concentrations. Eight of the remaining 17 compounds were detected in only a single run, and hence these results are not considered reliable since total uncertainty cannot be determined. With the exception of 1,4-diethylbenzene, all of these are within a factor of five of the MDL and/or not significantly greater than the DSB and/or the ambient air.

At low load, 14 VOCs with carbon number of 8 and greater were detected in all three test runs, only three of which were detected at concentrations significantly higher than the DSB and/or ambient air (Table 4-13). Twenty-four VOCs were detected in two of the test runs, but none of these was detected at concentrations significantly higher than the DSB and/or ambient air.

Table 4-13. Particulate Carbon Precursor Concentrations – Low Load (Site Echo).

Parameter	Value							
	mg/dscm				(%)	mg/dscm		
Run Number	Alpha-Lo-R1	Alpha-Lo-R2	Alpha-Lo-R3		Stack Average	RSD	Ambient	MDL
Date	17-May-03	18-May-03	19-May-03				21-May-03	(1)
<u>Particulate Carbon Precursors (VOC with Carbon Number 8 or greater)</u>								
2,2,5-trimethylhexane	2.1E-2	1.5E-2	3.5E-2		2.4E-2 a	43	7.8E-4	3.7E-4
o-ethyltoluene	1.5E-3	2.3E-2	3.7E-3		9.5E-3 a d	126	1.1E-4	3.7E-4
m- & p-xylene	7.2E-3	6.4E-3	1.2E-2		8.6E-3 a	37	6.7E-4	3.7E-4
Limonene	7.5E-4	4.1E-3	1.9E-2		8.0E-3 a d	122	2.1E-5	3.7E-4
2-methyloctane	1.9E-3	1.9E-2	1.8E-3		7.7E-3 a d	131	1.7E-4	3.7E-4
1,4-diethylbenzene	4.9E-3	8.6E-3	8.1E-3		7.2E-3 a	28	1.3E-4	3.7E-4
2,3-trimethylpentane	4.9E-3	3.4E-3	4.4E-3		4.2E-3 a	19	2.4E-4	3.7E-4
2,2,4-trimethylpentane	3.4E-3	3.7E-3	4.4E-3		3.9E-3	14	5.2E-4	3.7E-4
1,2,4-trimethylbenzene	1.1E-3	6.0E-3	2.9E-3		3.4E-3 a d	73	9.3E-5	3.7E-4
Ethylbenzene	3.0E-3	2.2E-3	3.7E-3		3.0E-3 a	24	2.5E-4	3.7E-4
3-methylheptane	2.3E-3	1.5E-3	3.7E-3		2.5E-3	45	6.2E-5	3.7E-4
Styrene + heptanal	7.5E-4	3.0E-3	1.5E-3		1.7E-3 a d	66	3.1E-5	3.7E-4
Octene-1	7.5E-4	3.0E-3	1.5E-3		1.7E-3 a d	66	5.2E-5	3.7E-4
3,3-dimethylheptane	3.8E-4	1.1E-3	7.4E-4		7.5E-4	50	3.1E-5	3.7E-4
alpha-pinene	2.3E-2	ND	4.3E-2		< 3.3E-2 a d	42	7.4E-4	3.7E-4
3-methyloctane	3.5E-2	ND	2.1E-2		< 2.8E-2 a d	37	3.5E-4	3.7E-4
3,6-dimethyloctane	4.1E-3	4.8E-2	ND		< 2.6E-2 a d	119	8.3E-5	3.7E-4
1,2,3-trimethylbenzene	5.3E-3	ND	1.8E-2		< 1.2E-2 a d	77	4.3E-4	3.7E-4
Nonanal	3.8E-3	ND	7.0E-3		< 5.4E-3 a d	42	1.1E-4	3.7E-4
beta-pinene	2.3E-3	ND	8.5E-3		< 5.4E-3 a d	82	3.1E-4	3.7E-4
o-xylene	2.3E-3	ND	5.2E-3		< 3.7E-3 a d	55	2.9E-4	3.7E-4
2,4-dimethylhexane	1.5E-3	ND	5.9E-3		< 3.7E-3 a d	84	1.5E-4	3.7E-4
3-ethylpentane	3.4E-3	ND	2.6E-3		< 3.0E-3 a	19	9.3E-5	3.7E-4
2,3-dimethylhexane	1.9E-3	ND	3.3E-3		< 2.6E-3 a d	39	6.2E-5	3.7E-4
p-ethyltoluene	1.1E-3	ND	4.0E-3		< 2.6E-3 a d	80	1.3E-4	3.7E-4
2,3,5-trimethylhexane	1.9E-3	ND	1.8E-3		< 1.9E-3 a	2	5.2E-5	3.7E-4
Isobutylbenzene	1.1E-3	1.9E-3	ND		< 1.5E-3 a	35	ND	3.7E-4
Isopropylbenzene	1.1E-3	ND	1.8E-3		< 1.5E-3 a d	34	3.1E-5	3.7E-4
m-ethyltoluene	7.5E-4	ND	1.8E-3		< 1.3E-3 a d	59	8.3E-5	3.7E-4
2,6-dimethylheptane	1.1E-3	ND	1.1E-3		< 1.1E-3 a	2	5.2E-5	3.7E-4
Isopropylcyclohexane	1.1E-3	ND	7.4E-4		< 9.3E-4 a d	30	3.1E-5	3.7E-4
Nonene-1	7.5E-4	ND	1.1E-3		< 9.3E-4 a d	27	9.3E-5	3.7E-4
n-octane	7.5E-4	ND	1.1E-3		< 9.3E-4 a d	27	2.0E-4	3.7E-4
1,2-diethylbenzene	7.5E-4	ND	7.4E-4		< 7.5E-4 a	2	ND	3.7E-4

Shading indicates substances not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Table 4-13 (continued). Particulate Carbon Precursor Concentrations – Low Load (Site Echo).

Parameter	Value							
	mg/dscm				(%)	mg/dscm		
Run Number	Alpha-Lo-R1	Alpha-Lo-R2	Alpha-Lo-R3	Stack Average	RSD	Ambient	MDL	MDL
Date	17-May-03	18-May-03	19-May-03					
Particulate Carbon Precursors (VOC with Carbon Number 8 or greater)								
n-propylbenzene	7.5E-4	ND	7.4E-4	< 7.5E-4 a	2	3.1E-5	3.7E-4	3.7E-4
Indene	7.5E-4	ND	7.4E-4	< 7.5E-4 a	2	3.1E-5	3.7E-4	3.7E-4
n-nonane	3.8E-4	ND	1.1E-3	< 7.4E-4 a d	69	3.1E-5	3.7E-4	3.7E-4
1,3,5-trimethylbenzene	3.8E-4	ND	7.4E-4	< 5.6E-4 a d	46	4.1E-5	3.7E-4	3.7E-4
n-undecane	ND	6.7E-3	ND	< 6.7E-3 e	n/a	2.1E-5	3.7E-4	3.7E-4
Octanal	ND	6.7E-3	ND	< 6.7E-3 e	n/a	ND	3.7E-4	3.7E-4
1,1-dimethylcyclohexane	3.4E-3	ND	ND	< 3.4E-3 e	n/a	3.1E-5	3.7E-4	3.7E-4
Naphthalene	ND	2.6E-3	ND	< 2.6E-3 e	n/a	ND	3.7E-4	3.7E-4
2-methylheptane	ND	ND	2.6E-3	< 2.6E-3 e	n/a	2.1E-5	3.7E-4	3.7E-4
4-methylheptane	1.9E-3	ND	ND	< 1.9E-3 e	n/a	3.1E-5	3.7E-4	3.7E-4
2,5-dimethylhexane	ND	ND	1.5E-3	< 1.5E-3 e	n/a	1.5E-4	3.7E-4	3.7E-4
sec-butylbenzene	1.1E-3	ND	ND	< 1.1E-3 e	n/a	ND	3.7E-4	3.7E-4
4,4-dimethylheptane	1.1E-3	ND	ND	< 1.1E-3 e	n/a	3.1E-5	3.7E-4	3.7E-4
n-decane	7.5E-4	ND	ND	< 7.5E-4 e	n/a	5.2E-5	3.7E-4	3.7E-4
n-dodecane	ND	ND	7.4E-4	< 7.4E-4 e	n/a	2.1E-5	3.7E-4	3.7E-4
Indan	3.8E-4	ND	ND	< 3.8E-4 e	n/a	ND	3.7E-4	3.7E-4
1,3-diethylbenzene	ND	ND	3.7E-4	< 3.7E-4 e	n/a	1.0E-5	3.7E-4	3.7E-4

Shading indicates substances not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Other VOCs

Other VOCs were measured in the canister samples to quantify VOCs that could contribute to OC measurement artifacts and selected hazardous air pollutants (HAPs). Most of the detected VOCs are fuel fragments and combustion intermediates or byproducts. 49 VOCs (excluding methane and ethane) were detected in three or more test runs ranging from 1 to 255, with an average of 20, a median of 8 and 90th percentile of 47, parts per *billion* (ppb) at high load (Table 4-14, in mg/dscm). Only four of these VOCs totaling 33 ppb were detected at levels significantly greater than the DSB and/or the ambient air. Only three of the VOCs detected in any high load run were not also detected in the ambient air.

At low load, 31 VOCs (excluding methane and ethane) detected in three test runs ranged from less than 1 to 170, with an average of 26, a median of 12 and 90th percentile of 65, ppb (Table 4-15, in mg/dscm). Only three of these, totaling 75 ppb, were detected at levels significantly greater than the DSB and/or the ambient air. Only one of the VOCs detected in any low load run was not also detected in the ambient air.

Methane levels reported in the stack gas samples are uncharacteristically high for this type of source (approximately 70 parts per million (ppm) in-stack equivalent, compared to typical levels of less than 1 ppm). Since methane levels in the raw (uncorrected for dilution air) blanks, ambient air sample and stack gas samples are approximately equal, this is probably a result of laboratory contamination or an error in the sample analysis. The methane results should be considered highly suspect and not used for any purpose.

Elements

Element concentrations were determined by XRF analysis of the TMFs used in the Alpha and Beta dilution samplers. Mg and Na results are considered semiquantitative because they are not reliably determined by XRF. S and Si are the most abundant elements in the stack gas (Tables 4-16 and 4-17), accounting for approximately 80 percent of the total element mass in all test runs. S is the only element that consistently appears in all runs at average concentrations significantly above the DSB, ambient air, and/or MDL among the four sets of results. The $\text{SO}_4^{=}$ results presented earlier are approximately a factor of two greater than the S concentrations by XRF, which is lower than as expected based on relative molecular weights (a factor of three is expected). Barring any undetected measurement errors, and since all of the particulate S is expected to be captured and analyzed as $\text{SO}_4^{=}$, this suggests a bias in either the S or the $\text{SO}_4^{=}$ results.

Carbonyls

Carbonyls were measured because they can contribute to heterogeneous secondary organic aerosol production in the aerosol phase and some are HAPs. Carbonyls were captured with the dilution sampler using two DNPH-impregnated silica gel cartridges assembled in series, and subsequently analyzed in the lab by HPLC. The results reported are the sum of the two

Table 4-14. Other VOC Concentrations – High Load (Site Echo).

Parameter	Value							MDL (1)
	mg/dscm					(%)	mg/dscm	
Units								
Run Number	Alpha-Hi-R1 (i)	Alpha-Hi-R2 (i)	Alpha-Hi-R3 (i)	Alpha-Hi-R4	Stack Average	RSD	Alpha-Hi-Ambient	
Date	12-May-03	13-May-03	14-May-03	15-May-03			21-May-03	
Other VOCs (Carbon Number 7 or less)								
Methane	4.5E+1	4.7E+1	4.6E+1	4.6E+1	4.6E+1 a	2	1.3E+0	3.7E-4
Methanol	1.3E-1	1.4E-1	4.5E-1	1.3E-1	2.1E-1 a	74	5.3E-3	3.7E-4
Ethane	1.5E-1	2.3E-1	1.7E-1	9.1E-2	1.6E-1 a	36	5.1E-3	3.7E-4
Toluene	2.2E-1	1.4E-1	8.0E-2	1.8E-2	1.1E-1 a	76	4.5E-3	3.7E-4
F 12	8.2E-2	1.0E-1	7.9E-2	8.0E-2	8.5E-2	12	2.6E-3	3.7E-4
Methylene chloride	7.6E-2	1.4E-1	1.1E-1	5.3E-3	8.4E-2 a	70	1.6E-3	3.7E-4
Propane	7.2E-2	1.0E-1	6.6E-2	4.7E-2	7.2E-2 a	33	3.4E-3	3.7E-4
trans-1,2-dichloroethylene	8.9E-2	5.4E-2	2.5E-2	2.7E-2	4.9E-2 a	61	8.6E-4	3.7E-4
Isopentane	1.0E-2	7.3E-2	3.6E-2	5.6E-3	3.1E-2 a	d 99	4.7E-3	3.7E-4
Acetylene	3.0E-2	5.1E-2	2.3E-3	3.8E-2	3.1E-2 a	68	1.4E-3	3.7E-4
n-pentane	1.2E-2	6.6E-2	2.7E-2	1.9E-3	2.7E-2 a	d 105	1.7E-3	3.7E-4
n-butane	6.2E-3	2.7E-2	4.8E-2	4.1E-3	2.1E-2 a	d 96	2.9E-3	3.7E-4
F 11	3.5E-2	1.9E-2	1.7E-2	1.3E-2	2.1E-2 a	47	1.7E-3	3.7E-4
n-hexane	3.1E-2	2.3E-2	2.2E-2	3.0E-3	2.0E-2 a	61	9.5E-4	3.7E-4
Ethene	1.8E-2	2.5E-2	2.6E-2	1.5E-3	1.8E-2 a	64	1.1E-3	3.7E-4
2,2,3-trimethylbutane	1.7E-2	3.7E-2	5.7E-3	1.5E-3	1.5E-2 a	d 103	3.3E-4	3.7E-4
2-methylhexane	2.7E-2	2.0E-2	7.6E-4	7.5E-3	1.4E-2 a	d 86	8.6E-4	3.7E-4
Propene	1.0E-2	1.5E-2	2.0E-2	7.5E-3	1.3E-2 a	43	6.7E-4	3.7E-4
Benzene	1.7E-2	1.2E-2	6.8E-3	3.4E-3	9.8E-3 a	62	7.0E-4	3.7E-4
F 113	1.4E-2	8.6E-3	8.7E-3	5.6E-3	9.2E-3 a	37	9.5E-4	3.7E-4
3-methylpentane	1.0E-2	9.0E-3	1.1E-2	4.5E-3	8.6E-3 a	33	1.1E-3	3.7E-4
c-2-hexene	7.7E-3	1.7E-2	ND	7.5E-4	< 8.6E-3 a	d 97	1.6E-4	3.7E-4
Isoprene	1.4E-2	4.1E-3	6.8E-3	ND	< 8.2E-3 a	d 59	1.8E-4	3.7E-4
Methylcyclopentane	1.2E-2	9.8E-3	7.6E-3	1.5E-3	7.6E-3 a	58	8.0E-4	3.7E-4
Cyclopentane	2.6E-3	5.6E-3	1.4E-2	8.3E-3	7.5E-3 a	62	3.0E-4	3.7E-4
Carbon tetrachloride	1.1E-2	7.1E-3	4.9E-3	4.9E-3	7.1E-3 a	43	7.8E-4	3.7E-4
2,3-dimethylpentane	5.9E-3	1.1E-2	6.8E-3	2.6E-3	6.5E-3 a	50	3.5E-4	3.7E-4
Iso-butene	8.8E-3	5.6E-3	4.9E-3	3.0E-3	5.6E-3 a	43	3.1E-4	3.7E-4
1,3-dimethylcyclopentane	5.9E-3	5.3E-3	5.7E-3	5.3E-3	5.5E-3 a	5	1.8E-4	3.7E-4
Chloroform	1.6E-2	1.9E-3	1.9E-3	1.9E-3	5.4E-3 a	d 131	1.6E-4	3.7E-4
Hexanal	5.1E-3	4.5E-3	4.9E-3	3.4E-3	4.5E-3 a	17	1.2E-4	3.7E-4
1-pentene	2.2E-3	4.9E-3	ND	5.6E-3	< 4.2E-3	43	2.0E-4	3.7E-4
c-3-hexene	1.0E-2	ND	7.6E-4	7.5E-4	< 3.9E-3 a	d 140	5.2E-5	3.7E-4
Methylcyclohexane	7.7E-3	4.1E-3	3.0E-3	7.5E-4	3.9E-3	74	3.5E-4	3.7E-4

Shading indicates substances not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

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< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

(i) High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

Table 4-14 (continued). Other VOC Concentrations – High Load (Site Echo).

Parameter	Value							
	mg/dscm					(%)	mg/dscm	
Units								
Run Number	Alpha-Hi-R1 (i)	Alpha-Hi-R2 (i)	Alpha-Hi-R3 (i)	Alpha-Hi-R4	Stack Average	RSD	Alpha-Hi-Ambient	MDL
Date	12-May-03	13-May-03	14-May-03	15-May-03			21-May-03	(1)
Other VOCs (Carbon Number 7 or less)								
Cyclohexene	4.0E-3	4.9E-3	4.2E-3	2.3E-3	3.8E-3 a	29	2.6E-4	3.7E-4
Methyl chloroform	5.5E-3	3.8E-3	3.8E-3	1.9E-3	3.7E-3 a	40	2.1E-4	3.7E-4
p-dichlorobenzene	4.4E-3	4.5E-3	2.3E-3	ND	< 3.7E-3 a	34	1.2E-4	3.7E-4
2,4-dimethylpentane	3.3E-3	5.3E-3	3.0E-3	1.5E-3	3.3E-3 a	47	1.2E-4	3.7E-4
2,3-dimethylbutane	1.8E-3	1.9E-3	2.6E-3	6.0E-3	3.1E-3 a	64	3.0E-4	3.7E-4
Cyclohexane	3.7E-3	4.9E-3	1.9E-3	3.8E-4	2.7E-3 a	d 73	3.8E-4	3.7E-4
Perchloroethylene	2.6E-3	2.6E-3	2.6E-3	2.6E-3	2.6E-3 a	1	7.2E-5	3.7E-4
F 114	2.6E-3	2.6E-3	2.6E-3	2.6E-3	2.6E-3 a	1	2.2E-4	3.7E-4
n-heptane	5.9E-3	1.9E-3	1.5E-3	7.5E-4	2.5E-3 a	d 92	1.8E-4	3.7E-4
Methyl bromide	1.5E-3	1.5E-3	3.0E-3	3.0E-3	2.2E-3 a	39	3.2E-4	3.7E-4
1-butene	2.2E-3	2.3E-3	2.6E-3	1.5E-3	2.1E-3 a	22	1.3E-4	3.7E-4
1,3-butadiene	2.6E-3	2.6E-3	1.5E-3	7.5E-4	1.9E-3 a	48	5.2E-5	3.7E-4
Chlorobenzene	2.2E-3	1.1E-3	1.1E-3	ND	< 1.5E-3 a	41	8.3E-5	3.7E-4
t-2-pentene	2.6E-3	1.1E-3	3.8E-4	ND	< 1.4E-3 a	d 82	7.2E-5	3.7E-4
1-hexene	1.1E-3	1.1E-3	1.1E-3	1.9E-3	1.3E-3 a	29	6.2E-5	3.7E-4
2-methyl-2-butene	2.6E-3	1.1E-3	1.1E-3	3.8E-4	1.3E-3	70	7.2E-5	3.7E-4
Acetonitrile	5.5E-2	ND	ND	ND	< 5.5E-2 e	n/a	7.2E-4	3.7E-4
1,2-dichloroethane	1.9E-2	1.4E-2	ND	ND	< 1.6E-2 a	d 25	2.9E-4	3.7E-4
2,2-dimethylpentane	ND	1.9E-2	ND	5.3E-3	< 1.2E-2	d 80	5.4E-4	3.7E-4
t-3-hexene + chloroform	4.4E-3	ND	1.9E-3	ND	< 3.1E-3 a	d 56	9.3E-5	3.7E-4
Cyclopentene	1.5E-3	ND	ND	4.1E-3	< 2.8E-3 a	d 67	2.1E-5	3.7E-4
3,3-dimethylpentane	3.7E-3	ND	3.8E-4	ND	< 2.0E-3 a	d 115	1.7E-4	3.7E-4
t-2-hexene	1.8E-3	ND	ND	ND	< 1.8E-3 e	n/a	4.1E-5	3.7E-4
1,1,2-trichloroethane	1.8E-3	ND	ND	ND	< 1.8E-3 e	n/a	ND	3.7E-4
Ethanol + ACN	ND	ND	ND	1.5E-3	< 1.5E-3 e	n/a	ND	3.7E-4
t-2-butene	ND	2.3E-3	ND	3.8E-4	< 1.3E-3 a	d 101	5.2E-5	3.7E-4
2-methyl-1-pentene	ND	ND	ND	1.1E-3	< 1.1E-3 e	n/a	6.2E-5	3.7E-4
Benzaldehyde	1.1E-3	ND	ND	1.1E-3	< 1.1E-3	2	1.0E-5	3.7E-4
c-2-pentene	1.1E-3	ND	ND	ND	< 1.1E-3 e	n/a	3.1E-5	3.7E-4
c-2-butene	ND	1.1E-3	ND	7.5E-4	< 9.4E-4 a	d 28	3.1E-5	3.7E-4
2-methyl-1-butene	7.3E-4	7.5E-4	ND	ND	< 7.4E-4	2	4.1E-5	3.7E-4
2-methyl-2-pentene	7.3E-4	ND	ND	ND	< 7.3E-4 e	n/a	2.1E-5	3.7E-4
trans-3-methyl-2-pentene	ND	7.5E-4	ND	3.8E-4	< 5.6E-4	d 47	1.0E-5	3.7E-4
t-3-heptene	7.3E-4	ND	ND	3.8E-4	< 5.5E-4 a	d 45	2.1E-5	3.7E-4
3-methyl-1-butene	3.7E-4	ND	3.8E-4	ND	< 3.7E-4 a	2	3.1E-5	3.7E-4
2-methylpropanal	3.7E-4	ND	ND	ND	< 3.7E-4 e	n/a	ND	3.7E-4
4-methylhexene	3.7E-4	ND	ND	ND	< 3.7E-4 e	n/a	2.1E-5	3.7E-4

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

(i) High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

Table 4-15. Other VOC Concentrations – Low Load (Site Echo).

Parameter	Value							
	mg/dscm				(%)	mg/dscm		
Units								
Run Number	Alpha-Lo-R1	Alpha-Lo-R2	Alpha-Lo-R3		Stack Average	RSD	Ambient	MDL
Date	17-May-03	18-May-03	19-May-03				21-May-03	(1)
Other VOCs (Carbon Number 7 or less)								
Methane	4.7E+1	4.5E+1	5.2E+1		4.8E+1 a	8	1.3E+0	3.7E-4
Ethane	3.1E-1	1.7E-1	7.8E-1		4.2E-1 a d	77	5.1E-3	3.7E-4
Propane	7.6E-2	1.2E-2	2.2E-1		1.0E-1 a d	105	3.4E-3	3.7E-4
trans-1,2-dichloroethylene	1.1E-1	5.6E-2	1.0E-1		8.9E-2 a	32	8.6E-4	3.7E-4
F 12	8.4E-2	3.1E-2	9.8E-2		7.1E-2 a	49	2.6E-3	3.7E-4
Toluene	7.6E-2	4.4E-2	9.4E-2		7.1E-2 a	36	4.5E-3	3.7E-4
Acetylene	4.2E-2	2.0E-2	5.6E-2		3.9E-2 a	45	1.4E-3	3.7E-4
Ethene	2.8E-2	1.5E-2	7.1E-2		3.8E-2 a d	79	1.1E-3	3.7E-4
2,2-dimethylpentane	5.4E-2	2.9E-2	2.7E-2		3.7E-2	41	5.4E-4	3.7E-4
3-methylpentane	4.6E-2	5.6E-3	1.8E-2		2.3E-2 a d	89	1.1E-3	3.7E-4
Propene	1.3E-2	4.1E-3	4.0E-2		1.9E-2 a d	99	6.7E-4	3.7E-4
2-methylhexane	1.7E-2	4.1E-3	2.3E-2		1.5E-2 a d	66	8.6E-4	3.7E-4
Cyclohexane	1.9E-3	3.3E-2	3.3E-3		1.3E-2 a d	138	3.8E-4	3.7E-4
Isopentane	7.9E-3	2.2E-3	2.0E-2		1.0E-2 a d	90	4.7E-3	3.7E-4
n-butane	6.4E-3	3.0E-3	2.1E-2		1.0E-2 a d	93	2.9E-3	3.7E-4
F 11	1.1E-2	6.4E-3	1.3E-2		9.8E-3 a	32	1.7E-3	3.7E-4
Benzene	8.3E-3	6.7E-3	1.1E-2		8.8E-3 a	27	7.0E-4	3.7E-4
1,3-dimethylcyclopentane	2.6E-3	7.1E-3	1.4E-2		7.9E-3 a d	72	1.8E-4	3.7E-4
2,2,3-trimethylbutane	1.1E-2	8.6E-3	2.6E-3		7.2E-3 a d	57	3.3E-4	3.7E-4
1,1,2-trichloroethane	1.9E-3	1.6E-2	1.8E-3		6.7E-3 a	125	ND	3.7E-4
Iso-butene	6.4E-3	4.9E-3	8.8E-3		6.7E-3 a	30	3.1E-4	3.7E-4
F 113	5.7E-3	5.6E-3	8.5E-3		6.6E-3 a	25	9.5E-4	3.7E-4
n-pentane	3.0E-3	1.1E-3	9.2E-3		4.4E-3 a d	95	1.7E-3	3.7E-4
1-hexene	4.1E-3	3.4E-3	5.5E-3		4.3E-3	25	6.2E-5	3.7E-4
Carbon tetrachloride	4.9E-3	2.2E-3	4.8E-3		4.0E-3 a	38	7.7E-4	3.7E-4
2-methyl-1-pentene	3.4E-3	5.6E-3	2.6E-3		3.9E-3	41	6.2E-5	3.7E-4
1-butene	3.8E-3	2.6E-3	3.3E-3		3.2E-3 a	18	1.3E-4	3.7E-4
1-pentene	4.1E-3	1.9E-3	2.9E-3		3.0E-3 a	38	2.0E-4	3.7E-4
p-dichlorobenzene	2.3E-3	4.5E-3	2.2E-3		3.0E-3 a	44	1.2E-4	3.7E-4
F 114	2.6E-3	2.6E-3	2.6E-3		2.6E-3 a	1	2.2E-4	3.7E-4
1,3-butadiene	3.0E-3	3.0E-3	1.5E-3		2.5E-3 a	35	5.2E-5	3.7E-4
Chloroform	1.9E-3	1.9E-3	3.7E-3		2.5E-3 a	42	1.5E-4	3.7E-4
Methyl chloroform	1.9E-3	1.9E-3	1.8E-3		1.9E-3 a	1	2.1E-4	3.7E-4
Methanol	1.6E-1	ND	4.7E-1		< 3.1E-1 a d	70	5.3E-3	3.7E-4
Methyl bromide	1.3E-2	ND	1.6E-2		< 1.5E-2	13	3.2E-4	3.7E-4
Methylene chloride	1.2E-2	1.7E-2	ND		< 1.4E-2 a d	26	1.6E-3	3.7E-4
Isoprene	ND	3.0E-3	2.2E-2		< 1.2E-2 d	107	1.8E-4	3.7E-4
1,2-dichloroethane	4.5E-3	1.8E-2	ND		< 1.1E-2 a d	85	2.9E-4	3.7E-4
Cyclopentane	1.0E-2	ND	1.3E-2		< 1.1E-2 a	15	3.0E-4	3.7E-4
Cyclohexene	6.8E-3	ND	9.9E-3		< 8.4E-3 a d	27	2.6E-4	3.7E-4

Shading indicates substances not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Table 4-15 (continued). Other VOC Concentrations – Low Load (Site Echo).

Parameter	Value							
	mg/dscm				(%)	mg/dscm		
Units	Alpha-Lo-R1	Alpha-Lo-R2	Alpha-Lo-R3		Stack Average	RSD	Ambient	MDL
Run Number	17-May-03	18-May-03	19-May-03				21-May-03	(1)
Other VOCs (Carbon Number 7 or less)								
n-hexane	1.9E-3	ND	1.0E-2		< 6.1E-3 a d	98	9.5E-4	3.7E-4
Hexanal	5.3E-3	ND	6.3E-3		< 5.8E-3 a	12	1.2E-4	3.7E-4
c-2-hexene	1.5E-3	ND	9.6E-3		< 5.5E-3 a d	103	1.5E-4	3.7E-4
Methylcyclopentane	1.1E-3	ND	5.9E-3		< 3.5E-3 a d	96	8.0E-4	3.7E-4
c-3-hexene	2.6E-3	ND	3.3E-3		< 3.0E-3 a	16	5.2E-5	3.7E-4
2,4-dimethylpentane	2.3E-3	ND	3.3E-3		< 2.8E-3 a d	27	1.2E-4	3.7E-4
Methylcyclohexane	7.5E-4	ND	3.7E-3		< 2.2E-3 a d	93	3.5E-4	3.7E-4
Chlorobenzene	1.9E-3	ND	2.2E-3		< 2.0E-3 a	11	8.3E-5	3.7E-4
n-heptane	7.5E-4	ND	3.3E-3		< 2.0E-3 a d	89	1.8E-4	3.7E-4
2,3-dimethylbutane	2.6E-3	ND	7.4E-4		< 1.7E-3 a d	80	3.0E-4	3.7E-4
3,3-dimethylpentane	7.5E-4	1.5E-3	ND		< 1.1E-3 a d	47	1.7E-4	3.7E-4
4-methylhexene	1.1E-3	ND	1.1E-3		< 1.1E-3	2	2.1E-5	3.7E-4
t-3-heptene	1.1E-3	ND	7.4E-4		< 9.3E-4 a d	30	2.1E-5	3.7E-4
trans-3-methyl-2-pentene	3.8E-4	ND	1.1E-3		< 7.4E-4 a d	69	1.0E-5	3.7E-4
Acetonitrile	ND	8.4E-2	ND		< 8.4E-2 e	n/a	7.2E-4	3.7E-4
2,3-dimethylpentane	ND	ND	1.4E-2		< 1.4E-2 e	n/a	3.5E-4	3.7E-4
cis-1,2,-dichloroethylene	ND	1.2E-2	ND		< 1.2E-2 e	n/a	ND	3.7E-4
Perchloroethylene	ND	ND	2.6E-3		< 2.6E-3 e	n/a	7.2E-5	3.7E-4
m-dichlorobenzene	ND	2.2E-3	ND		< 2.2E-3 e	n/a	6.2E-5	3.7E-4
o-dichlorobenzene	ND	ND	2.2E-3		< 2.2E-3 e	n/a	ND	3.7E-4
Ethanol + ACN	1.5E-3	ND	ND		< 1.5E-3 e	n/a	ND	3.7E-4
Cyclopentene	ND	ND	1.5E-3		< 1.5E-3 e	n/a	2.1E-5	3.7E-4
c-2-pentene	ND	ND	1.1E-3		< 1.1E-3 e	n/a	3.1E-5	3.7E-4
c-2-butene	7.5E-4	ND	ND		< 7.5E-4 e	n/a	3.1E-5	3.7E-4
Benzaldehyde	7.5E-4	ND	ND		< 7.5E-4 e	n/a	1.0E-5	3.7E-4
t-2-butene	7.5E-4	ND	ND		< 7.5E-4 e	n/a	5.2E-5	3.7E-4
2-methyl-2-butene	ND	ND	7.4E-4		< 7.4E-4 e	n/a	7.2E-5	3.7E-4
3-methyl-1-butene	3.8E-4	ND	ND		< 3.8E-4 e	n/a	3.1E-5	3.7E-4
t-2-pentene	ND	ND	3.7E-4		< 3.7E-4 e	n/a	7.2E-5	3.7E-4

Shading indicates substances not detected in at least 3 valid test runs.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Table 4-16. Particulate Element Concentrations – High Load (Site Echo).

(a) Alpha Sampler

Parameter	Value							
	mg/dscm					%	mg/dscm	
Units	Alpha-Hi-R1 (i)	Alpha-Hi-R2 (i)	Alpha-Hi-R3 (i)	Alpha-Hi-R4	Average	RSD	Ambient	MDL
Run Date	12-May-03	13-May-03	14-May-03	15-May-03			21-May-03	(2)
S	1.2E-02	2.3E-2	2.2E-2	1.6E-2	1.8E-2	28	8.9E-4	3.6E-5
Na	4.9E-03	6.7E-3	4.8E-3	7.9E-3	6.1E-3	25	2.2E-4	(1)
Si	4.8E-03	1.3E-3	8.2E-4	6.6E-4	1.9E-3 a b c d	103	2.4E-4	4.2E-5
Mg	1.1E-03	1.6E-3	6.2E-4	1.5E-3	1.2E-3 b	36	3.6E-5	(1)
Al	1.9E-03	3.6E-4	4.6E-4	5.7E-4	8.1E-4 a d	87	6.0E-5	7.5E-5
Fe	1.3E-03	4.9E-4	3.4E-4	1.8E-4	5.8E-4 a b c d	86	1.5E-4	1.1E-5
K	4.9E-04	8.1E-4	3.6E-4	4.0E-4	5.1E-4	39	6.6E-5	4.5E-5
Ca	4.9E-04	3.8E-4	1.4E-4	2.7E-4	3.2E-4 a c	47	9.5E-5	3.3E-5
Zn	6.0E-04	1.2E-4	6.9E-5	4.6E-5	2.1E-4 a b c d	126	3.3E-5	8.1E-6
Br	2.8E-04	4.3E-5	4.0E-5	4.7E-5	1.0E-4 a d	116	3.7E-6	7.5E-6
Cu	1.0E-04	2.8E-5	1.2E-4	ND	< 8.1E-5 a d	57	1.1E-5	8.1E-6
Ni	1.2E-04	2.7E-5	2.6E-5	1.0E-5	4.6E-5 a d	108	7.2E-6	6.6E-6
Mn	4.7E-05	2.7E-5	2.8E-5	ND	< 3.4E-5 a	33	3.2E-6	1.2E-5
Co	1.6E-05	1.1E-5	2.1E-5	ND	< 1.6E-5 a c d	31	1.3E-6	6.6E-6
Sr	1.7E-05	1.1E-5	1.2E-5	1.4E-5	1.4E-5 a b	22	9.7E-7	8.4E-6
Ba	8.1E-04	ND	ND	ND	< 8.1E-4 e	n/a	ND	3.9E-4
Cl	ND	ND	ND	3.8E-4	< 3.8E-4 e	n/a	2.0E-5	7.8E-5
Pb	ND	ND	1.3E-4	ND	< 1.3E-4 e	n/a	2.7E-6	2.3E-5
Mo	ND	2.6E-5	1.0E-4	ND	< 6.4E-5 a b c	83	ND	2.0E-5
P	ND	ND	4.9E-5	ND	< 4.9E-5 e	n/a	ND	4.2E-5
V	ND	4.0E-5	5.2E-5	ND	< 4.6E-5 a d	18	1.1E-5	1.9E-5
Ti	ND	4.8E-5	4.2E-5	ND	< 4.5E-5 a c d	9	9.7E-6	2.2E-5
Cr	ND	1.5E-5	2.7E-5	ND	< 2.1E-5 a d	38	5.9E-6	1.4E-5
As	ND	ND	ND	ND	ND e	n/a	3.6E-7	1.2E-5
Se	ND	ND	ND	ND	ND e	n/a	8.6E-7	9.3E-6

(b) Beta Sampler

Parameter	Value							
	mg/dscm					%	mg/dscm	
Units	Beta-Hi-R1	Beta-Hi-R2	Beta-Hi-R3	Beta-Hi-R4	Average	RSD	Ambient	MDL
Run Date	12-May-03	13-May-03	14-May-03	15-May-03			21-May-03	(2)
S	9.4E-03	1.2E-2	9.1E-3	7.1E-3	9.3E-3	20	8.9E-4	2.4E-5
Na	1.9E-03	2.0E-3	5.8E-3	9.6E-4	2.7E-3 a b c d	81	2.2E-4	(1)
Si	5.6E-04	1.0E-3	6.6E-4	5.3E-4	7.0E-4 a	34	2.4E-4	2.8E-5
Mg	3.2E-04	3.9E-4	1.2E-3	5.2E-5	5.0E-4 a b c d	102	3.6E-5	(1)
K	5.6E-04	3.0E-4	2.5E-4	1.8E-4	3.2E-4 a	50	6.6E-5	3.0E-5
Fe	2.3E-04	3.3E-4	2.6E-4	1.5E-4	2.4E-4 a	29	1.5E-4	7.7E-6
Ca	2.8E-04	2.5E-4	2.5E-4	1.8E-4	2.4E-4 a	18	9.5E-5	2.2E-5
Al	8.6E-05	2.0E-4	3.4E-4	2.9E-4	2.3E-4 a b	49	6.0E-5	5.0E-5
Br	2.4E-04	2.5E-5	1.5E-5	1.3E-5	7.3E-5 a d	152	3.7E-6	5.0E-6
Zn	1.9E-05	4.5E-5	1.0E-4	5.0E-5	5.4E-5 a c d	66	3.3E-5	5.5E-6
Co	1.1E-05	7.6E-6	1.1E-5	ND	< 9.7E-6 c	19	1.3E-6	4.4E-6
Ni	1.1E-05	1.2E-5	8.3E-6	6.0E-6	9.2E-6 a d	27	7.2E-6	4.4E-6
Sr	1.1E-05	8.9E-6	ND	6.0E-6	< 8.7E-6 a	30	9.7E-7	5.7E-6
Cl	ND	ND	9.5E-4	1.1E-3	< 1.0E-3	9	2.0E-5	5.3E-5
Ba	2.5E-04	ND	ND	5.6E-4	< 4.1E-4	54	ND	2.6E-4
Mo	1.4E-05	ND	6.0E-5	ND	< 3.7E-5 c	87	ND	1.4E-5
Ti	ND	3.1E-5	ND	ND	< 3.1E-5 e	n/a	9.7E-6	1.5E-5
V	ND	1.6E-5	ND	ND	< 1.6E-5 e	n/a	1.1E-5	1.3E-5
Mn	ND	1.5E-5	9.8E-6	ND	< 1.2E-5 a d	28	3.2E-6	8.1E-6
As	ND	ND	1.1E-5	ND	< 1.1E-5 e	n/a	3.6E-7	7.9E-6
Cu	7.0E-06	ND	ND	ND	< 7.0E-6 e	n/a	1.1E-5	5.5E-6
Rb	ND	4.4E-6	ND	ND	< 4.4E-6 e	n/a	ND	4.8E-6
Cr	ND	ND	ND	ND	ND e	n/a	5.9E-6	9.7E-6
Pb	ND	ND	ND	ND	ND e	n/a	2.7E-6	1.5E-5
Se	ND	ND	ND	ND	ND e	n/a	8.6E-7	6.3E-6

(1) No detection limits given. Zeroes treated as non-detect. Data is semi-quantitative.
 (2) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.
 MDL- Method Detection Limit
 n/a- not applicable
 ND - Not Detected
 RSD- Relative Standard Deviation
 < - detected in fewer than all test runs
 a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.
 b - 95% Confidence Lower Bound of the Average concentration is less than the Field Blank concentration.
 c - 95% Confidence Lower Bound of the Average concentration is less than the Trip Blank concentration.
 d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.
 e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).
 (i) High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

Table 4-17. Particulate Element Concentrations – Low Load (Site Echo).

(a) Alpha Sampler

Parameter	Value							
	mg/dscm					%	mg/dscm	
Units	Alpha-Lo-R1	Alpha-Lo-R2	Alpha-Lo-R3	0.0E+00	Average	RSD	Ambient	MDL
Run Date	17-May-03	18-May-03	19-May-03	01-Jan-04			21-May-03	(2)
S	1.0E-02	1.2E-2	1.2E-2		1.1E-2	10	8.9E-4	4.8E-5
Na	3.0E-03	6.1E-3	5.0E-3		4.7E-3 a c	33	2.2E-4	(1)
Mg	9.5E-04	4.3E-4	5.3E-4		6.4E-4 a b c d	44	3.6E-5	(1)
Si	4.5E-04	6.2E-4	6.8E-4		5.8E-4 a	20	2.4E-4	5.6E-5
K	3.8E-04	2.2E-4	2.2E-4		2.7E-4 a c	33	6.6E-5	6.0E-5
Ca	2.2E-04	2.4E-4	2.2E-4		2.3E-4 a c	5	9.5E-5	4.4E-5
Fe	9.0E-05	1.3E-4	2.0E-4		1.4E-4 a b c d	41	1.5E-4	1.5E-5
Br	1.0E-04	9.4E-5	3.7E-5		7.8E-5 a	46	3.7E-6	1.0E-5
Zn	6.0E-05	2.9E-5	2.9E-5		3.9E-5 a b c d	46	3.3E-5	1.1E-5
Cl	1.6E-03	ND	ND		< 1.6E-3 e	n/a	2.0E-5	1.0E-4
Al	2.2E-04	ND	1.5E-4		< 1.9E-4 d	24	6.0E-5	1.0E-4
Cu	ND	2.6E-5	ND		< 2.6E-5 e	n/a	1.1E-5	1.1E-5
V	ND	ND	2.0E-5		< 2.0E-5 e	n/a	1.1E-5	2.5E-5
Ni	ND	ND	1.1E-5		< 1.1E-5 e	n/a	7.2E-6	8.9E-6
Sr	1.2E-05	ND	9.5E-6		< 1.1E-5 a b d	15	9.7E-7	1.1E-5
Rb	ND	8.4E-6	ND		< 8.4E-6 e	n/a	ND	9.7E-6
Ti	ND	ND	ND		< ND e	n/a	9.7E-6	2.9E-5
Cr	ND	ND	ND		< ND e	n/a	5.9E-6	1.9E-5
Mn	ND	ND	ND		< ND e	n/a	3.2E-6	1.6E-5
Pb	ND	ND	ND		< ND e	n/a	2.7E-6	3.1E-5
Co	ND	ND	ND		< ND e	n/a	1.3E-6	8.9E-6
Se	ND	ND	ND		< ND e	n/a	8.6E-7	1.2E-5
As	ND	ND	ND		< ND e	n/a	3.6E-7	1.6E-5

(b) Beta Sampler

Parameter	Value							
	mg/dscm					%	mg/dscm	
Units	Beta-Lo-R1	Beta-Lo-R2	Beta-Lo-R3	0.0E+00	Average	RSD	Ambient	MDL
Run Date	17-May-03	18-May-03	19-May-03	01-Jan-04			21-May-03	(2)
S	5.9E-03	6.8E-3	7.0E-3		6.6E-3	9	8.9E-4	4.0E-5
Na	5.2E-03	3.0E-3	4.3E-3		4.1E-3 a c	26	2.2E-4	(1)
Si	4.7E-04	8.2E-4	4.7E-4		5.8E-4 a c d	35	2.4E-4	4.7E-5
Cl	1.3E-03	8.6E-5	3.5E-4		5.7E-4 a b c d	109	2.0E-5	8.7E-5
Mg	6.5E-04	3.7E-4	4.7E-4		5.0E-4 a c	29	3.6E-5	(1)
Fe	2.5E-04	2.4E-4	2.2E-4		2.4E-4 a	6	1.5E-4	1.3E-5
Ca	2.0E-04	1.6E-4	2.6E-4		2.1E-4 a c	25	9.5E-5	3.7E-5
K	2.0E-04	1.6E-4	2.0E-4		1.9E-4 a	13	6.6E-5	5.0E-5
Br	7.1E-05	7.3E-5	6.9E-5		7.1E-5 a	3	3.7E-6	8.4E-6
Zn	3.3E-05	1.7E-5	3.7E-5		2.9E-5 a c d	36	3.3E-5	9.1E-6
Ni	1.4E-05	8.1E-6	1.5E-5		1.2E-5 a d	29	7.2E-6	7.4E-6
Al	2.4E-04	3.1E-4	ND		< 2.8E-4 a b d	17	6.0E-5	8.4E-5
La	4.4E-04	ND	ND		< 4.4E-4 e	n/a	ND	5.4E-4
V	ND	ND	2.4E-5		< 2.4E-5 e	n/a	1.1E-5	2.1E-5
Mn	ND	ND	1.2E-5		< 1.2E-5 e	n/a	3.2E-6	1.3E-5
Co	9.4E-06	ND	7.2E-6		< 8.3E-6 c d	19	1.3E-6	7.4E-6
Cu	ND	ND	ND		< ND e	n/a	1.1E-5	9.1E-6
Ti	ND	ND	ND		< ND e	n/a	9.7E-6	2.5E-5
Cr	ND	ND	ND		< ND e	n/a	5.9E-6	1.6E-5
Pb	ND	ND	ND		< ND e	n/a	2.7E-6	2.6E-5
Sr	ND	ND	ND		< ND e	n/a	9.7E-7	9.4E-6
Se	ND	ND	ND		< ND e	n/a	8.6E-7	1.0E-5
As	ND	ND	ND		< ND e	n/a	3.6E-7	1.3E-5

(1) No detection limits given. Zeroes treated as non-detect. Data is semi-quantitative.

(2) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the Field Blank concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Trip Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

separately analyzed cartridges. This is the same principle employed in EPA Method TO-11A (ambient air reference method for formaldehyde and other aldehydes and ketones). The use of this method for source dilution measurements in these tests should be considered exploratory, since (a) method performance has not been previously evaluated for this application and (b) this is the first use of the field sampling method by the authors (the laboratory analysis team has extensive experience). Note, this method is not considered valid for acrolein.

Acetaldehyde and acetone were detected in most of the stack samples and in the ambient air sample at concentrations generally close to the MDL (Table 4-18). Formaldehyde was detected in three runs at low load at levels barely above the detection limit, but in only two runs at high load, and the average concentrations are not significantly greater than the ambient air. The RSDs for all of these compounds indicate it is likely that their average concentrations are not significantly higher than in the ambient air sample, the DSB and/or the FB. No differences between high load and low load results are evident.

The second cartridge of each pair was used to check for breakthrough. In most cases, the amount in the second cartridge comprises a significant part (more than 20 percent) of the total stack sample. This indicates a potential problem with the method performance in this application (introductory comments on Method TO-11A note possible interferences from ozone, liquid water and sunlight that can degrade performance in ambient air applications).

Acetaldehyde and acetone were detected in the FBs at very significant levels compared to the samples, therefore the FB results are subtracted from the stack results. Two dilution system blanks (DSBs) also was performed, one at the beginning of the field campaign and one at the end, where the sample inlet was capped and an ambient sample was drawn through the dilution air filters and the dilution sampler. Formaldehyde, acetone and acetaldehyde, glyoxol and hexanaldehyde were detected in both the system blank and the ambient air sample.

Comparing the DSB and ambient air results indicates that the dilution air filtration system removal efficiency is approximately 67 to 98 percent for formaldehyde, 0 to 100 percent for acetaldehyde, 77 to 100 percent for propionaldehyde, 90 to 99 percent for glyoxol and 58 to 95 percent for hexanaldehyde. The high variability in removal efficiency for acetaldehyde is

Table 4-18. Particulate Carbon Precursor (Carbonyl) Concentrations (Site Echo).

(a) Alpha tunnel - High load

Run		Alpha-Hi-R1 (i)	Alpha-Hi-R2 (i)	Alpha-Hi-R3 (i)	Alpha-Hi-R4			Ambient	MDL	
Date	Units	12-May-03	13-May-03	14-May-03	15-May-03	Average	RSD (%)	21-May-03	(1)	
Formaldehyde	mg/dscm	ND	ND	1.4E-1	2.9E-2	< 8.7E-2	d	95	7.8E-3	1.0E-2
	ppb	ND	ND	116	23	69		95	6	8
Acetaldehyde	mg/dscm	ND	9.7E-3	1.1E-2	4.4E-2	< 2.2E-2	b d	92	5.2E-3	8.6E-3
Acetone	mg/dscm	1.1E-1	ND	6.3E-1	4.6E-1	< 4.0E-1	a b d	66	6.1E-3	3.1E-2
Glyoxal	mg/dscm	ND	ND	4.8E-3	4.8E-3	< 4.8E-3		0	1.6E-3	2.3E-3
M-Tolualdehyde	mg/dscm	ND	ND	1.6E-2	9.9E-3	< 1.3E-2		33	ND	6.7E-3
Benzaldehyde	mg/dscm	ND	ND	7.4E-3	ND	< 7.4E-3	e	n/a	ND	6.2E-3
Propionaldehyde	mg/dscm	ND	ND	ND	ND	ND	e	n/a	6.1E-4	3.3E-3
Butyraldehyde	mg/dscm	ND	ND	ND	ND	ND	e	n/a	5.4E-4	2.9E-3
Valeraldehyde	mg/dscm	ND	ND	ND	ND	ND	e	n/a	1.9E-4	5.4E-3
Hexanaldehyde	mg/dscm	ND	ND	ND	ND	ND	e	n/a	5.8E-4	6.0E-3

(b) Alpha tunnel - Low load

Run		Alpha-Lo-R1	Alpha-Lo-R2	Alpha-Lo-R3	--			Ambient	MDL	
Date	Units	17-May-03	18-May-03	19-May-03	--	Average	RSD (%)	21-May-03	(1)	
Formaldehyde	mg/dscm	1.2E-2	1.9E-2	1.5E-2	--	1.5E-2	a d	24	7.8E-3	9.4E-3
	ppb	10	15	12	--	12		24	6	8
Acetaldehyde	mg/dscm	1.3E-2	1.3E-2	1.7E-2	--	1.4E-2	a b	15	5.2E-3	8.3E-3
Acetone	mg/dscm	2.1E-1	1.9E-1	2.6E-1	--	2.2E-1	a b	18	6.1E-3	2.9E-2
Propionaldehyde	mg/dscm	ND	ND	ND	--	ND	e	n/a	6.1E-4	3.1E-3
Butyraldehyde	mg/dscm	ND	ND	ND	--	ND	e	n/a	5.4E-4	2.7E-3
Glyoxal	mg/dscm	ND	ND	ND	--	ND	e	n/a	1.6E-3	2.2E-3
Valeraldehyde	mg/dscm	ND	ND	ND	--	ND	e	n/a	1.9E-4	5.2E-3
Hexanaldehyde	mg/dscm	ND	ND	ND	--	ND	e	n/a	5.8E-4	5.8E-3

Shaded area represents substances not detected in at least 3 valid test runs.

* All results are field blank corrected.

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the average Field Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

(i) High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

attributed to the measured levels being very near the MDL. These results indicate that the stack emission values may be positively biased for those substances with removal efficiencies across the dilution air purification system less than 100 percent. Acetone was detected in the both DSBs at levels significantly higher than in the ambient air sample or the FB. This could indicate a problem with residual acetone contamination in the field (acetone was used to rinse the probe, nozzle, connecting line and venturi between runs). Therefore, acetone results are not considered valid.

Because it appears likely that the stack sample results are positively biased due to incomplete removal of the analytes from the dilution air or otherwise potentially biased by background

levels in the samples, these results are considered qualitative, highly uncertain and should be used only with extreme caution. Based on these results, the method performance does not appear adequate, in its present stage of development, for measuring the extremely low concentrations of carbonyls present in these tests. Further evaluation and development of the method is recommended to assess dilution air purification efficiency, potential interferences and other method performance issues before further use at extremely low carbonyl concentrations.

Inorganic Fine Particle Precursors

NO_x, SO₂ and NH₃ emitted as gases can form secondary fine particles in the atmosphere through photochemical and other reactions. NO_x emissions were characterized using the plant's existing continuous emissions monitoring system. Gaseous NH₃ was captured by two different methods: (1) on citric acid-impregnated cellulose-fiber filter placed downstream of a QFF (to remove any particulate ammonium salts) in both the Alpha and Beta dilution samplers; and (2) by absorption from raw (undiluted) stack gas samples, after coarse particle filtration through a quartz wool filter, in wet impingers containing 0.1 N HCl solution. SO₂ was captured on a K₂CO₃-impregnated cellulose-fiber filter downstream of a QFF in the Alpha sampler.

NO_x concentration averaged approximately 2.5 ppm (dry, as measured) during the tests (Table 4-19), corresponding to an average of 2.0 ppm corrected to 15 percent O₂ (dry). This is approximately consistent with previous tests at Site Echo and with expected levels from units equipped with SCR systems.

The high load dilution sampler NH₃ results show high RSDs in both the Alpha and Beta sampler, attributed to a high result for Run 1 (Table 4-19). The impinger method results are much more consistent from run to run. The average high load NH₃ concentration from the Alpha and Beta dilution samplers is similar, however both are significantly higher than the impinger method result. If Run 1 is excluded, the dilution samplers and impinger method results are in somewhat better agreement. This suggests an anomaly in the high load Run 1 dilution sampler NH₃ results, although no explanation was revealed on investigation. At low load, the dilution sampler results also appear to have a slight positive bias compared to the

Table 4-19. Inorganic Secondary Particle Precursor Concentrations (Site Echo).

(a) High Load

Parameter	Units	Value							
		Hi-R1 (i)	Hi-R2 (i)	Hi-R3 (i)	Hi-R4	Average	RSD (%)	Ambient 21-May-03	MDL (1)
Run Number	-								
Date	-	11-May-03	12-May-03	13-May-03	14-May-03				
Ammonia (Alpha DS)	mg/dscm	8.7E+0	2.6E+0	1.5E+0	1.5E+0	3.6E+0 a b c d	97	3.6E-3	1.0E-3
	ppm	1.2E+1	3.7E+0	2.1E+0	2.1E+0	5.1E+0	97	5.1E-3	--
	lb/hr	2.5E+1	7.6E+0	4.3E+0	4.5E+0	1.0E+1	97	n/a	--
Ammonia (Beta DS)	mg/dscm	8.1E+0	3.2E+0	2.7E+0	2.4E+0	4.1E+0 a	66	3.6E-3	6.8E-4
	ppm	1.1E+1	4.5E+0	3.9E+0	3.3E+0	5.8E+0	66	5.1E-3	--
	lb/hr	2.3E+1	9.2E+0	7.9E+0	7.0E+0	1.2E+1	65	n/a	--
Ammonia (BAAQMD ST-1b)	mg/dscm	2.6E+0	2.7E+0	2.4E+0	2.3E+0	2.6E+0	8	--	--
	ppm	3.6E+0	3.8E+0	3.3E+0	3.3E+0	3.6E+0	8	--	--
	lb/hr	7.5E+0	7.9E+0	6.8E+0	7.0E+0	7.4E+0	7	--	--
Sulfur Dioxide (Alpha DS)	mg/dscm	1.3E-1	1.6E-1	2.5E-1	3.1E-1	2.1E-1	38	1.3E-2	2.5E-3
	ppm	4.9E-2	6.0E-2	9.3E-2	1.2E-1	7.9E-2	38	5.0E-3	--
	lb/hr	3.8E-1	4.6E-1	7.1E-1	9.1E-1	6.2E-1	40	n/a	--
NO _x (as NO ₂) (CEMS)	mg/dscm	4.4E+0	5.1E+0	5.1E+0	4.7E+0	4.8E+0	7	--	--
	ppm	2.3E+0	2.7E+0	2.6E+0	2.5E+0	2.5E+0	7	--	--
	lb/hr	1.3E+1	1.5E+1	1.5E+1	1.4E+1	1.4E+1	7	--	--

(b) Low Load

Parameter	Units	Value							
		Lo-R1	Lo-R2	Lo-R3	--	Average	RSD (%)	--	MDL (1)
Run Number	-								
Date	-	16-May-03	17-May-03	18-May-03	--				
Ammonia (Alpha DS)	mg/dscm	2.5E+0	3.9E+0	3.2E+0		3.2E+0 a	21	--	1.4E-3
	ppm	3.6E+0	5.5E+0	4.5E+0		4.5E+0	21	--	--
	lb/hr	5.6E+0	8.6E+0	7.1E+0		7.1E+0	21	--	--
Ammonia (Beta DS)	mg/dscm	3.2E+0	3.9E+0	5.1E+0		4.1E+0 a	25	--	1.1E-3
	ppm	4.5E+0	5.5E+0	7.3E+0		5.7E+0	25	--	--
	lb/hr	7.0E+0	8.5E+0	1.1E+1		9.0E+0	25	--	--
Ammonia (BAAQMD ST-1b)	mg/dscm	2.7E+0	2.5E+0	2.2E+0	--	2.5E+0	10	--	--
	ppm	3.7E+0	3.4E+0	3.0E+0	--	3.4E+0	10	--	--
	lb/hr	5.9E+0	5.4E+0	4.8E+0	--	5.4E+0	10	--	--
Sulfur Dioxide (Alpha DS)	mg/dscm	1.7E-1	2.3E-1	2.4E-1		2.1E-1	16	--	3.4E-3
	ppm	6.5E-2	8.5E-2	8.9E-2		8.0E-2	16	--	--
	lb/hr	3.8E-1	5.0E-1	5.2E-1		4.7E-1	16	--	--
NO _x (as NO ₂) (CEMS)	mg/dscm	4.5E+0	4.7E+0	4.6E+0	--	4.6E+0	2	--	--
	ppm	2.4E+0	2.5E+0	2.4E+0	--	2.4E+0	2	--	--
	lb/hr	1.0E+1	1.1E+1	1.0E+1	--	1.0E+1	3	--	--

CEMS - Continuous Emissions Monitoring System.

DS - Dilution Sampler

(1) Average MDL for dilution ratio. Ambient sample MDLs are smaller than test runs MDLs due to 1:1 dilution ratio.

MDL- Method Detection Limit

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

< - detected in fewer than all test runs

a - 95% Confidence Lower Bound of the Average concentration is less than the Dilution Sampler Blank concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the Field Blank concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Trip Blank concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

⁽ⁱ⁾ High winds interfered with dilution sampler bypass flow measurement, results may be positively biased (see text).

impinger method results. It should be noted that NH_3 was detected in the DSB, and the lower 95 percent confidence bound of all of the average dilution sampler NH_3 results is less than the DSB. Therefore, the dilution sampler results may be positively biased and the impinger method results are considered the most reliable.

Average SO_2 concentration was similar for high load and low load (0.21 mg/dscm) and is about 40 percent of the expected value based on fuel S analysis. The discrepancy between the expected and measured SO_2 values is surprising since practically all the fuel S is expected to be converted to SO_2 during combustion. Previous tests indicated that the expected SO_2 concentration in the stack is well below the carrying capacity of the K_2CO_3 -impregnated filters, so it is unlikely the filters were overloaded and no problems with the sampling or analysis of SO_2 were identified. Particulate SO_4^{2-} and elemental S levels presented earlier account for approximately 3 to 7 percent of the fuel S, leaving slightly more than half of the fuel S unaccounted for. This indicates a possible low bias in the stack SO_2 measurement, or a high bias in the fuel S measurement.

Ambient levels of SO_2 from a monitoring station near the plant location averaged 1.7 ppb during 2001 with a maximum 24-hour concentration of 16 ppb. The results from the ambient sample for this test were 5 ppb, which is within the range of the historical annual average.

5. EMISSION FACTORS AND SPECIATION PROFILES

Emission factors are a cost-effective means of developing area-wide emission inventories, which are one of the fundamental tools for air quality management. They also are useful for estimating emissions impacts of new facilities. In response to requests from the U.S. Congress and the U.S. EPA, the National Research Council (NRC) established the Committee on Research Priorities for Airborne Particulate Matter. The blue-ribbon panel of experts from industry, academia and the regulatory community identified characterization of source emissions as one of the ten key national research priorities, especially the size distribution, chemical composition, and mass emission rates of particulate matter, and the emissions of reactive gases that lead to secondary particle formation through atmospheric chemical reactions (NRC, 1999). Emission factors were derived from the results of these tests to facilitate data analysis and application.

EMISSION FACTOR DEVELOPMENT

Source-specific emission factors were determined by dividing the emission rate, in lb/hr, by the measured heat input, in million British thermal units per hour (MMBtu/hr), to give pounds per million British thermal units (lb/MMBtu) for each test run. Heat input is the product of the measured fuel flow rate and the average fuel heating value, obtained from the plant process data. Average emission factors were determined by taking the arithmetic mean of the detected data for valid test runs. Undetected data were excluded from calculations. This treatment of undetected data differs from the procedure used by EPA for development of emission factor documents (U.S. EPA, 1997b), in which one-half of the MDL is substituted for undetected data and used in sums and averaged data. The approach used in this report was chosen to avoid ambiguity when using the results for source apportionment analysis. Because one-half the detection limit is not included in the average results, and uncertainty cannot be determined based on a single datum, emission factors are reported for only those substances detected in at least two of the four test runs. Emission factors based on data detected in at least three test runs are considered the most reliable. None of the emission factors based on only two test runs is reported here because the results did not meet other screening criteria.

Speciation Profiles

A slightly different procedure for handling undetected results was used for calculating speciation profiles. Undetected data are treated as zeros in the speciation profiles so that both the sum of mass fractions for each run and the sum of the average mass fractions are equal to one. This also minimizes bias in the mass fraction average and uncertainty from compounds that are seldom detected since zero is counted as a real number in the calculations.

Uncertainty and Representativeness

As a measure of emission factor reliability, the bias (accuracy or systematic uncertainty) and precision (variability or random uncertainty) of the results, the total relative uncertainty (at the 95 percent confidence level) and 95 percent confidence upper bound were calculated for each emission factor and mass fraction using standard error analysis procedures (American Society of Mechanical Engineers, ASME, 1998).

The total emission factor uncertainty includes uncertainty in the sample volumes, dilution ratios, fuel flow rate, fuel heating value and run-to-run variability in addition to the analytical uncertainty. In the tables that follow, the reported results, the total relative uncertainty, and a 95 percent confidence upper bound are given for each of the substances of interest. The total relative uncertainty represents the 95 percent confidence interval based on a two-tailed Student “t” distribution. The 95 percent confidence upper bound estimate is based on the single-tailed Student “t” distribution at the 95 percent confidence level. Uncertainty cannot be determined for substances that were detected in only one of the four test runs; therefore, emission factors are not reported for these substances.

Except for substances of special interest for source apportionment or data analysis (e.g., OC, EC, ions), compounds with relative uncertainty greater than 100 percent are excluded. Relative uncertainty greater than 100 percent indicates it is likely that actual emissions are different from the reported value, and they cannot be distinguished from zero or the MDL with high confidence. Emission factors with an uncertainty greater than 100 percent should be considered potentially unrepresentative and data users should apply appropriate caution when using them. Although the absolute value of the emission factor is therefore uncertain, the 95 percent confidence upper bound represents a plausible upper bound for emissions (i.e., it is likely that the actual emissions

are below the upper bound). The reported uncertainty does not include the potential uncertainty associated with different plant configurations, operating conditions, geographical locations, fuel variations, etc.

Blanks and Ambient Air Samples

Three types of blanks for the dilution sampler measurements were collected in the field during these tests to assess sampling bias: DSBs (two for each sampler, total of four), FBs (one for each sampler, total of two) and TBs (one for the field campaign). In addition, a single ambient air sample was collected. Blanks and the ambient air sample were analyzed for all substances measured in the stack samples. The average and lower 95 percent confidence bounds of the stack sample results were compared to the maximum blank value for screening purposes as follows:

- The high load results were compared to the highest result measured in the first two DSBs (from the Alpha and Beta samplers). These DSBs represent a “clean” system at the beginning of the test before any stack samples were collected. The low load results were compared to the second two DSBs collected after the last low load test run. These DSBs represent the clean system plus any cross-run contamination from the preceding high load runs that may have been present.
- If the average stack sample result is less than the highest blank, the emission factor is excluded.
- If the lower 95 percent confidence bound of the average stack result is less than the highest DSB, FB or TB result, the emission factor is flagged with a footnote “a”, “b”, or “c”, respectively.
- If the lower 95 percent confidence bound of the average stack sample result is less than the ambient air result, the emission factor is flagged with a footnote “d”.
- For organic compounds, if the average stack sample result is less than five times the highest blank result, the emission factor is flagged with a footnote “B”.
- If a substance was not detected in any of the valid test run samples, the emission factor is flagged with the symbol “<”.

Refer to Section 6 for presentation of blank results.

Emission Factor Quality

This test represents one of the first applications of dilution sampling to this type of source and in many cases the extremely low concentrations of particulate matter and other pollutants challenged the limits of the state-of-the-art methods employed. In addition, because all of the emission measurements were made at the stack downstream of supplementary burners and post-combustion air pollution controls, the results do not represent emissions from the gas turbine alone. The resulting emission factors are not considered representative of any particular operating condition at this plant, but rather are the average of the operating conditions during this test. Consequently, data users should apply considerable caution when using these results.

Emission factors derived from a test of a single unit should be used with considerable caution. Such results do not necessarily represent results from a random sample of an entire source category population due to differences in design, configuration, emission controls, maintenance condition, operating conditions, geographic location, fuel compositions, ambient/weather conditions and other factors. The source-specific emission factors derived from this test should not be considered representative of all NGCC-SFs, and may best be used in conjunction with test results from other units within the same source category population to develop more robust, reliable emission factors.

The test data quality for these tests is considered high because the dilution sampling and sample collection/analysis methods are well documented in the peer-reviewed scientific literature and/or in published EPA test methods and protocols. Moreover, the test methods and data quality are extensively documented in this test report in sufficient detail for others to replicate the tests. However, it should be noted that whereas dilution sampling is widely accepted for demonstrating compliance with mobile source particulate emission standards and for stationary source receptor and source apportionment analysis, it is not currently accepted by regulatory agencies for demonstrating compliance with stationary source particulate with aerodynamic diameter less than 10 μm (PM₁₀) emission standards or permit limits. Widely recognized standard methods for stationary source dilution sampling do not presently exist.

The quality of the emission factors derived from this test should not be considered high because the emission factors are based on a single test or a single unit that may not be representative of

the entire source category population. This does not mean that these test results are not of value or high quality, but rather indicates that more tests are needed to corroborate the results before they are widely applied. As noted above, the emission factors derived from these test results may best be used in conjunction with test results from other units within the source category population to develop more robust, reliable emission factors.

EMISSION FACTORS

Primary PM_{2.5} Mass, Elements and Ions Emission Factors

Emission factors for primary PM_{2.5} mass, elements and ions were derived from the dilution sampling results. In Section 4, results of measurements from the Alpha and Beta dilution samplers were shown to give similar PM_{2.5} mass results that are not significantly different at the 95 percent confidence level. Therefore, the results of the Alpha and Beta stack samples were combined for determining average source-specific emission factors so that the resulting factors include both measurement and process variability. Note, the emission factors include any positive bias for some of the results that may have been caused by the wind interference discussed in Section 4. The Beta T1 filter results were used, because this filter pack included speciated results, whereas the T2 filter did not, and the T2 filter used a less accurate sample flow meter. Data from all valid runs were combined to determine average results separately for high load and low load

Emission factors for PM_{2.5} mass, S, SO₄⁼ and NH₄⁺ are reported for both high and low loads (Table 5-1). Cl, Cl⁻, NO₃⁻ and soluble Na emission factors also are reported, however the measured concentrations of these substances are not be significantly greater than the highest DSB (flagged “a”) so these results should be viewed with caution. The low load PM_{2.5} emission factor also is flagged “a” because of a high DSB result in the second Alpha sampler DSB. This DSB result appears to be an outlier compared to all the other DSB results, so this may not be typical of the background level in the stack samples. The PM_{2.5} mass emission factor for high load (0.00015 lb/MMBtu) is approximately 36 percent greater than the low load emission factor (0.00011 lb/MMBtu), however the confidence intervals overlap and therefore the difference is not significant at the 95 percent confidence level.

Table 5-1. Primary Emission Factors – Particulate Mass, Elements and Ions - Alpha and Beta Samplers (Site Echo).

(a) High Load.

Substance		Emission Factor (lb/MMBtu)	Uncertainty at 95% Confidence Level (%) (1)	95% Confidence Upper Bound (%) (2)	5th Percentile	95th Percentile	Number of Detected Runs	
Particulate Mass	PM2.5 mass	1.4E-4	41	1.9E-4	5.4E-5	2.1E-4	8	
Elements	Cl	< 1.3E-6	a	115	2.4E-6	7.3E-7	1.8E-6	3
	S	2.3E-5		39	3.0E-5	1.3E-5	3.7E-5	8
	Sr	< 1.9E-8	a b	52	2.8E-8	1.1E-8	2.7E-8	7
Ions	NO ₃ ⁻	6.6E-6	a	27	8.3E-6	5.6E-6	8.1E-6	8
	SO ₄ ⁼	4.3E-5		29	5.4E-5	2.9E-5	6.3E-5	8
	NH ₄ ⁺	2.4E-5		33	3.1E-5	1.6E-5	3.6E-5	8
	Soluble Na	4.0E-6	a	35	5.2E-6	2.4E-6	6.3E-6	8

(b) Low Load.

Substance		Emission Factor (lb/MMBtu)	Uncertainty at 95% Confidence Level (%) (1)	95% Confidence Upper Bound (%) (2)	5th Percentile	95th Percentile	Number of Detected Runs	
Particulate Mass	PM2.5 mass	1.1E-4	a	37	1.5E-4	8.2E-5	1.5E-4	6
Elements	Al	< 4.0E-7	a b	79	7.0E-7	2.9E-7	5.2E-7	4
	S	1.6E-5		35	2.0E-5	1.1E-5	2.1E-5	6
Ions	Cl ⁻	1.5E-5	a b c	43	2.2E-5	1.2E-5	1.8E-5	6
	SO ₄ ⁼	2.8E-5		35	3.6E-5	2.0E-5	3.8E-5	6
	NH ₄ ⁺	1.9E-5		32	2.4E-5	1.4E-5	2.4E-5	6

(1) Uncertainty is calculated at the 95% confidence level using the two-tailed Student t distribution. The 95 percent confidence interval of the emission factor is two times the uncertainty (i.e., mean +/- uncertainty). Uncertainty greater than 100% indicates it is likely actual emissions differ from the reported emission factor value. Data users should exercise appropriate caution.

(2) 95% upper confidence bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% upper confidence bound provides a plausible upper bound (i.e. it is likely emissions are lower) for emissions.

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

< - detected in fewer than all test runs

Particulate Carbon Emission Factors

OC emission factors for high load and low load are similar, 0.00024 and 0.00021 lb/MMBtu, respectively (Table 5-2). None of the SVOCs reported in Section 4 met the aforementioned criteria for reporting emission factors reflecting the extremely low concentrations of SVOCs in these samples, at or near the ability to detect them. EC was detected only in half of the high load stack samples at levels barely above the MDL. The EC emission factor is approximately 1/20 of the OC emission factor, and the uncertainty for this value exceeds 100 percent. OC and EC concentrations are not significantly greater than the blanks, so these emission factors should be considered potentially unrepresentative and viewed with caution. The OC emission factors are

greater than those for PM_{2.5} mass, which reflects both the low concentrations of both total PM_{2.5} mass and particulate carbon and potential positive bias in the OC measurement.

As noted in Section 4, it is very likely the OC results are positively biased due to adsorption of VOCs on the sampling media. This artifact is significant in these tests because of the extremely low OC concentrations present in the exhaust, much lower even than the trace concentrations of VOC that were measured. Backup OC (also shown on Table 5-2) is a separate measurement used as an indicator of the potential artifact. The emission factors based on OC and backup OC measurements are very similar, well within the uncertainties of the means, indicating the OC results are highly suspect and, at best, represent a conservative upper bound for actual emissions. The OC artifact is the subject of ongoing studies by others (e.g., Turpin, Huntzinger and Hering, 1994; Kirshstetter, Corrigan and Novakov, 2001); and, because the artifact is not well understood, it is the current convention not to subtract the backup OC from the primary result. Despite these limitations of the test results, it is clear from the results that particulate carbon emissions from this NGCC-SF are extremely low. Data users should apply appropriate caution when using these results.

Table 5-2. Primary Emission Factors: Particulate Carbon—Alpha and Beta Samplers (Site Echo)

(a) High Load.

Substance	Emission Factor (lb/MMBtu)	Uncertainty at 95% Confidence Level (%) (1)	95% Confidence Upper Bound (%) (2)	5th Percentile	95th Percentile	Number of Detected Runs
Organic Carbon (OC)	2.3E-4 a	37	3.0E-4	1.1E-04	3.5E-04	8
Elemental Carbon (EC)	< 1.2E-5 a d	106	2.3E-5	6.7E-06	1.9E-05	4
OC Backup	2.1E-4 a b c	35	2.7E-4	1.3E-04	2.9E-04	8

(b) Low Load.

Substance	Emission Factor (lb/MMBtu)	Uncertainty at 95% Confidence Level (%) (1)	95% Confidence Upper Bound (%) (2)	5th Percentile	95th Percentile	Number of Detected Runs
Organic Carbon (OC)	2.1E-4 a b	27	2.6E-4	1.6E-4	2.7E-4	6
OC Backup	2.3E-4 a b c	20	2.7E-4	2.0E-4	2.5E-4	6

(1) Uncertainty is calculated at the 95% confidence level using the two-tailed Student t distribution. The 95 percent confidence interval of the emission factor is two times the uncertainty (i.e., mean +/- uncertainty). Uncertainty greater than 100% indicates it is likely actual emissions differ from the reported emission factor value. Data users should exercise appropriate caution.

(2) 95% upper confidence bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% upper confidence bound provides a plausible upper bound (i.e. it is likely emissions are lower) for emissions.

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

Secondary Particle Precursor Emission Factors

Emissions of NO_x , SO_2 , NH_3 and VOC with carbon number greater than seven (VOC_{8+}) are considered secondary fine particle precursors (Table 5-3). The emission factor for NO_x is derived from the plant's continuous emission monitoring results. Emission factors for SO_2 and VOC_{8+} are derived from the dilution sampler canister results. The NH_3 emission factor is derived from the wet impinger method results because the dilution sampler results appears to be biased due to an unknown cause and the wet impinger method is widely accepted. Note, the NH_3 emission factor does not include particulate NH_4^+ results from Table 5-1 because the test objective was to measure $\text{PM}_{2.5}$ and $\text{PM}_{2.5}$ precursors separately.

With the exception of nonanal and 3,6-dimethyloctane, all of the VOC_{8+} were detected in the blanks at significant levels compared to the stack samples. The VOC_{8+} emission factors therefore should be viewed as potentially unrepresentative and used only with appropriate caution.

Other VOC Emission Factors

Emission factors for VOCs with a carbon number of seven or lower are presented in Table 5-4. All of the VOCs were detected in the blanks at significant levels compared to the stack samples. Therefore, the result should be viewed as potentially unrepresentative and used only with appropriate caution.

PM_{2.5} SPECIATION PROFILES

Speciation profiles for particulate matter provide a means of estimating the emissions of PM species based on a measurement or emission factor for total PM emissions. One of the principal applications of speciation profiles is for source-receptor and source apportionment models, such as CMB8 (Watson et al., 1997). Receptor models require profiles that express the speciated substance abundances in terms of the mass fraction of the substance in the total emissions stream and the uncertainty associated with that mass fraction. Speciated PM emission factors also are useful for estimating impacts of PM species emissions on air quality, e.g., atmospheric visibility (Ryan, 2002). EPA's SPECIATE database contains one of the largest compilations of speciation

Table 5-3. Secondary Particle Precursor Emission Factors (Site Echo).

(a) High Load

	Emission Factor (lb/MMBtu)	Relative Uncertainty at 95% Confidence Level (%) (1)	95% Confidence Upper Bound (lb/MMBtu) (2)	5th Percentile	95th Percentile	Number of Detected Runs
NO _x as NO ₂ (Plant CEMS)	7.9E-3	17	9.1E-3	7.3E-3	8.4E-3	4
NH ₃ (BAAQMD ST-1B)	4.2E-3	18	5.2E-3	3.9E-3	4.5E-3	4
SO ₂ (Alpha Sampler)	3.5E-4	63	5.1E-4	2.2E-4	4.9E-4	4
<u>VOC₈₊ (Alpha Sampler) (3)</u>						
2,2,5-trimethylhexane	4.9E-5 B a	82	8.0E-5	3.2E-5	7.8E-5	4
beta-pinene	2.9E-5 B a	78	4.7E-5	2.0E-5	4.6E-5	4
m- & p-xylene	2.7E-5 B a	87	4.5E-5	1.0E-5	3.9E-5	4
Nonanal	1.2E-5	70	1.8E-5	5.9E-6	1.5E-5	4
2,3,5-trimethylhexane	1.2E-5 B a	84	1.9E-5	4.6E-6	1.6E-5	4
o-xylene	1.0E-5 B a	90	1.7E-5	4.1E-6	1.5E-5	4
3,6-dimethyloctane	9.5E-6	38	1.3E-5	7.7E-6	1.1E-5	4
2,3-dimethylhexane	8.8E-6 B a	82	1.4E-5	4.4E-6	1.3E-5	4
1,4-diethylbenzene	7.7E-6 B	48	1.1E-5	5.7E-6	9.7E-6	4
1,2,4-trimethylbenzene	6.7E-6 B	69	1.0E-5	4.1E-6	9.8E-6	4
2,3-trimethylpentane	5.4E-6 B	46	7.4E-6	4.4E-6	6.9E-6	4
2,2,4-trimethylpentane	5.2E-6 B a	86	8.6E-6	3.2E-6	8.4E-6	4
n-octane	2.1E-6 B a	82	3.5E-6	1.2E-6	3.1E-6	4
Styrene + heptanal	< 2.0E-6 B a	88	3.3E-6	1.4E-6	2.5E-6	3
3-ethylpentane	2.0E-6 B a	94	3.4E-6	1.2E-6	3.4E-6	4
n-propylbenzene	1.4E-6 B a	74	2.2E-6	7.0E-7	1.9E-6	4
3,3-dimethylheptane	< 6.1E-7	36	7.9E-7	6.0E-7	6.2E-7	2
n-nonane	< 6.1E-7	36	7.9E-7	6.0E-7	6.2E-7	2
2-methylheptane	< 6.1E-7	35	7.9E-7	6.0E-7	6.2E-7	2
Total VOC ₈₊	< 1.9E-4	77	3.1E-4	1.1E-4	2.8E-4	3+

(a) Low Load

	Emission Factor (lb/MMBtu)	Relative Uncertainty at 95% Confidence Level (%) (1)	95% Confidence Upper Bound (lb/MMBtu) (2)	5th Percentile	95th Percentile	Number of Detected Runs
NO _x as NO ₂ (Plant CEMS)	8.1E-3	14	9.1E-3	8.0E-3	8.3E-3	3
NH ₃ (BAAQMD ST-1B)	4.2E-3	29	5.2E-3	3.8E-3	4.6E-3	3
SO ₂ (Alpha Sampler)	3.7E-4	42	4.8E-4	3.1E-4	4.1E-4	3
<u>VOC₈₊ (Alpha Sampler) (3)</u>						
1,4-diethylbenzene	1.3E-5 B a	74	1.9E-5	9.2E-6	1.5E-5	3
2,3-trimethylpentane	7.4E-6 B a	53	1.0E-5	6.1E-6	8.5E-6	3
2,2,4-trimethylpentane	6.8E-6 B	42	9.1E-6	6.0E-6	7.6E-6	3
2,6-dimethylheptane	< 2.0E-6 B a	30	2.5E-6	1.9E-6	2.0E-6	2
n-propylbenzene	< 1.3E-6 B a	30	1.7E-6	1.3E-6	1.3E-6	2
Total VOC ₈₊	3.0E-5 B	57	4.3E-5	2.4E-5	3.4E-5	3

Shaded area represents substances detected in fewer than 3 valid test runs. Average not considered reliable for quantitative analysis.

(1) Uncertainty is calculated at the 95% confidence level using the two-tailed Student t distribution. The 95 percent confidence interval of the emission factor is two times the uncertainty (i.e., mean +/- uncertainty). Uncertainty greater than 100% indicates it is likely actual emissions differ from the reported emission factor value. Data users should exercise appropriate caution.

(2) 95% upper confidence bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% upper confidence bound provides a plausible upper bound (i.e. it is likely emissions are lower) for emissions.

(3) VOC with carbon number 8 or greater

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

< - detected in fewer than all test runs

B - Stack average is less than five times the Dilution System Blank, Field Blank, or Trip Blank (as applicable).

Table 5-4. Other VOC Emission Factors (Site Echo).

(a) High Load

	Emission Factor (lb/MMBtu)		Uncertainty at 95% Confidence Level (%) (1)	95% Confidence Upper Bound (%) (2)	5th Percentile	95th Percentile	Number of Detected Runs
Ethane	2.6E-4	B a	63	3.9E-4	1.6E-4	3.6E-4	4
Propane	1.2E-4	B a	59	1.7E-4	8.2E-5	1.6E-4	4
Propene	2.2E-5	B a	72	3.4E-5	1.3E-5	3.2E-5	4
Carbon tetrachloride	1.2E-5	B a	73	1.8E-5	8.0E-6	1.8E-5	4
2,3-dimethylpentane	1.1E-5	B a	84	1.7E-5	5.1E-6	1.6E-5	4
1,3-dimethylcyclopentane	9.1E-6	B a	27	1.1E-5	8.7E-6	9.6E-6	4
Cyclohexene	6.3E-6	B a	53	9.0E-6	4.2E-6	7.9E-6	4
Methyl chloroform	6.1E-6	B a	68	9.4E-6	3.6E-6	8.6E-6	4
p-dichlorobenzene	< 6.1E-6	B a	88	1.0E-5	4.1E-6	7.4E-6	3
Perchloroethylene	4.3E-6	B a	26	5.4E-6	4.2E-6	4.3E-6	4
Methyl bromide	3.7E-6	B a	68	5.7E-6	2.4E-6	5.0E-6	4
1,3-butadiene	3.1E-6	B a	81	5.0E-6	1.4E-6	4.3E-6	4
Benzaldehyde	< 1.8E-6		36	2.4E-6	1.8E-6	1.9E-6	2
2-methyl-1-butene	< 1.2E-6		35	1.6E-6	1.2E-6	1.2E-6	2
3-methyl-1-butene	< 6.1E-7	B a	37	7.9E-7	6.0E-7	6.2E-7	2

(b) Low Load.

	Emission Factor (lb/MMBtu)		Uncertainty at 95% Confidence Level (%) (1)	95% Confidence Upper Bound (%) (2)	5th Percentile	95th Percentile	Number of Detected Runs
Iso-butene	1.2E-5	B a	79	1.8E-5	8.8E-6	1.5E-5	3
1-hexene	7.6E-6	B	68	1.1E-5	6.0E-6	9.4E-6	3
1-butene	5.7E-6	B a	51	7.9E-6	4.7E-6	6.5E-6	3
Methyl chloroform	3.3E-6	B a	26	4.1E-6	3.2E-6	3.3E-6	3
4-methylhexene	< 2.0E-6	B	30	2.5E-6	1.9E-6	2.0E-6	2

Shaded area represents substances detected in fewer than 3 valid test runs. Average not considered reliable for quantitative analysis.

(1) Uncertainty is calculated at the 95% confidence level using the two-tailed Student t distribution. The 95 percent confidence interval of the emission factor is two times the uncertainty (i.e., mean +/- uncertainty). Uncertainty greater than 100% indicates it is likely actual emissions differ from the reported emission factor value. Data users should exercise appropriate caution.

(2) 95% upper confidence bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% upper confidence bound provides a plausible upper bound (i.e. it is likely emissions are lower) for emissions.

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

B - Stack average is less than five times the Dilution System Blank, Field Blank, or Trip Blank (as applicable).

< - detected in fewer than all test runs

profiles (U.S. EPA, 2002a). Many of the profiles currently in SPECIATE are drawn from results generated in the 1980's and in some cases the 1970's and it is debatable whether these represent current source emissions. For example, prior to the 1999 update, the PM profile for natural gas-fired combustion turbines was based on results of a poorly documented jet engine test; this profile was removed in the 1999 update with no data to replace it. Due to the pending implementation of the PM2.5 NAAQS, EPA added 13 new PM profiles (some replaced older profiles) to SPECIATE in 1999 (U.S. EPA, 2002b), and is currently seeking to identify new profiles for eventual inclusion in a future update (Hodan, 2002). It is expected that a significant number of new profiles will be added to SPECIATE because of this search. Most of the new

profiles in SPECIATE will be drawn from articles published in peer-reviewed journals. EPA has not developed a formal procedures manual or acceptance criteria for preparing speciation profiles, however EPA has provided reviews of 178 articles published between 1990 and 2002 that provides insight into their process (Hodan, 2002).

EPA convened an expert panel of potential SPECIATE users and data suppliers in October 2002 to re-evaluate speciation needs (Hodan, 2002). Members of that group recommended that no hot stack samples or hot filter/iced impinger results should be used for PM speciation profiles because they do not represent actual condensed particle emissions (Watson and Chow, 2002). It was recommended that PM speciation profiles include, as a minimum, major elements (at least those reported by the IMPROVE and PM2.5 Speciation Trends networks), major water-soluble ions— SO_4^- and NO_3^- at a minimum, preferably also NH_4^+ , potassium (K), Na, Cl^- , fluoride (F^-), phosphate (PO_4^-), calcium (Ca), magnesium (Mg)— and carbon fractions—total carbon (TC), OC, and EC, preferably with other fractions that are defined by the method such as the eight IMPROVE fractions, and carbonate carbon. Organic fractions, isotopic abundances, organic compounds, and single particle properties should be included where they are well-defined, and can be normalized to PM or organic mass. The speciation profiles reported here are intended to be consistent with these recommendations.

PM2.5 Mass Speciation Profile (Dilution Sampler)

Because of the very low concentrations of total PM mass measured by the dilution sampler in these tests, it is considered more appropriate to normalize the PM2.5 speciation profile using the reconstructed PM2.5 mass. The reconstructed PM2.5 mass is determined from the individual species measurements with adjustments for assumed oxidation state and hydrocarbon speciation. The average reconstructed PM2.5 mass is greater than the measured mass by a factor of 2.5 to 2.8. While this is not entirely surprising for total mass below 500 μg (Chow et al., 2004), there is considerable suspicion regarding the reliability of the OC mass that comprises most of the reconstructed mass and this probably accounts for most of the discrepancy (see Sections 4, 6 and 7 for additional discussion). The OC mass was multiplied by a factor of 1.08 to account for hydrocarbon speciation (based on the total carbon fraction of all the SVOCs detected in any run). Elements are generally converted to the highest stable oxide form during combustion, except for

S, Cl and fixed nitrogen, which are assumed to be present as SO_4^- , Cl^- , NO_3^- and NH_4^+ (the IC rather than the ED-XRF analysis results are used for these ions/anions). Mg is not included in the reconstructed mass because the ED-XRF analysis is semi-quantitative for this element, and only soluble Na is included for the same reason. Undetected target substances are included as zeros in the reconstructed mass and for uncertainty calculations.

The speciation profiles for high load and low load are dominated by OC (Table 5-5 and Figures 5-1 and 5-2). 68 to 73 percent of the reconstructed mass is accounted for by OC, with SO_4^- plus NH_4^+ accounting for 15 to 20 percent of the remainder. Backup OC represents 62 to 79 percent of the reconstructed mass, which indicates the potential magnitude of positive bias in the OC result due to the VOC adsorption artifact (discussed elsewhere in this report). This simply underscores that data users need to apply appropriate caution when using the OC and other species mass fraction results.

Table 5-5. Speciation Profile for Primary Emissions- Dilution Sampler Results (Site Echo).

(a) High Load.

Substance		Average Mass Fraction (1) (2) (%)	Uncertainty at 95% Confidence Level (%) (3)	95% Confidence Upper Bound (%) (4)	Number of Detected Runs
Organic Carbon (OC) (5)	a	68	12	76	8
SO ₄ ⁼		13	30	16	8
NH ₄ ⁺		7.0	24	8.5	8
Soluble Na	a	2.9	42	3.9	8
Cl ⁻	a b c	2.0	72	3.3	6
NO ₃ ⁻	a	2.0	42	2.8	8
Elemental Carbon (EC)	a d	1.8	138	4.0	4
Si	a	1.2	62	1.8	8
Al	a b	0.41	64	0.63	8
K	a	0.35	29	0.43	8
Fe	a b	0.25	48	0.35	8
Ca	a c	0.24	26	0.29	8
Ba		0.14	216	0.42	3
Zn	a b c d	0.08	90	0.14	8
Br	a	0.05	97	0.09	8
Backup OC (6)	a b c	62	16	71	8

(b) Low Load.

Substance		Average Mass Fraction (1) (2) (%)	Uncertainty at 95% Confidence Level (%) (3)	95% Confidence Upper Bound (%) (4)	Number of Detected Runs
Organic Carbon (OC) (5)	a b	73	13	83	6
SO ₄ ⁼		8.7	21	10	6
NH ₄ ⁺		5.9	21	7.0	6
Cl ⁻	a b c	5.1	51	7.4	6
Soluble Na	a	2.7	52	3.8	6
NO ₃ ⁻	a	1.2	125	2.4	3
Si	a	0.72	39	0.95	6
K	a	0.23	27	0.28	6
Ca	a c	0.22	23	0.26	6
Al	a b	0.18	127	0.38	4
Fe	a b c d	0.16	52	0.23	6
Br	a	0.06	32	0.07	6
Backup OC (6)	a b c	78	16	90	6

(1) Mass fraction is emission factor (EMF) of species divided by reconstructed mass - calculated from highest stable oxide form of elements. OC is corrected for carbon speciation based on SVOC results. NDs are included as zeros in speciation calculations. The average reconstructed PM2.5 mass is 2.8 times greater than average measured PM2.5 mass, OC results are probably biased high.

(2) **IMPORTANT:** These speciation profiles should only be applied to PM2.5 mass results measured with a dilution sampler. They should not be applied to PM emissions factors measured by other methods (e.g. hot filter, wet impinger). When dilution sampler results for PM2.5 mass are not available, use species emission factors given in Tables 5-1 and 5-2.

(3) Uncertainty is calculated at the 95% confidence level using the two-tailed Student t distribution. The 95 percent confidence interval of the mass fraction is two times the uncertainty (i.e., mean +/- uncertainty). Uncertainty greater than 100% indicates it is likely the reported mass fraction is not representative of actual emissions. Data users should exercise appropriate caution.

(4) 95% upper confidence bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% upper confidence bound provides a plausible upper bound (i.e., it is likely actual mass fraction is lower) for mass fraction.

(5) OC measurements are subject to a potential positive bias from adsorption of VOC species. Refer to footnote (6) and Section 7 for further discussion.

(6) OC measured on back up filter as measure of potential artifact. OC artifact not included in reconstructed mass. Refer to Sections 4, 6 and 7 for further discussion of OC artifact.

< - not detected in all valid tests.

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

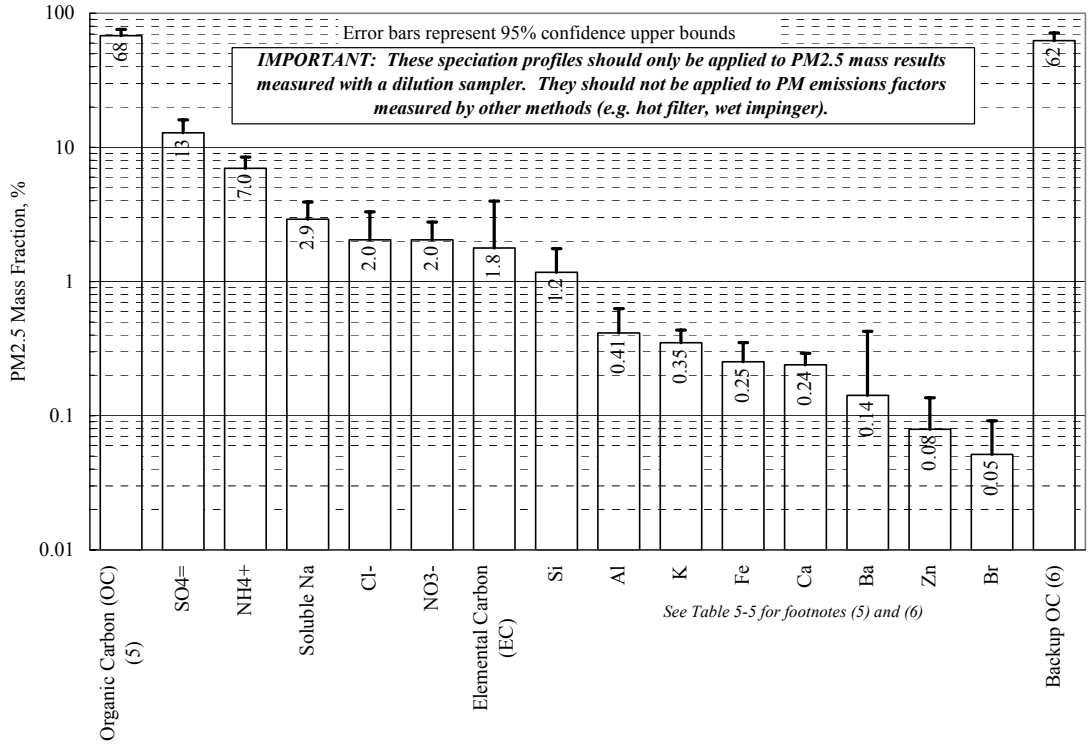


Figure 5-1. PM2.5 speciation profile, as measured by the dilution sampler, normalized by reconstructed PM2.5 mass – High Load (Site Echo).

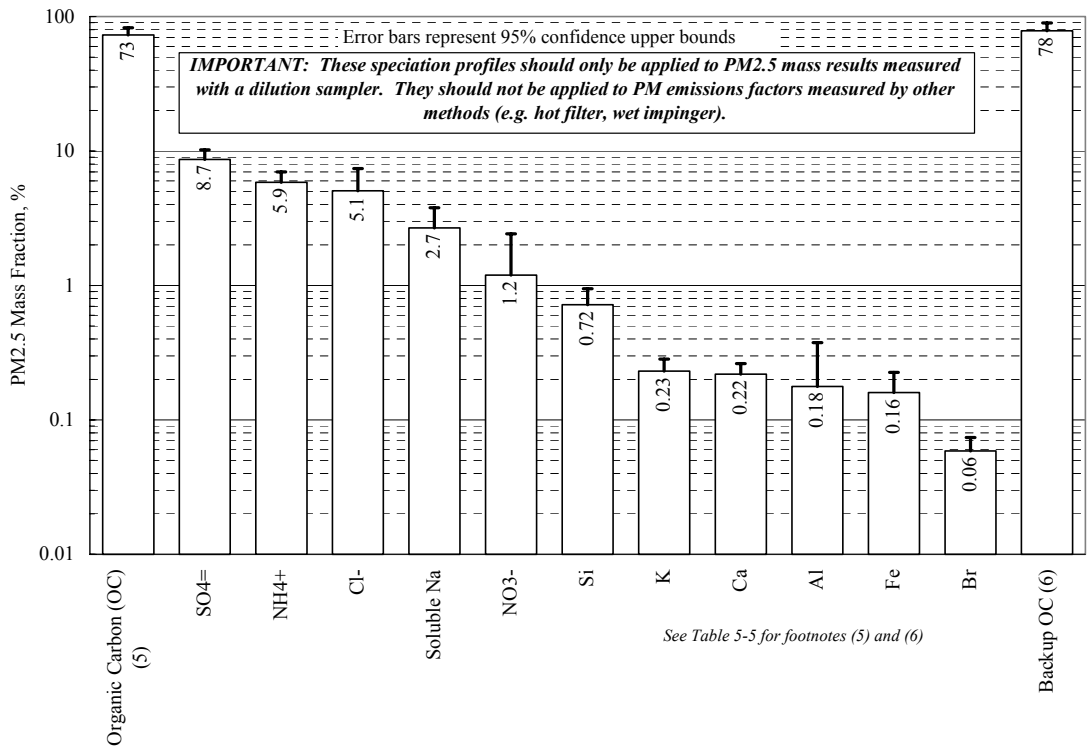


Figure 5-2. PM2.5 speciation profile, as measured by the dilution sampler, normalized by reconstructed PM2.5 mass – Low Load (Site Echo).

6. QUALITY ASSURANCE

This section summarizes the results of quality assurance activities performed during the test program, including analysis of blanks and other issues.

SAMPLE STORAGE AND SHIPPING

All samples requiring refrigerated storage were stored on-site in a refrigerator prior to shipment to the lab for analysis. All of the samples were shipped via overnight shipment to the lab in an ice chest with blue ice. Upon receipt of samples at the lab, those requiring refrigeration were stored at 4° C (nominal). Samples were stored and shipped in a manner to prevent breakage.

DILUTION SAMPLER SAMPLES

A variety of QA samples associated with the dilution sampler were collected and analyzed to assess data quality:

- Dilution sampler system blanks (DSBs) provide an indication of contamination resulting from residual deposits on the dilution sampler surfaces and/or dilution air purification system (HEPA/carbon filter) breakthrough. Two DSBs were collected on-site, one before and one after the emissions sampling. The first DSB was used to represent high load tests and the second DSB was used to represent low load tests. The DSBs were obtained by plugging the sample probe inlet and drawing air through the dilution air filters (HEPA and activated carbon), through the rest of the dilution sampler and collecting samples for the same duration (6 hours) and in the same manner as the stack samples were collected. The same full set of sampling media as used for stack sampling was collected with each the Alpha and Beta dilution samplers. Comparing DSB and ambient air sample results provides an assessment of dilution air purification system breakthrough. The DSB results are presented here as in-stack equivalent concentrations by applying the DSB analytical results to the average sample volumes and dilution ratios for each test condition (i.e., high and low load);
- FBs provide an indication of contamination during the handling and transport of the sampling media plus any contamination in the reagents. A single FB was collected for the test campaign by setting up and breaking down the dilution sampler sampling equipment without drawing gas through the sampling media. FBs were collected for all sample types except canisters. The FB results are presented as in-stack equivalents by applying the FB analytical results to the average sample volumes and dilution ratios for each test condition (i.e., high and low load);
- TBs provide an indication of contamination during the transport of the sampling media plus any contamination in the reagents. TBs are sampling media that are shipped from

the lab to the test site and back but are not opened. A single TB was collected for each sample type except canisters. The TB results are presented as in-stack equivalents by applying the TB analytical results to the average sample volumes and dilution ratios for each test condition (i.e., high and low load).

Blank results were compared to the 95 percent confidence lower bound of the average stack sample results. If the blank level is greater than the 95 percent lower bound, the stack emission and blank results are flagged. Flags indicate the data user should exercise caution since the field data may not be significantly different from the blanks.

Gravimetric Analysis

Prior to testing, unused filters were stored for at least one month in a controlled environment, followed by one week of equilibration in the weighing environment, to achieve stable filter tare weights. New and used filters were equilibrated at 20 ± 5 °C and a RH of 30 ± 5 percent for a minimum of 24 hours prior to weighing. Weighing was performed on a Cahn 31 electro-microbalance with ± 1 μg sensitivity. The electrical charge on each filter was neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance was calibrated with a 20 mg Class M weight and the tare was set prior to weighing each batch of filters. After every 10 filters were weighed, the calibration and tare were rechecked. If the results of these performance tests deviated by more than ± 5 μg , the balance was recalibrated. If the difference exceeded ± 15 μg , the balance was recalibrated and the previous 10 samples were reweighed. One hundred percent of initial weights and at least 30 percent of exposed weights were checked by an independent technician and samples were reweighed if these check-weights did not agree with the original weights within ± 0.015 mg. Pre- and post-weights, check weights and reweights (if required) were recorded on data sheets, as well as being directly entered into a database via an RS232 connection.

Net weights for all dilution sampler stack sample TMFs were positive and range from 9 to 54 μg . The middle range of the net filter weights falls between 19 and 39 μg (25th to 75th percentile). Compared to the reported analytical uncertainty (6.4 μg), the stack sample weights are greater than the analytical limits of qualifications (LOQ).

The six net filter weights on the DSBs ranged from 7 to 33 μg (Alpha and Beta samplers). The high DSB value, which corresponds to the Alpha tunnel low load condition, is clearly an outlier compared to the other five weights, which range from 7 to 18 μg and are otherwise normally distributed. The in-stack equivalent of this anomalous DSB result exceeded the average stack sample concentration 95 percent confidence lower bound for the Alpha tunnel low load condition (Table 6-1). This also led to a high relative percent difference (RPD) between the two Alpha sampler DSBs. Similarly, the anomalous low sample weight for the Beta sampler high load T1 filter (9 μg) resulted in high stack sample RSD and caused the DSB result (18 μg) to exceed the 95 percent confidence lower bound for that condition. If the DSB results and sample results are pooled irrespective of the individual samplers and test conditions and compared by use of a statistical 2-sample t-test, the 21 sample weights are significantly greater than the six DSB weights with very high (greater than 99 percent) confidence. The FB and ambient sample results are within an order of magnitude of each other, and both are lower than the DSBs are. PM_{2.5} was not detected in the TB.

Table 6-1. PM_{2.5} Mass Blank Results: (Site Echo).

(a) Alpha Sampler

	Alpha DSB (High Load) mg/dscm	Alpha DSB (Low Load) mg/dscm	Alpha DSB (average) mg/dscm	Alpha DSB RPD %	Alpha FB (High Load) mg/dscm	Alpha FB (Low Load) mg/dscm	Alpha Trip Blank (High Load) mg/dscm	Alpha Trip Blank (Low Load) mg/dscm
PM _{2.5} mass	3.0E-2	8.4E-2 ^a	5.7E-2	94.46	2.5E-2	2.5E-2	ND	ND

(b) Beta Sampler

	Beta DSB (High Load)	Beta DSB (Low Load)	Beta DSB (average)	Beta DSB (RPD)	Beta FB (High Load) mg/dscm	Beta FB (Low Load) mg/dscm	Beta Trip Blank (High Load) mg/dscm	Beta Trip Blank (Low Load) mg/dscm
PM _{2.5} mass (T1)	3.0E-2 ^a	1.9E-02	2.4E-2	48	6.8E-3	6.8E-3	ND	ND
PM _{2.5} mass (T2)	2.6E-2	1.5E-02	2.0E-2	53	8.5E-3	8.5E-3	ND	ND

RPD - relative percent difference (difference divided by mean)

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

Ions and Inorganic Secondary PM Precursors Analysis

The primary standard solutions were prepared with reagent grade salts, that were dried in an oven at 105 °C for one hour and then brought to room temperature in a desiccator. These

anhydrous salts were weighed to the nearest 0.10 mg on a routinely calibrated analytical balance under controlled temperature (approximately 20 °C) and RH (± 30 percent) conditions. These salts were diluted in precise volumes of DI water. Calibration standards were prepared at least once within each month by diluting the primary standard solution to concentrations covering the range of concentrations expected in the filter extracts and stored in a refrigerator. The calibration concentrations prepared were at 0.1, 0.2, 0.5, 1.0, and 2.0 μg per mL ($\mu\text{g}/\text{mL}$) for each of the analysis species. Calibration curves were performed weekly. Chemical compounds were identified by matching the retention time of each peak in the unknown sample with the retention times of peaks in the chromatograms of the standards. A DI water blank was analyzed after every 20 samples and a calibration standard was analyzed after every 10 samples. These quality control checks verified the baseline and calibration, respectively. Environmental Research Associates (ERA, Arvada, CO) standards were used daily as an independent QA check. These standards (ERA Wastewater Nutrient and ERA Mineral WW) were traceable to National Institute of Standards and Technology (NIST) simulated rainwater standards. If the values obtained for these standards did not coincide within a pre-specified uncertainty level (typically three standard deviations of the baseline level or ± 5 percent), the samples between that standard and the previous calibration standards were reanalyzed.

After analysis, the printout for each sample in the batch was reviewed for the following: 1) proper operational settings; 2) correct peak shapes and integration windows; 3) peak overlaps; 4) correct background subtraction; and 5) quality control sample comparisons. When values for replicates differed by more than ± 10 percent or values for standards differed by more than ± 5 percent, samples before and after these quality control checks are designated for reanalysis in a subsequent batch. Individual samples with unusual peak shapes, background subtractions, or deviations from standard operating parameters are also designated for reanalysis.

Table 6-2 lists the blanks and ambient sample concentrations for ions and the secondary PM gaseous precursors. Cl^- , NH_3 , and soluble Na were detected in the TB and FB indicating probably laboratory or reagent contamination for these substances. In most cases, levels of these substances are significant compared to the stack sample results. All target inorganics were detected in the DSBs except SO_2 . Cl^- , NO_3^- , NH_3 , and soluble Na were detected in the DSBs at levels greater than the respective 95 percent confidence lower bounds of the stack sample

average results for at least one case; therefore, stack sample results for these substances are probably biased high and should be used with caution.

Table 6-2. PM Ions and Inorganic Secondary PM Precursor Blank Results (Site Echo).

	Alpha DSB (High Load) mg/dscm	Alpha DSB (Low Load) mg/dscm	Alpha DSB (average) mg/dscm	Alpha DSB RPD %	Alpha FB (High Load) mg/dscm	Alpha FB (Low Load) mg/dscm	Alpha Trip Blank (High Load) mg/dscm	Alpha Trip Blank (Low Load) mg/dscm
Cl ⁻	8.8E-3 a	8.6E-3 a	8.7E-3	2	6.6E-3 b	6.7E-3 b	7.2E-3 c	7.3E-3 c
NO ₃ ⁻	ND	4.3E-3 d	4.3E-3	n/a	ND	ND e	ND	ND
SO ₄ ⁼	ND	9.4E-3	9.4E-3	n/a	ND	ND	ND	ND
NH ₄ ⁺	3.8E-3	7.3E-3	5.6E-3	62	ND	ND	ND	ND
NH ₃	4.5E+0 a	7.1E+0 a	5.8E+0	44	2.5E-3 b	2.5E-3	2.2E-3 c	2.2E-3
SO ₂	ND	ND	ND	n/a	ND	ND	ND	ND
Soluble Na	2.3E-3 a	3.1E-3 a	2.7E-3	29	1.1E-3	1.1E-3 b	7.9E-4	8.0E-4 c

	Beta DSB (High Load)	Beta DSB (Low Load)	Beta DSB (average)	Beta DSB RPD	Beta FB (High Load) mg/dscm	Beta FB (Low Load) mg/dscm	Beta Trip Blank (High Load) mg/dscm	Beta Trip Blank (Low Load) mg/dscm
Cl ⁻	ND	5.3E-3 a	5.3E-3	n/a	6.1E-3 b	7.6E-3 b	4.9E-3 c	6.1E-3 c
NO ₃ ⁻	3.0E-3 a	5.7E-3 a	4.4E-3 a	61	ND	ND	ND	ND
SO ₄ ⁼	2.7E-3	5.0E-3	3.9E-3	59	ND	ND	ND	ND
NH ₄ ⁺	ND	5.9E-3	5.9E-3	n/a	ND	ND	ND	ND
NH ₃	2.8E+0 a	7.8E+0 a	5.3E+0 a	94	1.5E-3	1.8E-3	1.5E-3	1.8E-3
Soluble Na	9.3E-4	2.3E-3 a	1.6E-3	86	ND	ND	5.4E-4	6.7E-4 c

RPD - relative percent difference (difference divided by mean)

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

d - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Elemental (XRF) Analysis

Three types of XRF standards were used for calibration, performance testing and auditing: 1) vacuum-deposited thin-film elements and compounds (supplied by Micromatter, Deer Harbor, WA); 2) polymer films; and 3) NIST thin-glass films. The vacuum deposit standards cover the largest number of elements and were used as calibration standards. The polymer film and NIST standards were used as quality control standards. Standards from the NIST are the definitive standard reference material, but are only available for the species Al, Ca, Co, Cu, Mn, and Si (Standard Reference Material (SRM) 1832) and Fe, Pb, K, Si, Ti, and Zn (SRM 1833). A separate Micromatter thin-film standard was used to calibrate the system for each element.

A quality control standard and a replicate from a previous batch were analyzed with each set of 14 samples. When a quality control value differed from specifications by more than ± 5 percent or when a replicate concentration differed from the original value (when values exceed 10 times the detection limits) by more than ± 10 percent, the samples were reanalyzed. If further tests of standards showed that the system calibration had changed by more than ± 2 percent, the instrument was recalibrated as described above. All XRF results were entered directly into the DRI databases.

Br, Ca, Fe, K, Mg, Na, S, Si and Zn were detected in all four of the DSB samples and Al, Cl, Cr and Ni were detected in at least one DSB sample (Table 6-3). In most cases, the detected concentrations are very close to the MDL. Where these also were detected in more than 2 stack samples, in almost all cases the concentrations are greater than the 95 percent confidence lower bound of the respective stack sample results. Ca, Fe, Mg, Na Si and Zn were found in the TBs and in most cases the FBs. Mg and Na are not reliably determined by XRF analysis due to interferences. The presence of Fe and Zn in the both TBs and FBs probably indicates trace laboratory and/or reagent contamination. In most cases where the above substances also were measured in at least two stack samples, they were found in the blanks at levels greater than the 95 percent confidence lower bound of the average stack sample results. Therefore, it is likely that stack sample results for these substances are positively biased and they should be used with caution.

OC and EC Analysis

The TOR system was calibrated by analyzing samples of known amounts of methane, carbon dioxide, and potassium hydrogen phthalate (KHP). The FID response was compared to a reference level of methane injected at the end of each sample analysis. Performance tests of the instrument calibration were conducted at the beginning and end of each day's operation. Intervening samples were reanalyzed when calibration changes of more than ± 10 percent were found.

Table 6-3. XRF Elemental Analysis Blank Results (Site Echo).

(a) Alpha Sampler

	Alpha DSB (High Load) mg/dscm	Alpha DSB (Low Load) mg/dscm	Alpha DSB (average) mg/dscm	Alpha DSB RPD %	Alpha FB (High Load) mg/dscm	Alpha FB (Low Load) mg/dscm	Alpha Trip Blank (High Load) mg/dscm	Alpha Trip Blank (Low Load) mg/dscm
Al	4.0E-4	ND	4.0E-4	n/a	ND	ND	ND	ND
Au	8.9E-5	ND	8.9E-5	n/a	ND	ND	ND	ND
Br	1.0E-4	1.5E-4	1.3E-4	37	ND	ND	ND	ND
Ca	2.4E-4	6.7E-4	4.5E-4	95	1.1E-4	1.1E-4	2.7E-4	2.7E-4
Cl	2.5E-4	9.4E-4	6.0E-4	116	ND	ND	1.8E-4	1.8E-4
Co	1.8E-5	ND	1.8E-5	n/a	ND	ND	8.8E-6	8.9E-6
Cr	1.0E-4	ND	1.0E-4	n/a	ND	ND	ND	ND
Cu	1.0E-3	3.0E-5	5.3E-4	188	ND	ND	ND	ND
Fe	6.5E-4	5.3E-4	5.9E-4	20	2.3E-4	2.3E-4	1.8E-4	1.8E-4
K	1.2E-4	5.2E-4	3.2E-4	124	4.6E-5	4.6E-5	1.5E-4	1.5E-4
Mg	ND	4.5E-4	4.5E-4	n/a	9.1E-4	9.2E-4	6.0E-4	6.0E-4
Mn	5.2E-5	ND	5.2E-5	n/a	ND	ND	ND	ND
Mo	8.7E-5	ND	8.7E-5	n/a	2.1E-5	2.1E-5	2.1E-5	2.1E-5
Na	4.0E-3	2.9E-3	3.4E-3	33	1.3E-3	1.3E-3	2.7E-3	2.7E-3
Ni	5.7E-5	2.1E-5	3.9E-5	94	ND	ND	ND	ND
P	ND	ND	n/a	n/a	1.0E-4	1.0E-4	6.8E-5	6.9E-5
Pb	5.6E-5	ND	5.6E-5	n/a	ND	ND	2.4E-5	2.4E-5
S	2.3E-3	5.6E-3	3.9E-3	83	5.5E-5	5.6E-5	ND	ND
Se	1.2E-5	ND	1.2E-5	n/a	ND	ND	ND	ND
Si	6.4E-4	1.0E-3	8.2E-4	44	1.4E-4	1.4E-4	3.5E-4	3.5E-4
Sr	9.8E-6	1.7E-5	1.3E-5	54	1.0E-5	1.0E-5	ND	ND
Ti	6.2E-5	ND	6.2E-5	n/a	ND	ND	6.7E-5	6.8E-5
V	4.0E-5	ND	4.0E-5	n/a	ND	ND	ND	ND
Zn	3.1E-4	8.9E-5	2.0E-4	112	4.2E-5	4.2E-5	7.9E-5	7.9E-5

(b) Beta Sampler

	Beta DSB (High Load)	Beta DSB (Low Load)	Beta DSB (average)	Beta DSB RPD	Beta FB (High Load) mg/dscm	Beta FB (Low Load) mg/dscm	Beta Trip Blank (High Load) mg/dscm	Beta Trip Blank (Low Load) mg/dscm
Ag	2.7E-4	ND	2.7E-4	n/a	ND	ND	ND	ND
Al	3.8E-3	2.0E-04	2.0E-3	180	1.4E-4	1.7E-4	ND	ND
Br	1.5E-4	1.3E-04	1.4E-4	17	ND	ND	ND	ND
Ca	4.0E-4	4.4E-04	4.2E-4	9	5.1E-5	6.3E-5	1.8E-4	2.3E-4
Cl	3.5E-4	2.5E-04	3.0E-4	32	7.1E-5	8.9E-5	1.2E-4	1.5E-4
Co	ND	ND	n/a	n/a	ND	ND	5.9E-6	7.4E-6
Cr	4.2E-5	ND	4.2E-5	n/a	ND	ND	ND	ND
Cu	1.5E-5	ND	1.5E-5	n/a	ND	ND	ND	ND
Fe	6.0E-4	2.2E-04	4.1E-4	91	2.0E-5	2.5E-5	1.2E-4	1.5E-4
K	1.1E-3	2.1E-04	6.6E-4	137	6.1E-5	7.6E-5	1.0E-4	1.3E-4
Mg	2.7E-4	3.1E-04	2.9E-4	13	5.0E-5	6.2E-5	4.0E-4	5.0E-4
Mn	9.1E-6	ND	9.1E-6	n/a	ND	ND	ND	ND
Mo	ND	ND	n/a	n/a	ND	ND	1.4E-5	1.8E-5
Na	3.1E-3	2.4E-03	2.8E-3	25	1.5E-3	1.8E-3	1.8E-3	2.3E-3
Ni	3.3E-5	6.6E-06	2.0E-5	133	ND	ND	ND	ND
P	4.2E-5	ND	4.2E-5	n/a	6.5E-5	8.1E-5	4.6E-5	5.7E-5
Pb	ND	ND	n/a	n/a	ND	ND	1.6E-5	2.0E-5
S	1.4E-3	2.8E-03	2.1E-3	71	3.2E-5	4.0E-5	ND	ND
Sb	9.7E-5	ND	9.7E-5	n/a	ND	ND	ND	ND
Si	1.2E-3	5.9E-04	9.1E-4	70	3.0E-5	3.7E-5	2.3E-4	2.9E-4
Sn	9.4E-5	ND	9.4E-5	n/a	ND	ND	ND	ND
Sr	8.8E-6	ND	8.8E-6	n/a	ND	ND	ND	ND
Ti	ND	ND	n/a	n/a	ND	ND	4.5E-5	5.7E-5
Zn	4.2E-5	4.4E-05	4.3E-5	6	ND	ND	5.3E-5	6.6E-5

RPD - relative percent difference (difference divided by mean)

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Known amounts of American Chemical Society (ACS) certified reagent-grade crystal sucrose and KHP were committed to TOR as a verification of the OC fractions. Fifteen different standards were used for each calibration. Widely accepted primary standards for EC and/or OC are still lacking. Results of the TOR analysis of each filter were entered into the DRI database.

EC was not detected in the TBs or FBs, but was detected in half of the DSBs at levels only slightly above the MDL (Table 6-4). OC was detected in all of the DSBs, FBs and TBs. The OC levels found in all of the DSBs and some of the FBs and TBs are greater than the 95 percent confidence lower bound of the average stack results; in fact, the average OC concentration found in the DSB samples is greater than the average OC concentration measured in all of the stack samples. The QFFs used for OC/EC analysis have the potential for positive OC bias due to adsorption of VOCs on the filter. A backup QFF sampled behind the TMF to indicate the potential magnitude of the bias caused by this artifact showed high concentrations of OC that are significant in all the samples. The average OC concentration measured in the backup QFFs is identical to the average OC measured in the field samples. Therefore, the OC results are highly uncertain and should be used with extreme caution.

Table 6-4. OC and EC Blank Results (Site Echo).
(a) Alpha Sampler

	Alpha DSB (High Load) mg/dscm	Alpha DSB (Low Load) mg/dscm	Alpha DSB (average) mg/dscm	Alpha DSB RPD %	Alpha FB (High Load) mg/dscm	Alpha FB (Low Load) mg/dscm	Alpha Trip Blank (High Load) mg/dscm	Alpha Trip Blank (Low Load) mg/dscm
OC*	1.7E-1 a	2.0E-1 a	1.8E-1	13	1.1E-1	1.1E-1	9.3E-2	9.4E-2
EC	ND e	1.1E-2 e	1.1E-2	n/a	ND e	ND e	ND e	ND e
Backup Filter OC**	1.7E-1 a	2.0E-1 a	1.9E-1	18	1.5E-1	1.5E-1 b	1.8E-1 c	1.8E-1 c

(b) Beta Sampler

	Beta DSB (High Load)	Beta DSB (Low Load)	Beta DSB (average)	Beta DSB (RPD)	Beta FB (High Load) mg/dscm	Beta FB (Low Load) mg/dscm	Beta Trip Blank (High Load) mg/dscm	Beta Trip Blank (Low Load) mg/dscm
OC*	1.1E-1 a	1.3E-01 a	1.2E-1	15	6.7E-2 b	8.3E-2 b	6.3E-2 c	7.8E-2
EC	1.1E-2 a	ND e	1.1E-2	n/a	ND	ND e	ND	ND e
Backup Filter OC**	9.9E-2 a	1.2E-01 a	1.1E-1	20	1.2E-1 b	1.5E-1 b	1.2E-1 c	1.5E-1 c

RPD - relative percent difference (difference divided by mean)

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

SVOC Analysis

Prior to sampling, the XAD-4™ resin was Soxhlet extracted with methanol, followed by dichloromethane, each for 24 hours. The cleaned resin was dried in a vacuum oven heated to 40 °C and stored in sealed glass containers in a clean freezer. The PUF plugs were Soxhlet extracted with acetone, followed by 10 percent diethyl ether in hexane. The TIGF filters were cleaned by sonification in dichloromethane for 30 minutes followed by another 30-minute sonification in methanol. Then they were dried, placed in aluminum foil, and labeled. Each batch of precleaned XAD-4™ resin and approximately 10 percent of the precleaned TIGF filters and PUF plugs were checked for purity by solvent extraction and GC/MS analysis of the extracts. The PUF plugs and XAD-4™ resins were assembled into glass cartridges (10 g of XAD between two PUF plugs), wrapped in hexane-rinsed aluminum foil and stored in a clean freezer prior to shipment to the field.

Prior to extraction, the following deuterated internal standards were added to each filter-sorbent pair:

naphthalene-d8	9.76	nanograms per microliter (ng/μl)
acenaphthene-d8	10.95	ng/μl (for acenaphthene and acenaphthylene)
biphenyl-d10	7.56	ng/μl
phenanthrene-d10	4.61	ng/μl
anthracene-d10	3.5	ng/μl
pyrene-d10	5.28	ng/μl (for fluoranthene and pyrene)
chrysene-d12	3.54	ng/μl (for benz[a]anthracene and chrysene)
benzo[e]pyrene-d12	4.20	ng/μl
benzo[a]pyrene-d12	4.68	ng/μl
benzo[k]fluoranthene-d12	2.0	ng/μl
benzo[g,h]perylene-d12	1.0	ng/μl (for indeno[1,2,3-cd]pyrene, dibenzo[ah+ac]anthracene, benzo[ghi]perylene and coronene)

Calibration curves for the GC/MS/MID quantification were made for the molecular ion peaks of the PAH and all other compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. NIST SRM 1647 (certified PAH), with the addition of deuterated internal standards and compounds not present in the SRM, was used to make calibration solutions. Three

concentration levels for each analyte were employed, and each calibration solution was injected twice. After the three-level calibration was completed, a standard solution was injected to perform calibration checks. If deviation from the true value exceeded 20 percent, the system was recalibrated. The MSD was tuned daily for mass sensitivity using perfluorotributylamine. In addition, one level calibration solution was run daily. If the difference between true and measured concentrations exceeded 20 percent, the system was recalibrated.

Twenty-nine SVOCs were detected in at least one of the blanks (Table 6-5). Of the 31 SVOCs detected in any stack or ambient air sample, 24 were also detected in at least one of the blanks. Those seven SVOCs that were detected in a stack sample or the ambient air sample but not detected in the blanks were detected in fewer than three test runs, and hence the results are not considered reliable. 2-methylbiphenyl was detected in all of the blanks at levels greater than the 95 percent confidence lower bound of the stack sample average. 1-methylnaphthalene, 1+2-ethylnaphthalene, C-trimethylnaphthalene, E-trimethylnaphthalene, F-trimethylnaphthalene, B-trimethylnaphthalene and 3-methylbiphenyl also were detected in at least one blank at levels greater than the 95 percent confidence lower bound of their respective average stack sample concentrations. None of the SVOCs detected in three or more runs has an average concentration greater than 5 times its respective concentration in the highest blank. Therefore, all the SVOC results should be considered unsuitable for quantitative analysis.

VOC Analysis

Calibration curves were performed weekly. VOC were identified by matching the response factors of each unknown sample with the response factors of the standards. Tenax cartridges spiked with a mixture of paraffinic (in the C₉-C₂₀ range) and aromatic (C₄, C₅, and C₆ benzenes) hydrocarbons were periodically analyzed by GC/FID to verify quantitative recovery from the cartridges. Three to five different concentrations of the hydrocarbon (HC) standard and one zero standard were injected, and the response factors obtained. If the percent difference of the response factor from the mean was more than 5 percent, the response factors were corrected before proceeding with the analysis.

Table 6-5. PUF/XAD Tunnel and Field Blank Results (Site Echo).

	Alpha DSB (High Load) mg/dscm	Alpha DSB (Low Load) mg/dscm	Alpha DSB (average) mg/dscm	Alpha DSB RPD %	Alpha FB (High Load) mg/dscm	Alpha FB (Low Load) mg/dscm	Alpha Trip Blank (High Load) mg/dscm	Alpha Trip Blank (Low Load) mg/dscm
2-methylnaphthalene	4.2E-4 e	ND e	4.2E-4	n/a	1.1E-4 e	1.1E-4 e	3.0E-4 e	3.0E-4 e
1-methylnaphthalene	4.3E-4 a	ND e	4.3E-4	n/a	1.1E-4 b	1.1E-4 e	2.5E-4 c	2.6E-4 e
1+2-ethylnaphthalene	3.7E-4 a	ND e	3.7E-4	n/a	2.7E-4 b	2.7E-4 e	5.1E-4 c	5.1E-4 e
1,3+1,6+1,7-dimethylnaphthalene	4.9E-4 e	ND e	4.9E-4	n/a	ND e	ND e	ND e	ND e
1,2-dimethylnaphthalene	ND e	1.3E-4 e	1.3E-4	n/a	ND e	ND e	ND e	ND e
2-Methylbiphenyl	2.0E-3 a	1.6E-3 a	1.8E-3	22	1.6E-3 b	1.6E-3 b	2.3E-3 c	2.3E-3 c
3-Methylbiphenyl	ND	8.8E-4 e	8.8E-4	n/a	1.2E-3 b	1.2E-3 e	1.8E-3 c	1.8E-3 e
4-Methylbiphenyl	9.0E-5 e	4.2E-5 e	4.9E-5	72	1.0E-4 e	1.0E-4 e	6.0E-4 c	6.1E-4 e
B-trimethylnaphthalene	ND	2.9E-5 a	2.9E-5	n/a	ND	ND	9.2E-6 c	9.3E-6 c
C-trimethylnaphthalene	3.3E-5 a	3.4E-5 e	3.3E-5	4	ND	ND e	ND	ND e
E-trimethylnaphthalene	5.0E-6 a	3.4E-5 a	1.9E-5	148	ND	ND	9.2E-6 c	9.3E-6 c
F-trimethylnaphthalene	1.8E-5 a	5.9E-6 e	1.2E-5	103	ND	ND e	3.4E-6 c	3.4E-6 e
2,3,5-I-trimethylnaphthalene	7.5E-5 a	3.8E-4 a	2.3E-4	133	ND	ND	ND	ND
2,4,5-trimethylnaphthalene	4.9E-5 e	ND e	4.9E-5	n/a	ND e	ND e	ND e	ND e
1,4,5-trimethylnaphthalene	ND e	ND e	n/a	n/a	2.8E-4 e	2.8E-4 e	ND e	ND e
A-methylphenanthrene	1.0E-4 e	ND e	1.0E-4	n/a	ND e	ND e	ND e	ND e
2-methylphenanthrene	2.1E-5 e	ND e	2.1E-5	n/a	ND e	ND e	ND e	ND e
B-methylphenanthrene	2.8E-4 e	2.7E-5 e	1.5E-4	165	ND e	ND e	ND e	ND e
C-methylphenanthrene	5.6E-5 e	ND e	5.6E-5	n/a	ND e	ND e	ND e	ND e
Anthrone	4.9E-5 a	2.3E-5 a	3.6E-5	74	2.5E-6 b	2.5E-6 b	ND	ND
D-dimethylphenanthrene	ND e	1.6E-4 e	1.6E-4	n/a	ND e	ND e	3.6E-4 e	3.6E-4 e
E-dimethylphenanthrene	ND e	1.8E-4 e	1.8E-4	n/a	ND e	ND e	ND e	ND e
Fluoranthene	ND e	5.2E-5 e	5.2E-5	n/a	ND e	ND e	ND e	ND e
Benzonaphthothiophene	ND e	ND e	n/a	n/a	5.9E-6 e	5.9E-6 e	ND e	ND e
Benz(a)anthracene	ND e	ND e	n/a	n/a	4.9E-5 e	4.9E-5 e	2.7E-5 e	2.7E-5 e
7-methylbenz(a)anthracene	ND e	ND e	n/a	n/a	ND e	ND e	1.5E-5 e	1.5E-5 e
Benzanthrone	ND e	ND e	n/a	n/a	ND e	ND e	2.4E-5 e	2.4E-5 e
7-methylbenzo(a)pyrene	ND e	ND e	n/a	n/a	ND e	ND e	5.4E-5 e	5.4E-5 e
Benzo(a)pyrene	ND e	ND e	n/a	n/a	ND e	ND e	5.8E-5 e	5.8E-5 e

RPD - relative percent difference (difference divided by mean)

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Two canister DSBs were collected from the Alpha sampler. Of the 129 VOCs detected in at least one of the stack samples or the ambient air sample, 128 of them were also detected in one or more of the DSBs (Table 6-6). Ninety compounds were detected in one or more of the DSBs at concentrations higher than the 95 percent confidence lower bound of their respective stack sample average. Only five VOCs were detected at concentrations greater than five times the highest DSB concentration; of these, only limonene was detected in three or more runs but the extremely high variability of the limonene results (RSD=171 percent) makes this result not significantly higher than the blanks and therefore highly uncertain. Overall, the extremely low concentrations of VOCs in the stack and ambient air samples were in almost every case not significantly greater than then DSB samples.

Table 6-6. Canister VOC Blank Results (Site Echo).

	Alpha DSB (High Load) mg/dscm		Alpha DSB (Low Load) mg/dscm		Alpha DSB (average) mg/dscm	Alpha DSB RPD %
Methane	4.4E+1	a	4.8E+1	a	4.6E+1	8
Carbon monoxide	1.1E+1	a	1.2E+1	a	1.1E+1	11
Carbon dioxide	2.6E+4		2.8E+4		2.7E+4	9
Ethane	1.4E-1	a	7.2E-1	a	4.3E-1	135
Ethene	2.5E-2	a	2.6E-2	a	2.5E-2	4
Acetylene	5.1E-2	a	3.5E-2	a	4.3E-2	37
1-butene	3.5E-3	a	2.5E-3	a	3.0E-3	34
Iso-butene	7.0E-3	a	6.7E-3	a	6.8E-3	4
Propene	8.7E-3	a	1.6E-2	a	1.2E-2	60
Propane	5.0E-2	a	3.3E-1	a	1.9E-1	148
1,3-butadiene	1.0E-3	a	4.6E-3	a	2.8E-3	126
n-butane	2.1E-2	a	2.6E-2	a	2.3E-2	20
Methanol	1.2E-1	a	7.4E-2	a	9.8E-2	50
t-2-butene	7.0E-4	a	ND	e	7.0E-4	n/a
c-2-butene	1.7E-3	a	ND	e	1.7E-3	n/a
3-methyl-1-butene	3.5E-4	a	ND	e	3.5E-4	n/a
Ethanol + ACN	ND	e	2.1E-3	e	2.1E-3	n/a
Acetonitrile	3.6E-2	e	ND	e	3.6E-2	n/a
Isopentane	3.9E-2	a	2.2E-2	a	3.1E-2	53
1-pentene	3.5E-4		7.4E-3	a	3.9E-3	182
2-methyl-1-butene	ND		7.0E-4	e	7.0E-4	n/a
n-pentane	3.3E-2	a	3.9E-3	a	1.8E-2	158
Isoprene	4.9E-3	a	ND		4.9E-3	n/a
t-2-pentene	1.0E-3	a	7.0E-4	e	8.7E-4	39
c-2-pentene	7.0E-4	e	3.5E-4	e	5.2E-4	66
2-methyl-2-butene	ND		1.1E-3	e	1.1E-3	n/a
2-methylpropanal	ND	e	3.5E-4	e	3.5E-4	n/a
Cyclopentene	3.5E-4	a	1.4E-3	e	8.7E-4	121
Cyclopentane	5.9E-3	a	3.9E-3	a	4.9E-3	42
2,3-dimethylbutane	2.1E-3	a	2.1E-3	a	2.1E-3	1
3-methylpentane	3.2E-2	a	2.8E-3	a	1.7E-2	167
2-methyl-1-pentene	ND	e	1.1E-3		1.1E-3	n/a
1-hexene	1.7E-3	a	1.4E-3		1.6E-3	21
n-hexane	2.4E-2	a	2.1E-3	a	1.3E-2	167
t-3-hexene + chloroform	3.5E-3	a	7.0E-4	e	2.1E-3	133
t-2-hexene	3.5E-4	e	3.5E-4	e	3.5E-4	1
2-methyl-2-pentene	3.5E-4	e	3.5E-4	e	3.5E-4	1
c-3-hexene	6.3E-3	a	4.6E-3	a	5.4E-3	31
c-2-hexene	1.6E-2	a	2.5E-3	a	9.4E-3	148
trans-3-methyl-2-pentene	ND		3.5E-4	a	3.5E-4	n/a
Methylcyclopentane	9.0E-3	a	2.5E-3	a	5.7E-3	115
2,4-dimethylpentane	4.9E-3	a	3.2E-3	a	4.0E-3	43
2,2,3-trimethylbutane	9.0E-3	a	9.5E-3	a	9.3E-3	5
Benzene	1.7E-2	a	9.5E-3	a	1.3E-2	55
3,3-dimethylpentane	1.4E-3	a	2.1E-3	a	1.7E-3	41
Cyclohexane	3.1E-3	a	2.1E-3	a	2.6E-3	39
4-methylhexene	3.5E-4	e	3.5E-4		3.5E-4	1
2-methylhexane	1.7E-2	a	2.1E-2	a	1.9E-2	19
2,3-dimethylpentane	5.2E-3	a	3.2E-3	e	4.2E-3	49
Cyclohexene	3.5E-3	a	2.1E-3	a	2.8E-3	49
1,3-dimethylcyclopentane	5.2E-3	a	3.5E-3	a	4.4E-3	39
3-ethylpentane	7.0E-4	a	7.0E-4	a	7.0E-4	1
2,2,4-trimethylpentane	3.1E-3	a	2.1E-3		2.6E-3	39
t-3-heptene	3.5E-4	a	3.5E-4	a	3.5E-4	1

RPD - relative percent difference (difference divided by mean)

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Table 6-6 (continued). Canister VOC Blank Results (Site Echo).

	Alpha DSB (High Load) mg/dscm		Alpha DSB (Low Load) mg/dscm		Alpha DSB (average) mg/dscm		Alpha DSB RPD %
n-heptane	2.1E-3	a	2.5E-3	a	2.3E-3		16
Methylcyclohexane	ND		1.4E-3	a	1.4E-3		n/a
2,5-dimethylhexane	1.2E-2	a	4.6E-3	e	8.2E-3		89
2,4-dimethylhexane	1.7E-3	a	7.0E-4	a	1.2E-3		85
2,3-trimethylpentane	2.1E-3		3.9E-3	a	3.0E-3		60
Toluene	1.8E-1	a	1.1E-1	a	1.5E-1		47
2,3-dimethylhexane	3.1E-3	a	3.2E-3	a	3.1E-3		1
2-methylheptane	ND		3.5E-4	e	3.5E-4		n/a
4-methylheptane	7.0E-4	a	7.0E-4	e	7.0E-4		1
3-methylheptane	1.7E-3	a	3.5E-4		1.0E-3		133
Hexanal	4.5E-3	a	4.2E-3	a	4.4E-3		7
2,2,5-trimethylhexane	2.8E-2	a	2.9E-2	a	2.8E-2		3
Octene-1	1.7E-3	a	7.0E-4	a	1.2E-3		85
1,1-dimethylcyclohexane	7.0E-4	a	ND	e	7.0E-4		n/a
n-octane	7.0E-4	a	1.8E-3	a	1.2E-3		86
2,3,5-trimethylhexane	3.8E-3	a	3.8E-2	a	2.1E-2		163
4,4-dimethylheptane	7.0E-4	e	2.8E-3	e	1.7E-3		121
2,6-dimethylheptane	7.0E-4	a	1.1E-3	a	8.7E-4		41
Chlorobenzene	1.7E-3	a	1.1E-3	a	1.4E-3		49
Ethylbenzene	6.3E-3	a	9.1E-3	a	7.7E-3		37
m- & p-xylene	1.6E-2	a	1.2E-2	a	1.4E-2		24
2-methyloctane	4.5E-3	a	2.5E-3	a	3.5E-3		59
3-methyloctane	2.0E-2	a	7.4E-3	a	1.4E-2		93
Styrene + heptanal	7.0E-4	a	3.5E-3	a	2.1E-3		134
o-xylene	4.9E-3	a	8.1E-3	a	6.5E-3		49
Nonene-1	7.0E-4	a	2.1E-3	a	1.4E-3		101
n-nonane	ND		3.5E-4	a	3.5E-4		n/a
Isopropylbenzene	1.0E-3	a	2.1E-3	a	1.6E-3		67
Isopropylcyclohexane	3.5E-4	a	7.0E-4	a	5.2E-4		67
Benzaldehyde	ND		7.0E-4	e	7.0E-4		n/a
alpha-pinene	5.7E-2	a	4.4E-2	a	5.0E-2		25
3,6-dimethyloctane	ND		7.0E-3	a	7.0E-3		n/a
n-propylbenzene	7.0E-4	a	7.0E-4	a	7.0E-4		1
m-ethyltoluene	1.4E-3	a	2.1E-3	a	1.7E-3		41
p-ethyltoluene	4.2E-3	a	7.0E-3	a	5.6E-3		51
1,3,5-trimethylbenzene	7.0E-4	e	2.8E-3	a	1.7E-3		121
o-ethyltoluene	3.8E-3	a	6.7E-3	a	5.2E-3		54
Octanal	7.0E-4	a	1.4E-3	e	1.0E-3		67
beta-pinene	8.0E-3	a	2.8E-2	a	1.8E-2		111
1,2,4-trimethylbenzene	1.0E-3		5.6E-3	a	3.3E-3		137
n-decane	1.7E-3	a	4.2E-3	e	3.0E-3		83
Isobutylbenzene	7.0E-4	a	2.8E-3	a	1.7E-3		121
sec-butylbenzene	ND	e	7.0E-4	e	7.0E-4		n/a
1,2,3-trimethylbenzene	1.1E-2	a	1.1E-1	a	6.0E-2		164
Limonene	3.8E-3	a	2.1E-3	a	3.0E-3		58
Indan	7.0E-4	e	1.4E-3	e	1.0E-3		67
Indene	ND	e	1.1E-3	a	1.1E-3		n/a
1,3-diethylbenzene	ND		7.0E-4	e	7.0E-4		n/a
1,4-diethylbenzene	2.4E-3		7.0E-3	a	4.7E-3		97
1,2-diethylbenzene	ND		1.8E-3	a	1.8E-3		n/a
Isopropyltoluene	5.6E-3	a	2.9E-2	e	1.7E-2		135
Nonanal	1.0E-3		1.1E-2	a	6.0E-3		165
n-undecane	7.0E-4	a	4.6E-3	e	2.6E-3		147
1,2,4,5-tetramethylbenzene	ND	e	1.4E-3	e	1.4E-3		n/a

RPD - relative percent difference (difference divided by mean)

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Table 6-6 (continued). Canister VOC Blank Results (Site Echo).

	Alpha DSB (High Load) mg/dscm		Alpha DSB (Low Load) mg/dscm		Alpha DSB (average) mg/dscm	Alpha DSB RPD %
1,2,3,5-tetramethylbenzene	ND	e	1.4E-3	e	1.4E-3	n/a
Naphthalene	ND	e	1.1E-3	e	1.1E-3	n/a
n-dodecane	ND	e	1.1E-3	e	1.1E-3	n/a
Total Identified NMHC	1.4E+0	a	1.8E+0	a	1.6E+0	25
F 12	5.1E-2		9.9E-2	a	7.5E-2	63
F 114	2.4E-3	a	2.5E-3	a	2.4E-3	1
Methyl bromide	1.4E-3	a	4.2E-3		2.8E-3	101
F 11	2.3E-2	a	1.2E-2	a	1.8E-2	65
Methylene chloride	8.4E-2	a	1.7E-2	a	5.1E-2	132
F 113	1.1E-2	a	5.3E-3	a	8.0E-3	69
trans-1,2-dichloroethylene	6.0E-2	a	1.1E-1	a	8.5E-2	58
Chloroform	3.5E-3	a	3.5E-3	a	3.5E-3	1
1,2-dichloroethane	1.1E-2	a	1.6E-2	a	1.3E-2	35
Methyl chloroform	3.5E-3	a	1.8E-3	a	2.6E-3	66
Carbon tetrachloride	6.6E-3	a	4.6E-3	a	5.6E-3	37
1,1,2-trichloroethane	ND	e	1.8E-3	a	1.8E-3	n/a
Perchloroethylene	2.4E-3	a	ND	e	2.4E-3	n/a
p-dichlorobenzene	2.1E-3	a	2.1E-3	a	2.1E-3	1

RPD - relative percent difference (difference divided by mean)

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Carbonyls Analysis

Two DSBs, one FB and one TB were collected for the DNPH coated silica gel cartridges used to collect carbonyls. No carbonyls were detected in the TB. Acetaldehyde, acetone and methylethylketone (MEK) were detected in the FBs (Table 6-7). The concentrations of formaldehyde, acetaldehyde and acetone in the blanks are greater than the 95 percent confidence lower bound of their respective average stack sample results (detected in 3 or more runs). Comparing the DSB results to the ambient air result, the apparent removal efficiency of the dilution air purification system is less than 100 percent (see Section 4 for discussion), indicating that most of the carbonyl sample results are probably biased due to carbonyls entering with the dilution air.

Another measure of method performance is breakthrough between the first and second sample cartridges. When greater than 20 percent of the total amount measured in the sample is contained in the second cartridge, breakthrough typically becomes a concern since it indicates the possibility that some of the substance may have penetrated the second cartridge. Most of the stack sample carbonyl results showed significant breakthrough potential (Tables 6-8 and 6-9). In

Table 6-7. Carbonyl Blank Results (Site Echo).

	Alpha DSB (High Load) mg/dscm	Alpha DSB (Low Load) mg/dscm	Alpha DSB (average) mg/dscm	Alpha DSB RPD %	Alpha FB (High Load) mg/dscm	Alpha FB (Low Load) mg/dscm	Alpha Trip Blank (High Load) mg/dscm	Alpha Trip Blank (Low Load) mg/dscm
Formaldehyde	ND	8.8E-2 a	8.8E-2	n/a	ND	ND	ND	ND
Acetaldehyde	ND	1.7E-1 a	1.7E-1	n/a	8.3E-2 b	8.0E-2 b	ND	ND
Acetone	2.6E-1 a	3.2E-1 a	2.9E-1	23	1.7E-1 b	1.6E-1 b	ND	ND
MEK	ND e	ND e	n/a	n/a	1.3E-1 e	1.2E-1 e	ND e	ND e
Glyoxal	ND	6.8E-3 e	6.8E-3	n/a	ND	ND e	ND	ND e
Hexanaldehyde	6.9E-3 e	ND e	6.9E-3	n/a	ND e	ND e	ND e	ND e

RPD - relative percent difference (difference divided by mean)

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.

e - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration (i.e. zero or one valid run).

Table 6-8. Carbonyl Breakthrough – High Load (Site Echo)

	Percent of Total													
	Run 1		Run 2		Run 3		Run 4		DSB		FB		Ambient	
	Front	Back	Front	Back	Front	Back	Front	Back	Front	Back	Front	Back	Front	Back
Formaldehyde	ND	ND	ND	ND	52	48	41	59	ND	ND	ND	ND	100	ND
Acetaldehyde	ND	ND	ND	100	ND	100	43	57	ND	ND	49	51	89	11
Acetone	100	ND	ND	ND	95	5	88	12	100	ND	51	49	100	ND
Acrolein	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Propionaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100	ND
Crotonaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MEK	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	52	48	ND	ND
Methacrolein	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Butyraldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100	ND
Benzaldehyde	ND	ND	ND	ND	ND	100	ND	ND	ND	ND	ND	ND	ND	ND
Glyoxal	ND	ND	ND	ND	100	ND	ND	100	ND	ND	ND	ND	100	ND
Valeraldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100	ND
M-Tolualdehyde	ND	ND	ND	ND	100	ND	ND	100	ND	ND	ND	ND	ND	ND
Hexanaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	100	ND	ND	64	36

ND = not detected.

Table 6-9. Carbonyl Breakthrough – Low Load (Site Echo).

	Percent of Total													
	Run 1		Run 2		Run 3		DSB		FB		Ambient			
	Front	Back	Front	Back	Front	Back	Front	Back	Front	Back	Front	Back		
Formaldehyde	100	ND	100	ND	100	ND	75	25	ND	ND	100	ND		
Acetaldehyde	ND	100	100	ND	ND	100	40	60	49	51	89	11		
Acetone	100	ND	100	ND	100	ND	78	22	51	49	100	ND		
Acrolein	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Propionaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100	ND		
Crotonaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
MEK	ND	ND	ND	ND	ND	ND	ND	ND	52	48	ND	ND		
Methacrolein	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Butyraldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100	ND		
Benzaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Glyoxal	ND	ND	ND	ND	ND	ND	40	60	ND	ND	100	ND		
Valeraldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100	ND		
M-Tolualdehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Hexanaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	64	36		

ND = not detected.

the ambient air sample, the back cartridge is significant only for hexanaldehyde. Breakthrough appears to be more of a problem with the stack samples than with the ambient samples, indicating a potential interference from other substances present in the stack sample. Because results for formaldehyde, acetaldehyde and acetone may be biased by background levels, the breakthrough results are probably meaningless for these carbonyls.

Overall, the data quality for carbonyl measurements is poor. A number of method performance indicators suggest that the method may not be appropriate for such low concentrations as found in these samples. Further investigation is needed to determine if these limitations can be overcome or whether the method is inherently limited.

7. DISCUSSION AND FINDINGS

COMPARISON OF ALPHA AND BETA DILUTION SAMPLERS

PM_{2.5} mass and species results were obtained with two different dilution sampler designs. The Alpha sampler is based on the Hildemann et al. design (1989) and has been used extensively by researchers for more than a decade in stationary source applications. The unique feature of this design is an aging chamber designed to provide substantial residence time after dilution for condensation and growth of low concentration organic aerosols. Hildemann's original work characterized the performance of this design extensively, including the effects of dilution ratio and particle losses throughout the system as a function of particle size. Therefore, this design is considered the current benchmark for stationary source dilution sampler performance.

While the Hildemann design is well known and has been successfully applied to a wide range of source types, it is not considered widely applicable for routine source tests due to its large size and weight. In a separate task of this program, experiments were conducted to assess the effects of two important design parameters affecting size and weight that were not previously well characterized: particle concentration and residence time after dilution (Chang et al., 2004). The experiments also revisited the effects of dilution ratio as a function of particle concentration. The experiments indicated that results comparable to the Hildemann design should be achievable with shorter residence times and lower dilution ratio. Also, a recent study showed that the mixing rate between dilution air and the sample was not a first order effect so faster mixing rates than used in the original Hildemann design were considered acceptable (Lyyräinen et al, 2004). Based on these results, a new, more compact and lightweight dilution sampler design was constructed (the Beta sampler). PM_{2.5} mass measurements made using both Alpha and Beta samplers in a pilot-scale furnace showed generally good agreement between the systems at moderate to high particle concentrations (Chang and England, 2004).

The key differences of the Beta sampler compared to the original Hildemann design are:

- Shorter aging section residence time (10 seconds versus 80 seconds);
- More rapid mixing between the sample and dilution air (within one diameter versus 15 diameters);

- Lower diluted sample volumetric flow rate (113 L/min versus 336 L/min);
- Sample path (linear path versus convoluted path).

This test represents the first field comparison between the Alpha and Beta samplers on a gas-fired combustion source. Tests were conducted simultaneously with both samplers, at different sampling locations in the stack but after establishing the absence of significant stratification of gas concentrations in the stack.

The Beta sampler results on average are 27 percent low compared to the Alpha sampler. To assess whether this apparent bias is significant, statistical tests drawn from EPA Method 301 “Field Validation of Pollutant Measurement Methods from Various Waste Media (U.S. EPA, 1992) were applied. Note, the number of test runs performed in these tests (seven) is smaller than required by Method 301 (twelve), so the statistical test results are viewed as a preliminary indication rather than conclusive validation. Method 301 specifies statistical tests at the 95 percent confidence level to determine the equivalency of an alternative method (in this case, the Beta sampler) in comparison to an existing reference method (in this case, the Alpha sampler) when the methods are run simultaneously (as they were in these tests). Method 301 first applies the statistical F-test to determine whether the variances (precision) of the two sets of results are the same, and then applies the statistical paired sample t-test to determine if the bias is significant. According to Method 301, if the bias is not significant according to the paired sample t-test at the 95 percent confidence level, no bias correction factor needs to be applied to the alternative method results. If the bias is significant, a bias correction factor of up to 20 percent must be applied to the alternative method results. If the bias is significant and exceeds 20 percent, the alternative method is rejected. Method 301 does not specifically address situations where the apparent bias is greater than 20 percent but not significant at the 95 percent confidence level, but the implication is that this is irrelevant.

A statistical paired sample t-test using PM_{2.5} mass results from all seven test runs shows the differences between the Alpha and Beta sampler results are not significant at the 95 percent

confidence level (i.e., H_0^3 falls within the 95 percent confidence interval of the mean of the differences, Figure 7-1). Only the Beta sampler T1 results are included in the comparison, since the T2 filter sample flow is considered unreliable (see Section 4). The apparent bias between the two samplers is far smaller for low load than for high load. As noted in Section 4, it is likely that the Alpha sampler results for the first three high load runs are positively biased due to wind interference in the dilution bypass flow measurement. Excluding the first three high load runs and reapplying the paired sample t-test again shows that the differences are not significant at this confidence level (Figure 7-2).

Thus, although the number of tests is smaller than ideal, the preliminary indication from these tests is that the PM_{2.5} mass results produced by the Beta sampler can be considered equivalent to those from the Alpha sampler, without a correction for bias. Note, the statistical test results tend to be influenced by a small number of extreme data points; however, no data were excluded as outliers due to the small number of tests. A similar statistical analysis of SO_4^- results, which are relatively robust, shows a similar degree of bias that is significant at the 95 percent confidence level. Results for most other speciated measurements also show similar indications. The fact that the results for many different species show a bias of similar magnitude suggests that a systematic instrument error affecting all the measurements, e.g. an error in sample flow rate or measurements contributing to dilution air flow rate, may be the source of this bias rather than the design differences between the samplers themselves. Subsequent to these tests, some small discrepancies in calibration of the sample venturis and bypass fan orifice were identified and resolved, but it is not certain whether the changes in calibration occurred before or after the test. In addition, the flow rate through the bypass fans was at the extreme low end of the calibrated range, which could introduce an additional source of systematic error in the calculated dilution air flow rate. These tests indicated the need for direct measurement of dilution air flow rate to improve accuracy. Further resolution of these issues was not possible during these tests. Further tests, with more careful attention to comparability of instrument accuracy and calibration, are needed to completely validate these findings.

³ H_0 is the null hypothesis, a statistical term, which is a "baseline condition" that is presumed to be true in the absence of strong evidence to the contrary, e.g., in statistical t-test the null hypothesis is that the means of two data sets are the same within a specified interval of confidence. Refer to a good statistical analysis textbook or other reference (e.g., U.S. EPA, 2000) for further information.

(with Ho and 95% t-confidence interval for the mean)

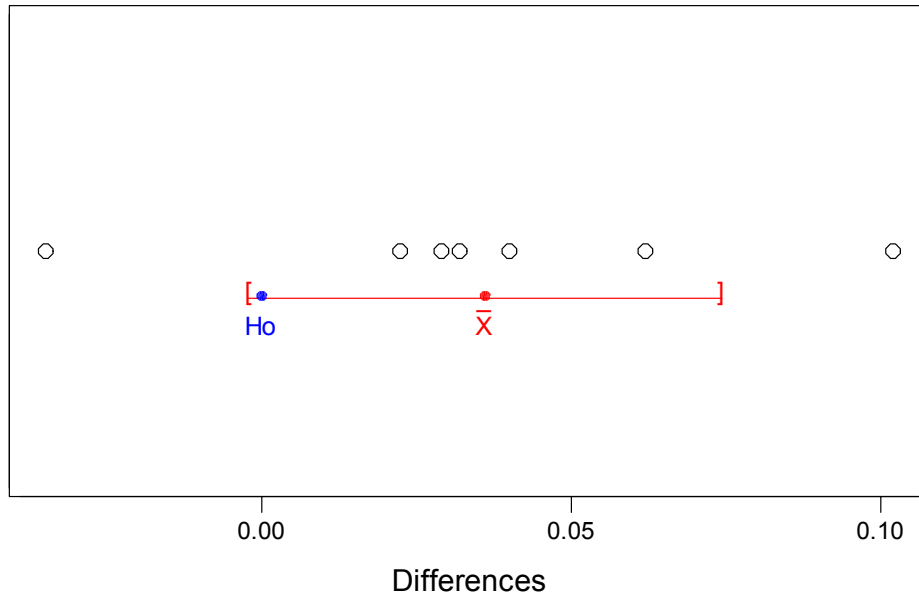


Figure 7-1. Differences between Raw Alpha and Beta Sampler PM2.5 Mass Results, All Runs (Site Echo)

(with Ho and 95% t-confidence interval for the mean)

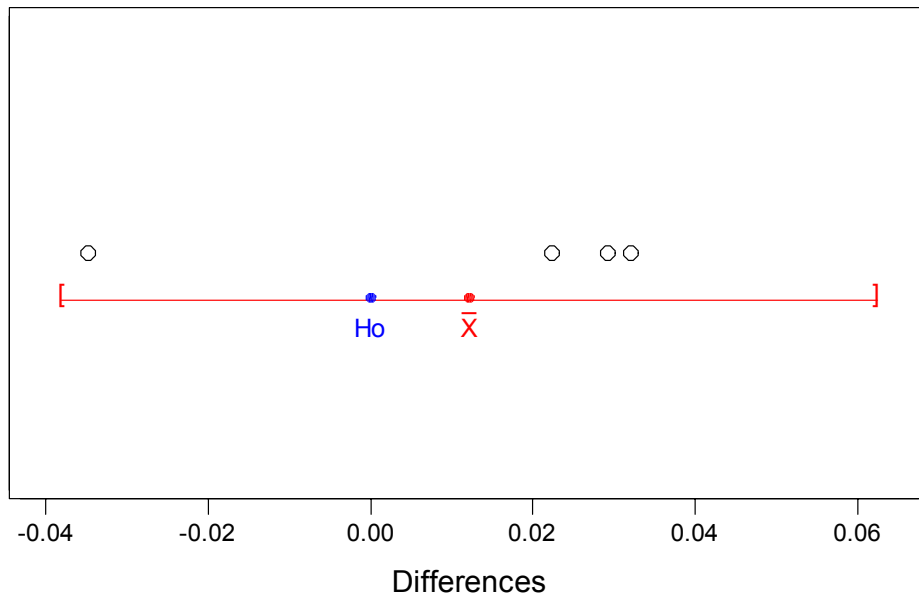


Figure 7-2. Differences Between Alpha and Beta Sampler PM2.5 Mass Results Excluding High Load Runs 1, 2 and 3 (Site Echo).

DILUTION METHOD PERFORMANCE

Accuracy

The accuracy of the dilution sampling method has been generally established based on the work of Hildemann et al. (1989), as discussed above. Based on the Hildemann particle loss experiments (the equivalent of analyte spiking), the most conservative PM_{2.5} mass accuracy using only the TMF results (ignoring sampling losses upstream of the TMF) can be expected to be in the range of approximately ± 10 to ± 20 percent (i.e., losses of 1.3 and 2.4 μm particles upstream of the filter were 7 and 21 percent, respectively). Hildemann's experiments and theoretical analysis show that losses decrease with decreasing particle size, so the average accuracy for a distribution of particle sizes below 2.5 μm is expected to be closer to the ± 10 percent range. Sampling bias in the PM_{2.5} mass concentration measurement is approximately five percent, based on typical performance criteria for the equipment used (reported accuracy of flow meters, temperature sensors, pressure transducers, etc.).

Hildemann's experiments showed that most of the losses occurred in the sample line and venturi, with very little loss (3 percent or less) occurring in the mixing and aging sections. Therefore, recovery of deposits from the sample line and venturi after sampling can significantly improve the overall accuracy. In this test, the sample nozzle, probe and transfer line and venturi deposits were recovered by rinsing with acetone and analyzed following procedures similar to EPA Method 5. The results, however, are dominated by background levels in the acetone indicating the acetone rinse procedure has insufficient sensitivity for this application. Probe/venturi recovery procedures need to be improved or revised to obtain sufficient sensitivity for quantitative analysis for gas combustion sources.

Comparing the Beta PM_{2.5} mass results to the Alpha results obtained in this project provides an indication of relative accuracy of two designs similar in concept (i.e., dilution plus aging) but with different design specifications. Using all the data from the Alpha and Beta samplers, the Beta sampler results appears to be biased by 62 percent compared to the Alpha sampler. However, it was noted earlier that Alpha sampler high load Runs 1, 2 and 3 are probably biased high due to wind interference with one of the key flow measurements during the test. Excluding these runs, the bias is approximately 19 percent, which is probably more representative of the

true accuracy. The t-test results for both sets of data show the bias is not significant at the 95 percent confidence level in either case.

Another estimate of accuracy was provided in the Beta sampler by attaching two TMFs in parallel to the sampling manifold. There is some question regarding the accuracy of the second filter (T2) results because a different type of flow meter was used (rotameter versus thermal mass flow meter) and the flow meter pressure was estimated from field notes rather than from periodic readings recorded on the field data sheets. Following the same statistical procedure to compare the two mass measurements shows that differences are not significant at the 95 percent confidence level. This comparison probably is not representative of the true accuracy, since the T2 results contain a comparatively large sampling uncertainty due to the type of flow meter that was used.

Finally, it should be noted that PM_{2.5} in the dilution air (based on DSB results) appears to contribute significantly to the measured stack PM_{2.5}. Further analysis of the results in the context of ambient air PM_{2.5} results from a nearby ambient monitoring station indicates that stack PM_{2.5} was strongly biased by penetration of ambient PM_{2.5} through the dilution air filters in these tests. The reader is referred to a separate report for further discussion of these results (England, 2004).

Precision

Precision can be assessed by calculating RSDs for the Alpha and Beta sampler results, and by comparing the homogeneity of variances using the statistical F-test. From Table 4-5, the RSD of the PM_{2.5} mass concentration results including all runs is 41 percent. Excluding high load Runs 1, 2 and 3, the RSD is 27 percent, which is probably more representative of the true measurement precision for the same reasons given above. Applying the F-test to all results shows the variances of the Alpha and Beta sampler results are not significantly different at the 95 percent confidence level (P-Value not less than 0.05, Figure 7-3). Excluding high load runs 1, 2 and 3 yields the same result (Figure 7-4). This implies similar measurement precision for the two different samplers.

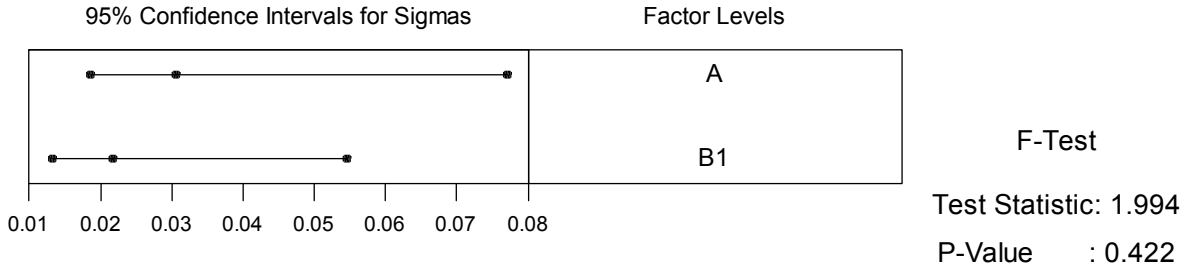


Figure 7-3. Homogeneity of Variances for Alpha (A) and Beta (B1) Sampler Results – All Runs (Site Echo).

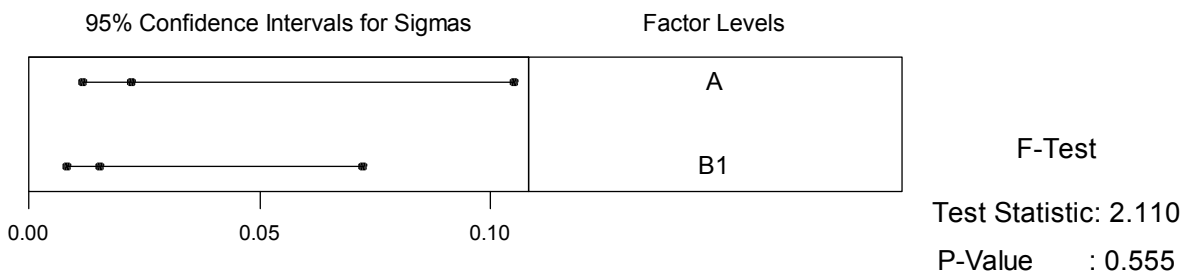


Figure 7-4. Homogeneity of Variances for Alpha (A) and Beta (B1) Sampler Results – Excluding High Load Runs 1, 2 and 3 (Site Echo).

Fuel S and SO₄⁼ Measurements

Because S is a relatively easily measured substance in all the samples, it can be used to assess the integrity of the measurements by calculating a S mass balance. S should be conserved in both the process and the measurement system, i.e.,

$$S_{\text{fuel}} [\text{MMBtu/hr}] = S_{\text{SO}_2} [\text{MMBtu/hr}]/2 + S_{\text{SO}_4} [\text{MMBtu/hr}]/3$$

Where S_{fuel} is the fuel total S content (as elemental S equivalent), S_{SO_2} is the measured stack gas SO₂ concentration and S_{SO_4} is the measured stack gas particulate SO₄⁼ content. A factor of 1/2 is applied to S_{SO_2} and 1/3 to S_{SO_4} to account for differences in molecular weight when comparing to fuel S. As expected, the majority—92 percent—of the S found in the stack is accounted for by gaseous SO₂ (Table 7-1). The stack S species measurements total approximately half of the calculated fuel input. This is in part because of the very low concentrations of S in both the fuel and the stack. Previous tests showed better agreement between fuel and stack measurements. The difference could not be traced to a specific problem in either the fuel or the stack S

measurements. The fuel measurements seem reasonable in comparison to typical heating value and S contents for natural gas, although fuel samples were not gathered concurrently with the stack samples and natural gas S content can vary significantly. This probably indicates a low bias in the stack SO₂ measurement.

Table 7-1. Comparison of S in Fuel to S Species in Stack (Site Echo).

Components	Units	Average High Load	Average Low Load	Average All
$S_{in} = S_{fuel}$	lb/MMBtu	4.1E-04		4.1E-04
$S_{SO_2}/2$	lb/MMBtu	1.9E-04	1.9E-04	1.9E-04
$S_{SO_4}/3$	lb/MMBtu	1.9E-05	1.2E-05	1.6E-05
$S_{out} = S_{SO_2}/2 + S_{SO_4}/3$	lb/MMBtu	2.0E-04	2.0E-04	2.0E-04
$100*(S_{out} - S_{in})/S_{in}$	%	-50	-52	-51

Particulate Carbon Measurements

OC is the largest component of the PM_{2.5} measured by the dilution sampler. There is currently heightened interest in particulate carbon from combustion sources due to PM₁₀ and PM_{2.5} NAAQS, the new Regional Haze rule and existing Visibility rules. Some states already have initiated development of PM_{2.5} State Implementation Plans in preparation for implementation of the 1997 PM_{2.5} NAAQS, and particulate carbon has been identified as having potential for adverse human health impacts. The National Park Service (NPS) is required to evaluate the visibility impact of new plants within 100 kilometers (km) of Class 1 Areas (national parks and wilderness areas). Primary EC and OC, SO₄⁻ and NO₃⁻ aerosols, and coarse (PM_{10-2.5}) and fine (PM_{2.5}) emissions are key factors in the visibility evaluation. Thus, reliable emission factors for particulate carbon emissions will be beneficial in conducting studies such as these.

QFFs were used to collect PM that was then analyzed for OC and EC by TOR using the IMPROVE protocol. Previous studies have shown that OC measurements on QFFs are susceptible to an artifact: adsorption of VOCs onto the filter media and collected PM, and devolatilization of organic PM, with the adsorptive artifact dominating and causing a positive bias (Mazurek et al., 1993). In this test, a QFF was placed downstream of a TMF during sample collection and subsequently analyzed for OC and EC to determine the extent of the VOC artifact (Turpin, 1994). The OC collected on this filter may be used to evaluate the potential significance of the VOC artifact relative to the OC collected on the front-loaded (primary) QFF. This is

commonly referred to as “backup OC”. In some cases, this approach may overestimate the extent of the VOC artifact because the adsorptive capacity of the filter media itself and the collected particles can affect the amount of VOC adsorbed on the filter (Kirchstetter, 2001). Attempts to eliminate the artifact, e.g. by addition of a denuder upstream of the QFF to remove VOC before the filter, may result in negative bias because some of the particulate OC is devolatilized as a result (Eatough et al., 1996; Cui et al., 1998). Therefore, it is current convention not to correct OC measurements for the backup filter/artifact results, but rather to present both sets of results and discuss the potential impact of the VOC artifact on the measured OC results.

Table 7-2 presents the data from the backup and primary QFFs used in this test. The corrected OC concentration—i.e., the OC mass measured on the backup QFF subtracted from the OC mass measured on the primary QFF—also is presented to illustrate the potential significance of the VOC artifact. For this test, the backup OC ranges from 59 to 136 percent and averages 99 percent of the primary OC stack results (97 percent of the average stack results). These results are qualitatively similar to the independent results of Hildemann et al. (1991), who determined speciated PM emissions from natural gas-fired home appliances using methods identical to those used in this program. Hildemann found that OC accounted for 84.9 percent of PM mass and that the backup OC accounts for 73 percent of the measured OC emissions, on average. Hildemann’s data are incorporated into EPA’s SPECIATE database, and are currently the only PM speciation data widely available for gas combustion. Thus, Hildemann’s results provide validation of the OC results measured in this study, and reinforce the need for caution when using the OC results.

Table 7-2. OC and Backup Filter OC Results for Site Echo (mg/dscm).

	Units	Run 1	Run 2	Run 3	Run 4	Stack Average	DSB	FB	Trip Blank	Ambient
OC	mg/dscm	2.2E-1	1.6E-1	1.6E-1	2.0E-1	1.8E-1	1.7E-1	1.1E-1	9.3E-2	1.1E-2
Backup OC	mg/dscm	1.7E-1	1.5E-1	1.7E-1	1.8E-1	1.7E-1	1.7E-1	1.5E-1	1.8E-1	7.0E-3
OC	mg/dscm	1.4E-1	1.0E-1	9.3E-2	5.3E-2	9.7E-2	1.1E-1	6.7E-2	--	--
Backup OC	mg/dscm	8.3E-2	8.9E-2	8.7E-2	7.2E-2	8.3E-2	9.9E-2	1.2E-1	--	--
OC	mg/dscm	1.4E-1	1.6E-1	1.3E-1	--	1.4E-1	2.0E-1	1.1E-1	--	--
Backup OC	mg/dscm	1.3E-1	1.5E-1	1.4E-1	--	1.4E-1	2.0E-1	1.5E-1	--	--
OC	mg/dscm	9.2E-2	1.0E-1	1.2E-1	--	1.0E-1	1.3E-01	8.3E-2	--	--
Backup OC	mg/dscm	1.2E-1	1.1E-1	1.3E-1	--	1.2E-1	1.2E-01	1.5E-1	--	--
Averages:										
OC	mg/dscm	1.5E-1	1.3E-1	1.2E-1	1.3E-1	1.3E-1	1.5E-1	9.2E-2	9.3E-2	1.1E-2
Backup OC	mg/dscm	1.2E-1	1.3E-1	1.3E-1	1.3E-1	1.3E-1	1.5E-1	1.4E-1	1.8E-1	7.0E-3
OC (corrected for Backup OC)	mg/dscm	2.4E-2	5.2E-3	-8.6E-3	-1.5E-3	4.2E-3	5.5E-3	-5.1E-2	-8.3E-2	3.8E-3
Backup OC/OC	%	84	96	107	101	97	96	156	189	64

Dilution Sampler Equipment and Method Improvements

During the course of these tests, a number of observations were made that suggest potential areas for improvements to the test procedures and or equipment in future tests to improve test accuracy and precision.

- Direct Measurement of Dilution Air Flow Rate. In the current equipment arrangement for both the Alpha and Beta samplers, dilution air flow, and hence dilution ratio, is measured indirectly by difference, measuring the diluted sample bypass flow and the sample media flow rates, then subtracting the undiluted sample flow rate from the sum. During these tests, high winds interfered with the measurement of the diluted sample bypass flow in the Alpha sampler (measured across an orifice at the exit of the HiVol bypass fan), resulting in a probable positive bias in measured concentrations for some of the test runs. A makeshift solution to eliminate the wind interference was identified. A direct measurement of dilution air flow rate using a venturi or flow orifice is recommended provide improved accuracy of dilution ratio under adverse conditions.
- Blanks/Contamination. The majority of elements and organic compounds were detected at levels comparable to the ambient air or background levels in the dilution system, and/or were near the minimum detection limits of the test methods. This indicates that the levels measured in the stack samples of these substances are not distinguishable from the ambient air or measurement background levels⁴. These findings strongly indicate the need for further development and validation of the dilution apparatus and method for measuring the extremely low concentrations of such substances that may be present in the stack emissions from combustion sources. It is recommended that future tests include at least one DSB for all measured substances and one DSB for each PM_{2.5} mass measurement to establish measurement background concentrations in the dilution air. These results could potentially be used to correct stack gas PM_{2.5} results for systematic bias due to background levels. In addition, the removal efficiency of the dilution air purification system (HEPA and activated carbon filters) should be determined by collecting an ambient air sample simultaneously with at least one DSB. Ambient air measurements also can provide data useful for evaluating the origin of substances detected in the stack gas. Improvements to the dilution air purification system to reduce background levels, larger sample volumes (longer run times), and/or the use of pure compressed or liquefied gases in place of purified ambient air for dilution (e.g., Battelle, 1994), should be explored for measuring organic compounds and elements from gas-fired sources. FBs and TBs for each measured substance also should be included as routine QA checks of the sample media and sample handling.

⁴ Note that this method was previously used to measure such pollutants at Site Bravo. At Site Bravo, a dilution sampler blank was not collected and analyzed; however, the measured stack concentrations of these substances at Site Echo and Site Bravo are similar. Further, many of the substances measured in the stack at site Bravo are indistinguishable from the ambient and field blanks collected at the site. Therefore, the levels measured in the stack samples at site Bravo for elemental and organic compounds may also be due to measurement background.

- Precision and Accuracy. The results of this test are very encouraging with regard to method precision and accuracy. After addressing the interference and contamination issues, further evaluation is recommended for a more rigorous assessment of precision and accuracy. The statistical tests (paired sample t-test and F-test) used in analyzing these test results are conventionally used evaluating method performance, however a larger number of valid samples is recommended. Typically, 9 to 12 simultaneous paired samples under a single operating condition are considered sufficient for establishing method performance. This was not feasible in the present test program due to the long run times (6 hours) needed for speciated measurements. However, a future test program could consider shorter runs for PM_{2.5} mass only. Paired sampling trains could include two Beta-type samplers with analyte spiking for evaluating bias, or one Beta sampler and one Alpha sampler using the Alpha sampler as the validated test method reference.

This test showed measurement background levels in the dilution air are significant for many substances relative to their respective concentrations in the stack gas samples. The results from this and previous tests suggest that variations in emissions due to source type or process operating conditions appear to be within the uncertainty of the measurements. Therefore, it is recommended that the above issues be addressed before undertaking further efforts to characterize the effects of process design and operation from other gas-fired combustion sources.

PROCESS OPERATION – PARAMETRIC EFFECTS

During these tests, four test runs were conducted at high load (without supplementary firing) and at low load (without supplementary firing). Including all test runs, the average PM_{2.5} emission factor is lower at low load than at high load; however, if high load Runs 1, 2 and 3 are excluded for reasons discussed previously, the apparent difference is much smaller. For both sets of data (including and excluding high load Runs 1, 2 and 3), the differences are not significant at the 95 percent confidence level based on a 2-sample t-test (Figure 7-5). Therefore, load has no significant effect on PM_{2.5} mass emission factors based on these results.

COMPARISON TO OTHER STUDIES

PM_{2.5} Emission Factors

Table 7-3 compares results of dilution sampler measurements for gas-fired process heaters, boilers steam generators, NGCC-SFs and natural gas-fired home appliances (Hildemann et al., 1991, API, 2001a; 2001b; 2001c; Wien et al., 2003; Wien et al., 2004a, 2004b, 2004c). Results from hot filter/iced impinger methods also are shown to demonstrate the correspondence in

results using these methods among the different tests and the striking difference between these and the dilution sampler results. The average Echo PM_{2.5} emission factor derived from the dilution

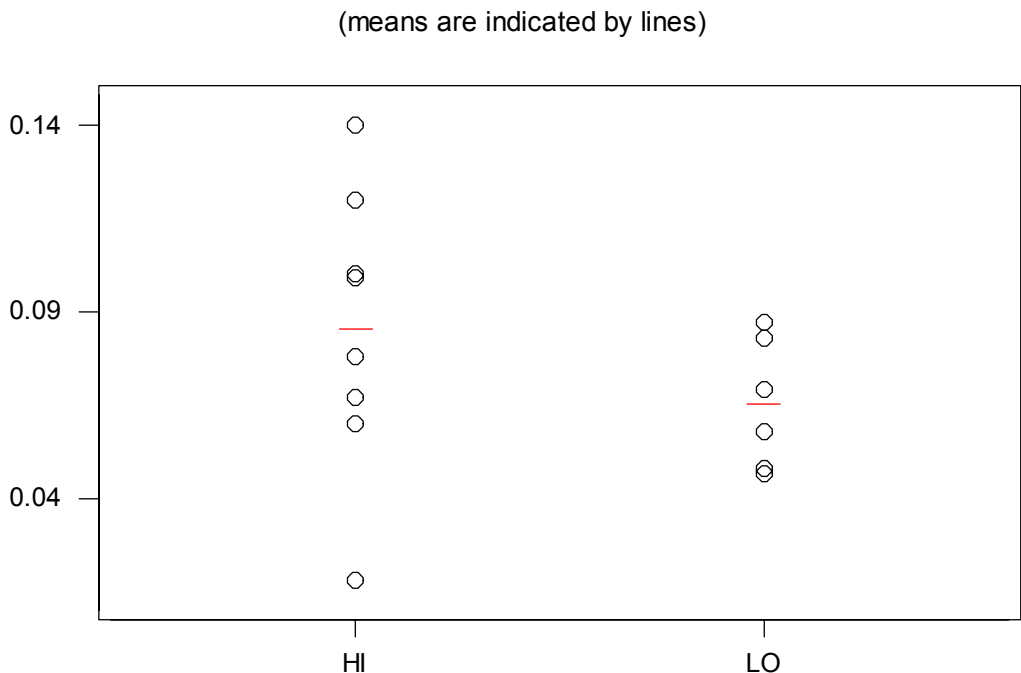


Figure 7-5. Comparison of High and Low Load PM_{2.5} Mass Results (Site Echo).

sampler results are at the near end of the range measured in other tests. The reasons for differences in PM_{2.5} concentration among the various dilution sampler tests are not well understood. Previous tests strongly suggest the hot filter/iced impinger method results are positively biased due to significant measurement artifacts (conversion of gaseous SO₂ to solid residue and excessive condensation of vapors in the iced impingers). Additional tests are needed to corroborate all of the recent dilution sampler test results. Despite the relatively small number of different tests, the striking difference between dilution sampling and hot filter/iced impinger results is very consistent.

The Hildemann PM_{2.5} results for natural gas-fired home appliances are significant in this context because they were obtained using the original sampler upon which the Alpha dilution sampler design used in this test is based. The sampling equipment and procedures are substantially the same as those used in this test. Hildemann's test results are the only published

results for natural gas combustion taken with a dilution sampler that the authors found prior to our own tests published in 2001. They have been used in recent source apportionment studies to assess the contribution of natural gas combustion sources to ambient PM_{2.5} concentrations (Zheng et al., 2002). Hildemann's PM speciation results are the only results for natural gas currently included in EPA's SPECIATE database. Despite the differences in the source types tested, the PM_{2.5} mass results for Site A, Site Bravo, Site Charlie, Site Echo and Hildemann are remarkably similar. The recent results obtained in this program highlight the variability inherent in the reported emission factors, which should be considered when applying the results to source apportionment studies.

Table 7-3. Comparison of Current Program and Other Data for Gas Combustion.

Source	Unit Type	Total PM10 lb/MMBtu	Filterable PM10		Condensable PM		PM2.5 (2) lb/MMBtu
			lb/MMBtu	% of Total PM10	lb/MMBtu	% of Total PM10	
AP-42	External Combustion: Natural Gas-Fired	0.0075 (3,4)	0.0019 (3)	25	0.0056 (4)	75	--
AP-42	Internal Combustion: Natural Gas-Fired Stationary Gas Turbine for Electricity Generation (Uncontrolled)	0.0066 (3,4)	0.0019 (3)	29	0.0047 (4)	71	--
Hildemann et al. (1991)	Natural gas-fired home appliances	-- --	-- --	--	-- --	--	0.00011
Site A (API, 2001a)	Refinery Gas-fired Boiler	0.0099 (1,4)	0.00016 (1)	2	0.0097 (4)	98	0.00036
Site B (API, 2001b)	Refinery Gas-fired Process Heater	0.0052 (1,4)	0.00064 (1)	12	0.0046 (4)	88	0.000054
Site C (API, 2001c)	Natural Gas-fired Steam Generator	0.0013 (1,4)	0.00008 (1)	6	0.0012 (4)	94	0.000056
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	0.0084 (1,4)	0.00059 (1)	7	0.0078 (4)	93	0.000052
Site Bravo (prior test, with duct burners) (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	--	0.00048 (3)	--	--	--	--
Site Bravo (prior test, without duct burners) (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	--	0.00120 (3)	--	--	--	--
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	0.0032 (1,4)	0.00029 (1)	9	0.0030 (4)	91	0.00025
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	0.0011 (1,4)	0.00010	9	0.0010 (4)	91	0.00016
Site Delta (Wien et al., 2004c)	Natural Gas-fired Institutional Boiler	0.0013 (5)	--	--	0.0013 (5)	--	0.00053 (6)
Site Echo (this test)	Natural Gas-fired Combined Cycle Power Plant with oxidation catalyst and SCR	--	--	--	--	--	0.00013

(1) Data collected using hot filter method (EPA Method PRE-4)

(2) Data collected using dilution tunnel method; data presented is for PM<2.5 microns and includes solid and condensed liquid PM.

(3) Data collected using hot filter methods (EPA Method 5, 201, or 201A)

(4) Data collected using wet impinger methods (e.g., EPA Method 202).

(5) SO₃ measured by controlled condensation method.

(6) High bias likely due to test following residual oil firing and high blank levels.

Particulate Carbon and Precursor Emission Factors

Particulate carbon—OC and EC—accounted for the vast majority of the reconstructed PM_{2.5} mass measured using the dilution sampler. It is believed, however, that the OC results are subject to positive bias from measurement artifacts (see discussion earlier in this section). The OC emission factor for Site Echo (0.00023 lb/MMBtu) is approximately equal to the average OC emission factor (0.00014 lb/MMBtu) from six previous tests by the authors and one independent test of gas-fired sources (Table 7-4). With the exception of Site C, all the OC results are within a factor of two of the mean. EC is somewhat more variable among the tests, but the levels are much lower than OC and results for all sites are within a factor of four of the average EC emission factor. The EC emission factor for Site Echo falls within the middle half of the data for other sources (between the 25th and 75th percentile), while the OC emission factor falls into the upper quartile. The total VOC₈₊ emission factor for Site Echo is comparable to the other results, falling into the second quartile (30th percentile) of the range.

Table 7-4. Average Particulate Carbon and Particulate Carbon Precursor Emission Factors for Gas-Fired Sources (lb/MMBtu).

Source	Unit Type	OC	Backup OC	EC	TC	All SVOCs	Total VOC ₈₊
Site A (API, 2001a)	Refinery Gas-fired Boiler	1.5E-4	--	9.4E-5	2.5E-4	4.1E-6	1.6E-4
Site B (API, 2001b)	Refinery Gas-fired Process Heater	2.8E-5	--	1.9E-5	3.4E-5	6.6E-7	4.0E-4
Site C (API, 2001c)	Natural Gas-fired Steam Generator	2.3E-4	--	9.2E-6	2.4E-4	1.5E-5	4.1E-5
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	6.7E-5	9.7E-5	7.3E-6	7.5E-5	1.7E-5	7.6E-4 *
Hildemann et al., 1991	Natural Gas-fired Home Appliances	9.0E-5	6.7E-5	7.1E-6	9.7E-5	--	--
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	2.0E-4	1.8E-4	1.9E-5	2.2E-4	6.0E-6	6.0E-4
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	1.9E-4	1.3E-4	3.6E-5	2.2E-4	3.0E-6	2.2E-4 *
Site Echo (this test)	Natural Gas-fired Combined Cycle Power Plant with oxidation catalyst and SCR	2.3E-4	2.3E-4	1.3E-5	2.4E-4	**	1.9E-4

*Excludes canister data.

**No SVOCs were measured above the blank concentrations.

EMISSION FACTOR QUALITY

The source-specific emission factors developed from this test generally have relative uncertainties below 50 percent, except for species such as EC and VOCs that were detected in only a few runs or that were detected at concentrations near the MDL or blank levels. The data sets are normally distributed, with some exceptions, so the arithmetic mean and uncertainty bounds are a reasonable representation of the data central tendency and distribution observed in this test. The 95 percent upper confidence bounds presented with the emission factors provides plausible upper bounds to emissions (i.e., the actual emission factor is very likely to be lower). The dilution sampling method has been validated in the peer-reviewed scientific literature (Hildemann et al., 1989), and the ambient air sample collection and analysis methods are well documented in published EPA test methods and/or guidelines. The data quality is well documented throughout this report, and sufficient details are provided for others to reproduce the tests. For these reasons, the data quality of these results is considered high. However, it should be noted that whereas dilution sampling is widely accepted for demonstrating compliance with mobile source particulate emission standards and for stationary source receptor and source apportionment analysis, it is not currently accepted by regulatory agencies for demonstrating compliance with stationary source PM₁₀ emission standards or permit limits. Widely recognized standard methods for stationary source dilution sampling do not presently exist. In a separate task of this program, efforts to develop a consensus standard method through ASTM International are underway at this writing.

It should be noted that emission factors with an uncertainty greater than 100 percent must be considered potentially unrepresentative. In addition, this test represents one of the first applications of these dilution samplers and sample collection methods to this type of source, and the results have not been corroborated by other independent tests. The reproducibility of the test results has been verified only qualitatively by comparison to other gas combustion sources tested within this program. In many cases, the extremely low concentrations of particulate matter and other pollutants challenged the LQLs of the state-of-the-art methods employed. Longer sampling times may alleviate the proximity to LQLs but this would reduce the method's practicality. Therefore, data users should exercise appropriate caution when using these results.

Uncertainty is presented with all emission factor and mass fraction results, including analytical, sample volume, and dilution ratio uncertainty. Although the data quality in this test is considered high, the emission factor quality is necessarily considered below average because they are source-specific emission factors based on a single test. The source-specific emission factors derived from this test may best be used in conjunction with similar test results from other units within the source category population to develop more robust, reliable emission factors. The results from this limited set of test data should not be interpreted as representative of the entire population of NGCC-SFs because of the wide range of designs, configurations, emission controls, operating conditions, ambient PM_{2.5} concentrations, weather conditions, fuel compositions, etc. that exist. In addition, because all of the emission measurements were made at the stack downstream of post-combustion air pollution controls, the results do not represent emissions from the gas turbine alone. Although the operating conditions for each test run were very steady and consistent within the high load and low load test series, the resulting emission factors are not considered representative of any particular operating condition but rather are the average of the operating conditions during the test. Consequently, data users should apply appropriate caution when using these results.

FINDINGS

In summary, the main findings of this test are:

- The majority of elements and organic compounds were detected at levels comparable to the ambient air or background levels in the dilution system, and/or were near the minimum detection limits of the test methods. This indicates that the levels of these substances measured in the stack samples are not distinguishable from the ambient air or measurement background levels⁵. These findings strongly indicate the need for further development and validation of the dilution apparatus and method for measuring the extremely low concentrations of such substances that may be present in the stack emissions from gas-fired combustion sources.
- Particulate mass emissions from this NGCC-SF (including post-combustion emission controls) are extremely low, qualitatively consistent with levels expected for gaseous fuel combustion based on published emission factors and other independent tests. The low

⁵ Note that this method was previously used to measure such pollutants at Site Bravo. At Site Bravo, a dilution sampler blank was not collected and analyzed; however, the measured stack concentrations of these substances at Site Echo and Site Bravo are similar. Further, many of the substances measured in the stack at site Bravo are indistinguishable from the ambient and field blanks collected at the site. Therefore, the levels measured in the stack samples at site Bravo for elemental and organic compounds may also be due to measurement background.

particulate and related pollutant concentrations in the exhaust from the plant contribute to moderate uncertainties in most of the emission factors derived from these test results.

- The average source-specific PM_{2.5} mass emission factor obtained using dilution sampling is 0.00013 lb/MMBtu, which is approximately 1/50 of the published AP-42 PM₁₀ emission factor for similar sources. The test result is consistent with other tests of stationary gas-fired sources using dilution methods. Previous tests suggest the difference is largely due to measurement artifacts associated with the published emission factors (conversion of gaseous SO₂ to solid SO₄⁼ residue in the iced impinger method, excessive condensation of vapors that would not occur under ambient conditions) and other limitations (inadequate sensitivity of the hot filter method) of the hot filter/iced impinger methods. Therefore, dilution sampling results are considered the most representative of actual PM_{2.5} emissions during this test.
- Tests performed with dilution sampling at high load and low load show that the difference in PM_{2.5} concentrations is small, within the uncertainty of the average result (±41 percent, or ±0.00006 mg/dscm, at the 95 percent confidence level).
- Tests performed comparing a new dilution sampler design to an established benchmark design showed agreement within the uncertainty bounds of the results. The estimated accuracy of the new dilution sampler design is 19 percent and estimated precision is 27 percent compared to the benchmark design.
- OC and EC comprise approximately 71 and 1.8 percent of the average reconstructed PM_{2.5} mass, respectively, as measured using the dilution sampler. However, it is likely that the OC results are biased high due to an organic adsorption artifact on the QFFs, which is more pronounced for clean sources such as gas combustion. Back-up filter results indicate that 59 to 136 percent of the measured OC may be due to this artifact. Further research is needed to improve the reliability of OC measurements.
- SO₄⁼, Cl⁻, NO₃⁻, NH₄⁺ and soluble Na account for approximately 25 percent of the reconstructed PM_{2.5} mass; SO₄⁼ alone accounts for approximately 11 percent of the total PM_{2.5} mass.
- The reconstructed PM_{2.5} mass based on the sum of all measured chemical species is 2.5 times higher than the measured PM_{2.5} mass. The difference lends further support to the likelihood of a positive bias in the OC measurement due to measurement artifacts.
- Emission factors for secondary particle precursors are low and qualitatively consistent with published emission factors for gaseous fuel combustion, other literature, and previous plant test results.
- Additional tests on other similar sources are recommended to corroborate the results and findings from this test and verify dilution sampling method performance. The results of this test provide a plausible upper bound for the measured emissions.

- Exploratory measurements using a commercial laser photometer to measure real-time PM_{2.5} trends in the diluted sample and ambient air were made to determine if the technique could be used to optimize the filter mass loadings in the dilution sampler and to determine if any correlation between ambient PM_{2.5} and stack PM_{2.5} trends could be established. Results were equivocal because large swings in the stack laser photometer response could not be related to stack PM_{2.5} or any other measurements. Further evaluation of the technique is needed to assess whether it can be useful in this type of application.
- Further refinement and testing of the dilution sampling equipment and procedures is needed to minimize procedural errors and improve knowledge of method precision and accuracy.

The data in this report were developed using an experimental dilution test method applied to one source operating under two nominal conditions with different sources of emissions that are not necessarily representative of the source category or the typical operation of the specific source tested. Accordingly, GE Energy does not recommend using any emissions factors contained herein for any regulatory and/or commercial applications. The data in this report may be useful for future refinement and validation of the experimental dilution method for specific applications so that it may be applied in future tests to develop more robust emission factors.

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APPENDIX A LIST OF ABBREVIATIONS

<	less than (upper estimate of true emission)
°C	degree Celsius
°F	degree Fahrenheit
µg	microgram
µg/mL	microgram per milliliter
µm	micrometer (micron)
ACS	American Chemical Society
Ag	silver
Al	aluminum
ANSI	American National Standards Institute
API	American Petroleum Institute
As	arsenic
ASME	American Society of Mechanical Engineers
Au	gold
Ba	barium
BAAQMD	Bay Area Air Quality Management District
Br	bromine
C ₂	compounds with carbon number of 2
C ₄	compounds with carbon number of 4
C ₅	compounds with carbon number of 5
C ₆	compounds with carbon number of 6
C ₉	compounds with carbon number of 9
C ₂₀	compounds with carbon number of 20
Ca	calcium
Cd	cadmium
CEC	California Energy Commission
CEMS	continuous emission monitoring system
cfm	cubic foot per minute
Cl	chlorine
Cl ⁻	chloride ion
CO	carbon monoxide
Co	cobalt
CO ₂	carbon dioxide
Cr	chromium
Cu	copper
DI	distilled deionized
DNPH	dinitrophenylhydrazine
DOE	United States Department of Energy
DRI	Desert Research Institute
DSB	dilution system blank
EC	elemental carbon
ECD	electron capture detection
ED-XRF	energy dispersive x-ray fluorescence

EI	electron impact
EPA	Environmental Protection Agency
ERA	Environmental Research Associates
eV	electron volt
FB	field blank
Fe	iron
FID	flame ionization detection
Ga	gallium
GC	gas chromatography
GC/IRD/MSD	gas chromatography/infrared detector/mass selective detector
GC/MS	gas chromatography/mass spectrometry
GC/MS/MID	gas chromatography/mass spectrometry/multiple ion detection
GE	General Electric
GE EER	GE Energy and Environmental Research Corporation
GE MPA	GE Mostardi Platt Associates
gr	grain
gr/100 scf	grain per hundred standard cubic feet
GRI	Gas Research Institute
H ₀	null hypothesis, a statistical term, which is a "baseline condition" that is presumed to be true in the absence of strong evidence to the contrary (e.g., in statistical t-test the null hypothesis is that the means of two data sets are the same within a specified level of confidence).
HAP	hazardous air pollutant
HC	hydrocarbon
HCl	hydrochloric acid
HEPA	high efficiency particulate arrest
Hg	mercury
HPLC	high performance liquid chromatography
HRSG	heat recovery steam generator
IC	ion chromatography
In	indium
ISO	International Organization for Standardization
K	potassium
K ₂ CO ₃	potassium carbonate
keV	kiloelectron volt
KHP	potassium hydrogen phthalate
km	kilometer
L/min	liter per minute
La	lanthanum
lb/hr	pound per hour
lb/MMBtu	pound of pollutant per million British thermal units of gas fired
LOQ	limit of quantification
LQL	lower quantification limit
MDL	minimum detection limit
MEK	methylethylketone
Mg	magnesium

mg	milligram
mg/dscm	milligram per dry standard cubic meter
MID	multiple ion detection
mL	milliliter
mm	millimeter
MMBtu/hr	million British thermal units per hour
Mn	manganese
Mo	molybdenum
MSD	mass selective detector
MW	megawatt
N	normal
Na	sodium
Na ⁺	sodium ion
NAAQS	National Ambient Air Quality Standards
ND	not detected
NETL	National Energy Technology Laboratory
NGCC-SF	natural gas fired combined cycle plant with supplementary firing
NH ₃	ammonia
NH ₄ ⁺	ammonium ion
Ni	nickel
NIST	National Institute of Standards and Technology
nm	nanometer
NO ₃ ⁻	nitrate ion
NO _x	oxides of nitrogen (sum of nitric oxide and nitrogen dioxide)
NPS	National Park Service
NRC	National Research Council
NYSERDA	New York State Energy Research and Development Authority
O ₂	molecular oxygen
OC	organic carbon
P	phosphorus
PAH	polycyclic aromatic hydrocarbon
Pb	lead
Pd	palladium
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 micrometers
PM2.5	particulate with aerodynamic diameter less than 2.5 micrometers
ppb	part per billion
ppm	part per million
PUF	polyurethane foam
QA	quality assurance
QFF	quartz fiber filter
Rb	rubidium
RH	relative humidity
RPD	relative percent difference
RSD	relative standard deviation
S	sulfur

Sb	antimony
scf	standard cubic foot
SCR	selective catalytic reduction
Se	selenium
Si	silicon
SI	Système Internationale
Sn	tin
SO ₂	sulfur dioxide
SO ₄ ⁼	sulfate ion
Sr	strontium
SRM	standard reference material
SVOC	semivolatile organic compound
Ti	titanium
TIGF	Teflon [®] -impregnated glass fiber
Tl	thallium
TMF	Teflon [®] -membrane filter
TOR	thermal/optical reflectance
TSI	Thermo Scientific Incorporated
U	uranium
V	vanadium
VOC	volatile organic compound
VOC ₈₊	VOC with carbon number of eight and greater
XAD-4 [™]	Amberlite [®] sorbent resin (trademark)
XRF	x-ray fluorescence
Y	yttrium
Zn	zinc
Zr	zirconium

APPENDIX B SI CONVERSION FACTORS

	<u>English (US) units</u>	X	<u>Factor</u>	=	<u>SI units</u>
Area:	1 ft ²	x	9.29 x 10 ⁻²	=	m ²
	1 in ²	x	6.45	=	cm ²
Flow Rate:	1 gal/min	x	6.31 x 10 ⁻⁵	=	m ³ /s
	1 gal/min	x	6.31 x 10 ⁻²	=	L/s
Length:	1 ft	x	0.3048	=	m
	1 in	x	2.54	=	cm
	1 yd	x	0.9144	=	m
Mass:	1 lb	x	4.54 x 10 ²	=	g
	1 lb	x	0.454	=	kg
	1 gr	x	0.0648	=	g
Volume:	1 ft ³	x	28.3	=	L
	1 ft ³	x	0.0283	=	m ³
	1 gal	x	3.785	=	L
	1 gal	x	3.785 x 10 ⁻³	=	m ³
Temperature	°F-32	x	0.556	=	°C
	°R	x	0.556	=	K
Energy	Btu	x	1055.1	=	Joules
Power	Btu/hr	x	0.29307	=	Watts