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 SUPPLEMENTARY FIRING, OXIDATION CATALYST AND SCR AT SITE BRAVO

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TOPICAL REPORT: TEST RESULTS FOR A COMBINED CYCLE POWER PLANT WITH SUPPLEMENTARY FIRING, OXIDATION CATALYST AND SCR AT SITE BRAVO

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This report presents test results obtained on one source measured at several 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 BRAVO OPERATING CONDITIONS (a)

	Run 1	Run 2	Run 3	Run 4
GT (Load) (%)	100	100	93	85
Duct Burner	ON	ON	PARTIAL	OFF
SCR	ON	ON	ON	ON
Oxidation Catalyst	ON	ON	ON	ON
Power Augmentation	Yes	Yes	Yes	Yes

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

(b) Duct burner was firing during part (~30 min.) of the test run and shutoff during the remainder of the test run.

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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 (PM2.5). PM2.5 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 PM2.5 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 PM2.5 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 PM2.5 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; and
- Identify and characterize PM2.5 precursor compound emissions from stationary combustion sources 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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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 PM2.5. PM2.5 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. PM2.5 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 PM2.5 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 to 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 PM2.5 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 PM2.5 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 PM2.5 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

Innovative particulate emission measurements were performed 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 a single shaft design, with the single generator driven by a shaft common to both the gas and the steam turbines. The gas turbine is equipped with a lean premix combustion system for oxides of nitrogen (NO_x) emissions control and steam injection for power augmentation. The HRSG is equipped with natural gas-fired duct burners for additional steam production, 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 using both traditional hot filter/iced impinger methods and an innovative dilution sampling protocol. Thus, the results do not represent emissions from the gas turbine alone. The flue gas temperature at the stack measurement location was approximately 230 degrees Fahrenheit (°F) during the tests.

The dilution sampler design 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 PM2.5 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 PM10 (particles smaller than 10 μm) emission standards or permit limits. Widely accepted, standardized procedures for stationary source dilution sampling do not currently exist. Concurrent measurements also were made using EPA Methods PRE-4 (in-stack cyclones and filter) and 202 (iced impingers) for total particulate, PM10 and PM2.5 including condensable particles.

Four six-hour test runs were performed at the stack on separate, consecutive days under varying operating conditions (duct burners on and off, 82 to 102 percent of rated load) near full load. Because of the varying operating conditions, 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:

- Particulate mass emissions from the NGCC-SF (including supplementary firing and post-combustion emission controls) were 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 and a procedural error contribute to large relative uncertainties in the emission factors derived from these test results.

- Average PM2.5 mass emission results obtained using two different methods of determining the emission factor for primary PM2.5 mass differ by more than a factor of ten: 0.00025 pounds of pollutant per million British thermal units of gas fired (lb/MMBtu) using the dilution sampler[1]; and 0.0031 lb/MMBtu using traditional hot filter/iced impinger methods for filterable and condensable particulate matter. Despite high relative uncertainty associated with the average results, the difference is significant at the 95 percent confidence level.

- Both the PM2.5 mass and the speciated mass fractions measured using dilution sampling are substantially different from those measured by hot filter/iced impinger methods. Because of significant measurement artifacts (conversion of gaseous sulfur dioxide to solid sulfate residue in the impingers, excessive condensation of vapors that would not occur under ambient conditions) and other limitations (inadequate sensitivity of the hot filter method, high blanks) of the hot filter/iced impinger methods, dilution sampling results are considered the most representative of actual primary PM2.5 emissions during this test.

- Condensable particulate matter and filterable particulate PM10 emission factors derived from tests using conventional EPA methods are qualitatively consistent with published emission factors for external combustion of natural gas and natural gas-fired combustion turbines (U. S. EPA, 2000a). Most of the condensable particulate matter, which dominates total PM10 emissions, is attributed to sulfate compounds. Other studies (Wien et al., 2001) showed that a measurement artifact (conversion of gaseous sulfur dioxide to sulfate residue) could produce a relatively large positive bias in condensable particulate matter as measured by iced impinger methods when applied to gas combustion. The sulfur dioxide-to-sulfate conversion artifact can explain much of the observed difference between the dilution sampler and hot filter/iced impinger method results.

- Organic carbon and elemental carbon comprise approximately 73 and 2.9 percent of the average reconstructed PM2.5 mass, respectively, as measured using the dilution sampler. However, it is likely that the organic carbon results are biased high due to a volatile organic compound adsorption artifact on the quartz fiber filters, which is more pronounced for clean sources such as gas combustion. Back-up filter results indicate that

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[1] Subsequent tests at Site Echo (England et al., 2004; England, 2004) showed that background PM2.5 in the dilution air was large in relation to stack PM2.5, and that stack PM2.5 was indistinguishable from the ambient air PM2.5 concentration. Therefore, it is likely that Site Bravo PM2.5 results are biased high and also may be indistinguishable from ambient air PM2.5 concentration.

74 to 126 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 and soluble sodium ion together account for approximately 14 percent of the reconstructed PM2.5 mass derived from the dilution sampler results; sulfate alone accounts for approximately 4 percent.

- Iron, silicon, calcium, aluminum, and potassium account for approximately 8 percent of the reconstructed PM2.5 mass derived from the dilution sampler results. Smaller amounts of 16 other detected elements comprise another 5 percent.

- The measured PM2.5 mass and the reconstructed PM2.5 mass based on the sum of all measured chemical species derived from the dilution sampler results agreed within 34 percent. The difference between reconstructed and measured mass is not significant at the 95 percent confidence level.

- Most elements are not present at levels significantly above the background levels in the ambient air or the minimum detection limits of the test methods.

- Most organic compounds were not detected at levels significantly above background levels in the ambient air or field blanks. A few organic compounds were detected at extremely low levels approximately consistent with published emission factors, other literature, and previous plant test results.

- Emission factors for secondary particle precursors are low and approximately consistent with published emission factors for gaseous fuel combustion, other literature, and previous plant test results.

- Because of the high relative uncertainty of the emission factors derived from this test, additional tests on other similar sources are needed 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.

- Further refinement and testing of the dilution sampling equipment and procedures is needed to minimize procedural errors and establish acceptable levels of method performance. Due to the proximity of many of the stack results to ambient air levels, a dilution system blank for all measurements is recommended for future tests to verify that substances detected in the ambient air are not present in the dilution air.

The data in this report were developed using an experimental dilution test method applied to one source operating under several 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 PM2.5. PM2.5 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. PM2.5 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 PM2.5 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 PM2.5 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-fired combined cycle power plant (NGCC-SF) at Site Bravo on September 6-11, 2001 along with emissions data obtained simultaneously using traditional hot filter/iced impinger methods. 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 test 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 PM2.5 concentrations.

The goals of this program were to:

- Develop improved dilution sampling technology and test methods for PM2.5 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 PM2.5 precursor compound emissions that can be used in source-receptor and source apportionment analyses.

It should be noted that the project team chose to complete the NGCC-SF test in advance of a pilot scale study of the dilution sampler test method to address a compelling need for detailed data on NGCC-SF fine (PM2.5) and ultrafine (smaller than 0.1 μm) particle emissions. The pilot-scale study is evaluating dilution ratio and residence time design criteria established by Hildemann et al. (1989) as part of the development of a more compact and field portable sampler designed to produce comparable results. A dilution sampler closely based on the benchmark Hildemann design was used for this test.

PROJECT OBJECTIVES

The specific objectives of this test were to:

- Provide speciated primary fine particle emissions data for NGCC-SF equipped with lean premix combustors, supplementary firing, oxidation catalyst, and selective catalytic reduction (SCR) that can be used in source receptor, source apportionment and other analyses;

- Compare PM2.5 mass measured using an in-stack filter and iced impinger train (EPA Method PRE-4/202) and mass measured using a dilution sampler;

- Develop emission factors and speciation profiles for organic aerosols and PM2.5 mass for use in source receptor and source apportionment analysis;

- Characterize sulfate ion ($SO_4^{=}$), nitrate ion (NO_3^-), ammonium ion (NH_4^+), 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 8 and above, sulfur dioxide (SO_2); oxides of nitrogen (NO_X), and ammonia (NH_3) using ambient air methods with the dilution sampler;

- Characterize selected hazardous air pollutants, such as benzene, toluene, xylenes and aldehydes using ambient air methods with the dilution sampler;

- Evaluate the feasibility of the acetyl acetone (Celanese) colorimetric method (EPA Conditional Test Method 037) for determination of formaldehyde emissions;

- Compare condensable particulate matter (CPM) results obtained using two different methods: EPA Method 202 and a modified version of EPA Method 8 (the back-half isopropyl alcohol catch is dried and weighed);

- Quantify semivolatile organic compounds (SVOC) species that contribute to organic particle constituents (for PM2.5 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. The emissions testing included simultaneous collection and analysis of both in-stack and diluted stack gas samples. All emission samples were collected from the exhaust 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 were collected during the tests to document operating conditions.

Table 1-1. Overview of Sampling Scope (Site Bravo).

	Number of Samples	
Sampling Location	Stack	Ambient Air
Source Level (Undiluted):		
EPA Methods 1, 2, 3 and 4 (stack gas flow rate)	4	--
EPA Method PRE-4/202 train (FPM/CPM)	4	--
EPA Method 17/8 train (CPM)	4	--
EPA Conditional Test Method 037 train (NH_3)	4	--
Bay Area Air Quality Management District Method ST-1B train (formaldehyde)	4	--
NO_x, CO, O_2	Continuous (Plant)	--
Dilution sampler:		
Teflon® filter (mass, elements)	4	1
Quartz fiber filter (ions, OC/EC)	4	1
K_2CO_3-impregnated cellulose fiber filter (SO_2)	4	1
Citric acid-impregnated cellulose fiber filter (NH_3)	4	1
TIGF/PUF/XAD®-4 (SVOCs)	4	1
Tenax® (VOCs)	4	1
Stainless steel canisters (VOCs, C_2-C_{10})	4	1
DNPH-coated silica gel cartridges (carbonyls)	4	1
Process monitoring	Continuous (Plant)	--

TIGF - Teflon®-impregnated glass fiber filter
PUF - polyurethane foam
XAD®-4 - Amberlite® sorbent resin
DNPH – dinitrophenylhydrazine

Table 1-2. Summary of Analytical Targets.

Parameters	In-Stack				Dilution Sampler								
	Cyclones	Quartz fiber filter	Imp.	Gases	Quartz fiber filter	TIGF/ PUF/ XAD®	TMF	Tenax®	SS cans	DNPH sorbent tube	K_2CO_3 filter	Citric acid filter	Gases
Total PM mass	X	X											
PM10 $_{\text{mass}}$	X	X											
PM2.5 mass	X	X					X						
Condensable particulate mass			X										
Sulfate			X		X								
Chloride			X		X								
Ammonium			X		X								
Nitrate			X		X								
Elements			X				X						
Organic carbon					X								
Elemental carbon					X								
Semivolatile organic compounds						X							
Volatile organic compounds*								X					
Volatile organic compounds**									X				
Aldehydes			X							X			
Ammonia (gaseous)			X									X	
NO_x				X									
SO_2											X		
CO				X									
O_2				X									
Moisture or relative humidity			X										X
Velocity				X									
Temperature				X									X

TMF - Teflon® membrane filter
TIGF - Teflon®-impregnated glass fiber filter
DNPH – dinitrophenylhydrazine
SS cans – stainless steel canisters
Imp. – iced impinger train
*Carbon number of 7 or greater
**Carbon number of 2 to 10

Source Level (Undiluted Exhaust Gas) Samples

In-stack sampling and analysis for filterable particulate matter (total, PM10—particles with aerodynamic diameter smaller than 10 μm— and PM2.5), CPM, NH_3 and formaldehyde was performed using traditional stationary source test methods. In-stack cyclones and filters were used for determining filterable particulate matter. CPM, NH_3 and formaldehyde were determined using aqueous iced impinger methods. CPM speciation was determined by analyzing the impinger residue. NO_X, carbon monoxide (CO) and oxygen (O_2) were determined instrumentally using the plant's existing continuous emissions monitoring (CEM) system.

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 sample stream from the stack into a mixing chamber, where it was diluted approximately 31:1 with ambient air purified by passing through a high efficiency particulate arrest (HEPA) filter and activated carbon. Because PM2.5 behaves aerodynamically almost like a gas at typical stack conditions, the samples were extracted non-isokinetically. A slipstream of the mixed and diluted sample was conveyed to a residence time chamber where it resided for approximately 70 seconds 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 (QFF) for ions and carbon speciation, Teflon® membrane (TMF) for PM2.5 mass and elements, potassium carbonate-impregnated cellulose fiber for SO_2, citric acid-impregnated cellulose fiber for NH_3 and Teflon®-impregnated glass fiber (TIGF) filters for particle phase SVOCs; a polyurethane foam (PUF)/Amberlite® sorbent resin (XAD®-4)/PUF cartridge to collect gas phase SVOCs; Tenax® sorbent tubes to capture VOCs with a carbon number greater than seven; a stainless steel canister to capture VOCs with a carbon number greater than two; and dinitrophenylhydrazine (DNPH)-coated silica gel cartridges to capture carbonyls (aldehydes). Four samples were collected over six hours on four separate test days.

Ambient Air Samples

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.

KEY PERSONNEL

GE Energy and Environmental Research Corporation (GE EER) had overall 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 EER) – Field Team Leader
- Judith Chow, John Watson, and Barbara Zielinska (Desert Research Institute, DRI) – Consulting and Laboratory Analysis
- Karl Loos (Shell Global Solutions U.S.) – API Work Group Chairman
- Karin Ritter (API) – API Project Officer
- Jim McCarthy and Paul Drayton (GRI) – GRI Project Manager
- Guido Franco and Marla Mueller (CEC) – CEC Project Manager
- Dan Gurney and Kathy Stirling (DOE/NETL) – DOE/NETL Contracting Officer Representative
- Barry Liebowitz (NYSERDA) – NYSERDA Project Manager

2. PROCESS DESCRIPTION

Tests were performed on a NGCC-SF employing a heavy duty gas turbine with supplementary firing, steam augmentation and post-combustion emission control equipment. The unit is a single shaft design, with the single generator driven by a shaft common to both the gas and the steam turbine. Hot exhaust gases from the gas turbine pass through a heat recovery steam generator (HRSG) before venting to the atmosphere via the stack (Figure 2-1). The HRSG contains supplementary duct burners for additional steam production. The steam from the HRSG is used both for power generation using the steam turbine and to provide process steam for a neighboring manufacturing facility. The total nominal electrical generation capacity of the cogeneration facility is 240 megawatt (MW). The unit fired natural gas for these tests. The facility is equipped with a continuous emissions monitoring system (CEMS) for CO, O_2 and NO_X.

POLLUTION CONTROL EQUIPMENT

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, NH_3, is injected through a grid just upstream of the SCR catalyst.

SAMPLING LOCATIONS

The exhaust gases vent to atmosphere through a vertical, cylindrical stack that is 233 feet tall. Emissions sampling was conducted at this stack, downstream of all the pollution control equipment, which has an inside diameter of 16.5 feet (198.0 inches) and has numerous sampling ports, some of which are used for the plant CEMS. There are four six-inch diameter flanged ports positioned at 90 degrees to each other and located approximately 6 feet above the sampling

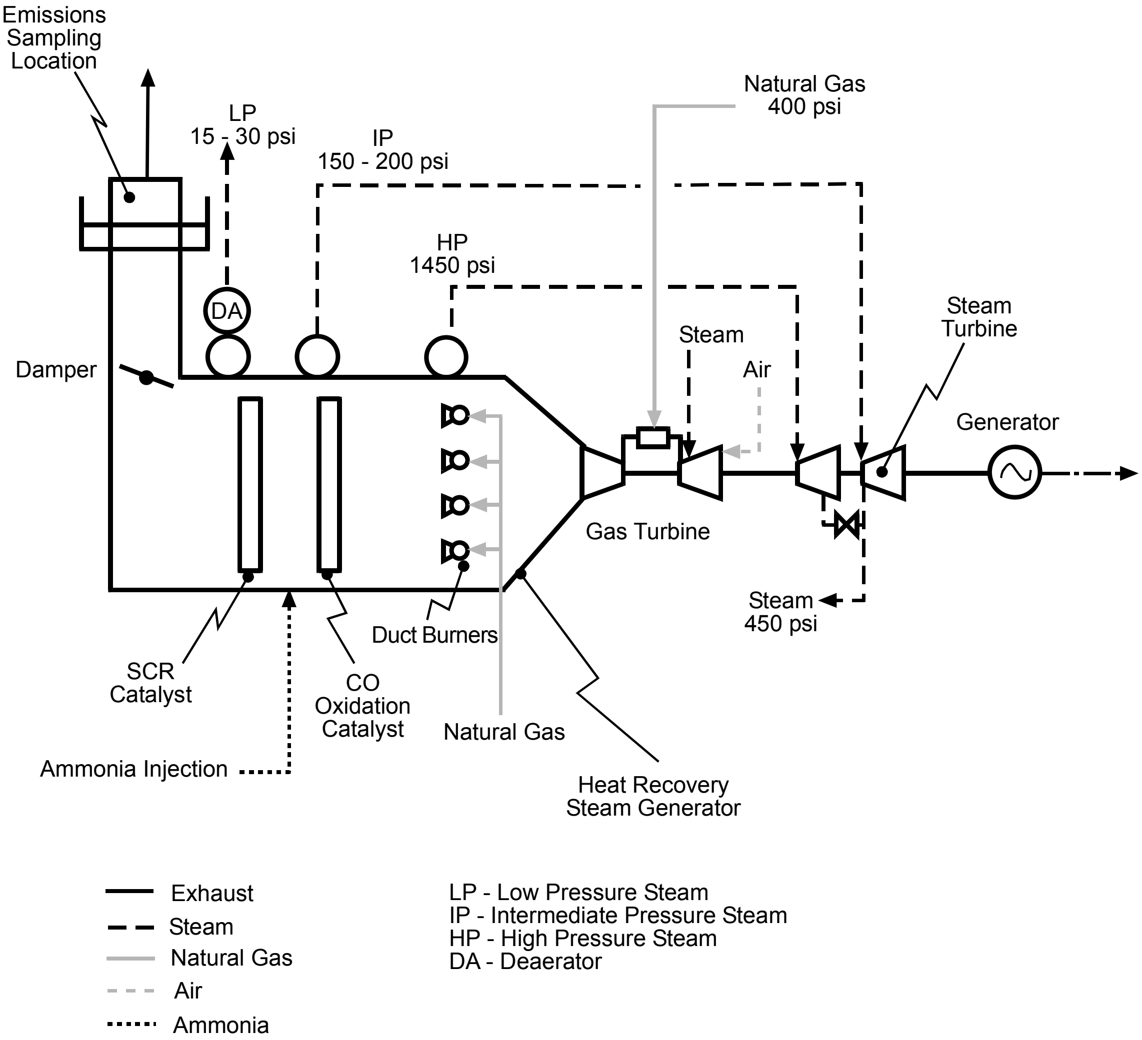

Figure 2-1. Site Bravo Process Overview.

platform. There are also four 4-inch ports offset from the 6-inch ports and located at 90 degrees to each other; the ports are flanged and located 4 feet above the platform. The ports are at least 60 feet (3.6 diameters) downstream from the last disturbance and 100 feet (6.1 diameters) upstream from the top of the stack. All ports are accessed from a single platform that is approximately 61 inches wide and approximately 128 feet above the ground. The stack gas O_2 concentration was uniform across the stack and there was no cyclonic flow present. Preliminary velocity traverses were performed to determine average velocity in the stack. Sampling was performed through three separate ports at single points of average flow, as determined by the preliminary velocity traverses; the Method 17/8 train and the dilution sampler probe were sampled through the same port so the sampling points could be co-located.

A single ambient air sample was collected adjacent to and at the same level as the air inlet for the turbine.

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, Method PRE-4/202 Run 1 began at 11:56 hours and finished at 17:56 hours on Thursday, September 6. Dilution sampling and in-stack testing were performed 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. Various quality assurance (QA) samples also were collected during the tests to assess contamination (trip blanks, reagent blanks, etc.), which are discussed in Section 6.

STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

Equal area sampling points across the stack diameter were determined according to EPA Method 1. An S-type Pitot tube was used to determine the stack gas temperature and velocity at each sampling point, from which the volumetric flow rate was calculated (EPA Method 2). Stack gas molecular weight was calculated in accordance with EPA Method 3. Moisture content of the sample was determined based on weight gain of the impingers used in the Method PRE-4/202 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. The measured stack gas flow rate was used with other measurements to calculate pollutant emission factors (see Section 5 for additional details).

O_2, CO, AND NO_X

Major gases and pollutant concentrations in the stack sample were monitored using the plant's CEMS, which is maintained, calibrated and operated consistent with 40 CFR 60 Appendix B.

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

Sampling Location	Measurements	Sampling Approach	Analysis Approach	Reference
Stack – source level (undiluted)	Temperature, velocity, moisture, flow rate	Pitot tube, thermocouple, gas sampling	Manometer, thermocouple readout, CEMS	U.S. EPA Methods 1, 2, 3A and 4 (40CFR60, App. A)
	Filterable total PM, PM10, PM2.5 mass	Hot in-stack series cyclones and filter	Gravimetry	U.S. EPA Method PRE-4 (U.S. EPA, 1999b)
	Condensable PM mass (organic and inorganic) and composition ($SO_4^=$, Cl^-, NO_3^-, NH_4^+, elements)	Iced impingers (DI water)	Organic extraction, titration and gravimetric analysis; ion chromatography, colorimetry, inductively coupled plasma atomic emission spectrometry	U.S. EPA Method 202, with supplemental analysis (U.S. EPA, 1996)
	Condensable PM mass and $SO_4^=$	Iced impingers (80% isopropanol)	Gravimetric; Ion chromatography	U.S. EPA Method 8, modified (40CFR60, App. A)
	NH_3	Acid Iced impingers (0.1N HCl)	Colorimetry	BAAQMD Method ST-1B (BAAQMD, 1982);
	Formaldehyde	Midget iced impingers (DI water) train	Colorimetry; DNPH extraction and HPLC	U.S. EPA CTM-037 (U.S. EPA, 2001)
Stack – dilution sampler (Hildemann et al., 1989)	PM2.5 mass and chemical composition	Ringed Teflon® membrane filter	Gravimetry	U.S. EPA, 1999a
	Elements	Ringed Teflon® membrane filter	X-ray fluorescence	U.S. EPA, 1999f
	OC and EC	Quartz fiber filter	Thermal-optical analysis	DRI, 2000
	Cations/anions ($SO_4^=$, Cl^-, NO_3^-, NH_4^+)	Quartz fiber filter	Ion chromatography	U.S. EPA, 1999a
	SO_2	K_2CO_3-impregnated cellulose-fiber filter	Ion chromatography	Johnson and Atkins, 1975
	NH_3	Citric acid-impregnated cellulose-fiber filter	Colorimetry	Chow and Watson, 1998
	Speciated VOC	Tenax® sorbent	Trap-purge/ cryogenic preconcentration HRGC with FID, MSD and FTIR	Zielinska et al., 1996
	Speciated VOC (C_2 and greater)	Stainless steel canisters	GC with FID and ECD	US EPA Method TO-15 (U.S. EPA, 1999e)
	Carbonyls	DNPH-coated silica gel cartridges	HPLC	UP EPA Method TO-11A (U.S. EPA, 1999c)
	Speciated SVOC	Filter/PUF/ XAD®-4/PUF	Electron impact GC with MSD and FTIR (multiple ion detection)	U.S. EPA Method TO-13A (U.S. EPA, 1999d)
Combustion air inlet – ambient air	PM2.5 mass	Ringed Teflon® membrane filter	Gravimetry	U.S. EPA, 1999a
	Elements	Ringed Teflon® membrane filter	X-ray fluorescence	U.S. EPA, 1999f
	OC and EC	Quartz fiber filter	Thermal-optical analysis	DRI, 2000
	Cations/anions ($SO_4^=$, Cl^-, NO_3^-, NH_4^+)	Quartz fiber filter	Ion chromatography	U.S. EPA 1999a
	NH_3	Citric acid-impregnated cellulose-fiber filter	Colorimetry	Chow and Watson, 1998
	SO_2	K_2CO_3-impregnated cellulose-fiber filter	Ion chromatography	Johnson and Atkins, 1975
	Speciated VOC	Tenax® sorbent	Trap-purge/ cryogenic preconcentration HRGC with FID, MSD and FTIR	Zielinska et al., 1996
	Speciated VOC (C_2 and greater)	Stainless steel canisters	GC with FID and ECD	US EPA Method TO-15 (U.S. EPA, 1999e)
	Carbonyls	DNPH-coated silica gel cartridges	HPLC	UP EPA Method TO-11A (U.S. EPA, 1999c)
	Speciated SVOC	Filter/PUF/ XAD®-4	Electron impact GC with MSD and FTIR (multiple ion detection)	U.S. EPA Method TO-13A (U.S. EPA, 1999d)

		Stack						Combustion Air Inlet
	Time	Velocity	Method PRE-4/202	Method 17/8	CTM-037	BAAQMD ST-1B	Dilution Sampler	Ambient Sample
06-Sep-01	8:00							
Thurs.	9:00	9:30						
	10:00							
	11:00		Run 1	Run 1	Run 1	Run 1	Run 1	
	12:00		11:56	11:55	11:55	11:55	11:55	
	13:00							
	14:00							
	15:00							
	16:00							
	17:00		17:56	17:55	17:55	17:55	17:55	
	18:00	18:15						
07-Sep-01	8:00	8:49						
Fri.	9:00		Run 2	Run 2	Run 2	Run 2	Run 2	
	10:00		10:26	10:25	10:25	10:25	10:25	
	11:00							
	12:00							
	13:00							
	14:00							
	15:00							
	16:00		16:26	16:25	16:25	16:25	16:25	
	17:00							
08-Sep-01	8:00	8:32	Run 3	Run 3	Run 3	Run 3	Run 3	
Sat.	9:00		9:11	9:10	9:10	9:10	9:10	
	10:00							
	11:00							
	12:00							
	13:00							
	14:00							
	15:00	15:43	15:11	15:10	15:10	15:10	15:10	
	16:00							
09-Sep-01	8:00	8:22	Run 4	Run 4	Run 4	Run 4	Run 4	
Sun.	9:00		9:01	9:00	9:00	9:00	9:00	
	10:00							
	11:00							
	12:00							
	13:00							
	14:00		15:01	15:00	15:00	15:00	15:00	
	15:00	15:45						
	16:00							

Figure 3-1. Chronology for NGCC-SF Tests (Site Bravo).

		Stack						Combustion Air Inlet
	Time	Velocity	Method PRE-4/202	Method 17/8	CTM-037	BAAQMD ST-1B	Dilution Sampler	Ambient Sample
10-Sep-01 Mon.	7:00						DSB	
	8:00						8:50	
	9:00							
	10:00							
	11:00							
	12:00							
	13:00							
	14:00						14:50	
	15:00							
11-Sep-01 Tues.	8:00							
	9:00							9:58
	10:00							
	11:00							
	12:00							
	13:00							
	14:00							
	15:00							15:58
	16:00							

DSB = dilution system blank

Figure 3-1. Chronology for NGCC-SF Tests (Site Bravo) (continued).

IN-STACK METHOD TESTS

Total particulate matter (PM), PM10 and PM2.5 that are filterable at stack temperature were determined using in-stack hot cyclone and filter methods. CPM, defined as the material collected in chilled impingers and which EPA defines as part of PM10 and PM2.5 emissions, also was measured for the in-stack samples. NH_3 and formaldehyde were measured using different sampling trains and methods described below.

In-Stack Total Filterable PM, PM10 and PM2.5

EPA Preliminary Method PRE-4 was used to measure filterable PM, PM10 and PM2.5 emissions. The method uses two in-stack cyclones (Andersen Model Case-PM10 and Case-PM2.5), the first with a cut point of 10 μm and the second with a cut point of 2.5 μm, followed by an in-stack QFF in series (Figure 3-2). The method is a variation of EPA Method 201A (40 CFR 51, Appendix M). EPA Method PRE-4 is identical to EPA Method 201A, except for the

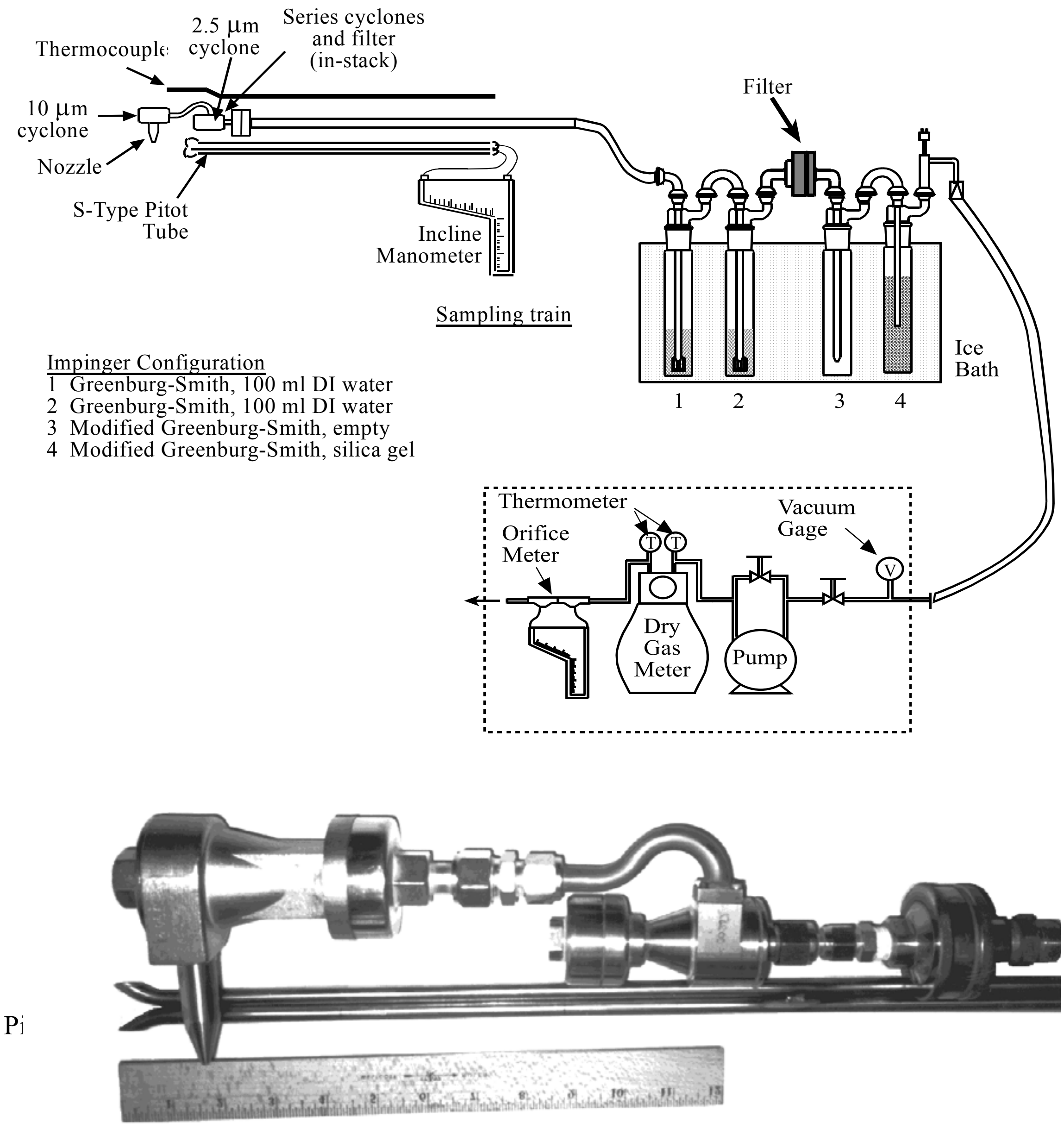

Figure 3-2. PM10/PM2.5 Train Configuration for Method PRE-4/202.

addition of a second cyclone with a cut point of 2.5 μm and separate recovery of the PM2.5-10 fraction of the sample. EPA Method 201A is accepted by state/local regulatory agencies for demonstrating compliance with statutory and permitted PM10 emission limitations. Often, the method is accepted for gas combustion without the cyclones using only the in-stack filter, assuming that all particles are smaller than 10 μm. This effectively becomes EPA Method 17.

EPA Method 5 and its variations, which uses no cyclones and employs filters heated to a specified temperature in an oven external to the stack, also are often accepted for demonstrating compliance with PM10 emission limits for gas combustion sources, based on the same assumption. Historical test data on gas-fired systems show a significant range of filterable PM emissions, which is thought to be due in part to coarse and large particles that occasionally appear in the exhaust due to spurious debris entering the system (Rubenstein, 2001). EPA Method PRE-4 was selected for these tests because:

- It enables determination of total particulate matter, PM10 and PM2.5 that are solids at stack temperature;
- It prevents spurious particles larger than 2.5 micrometers from being counted in the filterable PM2.5 fraction, thereby preserving a valid comparison of PM2.5 results measured by Method PRE-4 and the dilution sampler.

The sampling time was six hours at a sampling rate of approximately 0.4 cubic feet per minute (cfm) for each of the four runs. The sampling rate was selected based on the stack gas temperature and the volumetric flow rate necessary to achieve the target particle cut diameters in the cyclones. The long sampling time was selected to maximize sample volume due to the low PM concentration expected in the exhaust, while restricting the total duration of the daily tests to fit within a single crew shift. Sampling was performed according to the methods as published except for the following modifications and clarifications:

- The sample was collected from a single traverse point near a point of average velocity so that the dilution system and Method PRE4/202 sample probes could be co-located to preserve the integrity of the dilution sampling method comparison. It is assumed that any PM present is small enough to mix aerodynamically in the same manner as a gas[2]; therefore, the magnitude of the particle concentration profile was assumed to be similar to the gas concentration profile;
- A modified filter weighing procedure (API, 2001a, 2001b, 2001c) was employed in an effort to improve the precision of the gravimetric analysis for low particulate concentration. An O-ring, a filter and a filter support were all placed together in an aluminum foil pouch and weighed as a unit. All three components were recovered

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[2] Gas-particle slip is significant for typical exhaust gas conditions based on Stokes-Cunningham slip calculations and the experimental work of May (1967).

together into the same foil pouch after sampling to minimize negative bias due to filter breakage.

A second particulate sampling train was run in order to compare CPM measured by two different methods: a modified EPA Method 8 train and EPA Method 202. The front half of the second train employed an in-stack filter to determine total particulate emissions according to EPA Method 17. The front-half of the second train was not analyzed except for Runs 3 and 4 due to an inadvertent shortage of properly conditioned filters. The front-half measurements from the Method 17 train are not considered critical to these tests.

The particulate mass collected in the two cyclones and on the filter was determined gravimetrically. The QFFs (Pallflex Tissuequartz 2500QAT-UP-47 millimeter, mm) were weighed before and after testing on an analytical balance with a sensitivity of 10 micrograms (μg). In an effort to improve the accuracy and precision of the gravimetric results, the filters, filter support and stainless steel O-ring seals were weighed together to minimize post-test loss of filter matter during sample recovery. Pre- and post-test weighing was performed after drying the filters in a desiccator for a minimum of 72 hours, then repeat weighings were performed at a minimum of six-hour intervals until constant weight to within 0.5 milligrams was achieved. Probe and cyclone acetone rinses were recovered in glass sample jars for storage and shipment, and then transferred to tared beakers for evaporation and weighing. Acetone and filter blanks also were collected and analyzed. See Section 4 for discussion of data treatment.

Condensable Particulate Matter Mass and Chemical Analysis

EPA Method 202. CPM was determined using EPA Method 202. Total sampling time was six hours for all runs. After the in-stack filter used for the Method PRE-4 train, the sample passed through a heated Teflon® line to a series of four impingers placed in the ice bath. Impingers 1 and 2 were standard Greenburg-Smith impingers containing distilled deionized (DI) water; the third was a modified Greenburg-Smith impinger containing DI water; the fourth was an empty modified Greenburg-Smith impinger; and the fifth contained silica gel. A QFF (Pallflex Tissuequartz 2500 QAT-UP) was placed between the third and fourth impingers to improve capture efficiency for any aerosols that may have passed the first three impingers. The impinger train was purged with nitrogen for one hour at the conclusion of each test run to eliminate dissolved SO_2. The additional water impinger was included to accommodate the large amount of water expected due to the longer sampling run times. The contents of the impinger train were recovered with DI water followed by dichloromethane.

A number of optional procedures specified in Method 202 (Figure 3-3) were applied to improve the accuracy, precision and understanding of the results:

- An aliquot of the raw impinger sample was withdrawn and analyzed for $SO_4^{=}$ prior to the organic extraction;
- Following the organic extraction, the inorganic fraction was air dried at ambient temperature to prevent loss of chloride ion (Cl^-) and $SO_4^{=}$ before titration;
- The air-dried sample was titrated with ammonium hydroxide using phenylphthalein to stabilize sulfuric acid (H_2SO_4) and hydrochloric acid, if present, as ammonium sulfate and ammonium chloride, respectively. H_2SO_4 is very hygroscopic which can interfere with the constant weight procedure.
- The final dried residue was re-suspended and analyzed for Cl^-.

Previous tests (England et al., 2000; Corio and Sherwell, 2000) found that a majority of the particulate matter emissions from gas-fired sources consists of CPM. To obtain an understanding of the composition of the material collected in the impingers, additional analysis of the inorganic CPM residue was performed to speciate its constituents. After gravimetric analysis, the inorganic residue was re-suspended by sonicating in 100 milliliters (mL) of DI water, then an aliquot was analyzed for anions and cations (bromide, Cl^-, fluoride, NO_3^-, phosphate and $SO_4^{=}$) by ion chromatography, for NH_4^+ by colorimetry. The remaining sample was analyzed for elements by first digesting the sample in concentrated nitric acid and analyzing by inductively coupled plasma/mass spectrometry (ICP/MS).

EPA Method 8 (modified). CPM also was determined by EPA Method 8 (Figure 3-4), which uses a four-impinger train. In the standard form of the method, impinger 1 contains 80 percent

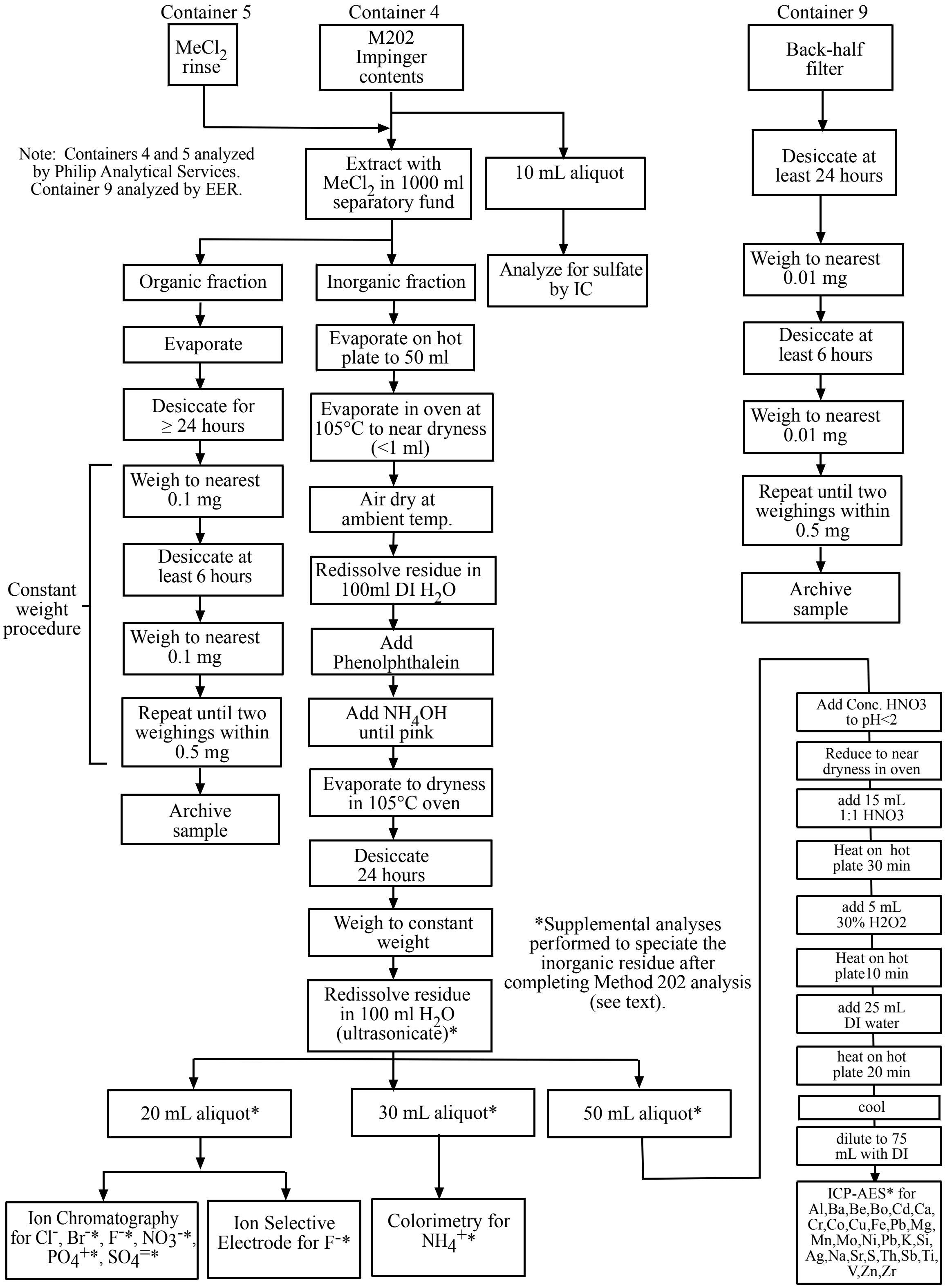

Figure 3-3. Modified Method 202 Sample Analysis Procedure.

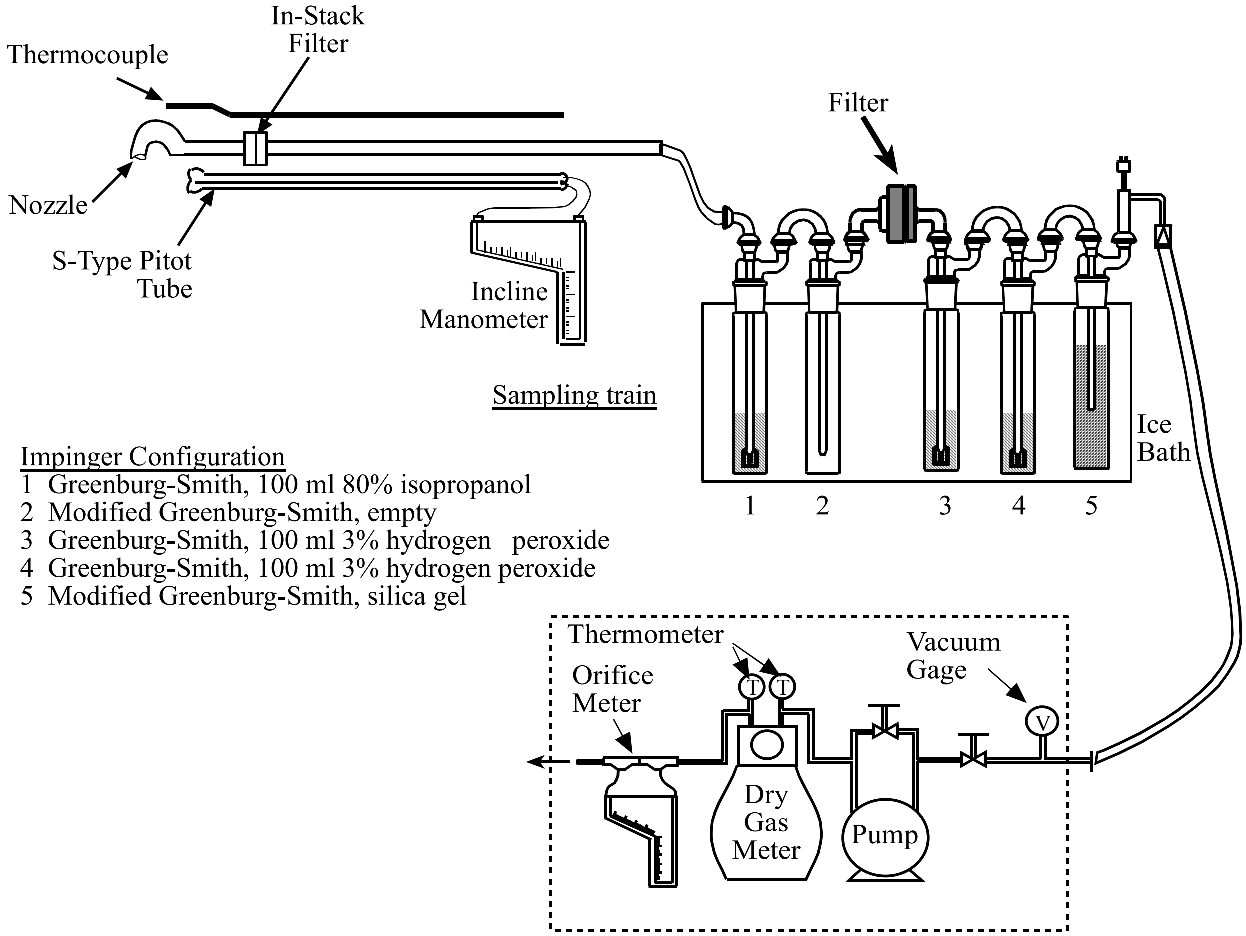

Figure 3-4. CPM Collection Train for Method 8 with In-stack Filter per Method 17.

reagent American Chemical Society (ACS) grade isopropanol (IPA) to capture H_2SO_4 mist; impingers 2 and 3 contain hydrogen peroxide to capture sulfur dioxide and impinger 4 contains silica gel. An empty impinger was added between impingers 1 and 2 to collect excess moisture during the long sample run. A filter was placed behind the empty impinger and analyzed for $SO_4^=$ content. The sampling rate was isokinetic for six hours at 0.4 cfm (to match the sample flow rate of the PRE-4/202 train). A 15-minute purge with ambient air at the average flow rate for the test was performed after sampling was completed. The contents of the IPA impinger and probe rinse were dried and weighed to determine CPM mass. The residue was then re-suspended with DI water and analyzed by barium-thorin titration to determine $SO_4^=$ content. The contents of the peroxide impingers were also analyzed using barium thorin titration to obtain SO_2 concentration.

NH_3

Concentrations of NH_3 were measured using Bay Area Air Quality Management District (BAAQMD) 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 3-5). The sampling train consists of four impingers connected in series. The first and second impingers contain a 0.1 normal solution (0.1N) of hydrochloric acid (HCl), the third impinger is empty, and the fourth impinger contains a weighed amount of silica gel. NH_3 in the sampled gas is collected in the impingers and in rinses of the sample probe and connecting glassware. Sampling occurred for six hours at a constant rate of 0.5 cfm.

After the test, the train was purged for five minutes with ambient air. 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. NH_3 content was determined by Nessler colorimetry.

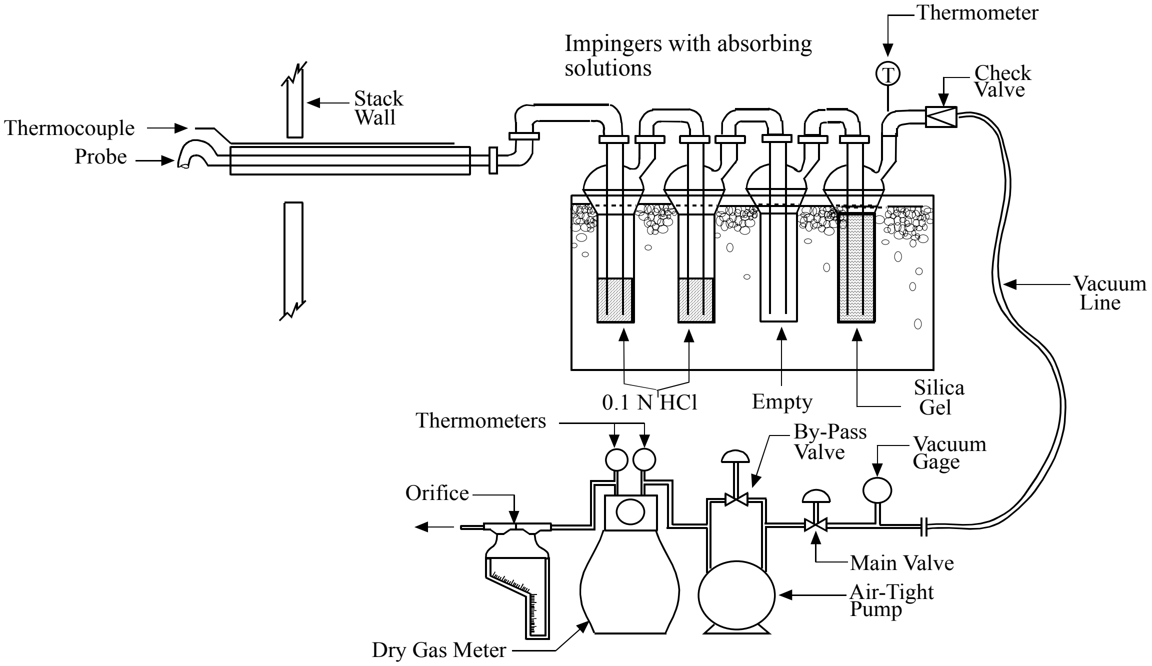

Figure 3-5. NH_3 Collection Train for BAAQMD Method ST-1B.

Formaldehyde

Formaldehyde in the stack gas was determined by the acetyl acetone derivitization method (EPA CTM-037), with supplemental analytical modifications to achieve lower detection limits. CTM-037 is approved by EPA as an alternative method for gas-fired internal combustion engines, and is accepted by a number of states (e.g., Mississippi) for ad hoc testing. Of interest to this test project was to assess its suitability for NGCC-SF testing and whether analytical enhancements might improve method performance. This method uses a series of midget impingers placed in an ice bath. The first impinger is empty to remove most of the moisture from the sample, followed by an impinger containing 10 mL of organic-free water and finally by an impinger containing silica gel to remove moisture. Sample runs were six hours long at a constant sampling rate of 0.2 to 0.4 liters per minute (L/min). Samples were analyzed by acetyl acetone derivitization and spectrophotometry according to the method. In addition, an experimental analysis using extraction with dinitrophenylhydrazine followed by analysis using high performance liquid chromatography (HPLC) was performed to determine if lower detection limits could be achieved.

NO_X, CO and O_2

The plant is equipped with a CEMS with instruments for monitoring NO_x, CO and O_2 concentrations. This system was used for determining NO_x emissions and for documenting process operating conditions during the tests. The CEMS extracts stack gas samples through a stainless steel probe, drawn by a sample pump located in the CEMS shelter at ground level. The sample is filtered at the stack and transported to the CEMS shelter through a heated sample line, where it is dried in a condenser (Teflon® coil in a refrigerated bath), filtered again, and further dried using a permeation dryer. The conditioned sample is then distributed to the instrumental gas analyzers for determining NO_x, CO and O_2 concentrations in the sample. A paramagnetic analyzer is used for O_2, a non-dispersive infrared absorption analyzer is used for CO, and a chemiluminescence analyzer is used for NO_x. The CEMS data are logged and transmitted to a centralized plant data system. The CEMS system is designed and operated in accordance with 40 CFR 60 Appendix A, Performance Specifications and with local requirements.

DILUTION SAMPLER TESTS

PM2.5 mass and chemical speciation in the stack gas was determined using a dilution sampler (Figure 3-6). A stainless steel probe with a buttonhook nozzle was used to withdraw the stack gas sample at a rate of approximately 25 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 and an activated carbon bed to remove gaseous organic compounds. After passing through a tube length equal to 10 sampler 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 through a sampling manifold of three cyclone separators to remove particles larger than 2.5 µm into a sampling module to provide a uniform gas stream for the sample collection media (TMF, QFF, potassium carbonate (K_2CO_3)-impregnated cellulose fiber filter, citric acid-impregnated cellulose-fiber filter, Tenax® tubes, DNPH-coated silica gel cartridges, stainless steel canisters and TIGF/PUF/ XAD®-4/PUF cartridge). The sample flow rate through the probe was monitored using a venturi flow meter and thermocouple. The venturi velocity head was measured continuously during the test using a pressure transducer and a Magnehelic® gauge. 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 six hours.

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 (ºC) 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 HiVol 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.

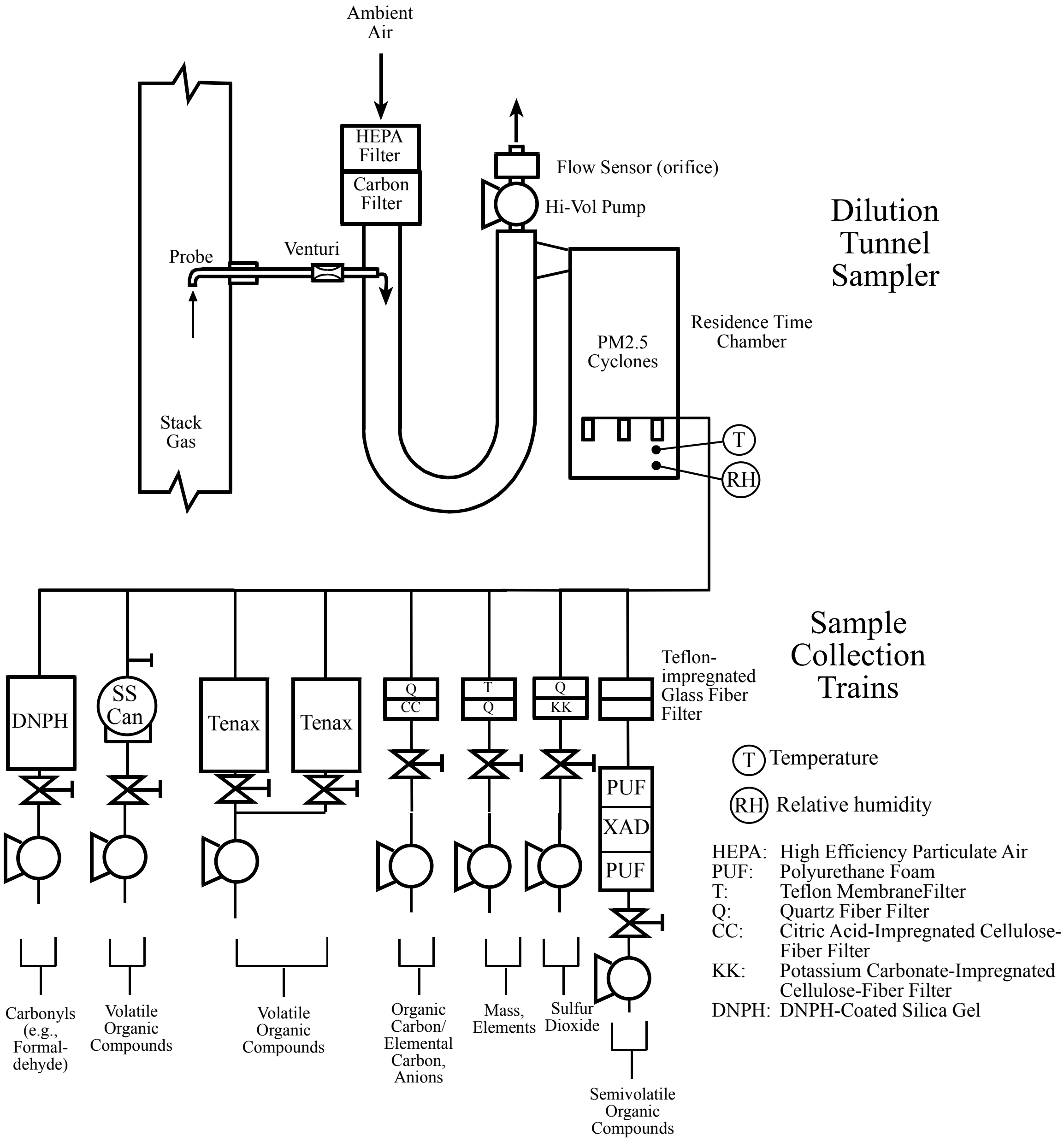

Figure 3-6. Dilution Sampling System.

The sample flow rate through the probe was monitored using a heated (150 ºC) venturi flow meter, with pressure transducer and thermocouple. The venturi velocity head was measured continuously during the test using a pressure transducer. 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 was initially 40:1 (dilution air:raw sample) based on Hildemann et al. (1989). The prior work of Hildemann et al. (1989) suggests that, in this design, mixing between the sample and the dilution air 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. 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 29 to 33 during the stack runs (Table 3-2), which resulted in average diluted sample temperatures of 25 to 35 degrees Celsius (°C; 77 to 95 degrees °F). Variations in dilution ratio within the range of these tests are expected to have no effect on mass of aerosols present at stack temperature and an effect on condensable organic compounds of less than 3 percent (Hildemann et al., 1989). The effect of sample temperature variations within the range of these tests is not known for this type of source and dilution sampler, although no correlation between diluted sample temperature and PM2.5 mass was found in prior tests (API, 2001a, 2001b, 2001c). Diluted sample temperatures are within 5 °C of the ambient air temperature. Aerosol growth due to moisture condensation is expected to be negligible below a relative humidity (RH) of approximately 70 percent (Seinfeld and Pandis, 1998). A 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. Dilution sampler design and operating parameters, including dilution ratio, are being evaluated in a separate pilot scale evaluation that will be discussed in a separate report.

A single ambient air sample was collected using the dilution sampler. The sampling setup was modified by attaching a three-cyclone manifold (similar to the one inside the residence time chamber) directly to the sampling module without the use of the dilution sampler. The ambient air sample was drawn into the module without dilution or filtration for a sampling period of six hours. The same sampling media were used as described below and in Figure 3-6. Ambient air was sampled at a location adjacent to the combustion air intake for the NGCC-SF.

Table 3-2. Dilution Sampler Operating Conditions (Site Bravo).

Parameter	Units	Run 1 06-Sep-01	Run 2 07-Sep-01	Run 3 08-Sep-01	Run 4 09-Sep-01	Ambient 11-Sep-01
Ambient Air Temp.	^{o}C	32.8	30.2	23.0	21.9	21.3
Ambient RH	%	17.3	26.2	46.2	50.8	55.8
Dilution Chamber Temp.	^{o}C	35.1	32.4	25.9	25.2	NA
Dilution Chamber RH*	%	12.1	24.6	46.6	49.5	NA
Stack Sample Flow Rate	dry slpm	14.1	14.9	17.0	14.9	NA
Dilution Ratio	--	33.0	32.9	29.5	29.3	NA
Teflon Filter Flow Rate (mass, elements)	dry slpm	73.9	73.5	73.8	73.7	73.6
Quartz Filter Flow Rate (ions, OC/EC)	dry slpm	71.0	71.3	73.5	73.7	73.2
Citric Acid Filter Flow Rate (NH_3)	dry slpm	71.0	71.3	73.5	73.7	73.2
K_2CO_3 Filter Flow Rate (SO_2)	dry slpm	74.0	74.2	74.1	73.7	74.3

RH = relative humidity

*RH sensor failed. Calculated from ambient air humidity, dilution ratio, stack gas moisture and sample temperature.

PM2.5 Mass

Samples for PM2.5 mass measurements were collected on a 47-mm diameter polymethylpentane ringed, 2.0 µm pore size, TMF (Gelman No. RPJ047) placed in a two-stage Savillex (Minnetonka, Minnesota) filter holder. The filter packs were plugged directly into the bottom of the sampling module to ensure that no handling of the filters was required in the field. The flow rate through the filter was set prior to sample collection at a target rate of 75 standard liters per minute (sL/min) with a needle valve and monitored during sampling using a Thermo Scientific Incorporated (TSI) mass flow meter (Model 4043). Weighing was performed on a Cahn 31 electro-microbalance with ± 1 microgram sensitivity.

Elements

Energy dispersive x-ray fluorescence (ED-XRF) analysis was performed on the TMFs 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), sulfur (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.

A Kevex Corporation Model 700/8000 energy dispersive x-ray fluorescence (ED-XRF) analyzer with a side-window, liquid-cooled, 60 kilo electron 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 millimeters, 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 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 of 16 samples under five excitation conditions required a total of approximately 6 hours.

$SO_4^=$, NO_3^-, Cl^- and $NH_4^\pm$

Samples for determining water-soluble Cl^-, NO_3^-, $SO_4^=$ and NH_4^+ were collected on 47 mm QFFs (Pallflex Tissuequartz 2500QAT-UP-47mm). The flow rate through the filter was set prior to sample collection at a target rate of 75 standard liters per minute (sL/min) with a needle valve and monitored during sampling using a TSI mass flow meter (Model 4043).

For analysis, each QFF was cut in half and one filter half was placed in a polystyrene extraction vial with 15 mL of DI water. The remaining half was used for determination of OC and EC as described below. 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. The associated filter half was archived in the original petri slide. Cl^-, NO_3^-, $SO_4^=$ and NH_4^+were measured with a

Dionex 2020i ion chromatograph (IC). Approximately 2 mL of the filter extract was injected into the IC.

Organic and Elemental Carbon

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 CO_2 by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO_2); 3) reduction of CO_2 to methane (CH_4) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantification of CH_4 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).

Volatile Organic Compounds

Tenax®. Glass tubes filled with Tenax®-TA (a polymer of 2,6-diphenyl-p-phenylene oxide) solid adsorbent were used to collect VOC samples. Two Tenax® cartridges in parallel were used simultaneously for each test run due to the low concentrations expected in the sample. Each cartridge contained approximately 0.2 grams of Tenax® resin. A sample rate of approximately 0.1 L/min through each Tenax® tube was used. The flow rate through the Tenax® cartridges was controlled and monitored with a mass flow controller during sampling.

The Tenax® samples were analyzed by the thermal desorption-cryogenic preconcentration method, followed by high-resolution gas chromatographic separation and FID to determine individual hydrocarbons for peak quantification, and/or combined mass selective/Fourier transform infrared detection (MSD/FTIR), for peak identification. The resultant peaks were quantified and recorded by the chromatographic data systems.

Canisters. In order to more fully speciate the VOCs, canister samples were taken to capture VOCs with a carbon number between two and ten. An integrated sample was collected in a canister downstream of the dilution sampler using a pump and flow control device to maintain a constant sample flow rate into the canister over the entire sampling period. The flow rate used is a function of the final desired sample pressure and the specified sampling period, for our purposes, 17 mL per minute (mL/min).

For analysis, a known volume of gaseous sample is passed through a cryogenically cooled trap, cooled with liquid argon, cryogenically trapping out carbon number of 2 (C_2) and heavier VOCs without trapping methane. The trap containing the condensed VOC is 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 is by FID while detection of the halogenated compounds is by electron capture detection (ECD), and the resultant peaks are quantified and recorded by an electronic integrator and by the chromatographic data system.

SVOCs

Samples were collected using a filter followed by an adsorbent cartridge. The media used for collecting SVOCs were 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 was transferred from the sampling manifold through a 3/8-inch copper manifold leading to a momentum diffuser chamber followed by the filter and cartridge holder. The flow through the sampler was monitored continuously by a mass flow meter and kept at a target flow rate of 113 L/min.

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 sample gas were collected by drawing sample through a cartridge impregnated with acidified 2,4-DNPH. The resulting products (hydrazones) in the cartridge are measured in the laboratory using HPLC to determine the levels of the carbonyl compounds originally present in sample. Typically, C_1-C_6 carbonyl compounds, including benzaldehyde, are measured effectively by this technique. The target flow rate used for this sample was 0.4 L/min.

Sulfur Dioxide

Filter packs containing a QFF followed by a potassium carbonate impregnated cellulose-fiber filters were used to collect SO_2 gas downstream of the dilution sampler. The target flow rate used for this sample was 75 L/min. These filters were extracted with hydrogen peroxide and then analyzed using IC.

NH_3

Filter packs containing a QFF followed by a citric acid impregnated cellulose-fiber filter were used to collect NH_3 gas downstream of the dilution sampler. The target flow rate used for this sample was 75 L/min. These filters were extracted with DI water and then analyzed using automated colorimetry.

4. TEST RESULTS

All stack emission results are presented in units of milligrams 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 is 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 minimum in-stack detection limits achieved for all measured substances are given in Table 4-1. 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 field blank results, are discussed in Sections 6 and 7.

PROCESS OPERATING CONDITIONS

NGCC-SF operating conditions during testing are summarized in Table 4-2. The operating conditions for each run varied with normal plant operation near full load, and included supplementary firing (duct burners on) for some of the runs. Therefore, the tests are not considered representative of any particular operating condition but rather are the average of the operating conditions during the test. The NGCC-SF operated an average of approximately 102 percent of the rated generator output for Runs 1 and 2. Runs 3 and 4 were performed on

Table 4-1. Approximate In-Stack Detection Limits Achieved for Site Bravo Tests.

Substance	Dilution Tunnel mg/dscm	In-stack methods mg/dscm	Substance	Dilution Tunnel mg/dscm	In-stack methods mg/dscm	Substance	Dilution Tunnel mg/dscm	Substance	Dilution Tunnel mg/dscm
Total FPM mass	--	6.1E-1	Pb	4.7E-5	5.7E-4	E-trimethylnaphthalene	1.7E-6	Pyrene	6.8E-6
FPM10 mass	--	4.3E-1	Pd	1.7E-4	--	F-trimethylnaphthalene	1.6E-6	9-Anthraldehyde	4.6E-5
FPM2.5 mass	1.2E-3	2.6E-1	Rb	1.6E-5	--	2,3,5+I-trimethylnaphthalene	5.1E-6	Retene	1.0E-4
Organic CPM	--	1.4E-1	S	7.8E-5	1.7E-3	2,4,5-trimethylnaphthalene	1.4E-5	Benzonaphthothiophene	3.4E-6
Inorganic CPM	--	1.4E-1	Sb	2.8E-4	1.4E-3	J-trimethylnaphthalene	1.4E-5	1-MeFl+C-MePy/Fl	2.7E-5
SO4=	1.9E-3	1.4E-2	Se	1.9E-5	--	1,4,5-trimethylnaphthalene	1.6E-4	B-MePy/MeFl	1.7E-6
NO3-	1.9E-3	1.4E-2	Si	9.9E-5	2.9E-3	Acenaphthylene	1.8E-4	C-MePy/MeFl	1.7E-6
NH4+	1.9E-3	1.4E-2	Sn	2.7E-4	--	Acenaphthene	4.4E-5	D-MePy/MeFl	1.7E-6
Cl-	1.9E-3	1.4E-2	Sr	1.7E-5	2.9E-5	Fluorene	2.1E-4	4-methylpyrene	3.4E-6
NH3	4.9E-4	1.3E-3	Ti	4.5E-5	2.9E-4	Phenanthrene	1.4E-5	1-methylpyrene	1.4E-5
SO2	1.2E-3	3.0E-1	Tl	3.9E-5	--	A-methylfluorene	1.8E-4	Benzo(c)phenanthrene	1.9E-5
Ag	1.9E-4	2.9E-4	U	3.6E-5	--	1-methylfluorene	1.1E-4	Benz(a)anthracene	1.0E-5
Al	1.6E-4	8.6E-4	V	3.9E-5	2.9E-4	B-methylfluorene	1.1E-4	7-methylbenz(a)anthracene	1.0E-5
As	2.5E-5	--	Y	2.0E-5	--	9-fluorenone	2.3E-4	Chrysene	3.4E-6
Au	4.9E-5	--	Zn	1.7E-5	2.9E-4	Xanthone	6.8E-6	Benzanthrone	1.5E-5
Ba	8.1E-4	2.9E-5	Zr	2.7E-5	2.9E-4	Acenaphthenequinone	1.0E-5	Benz(a)anthracene-7,12-dionene	6.3E-5
Br	1.6E-5	--	OC	1.4E-2	--	Perinaphthenone	1.7E-3	1,4-chrysenequinone	8.5E-6
Ca	7.0E-5	5.7E-3	EC	3.2E-3	--	A-methylphenanthrene	8.2E-5	Benzo(b+j+k)fluoranthene	1.7E-6
Cd	1.9E-4	5.7E-5	Naphthalene	1.7E-3	--	2-methylphenanthrene	3.4E-6	7-methylbenzo(a)pyrene	1.2E-5
Cl	1.6E-4	--	2-methylnaphthalene	1.1E-4	--	B-methylphenanthrene	1.9E-5	Benzo(e)pyrene	1.0E-5
Co	1.4E-5	2.9E-4	1-methylnaphthalene	6.5E-5	--	C-methylphenanthrene	4.8E-5	Perylene	3.4E-6
Cr	3.0E-5	1.1E-4	Biphenyl	1.1E-4	--	1-methylphenanthrene	3.8E-5	Benzo(a)pyrene	1.0E-5
Cu	1.7E-5	1.7E-4	1+2-ethylnaphthalene	2.2E-4	--	Anthrone	1.7E-6	Indeno[123-cd]pyrene	1.0E-5
Fe	2.3E-5	5.7E-4	2,6+2,7-dimethylnaphthalene	1.8E-4	--	Anthraquinone	9.2E-5	Benzo(ghi)perylene	1.0E-5
Ga	3.0E-5	--	1,3+1,6+1,7-dimethylnaphthalene	3.9E-4	--	2,3-Benzofluorene	1.1E-5	Dibenzo(ah+ac)anthracene	1.0E-5
Hg	4.1E-5	--	1,4+1,5+2,3-dimethylnaphthalene	1.7E-4	--	3,6-dimethylphenanthrene	8.0E-5	Coronene	1.0E-5
In	2.0E-4	--	1,2-dimethylnaphthalene	1.2E-4	--	A-dimethylphenanthrene	8.0E-5	Volatile Organic Compounds	9.6E-4
K	9.5E-5	2.9E-2	2-Methylbiphenyl	2.7E-4	--	B-dimethylphenanthrene	5.6E-5	Formaldehyde	4.7E-3
La	9.7E-4	--	3-Methylbiphenyl	3.9E-4	--	C-dimethylphenanthrene	5.6E-5	Acetaldehyde	1.3E-2
Mg	1.2E-13	1.4E-3	4-Methylbiphenyl	3.2E-5	--	1,7-dimethylphenanthrene	5.6E-5	Propionaldehyde	3.3E-3
Mn	2.5E-5	1.4E-4	Dibenzofuran	1.1E-4	--	D-dimethylphenanthrene	5.1E-5	Crotonaldehyde	4.7E-3
Mo	4.2E-5	1.4E-4	Bibenzyl	4.2E-3	--	E-dimethylphenanthrene	2.6E-5	MEK	4.7E-3
Na	1.2E-13	2.9E-3	A-trimethylnaphthalene	3.2E-6	--	Anthracene	0.0E+0	Glyoxal	3.0E-3
Ni	1.4E-5	5.7E-4	B-trimethylnaphthalene	1.7E-6	--	9-methylanthracene	7.8E-5	Valeraldehyde	5.4E-3
P	8.8E-5	2.9E-3	C-trimethylnaphthalene	1.4E-5	--	Fluoranthene	3.4E-6		

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

Parameter	Units	Run 1	Run 2	Run 3	Run 4	Average	RSD
Date	dd-mmm-yy	6-Sep-01	7-Sep-01	8-Sep-01	9-Sep-01		
Start time	hh:mm	11:55	10:25	9:10	9:00	--	--
End time	hh:mm	17:55	16:25	15:10	15:00	--	--
Turbine fuel flow rate	klb/hr	72.9	73.0	68.0	62.3	69.0	7%
Duct burner fuel flow rate*	klb/hr	8.1	8.7	0.12	0.00	4.23	114%
Total fuel flow rate	klb/hr	81.0	81.7	68.1	62.3	73.3	13%
Total fuel flow rate	scfm	30,948	30,107	22,340	20,438	25,958	21%
Steam power augmentation	--	Yes	Yes	Yes	Yes	--	--
Ambient air temperature	°F	73.9	71.1	62.8	62.6	67.6	9%
Gas turbine exit gas temperature	°F	1,139	1,139	1,131	1,126	1,134	1%
Compressor inlet air pressure	in. H2O	3.55	3.56	3.24	2.96	3.33	9%
Compressor inlet air temperature	°F	63.0	62.2	63.0	63.1	62.8	1%
Barometric pressure (plant data)	in. Hg	29.76	29.76	29.76	29.76	29.76	0%
Barometric pressure (stack test data)	in. Hg	29.85	29.90	29.90	29.85	29.88	0%
Compressor air discharge pressure	psig	212.7	213.6	196.3	185.5	202.0	7%
Inlet air humidity	lb H2O/lb air	0.0128	0.0128	0.0128	0.0128	0.0128	0%
Oxidation catalyst gas temperature	°F	688	691	638	627	661	5%
Ammonia feed rate	lb/hr	167	163	106	80	129	33%
Generator electrical output	MW	244.3	245.5	206.1	196.6	223.1	11%
Stack gas NO_x Concentration (dry, 15% O_2)	ppmv	4.0	4.0	2.5	1.5	3.0	40%
Stack gas CO Concentration (dry, 15% O_2)	ppmv	2.4	2.8	0.7	0.8	1.7	64%
Stack gas O_2 Concentration (dry, as measured)	%v	12.5	12.4	13.8	13.9	13.1	6%
Gross heat input	MMBtu/hr	1,906	1,921	1,602	1,465	1,723	13%
Process steam output flow rate	klb/hr	295	261	85	8	162	85%
Combustion reference temperature	°F	2,407	2,406	2,369	2,356	2,385	1%
Ambient temperature**	°F	91.0	86.3	73.5	71.3	80.5	12%
Ambient relative humidity**	%	17	26	46	51	35	45%

* Duct burners were on for Runs 1 and 2, intermittent for Run 3 (total of approx. 30 minutes) and off for Run 4

** Based on measurements by GE EER at the stack sampling location due to plant relative humidity sensor failure.

weekend days when power and steam demands were lower, and the NGCC-SF operated at approximately 82-85 percent of capacity. It should be noted that the HRSG duct burners were on during Runs 1 and 2, on briefly during of Run 3 and completely off during Run 4. Thus, although the plant output met the test plan goal of 80 percent of rated capacity or greater, conditions varied significantly during the tests.

The inlet air humidity sensor was reported by the facility to be malfunctioning during testing, and indicated the same value during all stack test runs. This did not affect the test results.

The average gross heat input (based on fuel higher heating value) to the unit during the tests was obtained from the fuel flow rate reported by plant process data. The average gross heat input is used to convert in-stack emission rates (lb/hr) to emission factors in pounds of pollutant per million British thermal units (lb/MMBtu) of gas fired, which are presented in Section 5.

Previous analyses of the natural gas used at the facility, from the same utility's gas distribution system as in these tests, indicate an average natural gas sulfur level of 0.25 to 0.30 grains/100 standard cubic feet (scf), with a maximum level of approximately 0.50 grains/100 scf (as elemental sulfur). Assuming an average natural gas gross (higher) heating value of 1020 British thermal units (Btu)/scf, this corresponds to an average sulfur level in the natural gas of approximately 3.5E-4 to 4.2E-4 lb/MMBtu, and a maximum of 7.0E-4 lb/MMBtu. Expressed as SO_2, these values correspond to an average level of 7.0E-4 to 8.4E-4 lb/MMBtu and a maximum of 1.4E-3 lb/MMBtu

PRELIMINARY TESTS

Preliminary tests were conducted to establish single point of average velocity through each of the sampling ports for sample collection. Stack traverses with the S-type Pitot probe before and after each test run were used to determine the average stack gas velocity for flow rate calculations.

STACK GAS CONDITIONS AND FLOW RATE

A summary of the stack conditions during testing is presented in Table 4-3. Stack gas temperature during the tests ranged from 224 to 236 °F.

Table 4-3. Average Stack Conditions (Site Bravo).

Parameter	Units	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD
Date		6-Sep-01	7-Sep-01	8-Sep-01	9-Sep-01		
Stack Temperature	°F	225	224	231	236	229	2%
Moisture	%v	12.5	13.6	8.5	8.5	10.8	25%
Velocity	ft/s	84	83	75	72	79	8%
	m/s	25.6	25.3	22.9	21.9	23.9	8%
Flow Rate	acfm	1,081,600	1,060,300	962,000	921,900	1,006,500	8%
	dscfm	723,600	721,000	667,600	634,500	686,700	6%
	dscmm	20,490	20,420	18,910	17,970	19,450	6%

(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

IN-STACK AND IMPINGER METHOD RESULTS

Particulate Mass

Filterable particulate matter (FPM). Filterable particulate matter (FPM) results as measured by Method PRE-4 and Method 17 are presented in Table 4-4. The acetone rinse results are corrected for the acetone field reagent blank, which caused the corrected net weights to become negative (-0.24 to –1.21 milligrams (mg)) for 9 of 15 samples. Net weights for all of the QFFs also are slightly negative (-0.40 to –0.83 mg, standard deviation 0.20 mg). These results are indicative of the limitations of these methods for such low PM concentrations. Negative net or blank-corrected weight results are reported as ”ND” and excluded from sums, averages and standard deviations. Some of the results are below the in-stack minimum detection limits (MDLs) given in Table 4-1. Special procedures were applied in an attempt to achieve the lowest practical MDLs, including use of a more sensitive balance (0.00001 grams) for weighing filters and special filter handling procedures. The total in-stack MDLs (sum of MDLs for each sample fraction) for FPM given in Table 4-1 assume that these results are near “zero” for this method (net or blank-corrected weights less than zero for several of the sample fractions indicates that this is a reasonable assumption). Therefore, in-stack MDLs are estimated using 3 times the sum of the standard deviation of the duplicate tare and final weight results (in mg) divided by the average sample gas volume of approximately 3.5 dry standard cubic meters (dscm) (see Section 7 for further details and discussion). This yields a somewhat lower MDL than using the standard deviation of the net weights themselves, and reflects more on the analytical capability of the method rather than on the overall capability of the method. It is not current convention to report FPM results below the MDL as simply “ND” since widely accepted MDLs for this method have not been established for low concentration applications. Therefore, the results in Table 4-4 are flagged “<” to indicate results for one or more of the fractions included in the total are below the estimated MDLs for this test program.

In Table 4-4 and subsequent tables throughout this report, the shaded area represents results detected in fewer than 3 of the test runs. These results are considered qualitative, for information only, and not suitable for use in quantitative analysis without further corroboration.

Method PRE-4. Total FPM, which includes all PM collected in the in-stack nozzle/cyclone assembly and on the in-stack filter, ranged from 0.06 to 1.18 mg/dscm. FPM smaller than (<) 10 µm, which includes the portion of total FPM collected downstream of the PM10 cyclone, is 0.06 to 0.47 mg/dscm. FPM < 2.5 µm, which includes the portion of FPM collected downstream of the PM2.5 cyclone and on the in-stack filter, is only present at levels above detection limits for one run after blank correction, at a level of 0.06 mg/dscm. These in-stack concentrations correspond to total weight gains in the sampling train of 0.2 to 4 milligrams (mg). Uncorrected (for blanks) net weights in each fraction of -0.8 to 4.8 mg. It should be noted that virtually all of the FPM weight gains are from the acetone rinses, because net weights for all of the filters are slightly negative. If negative net weights are not set to zero after blank correction, total PM weight gains would range from –1.4 to 2.8 mg.

Table 4-4. Filterable Particulate Matter Results (Site Bravo).

Parameter	Units	Results										
Run Number	-		Run 1 *(i)*		Run 2 *(i)*		Run 3 *(ii)*		Run 4 *(iii)*		Average	RSD
Date	-		6-Sep-01		7-Sep-01		8-Sep-01		9-Sep-01			
Total FPM**	mg/dscm	<	1.18	<	0.39	<	0.06	<	0.06	<	0.42	126%
(by Method PRE-4)	lb/hr	<	3.2	<	1.0	<	0.15	<	0.13	<	1.13	128%
Total FPM	mg/dscm	NA		NA		<	0.48	<	0.26	<	0.37	42%
(by Method 17)*	lb/hr					<	1.2	<	0.67	<	0.95	42%
FPM <10 µm**	mg/dscm	<	0.47	<	0.07	<	0.06	ND		<	0.20	117%
(by Method PRE-4)	lb/hr	<	1.3	<	0.19	<	0.15	ND		<	0.54	119%
FPM <2.5 µm**	mg/dscm	ND		ND		<	0.06	ND		<	0.06	n/a
(by Method PRE-4)	lb/hr	ND		ND		<	0.15	ND		<	0.15	n/a

Shaded area represents substances not detected in all valid test runs. Average not considered reliable for quantitative analysis.
< - one or more of the sample fractions are lower than the minimum detection limit.
n/a - not applicable
ND - not detected
NA - not analyzed
RSD - relative standard deviation
*Method 17 results are not considered reliable in this test due to problems with filter tare weights.
**Filter net weights were negative for all runs due to the extremely low particulate loading, and are treated as zeros in summing the data. All of the reported particulate mass is from the acetone rinses. FPM<2.5 um includes 1 acetone rinse, FPM<10 um includes 2 acetone rinses, and Total FPM includes 3 acetone rinses (see Method PRE-4 for further details).
(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

Acetone reagent blanks and filter blanks are significant relative to the samples. Acetone blank corrections ranged from 28 to more than 100 percent of the acetone rinse net weights. All filter weights are negative, with the field blank filter comprising from 36 to 76 percent of the negative mass. This result reflects the extremely low PM loading in the stack and suggests that the PM mass loading at the stack in these tests may be near or below the minimum detection and/or lower quantification limits of the overall method. Further discussion of PM mass detection limits and variability is presented in Section 7.

Method 17. The total FPM results obtained from Method 17 do not agree well with the results from Method PRE-4, on a run-to-run basis, with the Method 17 result being four to eight times higher than the Method PRE-4 result. This difference is most likely due to the low particulate loading of the source being at or below detection limits. The tare weights for these filters were not measured with sufficient resolution for reliable results. Therefore, the Method 17 data should be considered qualitative only and not representative of the actual emissions. The results are not suitable for use in emission factor development.

CPM. Since there has been much controversy over the most appropriate method of measuring CPM at the low levels encountered with gas-fired units, CPM was simultaneously measured using two different iced impinger methods for comparison purposes. The results are summarized in Table 4-5. For the purposes of this report, the MDL for CPM mass is defined as the tolerance (0.5 mg) for the gravimetric analysis procedure. The net weights of the inorganic impinger residues are generally higher than the MDL, while the most of the organic residue net weights are below the MDL. Results lower than the MDL are flagged "<" in Table 4-5.

> Method 202. The average total CPM, which is the sum of the evaporated organic extract (corrected for dichloromethane reagent blank), the inorganic residue (corrected for addition of ammonium hydroxide (NH_4OH) and water reagent blank) and the back-half filter, is 2.0 mg/dscm. The reagent blanks are not significant relative to the sample masses; the water reagent blank ranged from 12-28 percent of the uncorrected net weight and the dichloromethane blank is below detection limits. The total average inorganic CPM is 1.8 mg/dscm. $SO_4^=$ concentration was determined from an aliquot taken from the impinger catch and rinse before it was extracted with the organic solvent. 55 percent of the inorganic CPM is accounted for by $SO_4^=$, with a concentration of 0.99 mg/dscm. The average organic CPM concentration is 0.39 mg/dscm, with three of the four runs being

below detection limits (detection limit is approximately 0.29 mg/dscm). This result is lower than previous tests on a gas-fired boiler and gas-fired steam generator that had organic CPM concentrations of 0.6 and 0.8 mg/dscm, respectively.

Table 4-5. Condensable Particulate Matter Results (Site Bravo).

Parameter	Units	Value					
Run Number	-	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD
Date	-	6-Sep-01	7-Sep-01	8-Sep-01	9-Sep-01		
Inorganic CPM (Method 202)	mg/dscm	1.2	2.4	1.3	2.4	1.8	36%
	lb/hr	3.2	6.4	3.3	5.7	4.6	35%
Organic CPM (Method 202)	mg/dscm	0.39	ND	ND	ND	< 0.39	n/a
	lb/hr	1.0	ND	ND	ND	< 1.0	n/a
Total CPM (Method 202)	mg/dscm	1.7	< 2.4	< 1.3	< 2.4	< 2.0	28%
(corrected for NH_4^+ and H_2O)	lb/hr	4.6	< 6.5	< 3.3	< 5.8	< 5.1	28%
Total CPM (Method 8)	mg/dscm	1.7	1.7	0.87	1.7	1.5	26%
	lb/hr	4.7	4.4	2.3	4.2	3.9	27%
Sulfate (as $SO_4^=$) in	mg/dscm	1.1	1.1	0.76	0.99	0.99	16%
Impingers (Method 202)	lb/hr	3.0	3.0	1.9	2.3	2.5	21%
Sulfate (as $SO_4^=$) in	mg/dscm	1.2	1.1	0.79	1.1	1.0	17%
Impingers (Method 8)	lb/hr	3.2	3.1	2.0	2.7	2.8	20%

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

RSD - relative standard deviation

CPM - condensable particulate matter

< - one or more of the sample fractions are lower than the detection limit.

n/a - not applicable

(i) Duct burners on.

(ii) Duct burners on for first 30 minutes of 360 minute test run.

(iii) Duct burners off.

CPM concentration is approximately 33 times greater than FPM2.5, on average, however FPM2.5 is below detection limits in 3 of 4 runs, so this relationship has a high uncertainty. On average, approximately 91 percent of the CPM is found in the inorganic fraction, while 6 percent is found in the organic fraction; the remaining mass (3 percent) is accounted for in the impinger filter that was not speciated. The inorganic CPM results are somewhat variable from run to run, with a standard deviation equal to 36 percent of the arithmetic mean. Organic CPM was only found at detectable levels in one run. CPM results are corrected for dichloromethane and water recovery blank results. The inorganic CPM data also are corrected for NH_4^+ retained and combined water released in the acid base titration, as described in Method 202. These results are discussed further in Section 7.

Method 8. A modified version of EPA Method 8 was recently proposed by Rubenstein for measuring particulate emissions from natural gas-fired combustion turbines (2001). Tests using this method were conducted simultaneously with the Method 202 tests to provide a comparison. This method does not differentiate between organic and inorganic CPM, and presumes that the only true CPM from natural gas combustion is from H_2SO_4 arising from sulfur in the fuel, which will be collected in the first impinger (isopropanol solution). The average total CPM concentration is 1.5 mg/dscm, approximately equal to that determined from the Method 202 Train. The concentration of $SO_4^=$ reported by the two different methods is similar. However, a larger percentage of the CPM in the Method 8 train is accounted for by the $SO_4^=$ number, indicating that the Method 202 train perhaps is capturing something that the Method 8 train does not. This result indicates that the methods, when performed as indicated in this report, give similar results, but more study is needed to determine the reasons for the differences in results.

Additionally, the re-suspended inorganic residues of the Method 202 trains were analyzed for a broader range of elements and ions to more fully speciate the mass. These results are presented in Table 4-6; the results are corrected by subtracting the reagent blank, adjusted for relative volume. $SO_4^=$, Cl^-, NH_4^+, Na, and Ca are the five most abundant compounds in the inorganic CPM fraction. The $SO_4^=$ determined from the residue agrees well with the $SO_4^=$ determined from the raw impinger solution aliquot, indicating that $SO_4^=$ was conserved well during the analysis. Soluble $SO_4^=$, Na, Cl^- and NH_4^+ account for an average of 1.5 mg/dscm, or 84 percent, of the inorganic CPM mass as presented in Table 4-5 (Na accounts for 2 percent but was detected in only a single run so it is not considered reliable). The remaining elements that were detected account for an average of 0.009 mg/dscm, or 0.5 percent, of the average inorganic CPM mass. Agreement between the reconstructed mass based on the residue species and the gravimetric result is good; the reconstructed mass accounts for approximately 75 percent of the inorganic CPM mass, on average. The additional analysis also confirms that $SO_4^=$ is the dominant compound in the inorganic residue; it is believed the majority of $SO_4^=$ found in the impinger contents is an artifact resulting from oxidation of gaseous SO_2 in the stack gas (Wien et al., 2001). These results and issues are discussed further in Section 7.

Table 4-6. Speciation (mg/dscm) of Method 202 Back-Half Impinger Catch (Site Bravo).

	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD
$SO_4^=$	1.07E+0	1.08E+0	7.38E-1	9.69E-1	9.65E-1	16%
Cl^-	ND	4.52E-1	ND	2.46E-1	< 3.49E-1	42%
NH_4^+	7.42E-2	4.07E-1	3.10E-2	1.92E-1	1.76E-1	96%
Na	ND	ND	ND	2.88E-2	< 2.88E-2	n/a
Ca	ND	ND	ND	5.03E-3	< 5.03E-3	n/a
Zn	2.13E-4	3.50E-3	3.44E-3	4.88E-3	3.01E-3	66%
Mn	7.30E-4	1.23E-4	3.43E-4	5.26E-5	3.12E-4	98%
Sr	ND	ND	2.44E-4	3.20E-4	< 2.82E-4	19%
Ba	6.58E-5	4.50E-5	3.19E-5	4.62E-5	4.72E-5	30%

Shaded area represents substances not detected in all valid test runs. Average not considered reliable for quantitative analysis.
< - one or more blank corrected values less than zero
n/a-not applicable; two or more runs not detected
ND - blank corrected value less than zero
(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

Formaldehyde. EPA Method Conditional Test Method (CTM)-037 (also known as the acetyl acetone or Celanese method) for determining formaldehyde emissions originally was developed for the wood products industry and recently was validated by GRI and approved by EPA as an alternative method for natural gas-fired stationary combustion sources (U.S. EPA, 2001). A number of states recently have allowed its use during initial permit tests to gather background data on NGCC-SF emissions. Results using the acetyl acetone derivitization and spectrophotometric analysis procedure for formaldehyde are below the method limit of quantification (LOQ) (approximately 56 ppb for the sampling conditions in these tests) for all runs. An additional experimental analysis of the sample by HPLC did not yield any useful additional information; since levels in the field blanks and reagent blank are similar to levels in the samples. These results indicate that formaldehyde concentrations present during this test likely are below the capability of this method.

NH_3. NH_3 was measured using BAAQMD Method ST-1B. The results (presented later with other NH_3 results in Table 4-15) are consistent with previous tests on this unit.

DILUTION SAMPLER RESULTS

Particulate Mass

PM2.5 mass measurements using the dilution sampler 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.

Results from these measurements show that PM2.5 concentrations and emission rates average 0.18 mg/dscm and 0.48 lb/hr, respectively, with a relative standard deviation of 104 percent, based on TMF weight (Table 4-7). Run 2 dominates the average, and is almost an order of magnitude higher than the other two detected runs. The filter weight for Run 4 is negative. It is believed that a procedural error resulted in some of the filter cassettes being overtightened, leading to slight physical damage to the filters. Although no physical damage to the filter was detected on inspection, the data is flagged as undetected. This may also contribute to the relatively poor precision (compared to previous tests on other gas-fired sources with the same dilution sampler) of the PM2.5 mass results. These results are more than an order of magnitude lower than the sum of FPM2.5 and CPM measured by EPA Methods PRE-4 and 202, and despite the high relative standard deviation of the results, the absolute standard deviation is considerably smaller than for the Method PRE-4/202 results. On average, PM2.5 concentration measured in the stack gas is approximately five times higher using the dilution sampler than the concentration measured in the ambient air. The annual (2001) average ambient PM2.5 concentration at a monitoring station near the plant is 0.025 mg/dscm, which is (coincidentally) in exact agreement with the measured ambient PM2.5 value during these tests.

The concentration of PM2.5 using the dilution sampler is approximately two times higher than FPM <2.5 µm measured using Method PRE-4, however FPM2.5 is below detection limits in 3 of 4 runs, so this relationship has a high uncertainty. Concentration of PM2.5 using the dilution sampler is almost 33 times lower than CPM measured using Method 202. CPM is normally included in regulatory definitions of PM10. CPM emission measurements are strongly method dependent because the dilution sampler replicates conditions experienced by the stack emissions

Table 4-7. Dilution Sampler PM2.5 Results (Site Bravo).

	Units	Results						
Run Number	-	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD	Ambient
Date	-	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01		(%)	11-Sep-01
PM2.5 mass	mg/dscm	1.1E-01	3.8E-01	3.3E-02	NV	c 1.8E-01	104	2.5E-02
	lb/hr	3.0E-01	1.0E+00	8.3E-02	NV	4.8E-01	105	n/a

n/a-not applicable
NV - Test run Not Valid. Filter damaged due to overtightening of filter cassette.
RSD- Relative Standard Deviation
c - 95% Confidence Lower Bound of the Average concentration is lower than the Ambient concentration indicating it is likely the results are not significantly different at the 95% confidence level.
(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

as they mix with the atmosphere more accurately than Method 202. Due to the SO_2 and excessive condensation artifacts associated with Method 202, it is believed the dilution sampler results are more representative of the true primary PM2.5 emissions.

$SO_4^=$, NO_3^-, Cl^-, NH_4^+ and Soluble Na^+

QFFs were analyzed for $SO_4^=$, Cl^-, NO_3^-, NH_4^+ and sodium ion (Na^+). Of these, NO_3^- is highest in average concentration at 0.015 mg/dscm, followed by $SO_4^=$ at 0.013 mg/dscm (Table 4-8). NH_4^+ was not detected in two of the three valid runs. The TMF net weight (PM2.5 mass) is negative for Run 4. Ion speciation data from Run 4 showed qualitative agreement to the other runs; however, the reconstructed mass cannot be validated against the TMF results so the Run 4 PM2.5 ion speciation results are invalidated and flagged ("NV"). All ions in the field blank are present below detectable levels (see Section 6 for additional discussion of blanks).

The QFFs used for these measurements have the potential for a positive $SO_4^=$ bias due to adsorption and oxidation of gaseous SO_2. The average $SO_4^=$ is 2.9 times higher than the elemental S content measured on the TMF (see later discussion), which is in very good agreement with the expected value of 3.0 based on the ratio of molecular weights, indicating that any bias due to SO_2 adsorption is not significant. The average particulate $SO_4^=$ concentration from the dilution sampler is less than 1/100 of the average $SO_4^=$ concentration reported above for Method 202. This difference lends further support to the likelihood of a significant measurement artifact in Method 202 due to oxidation of gaseous SO_2 in the sample. Concentrations of particulate NO_3^{-}, $SO_4^{=}$ and Na^{+} measured in the stack gas are within an order of magnitude of their respective concentrations measured in the ambient air.

Table 4-8. Dilution Sampler $SO_4^{=}$, NO_3^{-}, Cl^{-} NH_4^{+} and Soluble Na^{+} Results (Site Bravo).

Parameter	Units	Value						
Run Number	-	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD (%)	Ambient
Date	-	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01			11-Sep-01
Sulfate	mg/dscm	4.8E-3	3.0E-2	2.7E-3	NV	c 1.3E-2	122	2.1E-03
	lb/hr	1.3E-2	8.2E-2	6.7E-3	NV	c 3.4E-2	123	n/a
Nitrate	mg/dscm	5.5E-3	3.9E-2	2.4E-3	NV	c 1.5E-2	130	2.1E-03
	lb/hr	1.5E-2	1.0E-1	6.0E-3	NV	c 4.2E-2	130	n/a
Chloride	mg/dscm	6.4E-3	2.2E-2	2.5E-3	NV	c 1.0E-2	100	8.2E-04
	lb/hr	1.7E-2	6.0E-2	6.2E-3	NV	c 2.8E-2	101	n/a
Ammonium	mg/dscm	ND	7.8E-3	ND	NV	< d 7.8E-3	n/a	4.9E-04
	lb/hr	ND	2.1E-2	ND	NV	< d 2.1E-2	n/a	n/a
Soluble Na	mg/dscm	3.5E-4	1.5E-3	3.3E-4	NV	c 7.3E-4	93	8.4E-05
	lb/hr	9.6E-4	4.1E-3	8.2E-4	NV	c 2.0E-3	95	n/a

Shaded area represents substances not detected in 3 valid test runs. Average not considered reliable for quantitative analysis.
n/a- not applicable
ND - Not Detected
NV - Test run Not Valid
RSD- Relative Standard Deviation
c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.
d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.
(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

The results for Run 2 show significantly higher concentrations of all ions compared to the other two valid runs. Element results, discussed later in this section of the report, also are elevated for Run 2. The in-stack method results for FPM do not show the same trend, while the inorganic CPM mass results for Run 2 do. None of the CPM residue speciation results follows the same trend. The elevated level of all ions and elements, rather than one or subset of them, suggests the possibility of a measurement error (e.g., an error in measurement of dilution ratio) or an unusual process or ambient air condition that occurred during this run. The latter possibility is mildly corroborated by the inorganic CPM mass results. The data were reviewed for potential explanations. While the trend remains somewhat perplexing, no conclusive or highly probable explanation could be found.

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 ranged from 0.079 to 0.19 mg/dscm, which is well above its concentration measured in the ambient air (Table 4-9) but still very low in absolute terms relative to other types of sources. EC was detected in only two of the test runs at concentrations of 0.0097 and 0.017 mg/dscm. The TMF for PM2.5 mass had a negative net weight for Run 4. Carbon speciation data from Run 4 showed qualitative agreement to the other runs, but should not be used for quantitative purposes, therefore the results from the chemical speciation of the PM2.5 are invalidated and flagged "NV" in the table for that run. OC accounts for approximately 94 percent of the total carbon mass. The average EC concentration measured in the stack gas is 15 times greater than in the ambient air; the average OC concentration in the stack gas is sixteen times greater than the ambient concentration. Although it is not possible to determine if the stack and ambient OC and EC concentrations are significantly different at the 95 percent confidence level because only a single ambient air sample was collected, the ambient concentrations are not within in two standard deviations of the stack result. This result indicates that the stack and ambient air results may be significantly different, but it is not possible to say that they are different with a known degree of confidence. OC and EC are below detection limits in the field blank (see Section 6 for additional discussion of blank results).

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 OC concentrations on the backup filter and on the primary filter are not significantly different at the 95 percent confidence level. Some individual VOCs were measured in the sample at concentrations similar to OC, and the sum of all the measured VOCs is several times greater than OC (see Section 5 of the report), so even adsorption of a small fraction of the VOCs could account for the measured OC. Therefore, the magnitude of any bias in the OC result is potentially significant, and may be on the same magnitude as the measured value. Contradicting this observation is the fact that the total PM2.5 mass is reasonably well accounted for by the reconstructed mass (within 34 percent), and on average OC comprises 80 percent of the reconstructed mass, albeit with high uncertainty associated with all the measurements. The OC artifact is the subject of ongoing studies, 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.

Table 4-9. OC/EC as Measured by the Dilution Sampler (Site Bravo).

Parameter	Units	Value						
Run Number	-	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average*	RSD	Ambient
Date	-	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01		(%)	11-Sep-01
Organic Carbon (OC) **	mg/dscm	1.9E-1	1.5E-1	7.9E-2	NV	a b 1.4E-1	41	8.8E-3
	lb/hr	5.2E-1	4.1E-1	2.0E-1	NV	a b 3.8E-1	44	n/a
Elemental Carbon (EC)	mg/dscm	9.7E-3	1.7E-2	ND	NV	< c 1.3E-2	38	8.9E-4
	lb/hr	2.6E-2	4.5E-2	ND	NV	< c 3.6E-2	38	n/a
Total Carbon (TC)	mg/dscm	2.0E-1	1.7E-1	7.9E-2	NV	< a b c 1.5E-1	42	9.6E-3
	lb/hr	5.5E-1	4.6E-1	2.0E-1	NV	4.0E-1	45	n/a
Backup Filter OC ***	mg/dscm	1.4E-1	1.4E-1	1.0E-1	NV	b 1.3E-1	18	3.1E-3
	lb/hr	3.9E-1	3.7E-1	2.5E-1	NV	b 3.4E-1	22	n/a

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

* TC Average calculated as average of TC runs, not OC Average + EC Average.

** OC measurements are subject to a potential positive bias from adsorption of VOC species. Refer to footnote *** and Sections 6 & 7 for further discussion.

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

n/a- not applicable
ND - Not Detected
NV - Test run Not Valid
RSD- Relative Standard Deviation
< - not detected in one or more runs
a - 95% Confidence Lower Bound of the Average concentration is less than the dilution system 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 ambient air concentration
(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

Particulate Carbon Speciation. SVOCs were measured to determine the extent to which OC measured on the QFFs could be speciated, and to identify specific particulate organic compounds that could serve as markers for source apportionment. SVOCs were determined on the combined TIGF/PUF/ XAD®-4/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. Only six substances were detected in three or more test runs (Table 4-10). Of these six, 1+2-ethylnaphthalene, phenanthrene, 2-methylphenanthrene and D-methylpyrene (MePy)/methylfluorene (MeFl) also were detected in the field blank at concentrations that are not significantly different (within 2 standard deviations) from the stack concentration, and hence are considered indistinguishable from the background of the measurement methods. Anthrone was not detected in the field blank, but the average stack concentration is less than 2 standard deviations above the MDL (hence not significantly above

Table 4-10. Primary Particulate Carbon Speciation Results (Site Bravo).

Parameter	In-stack Concentrations (mg/dscm)							Ambient
Run Number	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD	MDL	mg/dscm
Date	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01		(%)		11-Sep-01
1+2-ethylnaphthalene	5.2E-4	5.6E-4	3.9E-4	4.7E-4	b 4.9E-4	15	2.2E-4	2.9E-5
Phenanthrene	7.2E-4	9.3E-4	6.8E-5	8.8E-5	b c 4.5E-4	97	1.4E-5	1.3E-4
7-methylbenzo(a)pyrene	1.4E-4	8.1E-5	8.8E-5	1.6E-4	1.2E-4	34	1.2E-5	ND
2-methylphenanthrene	2.4E-4	4.8E-5	6.8E-6	3.8E-6	b c 7.4E-5	150	3.4E-6	1.1E-5
D-MePy/MeFl	8.5E-5	2.3E-5	6.8E-6	9.9E-6	b c 3.1E-5	117	1.7E-6	8.2E-7
Anthrone	4.8E-5	1.8E-5	2.4E-5	1.9E-5	2.7E-5	51	1.7E-6	3.0E-7
1,4+1,5+2,3-dimethylnaphthalene	2.9E-3	6.2E-4	ND	ND	< c 1.7E-3	91	1.7E-4	1.9E-5
2-methylnaphthalene	3.0E-4	1.2E-3	ND	ND	< c 7.5E-4	85	1.1E-4	1.9E-4
Acenaphthene	1.0E-3	2.8E-4	ND	ND	< b c 6.5E-4	81	4.4E-5	7.8E-5
1-methylnaphthalene	1.8E-4	6.4E-4	ND	ND	< c 4.1E-4	81	6.5E-5	8.9E-5
Xanthone	2.2E-5	3.3E-4	ND	ND	< b c 1.7E-4	124	6.8E-6	1.9E-6
Pyrene	2.0E-4	4.7E-5	ND	ND	< c 1.3E-4	89	6.8E-6	6.8E-6
Fluoranthene	1.1E-4	9.0E-5	ND	ND	< 1.0E-4	17	3.4E-6	1.2E-5
A-trimethylnaphthalene	1.1E-4	8.1E-5	ND	ND	< b c 9.5E-5	20	3.2E-6	1.0E-5
C-trimethylnaphthalene	8.8E-5	8.1E-5	ND	ND	< 8.5E-5	6	1.4E-5	7.4E-6
B-trimethylnaphthalene	5.4E-5	5.3E-5	ND	ND	< 5.3E-5	2	1.7E-6	8.2E-6
7-methylbenz(a)anthracene	2.2E-5	8.5E-5	ND	ND	< 5.3E-5	83	1.0E-5	ND
E-trimethylnaphthalene	4.1E-5	2.7E-5	ND	ND	< c 3.4E-5	28	1.7E-6	4.8E-6
F-trimethylnaphthalene	3.3E-5	3.0E-5	ND	ND	< 3.1E-5	8	1.6E-6	4.8E-6
1,3+1,6+1,7-dimethylnaphthalene	ND	5.5E-4	ND	ND	< d 5.5E-4	n/a	3.9E-4	6.5E-5
Dibenzofuran	ND	4.1E-4	ND	ND	< d 4.1E-4	n/a	1.1E-4	6.2E-5
2,6+2,7-dimethylnaphthalene	ND	3.1E-4	ND	ND	< d 3.1E-4	n/a	1.8E-4	4.0E-5
E-dimethylphenanthrene	ND	ND	ND	2.6E-4	< d 2.6E-4	n/a	2.6E-5	ND
Fluorene	ND	2.6E-4	ND	ND	< d 2.6E-4	n/a	2.1E-4	4.4E-5
Biphenyl	ND	2.3E-4	ND	ND	< d 2.3E-4	n/a	1.1E-4	3.6E-5
2,3,5+I-trimethylnaphthalene	ND	ND	ND	1.9E-4	< d 1.9E-4	n/a	5.1E-6	6.7E-6
C-methylphenanthrene	1.7E-4	ND	ND	ND	< d 1.7E-4	n/a	4.8E-5	3.6E-6
C-dimethylphenanthrene	1.5E-4	ND	ND	ND	< d 1.5E-4	n/a	5.6E-5	3.9E-6
1-methylphenanthrene	8.1E-5	ND	ND	ND	< d 8.1E-5	n/a	3.8E-5	3.0E-6
4-methylpyrene	4.4E-5	ND	ND	ND	< d 4.4E-5	n/a	3.4E-6	ND
2,4,5-trimethylnaphthalene	1.4E-5	ND	ND	ND	< d 1.4E-5	n/a	1.4E-5	1.8E-6
C-MePy/MeFl	ND	3.4E-6	ND	ND	< d 3.4E-6	n/a	1.7E-6	ND
Anthracene	8.5E-7	ND	ND	ND	< d 8.5E-7	n/a	0.0E+0	6.5E-6
Naphthalene	ND	ND	ND	ND	d ND	n/a	1.7E-3	2.1E-4
1,2-dimethylnaphthalene	ND	ND	ND	ND	d ND	n/a	1.2E-4	6.4E-6
J-trimethylnaphthalene	ND	ND	ND	ND	d ND	n/a	1.4E-5	1.5E-6
1,4,5-trimethylnaphthalene	ND	ND	ND	ND	d ND	n/a	1.6E-4	5.7E-6
A-methylfluorene	ND	ND	ND	ND	d ND	n/a	1.8E-4	6.0E-6
Acenaphthenequinone	ND	ND	ND	ND	d ND	n/a	1.0E-5	5.5E-7
A-methylphenanthrene	ND	ND	ND	ND	d ND	n/a	8.2E-5	5.6E-6
B-methylphenanthrene	ND	ND	ND	ND	d ND	n/a	1.9E-5	6.5E-7

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

n/a- not applicable; only one run within detectable limits.

MDL - In-stack minimum detection limit (based on minimum analytical detection limit, sample volume, and dilution ratio).

ND - Not Detected

RSD- Relative Standard Deviation

< not detected in all valid tests.

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 Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

(i) Duct burners on.

(ii) Duct burners on for first 30 minutes of 360 minute test run.

(iii) Duct burners off.

the MDL). The concentration of 7-methylbenzo(a)pyrene is significantly (greater than 2 standard deviations) above the MDL, and it was not detected in the field blank or ambient air sample; however, it is only a factor of 10 greater than the MDL and this may not be significantly higher than the LQL (See Chapter 6). LQLs could not be determined based on the single field blank collected in this field campaign, but will be assessed later in the final program report.

Of the remaining 27 SVOCs that were detected, 14 were detected in only one run and 13 were detected in 2 runs. Uncertainties cannot be determined for those detected in only one run, hence results for these SVOCs are not considered reliable indicators of actual emissions. Only six of the 13 substances detected in 2 runs are at concentrations significantly greater than the field blanks and MDLs, but they are within approximately a factor of 10 of the ambient air concentration or the MDL; hence, these are indistinguishable from the background with high confidence. Twenty-five of these 27 substances were detected in Run 1 and/or Run 2, when the duct burners were operating, and only 2 substances were detected in Run 3 and/or Run 4, when the duct burners were not operating (except for a brief period during Run 3).

In summary, it is 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 increased frequency of substances detected during runs when the duct burners were in operation indicates the possibility that slightly more particulate carbon species may be produced during duct burner operation, but the results of these tests are inconclusive due to the low concentrations present in the exhaust and small number of test runs. The SVOCs that were detected in two or more runs account for less than 3 percent of the corrected OC mass[3] measured on the QFFs.

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 eight carbon atoms are too volatile to form aerosols under atmospheric conditions. Tenax® sorbent was used to collect VOCs with a boiling point of approximately 40 °C and greater. The analysis of Tenax® focused only on VOCs with a carbon number greater than seven. An error during Run 1 sampling

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[3] "Corrected OC" equals measured OC multiplied by 1.08 to account for the measured hydrocarbon speciation.

prevented the Tenax® media from being exposed to the sample stream, invalidating the samples for Run 1. A backup sample was used for Run 2 and the ambient sample, so the results in the table for those samples are the sum of the concentrations in the front and backup tubes. The Tenax® sample media is susceptible to degradation from components in the sample stream, producing decomposition byproducts that obscure the actual concentrations in the exhaust gas. The Tenax® results should be viewed as highly uncertain, in particular, for benzaldehyde, benzoic acid, hexadecanoic acid, phenol and acetophenone, which are all believed to be Tenax® decomposition byproducts in these tests.

Seventeen VOCs were detected in only one run at concentrations generally very close (within a factor of 10) to the MDL, hence results for these compounds are not considered representative of actual emissions (Table 4-11). Of the remaining VOCs, the MDL and/or concentrations in the field blank are generally within two standard deviations of the stack concentration and hence the differences are not considered significant. Nonanal, decanal and 1-undecene are the only VOCs with carbon number greater than seven with concentrations significantly above the MDL, the field blank and the ambient air sample. However, these were detected in only two of the three valid test runs and the relative standard deviations are large.

<u>Other VOCs</u>. Other VOCs also were measured using stainless steel canisters to quantify VOCs with carbon number greater than 7 for which Tenax® may not work well, VOCs that could contribute to OC measurement artifacts, and selected hazardous air pollutants (HAPs). The analysis of the canister samples allows for detection of organic species with carbon numbers as low as two.

No ambient air sample was taken concurrent with any of the test runs. A dilution system blank (DSB) was not used or taken for the canister testing at Site Bravo. However, a DSB was subsequently analyzed at another similar site approximately 20 miles away, Site Echo. Site Echo also is a NGCC-SF with oxidation catalyst and SCR of very similar size and configuration. For Site Echo, the 95 percent confidence lower bound of the average concentration of both toluene and methanol was less than the DSB, indicating that they are not distinguishable from background levels. Since the levels of toluene and methanol in the stack samples at Bravo are similar to those at Echo, it is likely that the same conclusion can be drawn for Bravo in the

Table 4-11. Particulate Carbon Precursor (VOC with Carbon Number >8) Results (Site Bravo).

Parameter	In-Stack Concentrations							Ambient
Units	mg/dscm					%	mg/dscm	mg/dscm
Run Number	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD	MDL	
Date	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01				11-Sep-01
Hexadecanoic acid f	ND	* 4.8E-1	1.9E-1	3.0E-2	< b c f 2.3E-1	97	9.6E-04	1.5E-2
Benzaldehyde f	ND	2.1E-1	6.2E-2	4.3E-2	< b c f 1.0E-1	86	9.6E-04	4.8E-3
Acetophenone f	ND	6.1E-2	2.3E-2	2.0E-2	< b c f 3.5E-2	65	9.6E-04	1.4E-3
Styrene	ND	* 7.0E-2	2.0E-2	1.1E-2	< b c 3.3E-2	94	9.6E-04	1.4E-3
Pentadecane	ND	5.6E-2	1.7E-2	1.4E-2	< b c 2.9E-2	80	9.6E-04	1.3E-3
Heptadecane	ND	6.1E-2	3.8E-3	2.3E-3	< c 2.2E-2	149	9.6E-04	1.6E-4
Dodecane	ND	4.7E-2	1.1E-2	8.5E-3	< b c 2.2E-2	98	9.6E-04	9.3E-4
Tetradecane	ND	3.8E-2	1.2E-2	8.3E-3	< b c 1.9E-2	84	9.6E-04	6.8E-4
Phenol f	ND	3.5E-2	1.3E-2	1.0E-2	< b c f 1.9E-2	71	9.6E-04	6.4E-4
Hexadecane	ND	4.0E-2	6.2E-3	4.5E-3	< c 1.7E-2	119	9.6E-04	2.5E-4
Decane	ND	3.4E-2	8.6E-3	6.5E-3	< b c 1.6E-2	93	9.6E-04	1.8E-3
m & p-xylene	ND	2.7E-2	6.4E-3	3.6E-3	< b c 1.2E-2	103	9.6E-04	6.1E-3
Octadecane	ND	3.0E-2	2.4E-3	9.4E-4	< c 1.1E-2	148	9.6E-04	6.9E-5
p-isopropyltoluene	ND	2.4E-2	4.7E-3	3.3E-3	< b c 1.1E-2	107	9.6E-04	3.4E-4
Octanal	ND	1.3E-2	4.6E-3	1.1E-2	< 9.5E-3	46	9.6E-04	3.8E-4
Undecane	ND	1.9E-2	2.8E-3	2.7E-3	< b c 8.0E-3	114	9.6E-04	7.0E-4
Nonane	ND	1.7E-2	3.4E-3	3.1E-3	< b c 7.9E-3	102	9.6E-04	3.3E-3
Biphenyl	ND	1.1E-2	2.6E-3	4.0E-3	< b c 5.9E-3	78	9.6E-04	2.9E-4
Tridecane	ND	1.0E-2	2.5E-3	1.5E-3	< b c 4.8E-3	101	9.6E-04	3.7E-4
Ethylbenzene	ND	9.9E-3	2.5E-3	1.8E-3	< b c 4.8E-3	94	9.6E-04	3.0E-3
o-xylene	ND	8.9E-3	2.3E-3	1.0E-3	< b c 4.1E-3	104	9.6E-04	2.1E-3
1,2,4-trimethylbenzene	ND	7.7E-3	1.9E-3	1.1E-3	< b c 3.5E-3	102	9.6E-04	5.6E-4
m-ethyltoluene	ND	5.6E-3	1.6E-3	9.7E-4	< b c 2.7E-3	91	9.6E-04	5.3E-4
Naphthalene	ND	5.0E-3	1.6E-3	1.2E-3	< c 2.6E-3	80	9.6E-04	6.3E-4
Nonanal	ND	ND	3.3E-2	4.0E-2	< 3.6E-2	14	9.6E-04	4.7E-4
Decanal	ND	4.4E-2	2.5E-2	ND	< c 3.4E-2	40	9.6E-04	1.1E-3
1-undecene	ND	1.0E-2	6.9E-3	ND	< c 8.7E-3	29	9.6E-04	3.4E-4
Dodecene	ND	ND	2.7E-3	5.8E-3	< c 4.2E-3	50	9.6E-04	6.1E-5
3-methyloctane	ND	4.8E-3	1.8E-3	ND	< c 3.3E-3	65	9.6E-04	4.8E-4
Eicosane	ND	ND	4.2E-3	2.0E-3	< 3.1E-3	51	9.6E-04	ND
Cyclohexanone	ND	1.8E-2	ND	ND	< d 1.8E-2	n/a	9.6E-04	7.8E-4
Butyl acetate	ND	1.2E-2	ND	ND	< d 1.2E-2	n/a	9.6E-04	ND
1-nonene	ND	7.4E-3	ND	ND	< d 7.4E-3	n/a	9.6E-04	5.4E-5
1-decene	ND	7.4E-3	ND	ND	< d 7.4E-3	n/a	9.6E-04	ND
2-heptanone	ND	3.6E-3	ND	ND	< d 3.6E-3	n/a	9.6E-04	1.3E-4
Nonadecane	ND	ND	3.5E-3	ND	< d 3.5E-3	n/a	9.6E-04	2.9E-4
1,3-dichlorobenzene	ND	3.0E-3	ND	ND	< d 3.0E-3	n/a	9.6E-04	9.6E-5
2,3-benzofuran	ND	** 2.9E-3	ND	ND	< d 2.9E-3	n/a	9.6E-04	ND
2-methylnaphthalene	ND	2.6E-3	ND	ND	< d 2.6E-3	n/a	9.6E-04	2.0E-4
Propylbenzene	ND	2.2E-3	ND	ND	< d 2.2E-3	n/a	9.6E-04	1.6E-4
Dimethyloctane	ND	2.1E-3	ND	ND	< d 2.1E-3	n/a	9.6E-04	2.9E-4
o-ethyltoluene	ND	2.0E-3	ND	ND	< d 2.0E-3	n/a	9.6E-04	1.5E-4
1,3,5-trimethylbenzene	ND	1.9E-3	ND	ND	< d 1.9E-3	n/a	9.6E-04	2.2E-4
(+/-)-limonene	ND	1.7E-3	ND	ND	< d 1.7E-3	n/a	9.6E-04	1.7E-4
2-methyloctane	ND	1.5E-3	ND	ND	< d 1.5E-3	n/a	9.6E-04	2.6E-4
p-ethyltoluene	ND	1.4E-3	ND	ND	< d 1.4E-3	n/a	9.6E-04	1.7E-4
4-ethyl-o-xylene	ND	ND	9.9E-4	ND	< d 9.9E-4	n/a	9.6E-04	1.7E-4

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

* More than 50% of the compound was collected in the backup sample tube, indicating possible breakthrough

** The compound was detected in the backup sample tube but not detected in the first sample tube, indicating possible breakthrough

n/a- not applicable; detected in only one run; ND - Not Detected; RSD - Relative Standard Deviation

< not detected in all valid runs

MDL - In-stack minimum detection limit (based on analytical minimum detection limit, sample volume and dilution ratio)

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 Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

f - These are subject to contamination from the degradation of Tenax sorbent; therefore, results are highly uncertain.

(i) Duct burners on.

(ii) Duct burners on for first 30 minutes of 360 minute test run.

(iii) Duct burners off.

absence of more detailed data. In addition, the 95 percent confidence lower bound of the average concentration of methanol at Site Bravo was less than the MDL due to the high variability (relative standard deviation (RSD) = 162 percent) of detected concentrations in the stack samples, indicating poor reliability of the measured concentration. 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 these pollutants present in these tests.

The in-stack concentrations of detected compounds are extremely low, with an average of 27 parts per billion (ppb), median of 4 ppb, and 90th percentile of 54 ppb (Table 4-12, in mg/dscm). Most of the compounds are fuel fragments and combustion intermediates or byproducts. Only 7 of the 137 VOCs detected in the stack sample canisters were not detected in the ambient air. 12 VOCs were detected in only one run indicating these results are of questionable validity. 29 compounds were detected in fewer than 3 of the stack test samples. The 95 percent confidence lower bounds for 37 VOCs are less than the ambient air concentration, indicating it is likely they are not significantly different. Ninety-three of the VOCs detected in the stack sample canisters have 95 percent confidence lower bounds greater than the ambient sample. One hundred and eight compounds were detected in three or more valid test runs, most of which have high relative standard deviations contributing to high uncertainty for these compounds; of these, only 34 compounds have concentrations more than two standard deviations greater than their respective concentrations in the ambient air. These 34 compounds comprise 44 percent of the mass represented by all the compounds detected in 3 or more valid runs. Only six compounds (2,3,5-trimethylhexane, 1-decene, toluene, propane, ethane, and octanal) represent more than 80 percent of the mass of compounds that were detected in three or more runs and that are significantly higher than the ambient air concentration. Of these, only toluene is considered a HAP. Two other HAPs (methanol and acetone) also were detected at comparable levels to toluene, but very high relative standard deviations (greater than 100 percent) for these indicate poor reliability because they are not significantly greater than zero, the MDL or ambient air concentration.

Table 4-12. Volatile Organic Compound (VOC) Results from Canisters (Site Bravo).

Parameter	In-Stack Concentrations							Ambient
Units	mg/dscm					(%)	mg/dscm	mg/dscm
Run Number	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD	MDL	
Date	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01				11-Sep-01
Particulate Carbon Precursors (VOC with carbon number 8 and greater):								
2,3,5-trimethylhexane	1.7E-01	1.1E-01	1.4E-01	1.5E-01	1.4E-01	19	1.9E-04	4.4E-03
1-decene	1.6E-01	9.3E-02	1.3E-01	1.5E-01	1.3E-01	22	1.9E-04	4.2E-03
Octanal	4.7E-02	6.0E-02	2.4E-02	2.8E-02	4.0E-02	43	2.2E-04	2.6E-03
Nonanal	8.9E-02	1.2E-02	2.2E-02	2.4E-02	c f 3.7E-02	95	2.1E-04	3.9E-03
Styrene + heptanal	2.5E-02	5.7E-02	1.9E-02	2.7E-02	3.2E-02	53	1.8E-04	1.3E-03
m- & p-xylene	5.2E-02	3.8E-02	1.8E-02	1.2E-02	3.0E-02	61	1.8E-04	3.8E-03
o-xylene	3.7E-02	1.7E-02	9.7E-03	1.7E-02	2.0E-02	58	1.8E-04	1.8E-03
alpha-pinene	6.0E-02	2.1E-03	1.6E-02	1.0E-03	c f 2.0E-02	139	1.8E-04	2.9E-05
2,2,4-trimethylpentane	1.8E-02	1.4E-02	7.0E-03	9.1E-04	1.0E-02	76	1.9E-04	3.4E-04
n-dodecane	2.0E-02	1.0E-02	2.0E-03	5.3E-03	c f 9.4E-03	83	1.9E-04	1.7E-04
n-decane	1.3E-02	1.7E-02	3.8E-03	3.5E-03	9.3E-03	72	1.9E-04	7.0E-04
Ethylbenzene	1.7E-02	9.7E-03	5.6E-03	2.7E-03	c 8.7E-03	70	1.8E-04	1.9E-03
m-ethyltoluene	1.5E-02	9.9E-03	4.6E-03	2.9E-03	8.2E-03	69	1.8E-04	4.4E-04
1,2,3-trimethylbenzene	1.5E-02	7.2E-03	3.8E-03	3.1E-03	7.2E-03	73	1.8E-04	2.5E-04
1,4-diethylbenzene	1.3E-02	5.4E-03	3.3E-03	4.5E-03	6.5E-03	68	1.8E-04	3.6E-04
C10 paraffin A	1.4E-02	ND	4.0E-03	7.3E-04	< c f 6.3E-03	111	1.9E-04	1.6E-04
n-undecane	1.0E-02	9.5E-03	2.2E-03	3.3E-03	6.2E-03	65	1.9E-04	2.5E-04
n-octane	5.9E-03	1.3E-02	1.3E-03	4.4E-03	c f 6.2E-03	81	1.9E-04	2.3E-04
1,2,4-trimethylbenzene	1.1E-02	1.0E-02	1.5E-03	8.5E-04	c f 6.0E-03	93	1.8E-04	7.9E-05
n-nonane	9.2E-03	7.1E-03	2.6E-03	1.6E-03	5.1E-03	70	1.9E-04	6.3E-04
2,3,-trimethylpentane	8.4E-03	5.7E-03	2.9E-03	9.1E-04	4.5E-03	73	1.9E-04	ND
1,3,5-trimethylbenzene	7.6E-03	5.7E-03	2.1E-03	1.4E-03	4.2E-03	71	1.8E-04	3.3E-04
2,2,5-trimethylhexane	3.3E-03	4.3E-03	4.0E-03	3.6E-03	3.8E-03	12	1.9E-04	6.6E-05
p-ethyltoluene	7.1E-03	4.4E-03	2.2E-03	1.4E-03	3.8E-03	68	1.8E-04	1.9E-04
n-propylbenzene	5.7E-03	3.6E-03	1.9E-03	2.9E-03	3.5E-03	46	1.8E-04	1.7E-04
1,2,3,5-tetramethylbenzene	8.5E-03	2.3E-03	1.2E-03	1.5E-03	c f 3.4E-03	101	1.8E-04	5.7E-05
3-ethylpentane	4.7E-03	2.9E-03	1.3E-03	ND	< c f 2.9E-03	58	1.9E-04	1.2E-04
o-ethyltoluene	5.5E-03	3.4E-03	1.4E-03	1.2E-03	2.9E-03	71	1.8E-04	1.4E-04
Isopropyltoluene	6.3E-03	2.7E-03	1.4E-03	1.0E-03	c f 2.9E-03	85	1.8E-04	8.5E-05
1,2,3,4-trimethylbenzene	3.5E-03	2.3E-03	2.4E-03	3.1E-03	2.8E-03	20	1.8E-04	1.9E-04
2-methylheptane	3.7E-03	3.9E-03	7.3E-04	ND	< c f 2.8E-03	64	1.9E-04	1.6E-04
C11 paraffin B	2.2E-03	1.4E-03	ND	1.8E-03	< 1.8E-03	22	1.9E-04	3.6E-05
3,6-dimethyloctane	2.0E-03	1.0E-03	2.0E-03	ND	< 1.7E-03	35	1.9E-04	1.8E-05
Octene-1	4.4E-03	2.0E-03	1.4E-03	2.7E-03	2.6E-03	49	1.9E-04	1.1E-04

c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.
d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.
f - 95% Confidence Lower Bound of the Average concentration is less than the MDL.
g - For acetone and toluene, mean is less than 10 times the MDL; or, for all others, mean is less than 5 times the MDL.
(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

Table 4-12 (continued). Volatile Organic Compound (VOC) Results from Canisters (Site Bravo).

Parameter	In-Stack Concentrations							Ambient
Units	mg/dscm					(%)	mg/dscm	mg/dscm
Run Number	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD	MDL	
Date	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01				11-Sep-01
Naphthalene	5.7E-03	1.5E-03	1.2E-03	2.0E-03	c f 2.6E-03	82	1.7E-04	2.9E-04
Limonene	3.1E-03	1.9E-03	2.6E-03	2.4E-03	2.5E-03	19	1.8E-04	2.5E-04
3-methylheptane	2.9E-03	3.3E-03	1.3E-03	ND	< 2.5E-03	42	1.9E-04	1.1E-04
1,3-diethylbenzene	3.1E-03	3.1E-03	1.2E-03	1.5E-03	2.2E-03	44	1.8E-04	4.5E-05
1,2,4,5-tetramethylbenzene	5.4E-03	1.7E-03	6.9E-04	1.0E-03	c f 2.2E-03	98	1.8E-04	2.8E-05
2,6-dimethyloctane	1.4E-03	2.6E-03	2.6E-03	2.2E-03	2.2E-03	25	1.9E-04	1.1E-04
2,3-dimethylhexane	3.7E-03	2.2E-03	5.5E-04	ND	< c f 2.2E-03	73	1.9E-04	8.4E-05
Isopropylcyclohexane	4.0E-03	3.4E-03	3.6E-04	5.4E-04	c f 2.1E-03	91	1.9E-04	2.8E-04
2,5-diemthylhexane	3.3E-03	2.0E-03	9.2E-04	ND	< c f 2.1E-03	57	1.9E-04	7.2E-05
C10 paraffin C	1.4E-03	2.6E-03	ND	1.8E-03	< 2.0E-03	32	1.9E-04	2.4E-05
Isobutylbenzene	2.5E-03	2.9E-03	1.2E-03	1.0E-03	1.9E-03	48	1.8E-04	1.1E-04
2,4,4-trimethyl-1-pentene	2.0E-03	2.0E-03	1.4E-03	2.0E-03	1.9E-03	15	1.9E-04	3.0E-05
Isopropylbenzene	2.7E-03	1.9E-03	1.0E-03	8.5E-04	1.6E-03	52	1.8E-04	1.3E-04
Indan	2.6E-03	2.4E-03	6.8E-04	6.7E-04	1.6E-03	67	1.8E-04	1.2E-04
C10 aromatic 2	3.1E-03	1.7E-03	6.9E-04	6.9E-04	f 1.5E-03	73	1.8E-04	9.1E-05
C10 aromatic 4	3.1E-03	1.3E-03	8.6E-04	6.9E-04	f 1.5E-03	73	1.8E-04	4.0E-05
C8 paraffin 2	2.2E-03	1.4E-03	7.4E-04	ND	< f 1.5E-03	52	1.9E-04	5.4E-05
C10 aromatic 5	2.7E-03	7.7E-04	6.9E-04	ND	< c f 1.4E-03	82	1.8E-04	3.4E-05
beta-pinene	5.8E-04	2.7E-03	1.4E-03	5.2E-04	f 1.3E-03	78	1.8E-04	ND
C8 paraffin 3	2.0E-03	1.2E-03	3.7E-04	ND	< c f 1.2E-03	69	1.9E-04	2.4E-05
2-propyltoluene	2.1E-03	1.3E-03	8.6E-04	5.1E-04	1.2E-03	57	1.8E-04	2.3E-05
1,2-diethylbenzene	2.1E-03	1.3E-03	5.2E-04	6.9E-04	1.2E-03	62	1.8E-04	1.7E-05
4-methylheptane	1.4E-03	1.6E-03	1.8E-04	ND	< c f 1.1E-03	72	1.9E-04	6.0E-06
C9 olefin 1	1.0E-03	1.0E-03	5.4E-04	ND	< g 8.5E-04	31	1.9E-04	ND
Dodecene-1	1.6E-03	2.0E-04	ND	5.4E-04	< c f g 7.9E-04	94	1.9E-04	3.0E-05
C9 paraffin 3	4.1E-04	8.1E-04	7.3E-04	ND	< g 6.5E-04	33	1.9E-04	2.4E-05
C8 olefin 3	6.0E-04	ND	1.8E-04	3.6E-04	< f g 3.8E-04	56	1.9E-04	1.2E-05
C10 aromatic 1	1.9E-04	3.8E-04	ND	5.1E-04	< f g 3.6E-04	45	1.8E-04	ND
C10 olefin 2	9.8E-03	1.0E-03	ND	ND	< c f 5.4E-03	115	1.9E-04	6.5E-05
Indene	1.8E-04	2.2E-03	ND	ND	< c f 1.2E-03	120	1.7E-04	1.6E-05
1-methylindan	ND	1.1E-03	ND	8.4E-04	< f 9.9E-04	21	1.8E-04	2.2E-05
C11 aromatic 1	9.6E-04	ND	ND	6.9E-04	< c f g 8.3E-04	24	1.8E-04	5.7E-06
C9 paraffin 1	ND	ND	9.2E-04	7.3E-04	< g 8.2E-04	16	1.9E-04	ND
2,4-diemthylhexane	8.2E-04	8.1E-04	ND	ND	< g 8.2E-04	0	1.9E-04	6.0E-06

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

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

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

f - 95% Confidence Lower Bound of the Average concentration is less than the MDL.

g - For acetone and toluene, mean is less than 10 times the MDL; or, for all others, mean is less than 5 times the MDL.

(i) Duct burners on.

(ii) Duct burners on for first 30 minutes of 360 minute test run.

(iii) Duct burners off.

Table 4-12 (continued). Volatile Organic Compound (VOC) Results from Canisters (Site Bravo).

Parameter	In-Stack Concentrations							Ambient
Units	mg/dscm					(%)	mg/dscm	mg/dscm
Run Number	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD	MDL	
Date	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01				11-Sep-01
C11 aromatic 3	ND	5.8E-04	1.0E-03	ND	< f g 8.1E-04	41	1.8E-04	ND
1,1-dimethylcyclohexane	8.0E-04	4.0E-04	ND	ND	< c f g 6.0E-04	47	1.9E-04	1.2E-05
C9 olefin 4	4.0E-04	8.0E-04	ND	ND	< f g 6.0E-04	47	1.9E-04	ND
C9 paraffin 2	4.1E-04	6.1E-04	ND	ND	< c f g 5.1E-04	28	1.9E-04	3.6E-05
C8 olefin 1	4.0E-04	6.0E-04	ND	ND	< c f g 5.0E-04	28	1.9E-04	4.1E-05
C10 aromatic 6	1.9E-03	ND	ND	ND	< d 1.9E-03	n/a	1.8E-04	5.1E-05
4,4-dimethylheptane	1.8E-03	ND	ND	ND	< d 1.8E-03	n/a	1.9E-04	3.6E-05
2,6-dimethylheptane	1.4E-03	ND	ND	ND	< d 1.4E-03	n/a	1.9E-04	4.8E-05
Nonene-1	ND	1.2E-03	ND	ND	< d 1.2E-03	n/a	1.9E-04	2.4E-05
3,3-dimethylheptane	1.0E-03	ND	ND	ND	< d 1.0E-03	n/a	1.9E-04	4.8E-05
sec-butylbenzene	ND	3.8E-04	ND	ND	< d g 3.8E-04	n/a	1.8E-04	2.8E-05
C11 paraffin A	ND	ND	ND	ND	d ND	n/a	1.9E-04	1.2E-05
3-methyloctane	ND	ND	ND	ND	d ND	n/a	1.9E-04	1.8E-05
C8 olefin 2	ND	ND	ND	ND	d ND	n/a	1.9E-04	1.2E-05
Other VOC:								
Methanol	5.8E-01	1.7E-02	9.1E-03	ND	< f 2.0E-01	162	4.3E-04	ND
Toluene	1.8E-01	1.3E-01	8.2E-02	6.8E-02	1.2E-01	45	1.8E-04	4.2E-03
Acetone	3.2E-01	1.4E-02	7.5E-03	8.9E-03	c f 8.7E-02	176	2.6E-04	3.3E-04
Propane	9.9E-02	1.0E-01	7.4E-02	5.4E-02	8.2E-02	28	2.0E-04	4.5E-03
Ethane	8.8E-02	1.0E-01	7.1E-02	5.4E-02	7.9E-02	27	2.0E-04	9.5E-03
Isopentane	7.9E-02	1.1E-01	3.8E-02	1.2E-02	5.9E-02	72	2.0E-04	2.6E-03
Ethene	6.1E-02	7.9E-02	2.9E-02	1.3E-02	4.6E-02	65	1.9E-04	6.9E-04
n-hexane	3.5E-02	4.3E-02	7.5E-02	7.2E-03	4.0E-02	70	1.9E-04	5.6E-04
n-butane	3.0E-02	5.5E-02	4.1E-02	1.0E-02	3.4E-02	56	2.0E-04	2.2E-03
Hexanal	4.2E-02	4.3E-02	1.9E-02	2.5E-02	3.2E-02	37	2.3E-04	8.7E-04
Acetylene	4.6E-02	4.0E-02	2.2E-02	1.0E-02	3.0E-02	55	1.8E-04	5.8E-04
n-pentane	3.5E-02	5.3E-02	2.1E-02	7.2E-03	2.9E-02	67	2.0E-04	1.4E-03
2-methylpentane	3.0E-02	2.8E-02	1.1E-02	2.9E-03	1.8E-02	73	1.9E-04	7.5E-04
Isobutane	1.7E-02	2.9E-02	1.9E-02	6.9E-03	1.8E-02	50	2.0E-04	1.2E-03
Propene	2.0E-02	2.1E-02	1.6E-02	1.1E-02	1.7E-02	28	1.9E-04	3.3E-04
Benzene	2.6E-02	1.6E-02	1.0E-02	8.0E-03	1.5E-02	53	1.8E-04	6.5E-04
Methylcyclopentane	2.0E-02	2.0E-02	1.2E-02	2.2E-03	1.4E-02	62	1.9E-04	4.2E-04
3-methylpentane	2.0E-02	1.6E-02	6.8E-03	9.2E-04	1.1E-02	78	1.9E-04	3.9E-04
3-methylhexane + pentanal	1.4E-02	1.1E-02	6.3E-03	1.5E-03	8.0E-03	66	1.9E-04	3.3E-04

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

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

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

f - 95% Confidence Lower Bound of the Average concentration is less than the MDL.

g - For acetone and toluene, mean is less than 10 times the MDL; or, for all others, mean is less than 5 times the MDL.

(i) Duct burners on.

(ii) Duct burners on for first 30 minutes of 360 minute test run.

(iii) Duct burners off.

Table 4-12 (continued). Volatile Organic Compound (VOC) Results from Canisters (Site Bravo).

Parameter	In-Stack Concentrations							Ambient
Units	mg/dscm					(%)	mg/dscm	mg/dscm
Run Number	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD	MDL	
Date	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01				11-Sep-01
Cyclohexane	1.4E-02	9.0E-03	4.5E-03	1.8E-03	7.3E-03	73	1.9E-04	2.1E-04
Iso-butene	9.2E-03	9.4E-03	4.7E-03	5.2E-03	7.1E-03	36	1.9E-04	2.1E-04
n-heptane	1.1E-02	9.8E-03	4.6E-03	1.3E-03	6.6E-03	68	1.9E-04	3.6E-04
2-methylhexane	1.0E-02	7.6E-03	3.4E-03	9.0E-04	5.6E-03	76	1.9E-04	2.5E-04
Methylcyclohexane	8.0E-03	9.2E-03	3.8E-03	1.3E-03	5.6E-03	66	1.9E-04	3.1E-04
2,2-dimethylbutane	7.2E-03	6.6E-03	2.6E-03	ND	< 5.4E-03	46	1.9E-04	1.6E-04
2,3-dimethylbutane	8.2E-03	8.4E-03	3.7E-03	1.3E-03	5.4E-03	65	1.9E-04	2.1E-04
Isoprene	8.6E-03	6.6E-03	2.1E-03	1.0E-03	4.6E-03	78	1.8E-04	1.8E-04
2,3-dimethylpentane	8.0E-03	6.1E-03	2.9E-03	7.3E-04	4.4E-03	73	1.9E-04	2.1E-04
1,3-dimethylcyclopentane	5.8E-03	3.4E-03	1.4E-03	ND	< c f 3.6E-03	62	1.9E-04	1.2E-04
2,4-dimethylpentane	6.3E-03	4.1E-03	2.0E-03	5.5E-04	3.3E-03	78	1.9E-04	1.1E-04
Cyclopentane	4.6E-03	5.0E-03	1.8E-03	1.4E-03	3.2E-03	58	1.9E-04	1.1E-04
Chlorobenzene	3.2E-03	2.4E-03	1.7E-03	ND	< 2.4E-03	31	2.5E-04	1.6E-04
c-2-hexene	3.0E-03	2.0E-03	2.2E-03	1.8E-03	2.2E-03	24	1.9E-04	1.1E-04
1-butene	2.6E-03	2.6E-03	2.2E-03	1.3E-03	2.2E-03	30	1.9E-04	7.1E-05
Benzaldehyde	1.7E-03	1.1E-03	2.0E-03	2.7E-03	1.9E-03	36	2.1E-04	6.4E-05
2,2,3-trimethylbutane	3.1E-03	1.6E-03	1.5E-03	5.5E-04	1.7E-03	62	1.9E-04	6.6E-05
c-3-hexene	2.8E-03	2.2E-03	5.4E-04	5.4E-04	f 1.5E-03	76	1.9E-04	1.1E-04
1,3-butadiene	1.9E-03	1.7E-03	8.7E-04	6.9E-04	1.3E-03	47	1.8E-04	2.9E-05
2-methyl-1-butene	1.0E-03	1.8E-03	3.6E-04	ND	< c f 1.1E-03	68	1.9E-04	2.4E-05
Cyclopentene	9.7E-04	1.2E-03	3.5E-04	1.4E-03	9.7E-04	46	1.8E-04	6.3E-05
t-2-butene	1.0E-03	1.2E-03	1.1E-03	5.4E-04	9.6E-04	30	1.9E-04	3.0E-05
Cyclohexene	7.8E-04	7.8E-04	7.1E-04	ND	< g 7.6E-04	6	1.9E-04	1.2E-05
3,3-dimethylpentane	1.0E-03	8.2E-04	3.7E-04	ND	< f g 7.4E-04	45	1.9E-04	1.2E-05
C7 olefin 2	6.0E-04	8.0E-04	5.4E-04	ND	< g 6.5E-04	21	1.9E-04	1.8E-05
2-methyl-2-butene	6.0E-04	6.0E-04	9.0E-04	3.6E-04	g 6.2E-04	36	1.9E-04	4.7E-05
2-methyl-2-pentene	6.0E-04	6.0E-04	3.6E-04	ND	< g 5.2E-04	27	1.9E-04	2.4E-05
MTBE	5.3E-02	ND	ND	3.4E-03	< c f 2.8E-02	124	1.2E-03	1.1E-04
Ethanol + ACN	2.1E-02	ND	2.3E-02	ND	< 2.2E-02	7	6.2E-04	ND
c-2-butene	ND	ND	2.3E-03	2.2E-03	< 2.2E-03	6	1.9E-04	6.5E-05
2-methylpropanal	2.3E-03	ND	ND	1.6E-03	< c f 2.0E-03	25	2.4E-04	3.0E-05
2-methyl-1-pentene	4.0E-04	1.0E-03	ND	ND	< f g 7.0E-04	60	1.9E-04	ND
t-3-heptene	2.0E-04	4.0E-04	ND	ND	< c f g 3.0E-04	47	1.9E-04	1.8E-05
t-2-pentene	2.2E-03	ND	ND	ND	< d 2.2E-03	n/a	1.9E-04	ND

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

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

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

f - 95% Confidence Lower Bound of the Average concentration is less than the MDL.

g - For acetone and toluene, mean is less than 10 times the MDL; or, for all others, mean is less than 5 times the MDL.

(i) Duct burners on.

(ii) Duct burners on for first 30 minutes of 360 minute test run.

(iii) Duct burners off.

Table 4-12 (continued). Volatile Organic Compound (VOC) Results from Canisters (Site Bravo).

Run		Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*			RSD	Ambient	In-stack
Date	Units	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01		Average	%	11-Sep-01	MDL
Formaldehyde	mg/dscm	1.4E-1	1.4E-1	4.7E-2	5.5E-2	a b	9.7E-2	54	3.7E-3	4.7E-3
	ppb	113	115	38	44		78	54	3	4
Acetaldehyde	mg/dscm	1.7E-1	1.0E-1	4.6E-2	5.1E-2	a b	9.2E-2	63	5.3E-3	1.3E-2
Acetone	mg/dscm	3.1E-1	1.3E-1	6.0E-2	2.8E-2	a b c	1.3E-1	96	8.8E-3	
Glyoxal	mg/dscm	2.0E-2	3.6E-2	2.2E-2	2.4E-2		2.5E-2	28	2.0E-3	3.0E-3
MEK	mg/dscm	ND	ND	ND	5.0E-3	< d	5.0E-3	n/a	5.6E-4	4.7E-3

Notes:

-Shaded area represents substances not detected in 3 valid test runs. Average not considered reliable for quantitative analysis.
-Results are not considered quantitative due to high concentrations in system blanks. See discussion.
-All results are field blank corrected.

n/a- not applicable; only one run within detectable limits.
ND - Not Detected
RSD - Relative Standard Deviation
< - detected in fewer than all valid sample runs
MDL - minimum detection limit (in-stack)
MEK - methyl ethyl ketone
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 Ambient concentration.
d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.
(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

Elements

Element concentrations were measured by x-ray fluorescence (XRF) analysis of the TMFs used in the dilution sampler to determine potential elemental markers for gas combustion. Mg and Na results are considered semi-quantitative because of interferences in the XRF analysis. The TMF for PM2.5mass had a negative net weight for Run 4, therefore the results from the chemical speciation of the PM2.5 are invalidated and flagged “NV” in the table for that run. All elements except for Si, Mg and P were not detected in the field blank (see Section 6).

7 elements – Cl, Fe, Si, S, Zn, Cu and Ni - were found in all three valid test runs (Table 4-13), and these comprise 75 percent of the total mass (excluding Na and Mg). Cl is the most abundant element present. Although the concentrations in the stack for these 7 generally are greater than the MDL (approximately 70 times on average) and the respective concentrations in the ambient air (approximately 30 times on average), the relative standard deviation of all 7 elements is high, greater than 100 percent, indicating it is likely that the reported concentrations are not distinguishable from the MDL or concentrations in the ambient air. This is a result of the extremely low concentrations present in the exhaust gas. Despite high relative standard

deviation, the average S results are approximately one-third of the dilution sampler $SO_4^{=}$ results presented earlier, which is the expected ratio based on molecular weights assuming all particulate sulfur is soluble as $SO_4^{=}$. As, Au, Ba, Cd, Ga, Hg, In, La, Pd, Rb, Sb, Se, Sn, Tl, U and Y are below detectable levels for all sample runs. Those elements detected in fewer than 3 runs are generally at levels much closer to the MDL.

Table 4-13. Elements, as Measured by the Dilution Sampler (Site Bravo).

Parameter	In-Stack Concentrations							Ambient
Units	mg/dscm					%	mg/dscm	mg/dscm
Run	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD	MDL	
Date	09/06/01	09/07/01	09/08/01	09/09/01			(2)	9/11/2001
Cl	8.1E-03	2.1E-2	8.2E-4	NV	c 1.0E-2	103	1.6E-4	8.3E-4
Cu	1.7E-04	1.2E-3	3.7E-5	NV	c 4.7E-4	136	1.7E-5	7.2E-6
Fe	3.8E-03	1.4E-2	2.0E-4	NV	c 6.0E-3	119	2.3E-5	2.3E-4
Mg	1.1E-03	2.4E-3	7.3E-5	NV	b c 1.2E-3	97	(1)	1.2E-4
Na	3.8E-03	1.1E-2	1.2E-3	NV	c 5.3E-3	94	(1)	7.4E-4
Ni	3.9E-04	9.7E-5	3.4E-5	NV	c 1.7E-4	109	1.4E-5	3.4E-6
S	2.0E-03	1.0E-2	9.7E-4	NV	c 4.3E-3	114	7.8E-5	7.3E-4
Si	1.7E-03	1.4E-2	3.3E-4	NV	b c 5.3E-3	140	9.9E-5	3.5E-4
Zn	2.5E-04	1.4E-3	5.5E-5	NV	c 5.6E-4	128	1.7E-5	1.2E-5
Ag	8.1E-04	ND	ND	NV	< d 8.1E-4	n/a	1.9E-4	ND
Al	6.6E-04	3.5E-3	ND	NV	< c 2.1E-3	96	1.6E-4	1.0E-4
Br	1.8E-05	8.1E-5	ND	NV	< c 5.0E-5	89	1.6E-5	5.3E-6
Ca	8.9E-04	4.9E-3	ND	NV	< c 2.9E-3	98	7.0E-5	1.5E-4
Co	4.4E-05	ND	2.0E-5	NV	< 3.2E-5	53	1.4E-5	ND
Cr	6.4E-04	ND	ND	NV	< d 6.4E-4	n/a	3.0E-5	3.9E-6
K	3.5E-04	2.2E-3	ND	NV	< c 1.3E-3	102	9.5E-5	1.1E-4
Mn	1.1E-04	2.3E-4	ND	NV	< c 1.7E-4	53	2.5E-5	3.5E-6
Mo	7.1E-05	ND	ND	NV	< d 7.1E-5	n/a	4.2E-5	ND
P	ND	3.4E-4	ND	NV	< d 3.4E-4	n/a	8.8E-5	ND
Pb	6.8E-05	1.5E-4	ND	NV	< c 1.1E-4	54	4.7E-5	1.6E-5
Sr	ND	6.4E-5	ND	NV	< d 6.4E-5	n/a	1.7E-5	2.4E-6
Ti	2.0E-04	5.9E-4	ND	NV	< c 3.9E-4	70	4.5E-5	1.6E-5
V	7.4E-05	2.5E-4	ND	NV	< c 1.6E-4	76	3.9E-5	8.9E-6
Zr	ND	4.1E-5	ND	NV	< d 4.1E-5	n/a	2.7E-5	ND

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

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

(2) Average method detection limit for dilution ratio. Ambient sample MDLs are smaller due to 1:1 dilution ratio.

MDL - In-stack minimum detection limit (based on minimum analytical detection limit, sample volume, and dilution ratio).

n/a- not applicable; ND - not detected; NV - test run not valid; RSD - relative standard deviation

< - not detected in all valid test runs

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 Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

(i) Duct burners on.

(ii) Duct burners on for first 30 minutes of 360 minute test run.

(iii) Duct burners off.

Concentrations of all the elements that were detected in all three valid runs are elevated for Run 2 compared to the other valid runs. As noted earlier in this section (see discussion of Table 4-8), no conclusive explanation for this observation was found.

Carbonyls

Dilution Sampler. 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 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.

The second cartridge of each pair was used to check for breakthrough. In many cases, the amount in the second cartridge comprised 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).

Formaldehyde, acetaldehyde, acetone, and glyoxol were detected in all four stack samples and in the ambient air sample (Table 4-14). Methyl ethyl ketone (MEK) also was detected in one stack sample and the ambient air sample, but the concentration in the stack is right at the MDL and much lower than in the ambient air; this result is not considered representative of actual emissions. The relative standard deviations for all of these compounds except glyoxol indicate it is likely that their average concentrations are not significantly higher than in the ambient air. The reported concentrations of formaldehyde, acetaldehyde and acetone are slightly elevated in Runs 1 and 2 (during which the duct burners were operating) compared to Runs 3 and 4 (during which the duct burners were not operating except for a brief period during Run 3).

Table 4-14. Carbonyl Results (Site Bravo).

Run		Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*		RSD	Ambient	In-stack
Date	Units	06-Sep-01	07-Sep-01	08-Sep-01	09-Sep-01	Average	%	11-Sep-01	MDL
Formaldehyde	mg/dscm	1.4E-1	1.4E-1	4.7E-2	5.5E-2	a b 9.7E-2	54	3.7E-3	4.7E-3
	ppb	113	115	38	44	78	54	3	4
Acetaldehyde	mg/dscm	1.7E-1	1.0E-1	4.6E-2	5.1E-2	a b 9.2E-2	63	5.3E-3	1.3E-2
Acetone	mg/dscm	3.1E-1	1.3E-1	6.0E-2	2.8E-2	a b c 1.3E-1	96	8.8E-3	
Glyoxal	mg/dscm	2.0E-2	3.6E-2	2.2E-2	2.4E-2	2.5E-2	28	2.0E-3	3.0E-3
MEK	mg/dscm	ND	ND	ND	5.0E-3	< d 5.0E-3	n/a	5.6E-4	4.7E-3

Shaded area represents substances not detected in 3 valid test runs. Average not considered reliable for quantitative analysis.
Note, results are not considered quantitative due to high concentrations in system blanks. See discussion.
* All results are field blank corrected.
n/a- not applicable; only one run within detectable limits.
ND - Not Detected
RSD - Relative Standard Deviation
< - detected in fewer than all valid sample runs
MDL - minimum detection limit (in-stack)
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 Ambient concentration.
d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.
(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

Acetaldehyde and acetone were detected in the field blanks, therefore the field blank results are subtracted from the stack results. A DSB also was performed, 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 were detected in both the DSB and the ambient air sample. Comparing the two results indicates that the dilution air filtration system removal efficiency is approximately 56 percent for formaldehyde, 49 percent for acetone, and 84 percent for acetaldehyde. The levels present in the dilution sampler blank are large compared to the raw stack results. For example, approximately 50 to 130 percent of the formaldehyde measured in the stack samples could be accounted for by the trace amounts in the dilution air. With only single samples for the blanks and ambient air, it is not possible to determine if the differences are significant with a known degree of confidence.

The levels of formaldehyde in the stack samples are comparable to those in the DSB, ambient sample and field blank. For Site Bravo, the 95 percent confidence lower bound of the average concentration was less than the concentrations of both the DSB and the field blank. Formaldehyde measurements also were made in a subsequent test at another nearby and similar site, Site Echo. For Site Echo at high load, the 95 percent confidence lower bound of the average concentration was less than the ambient concentration; at low load the 95 percent confidence lower bound of the average concentration was less than the ambient and DSB concentrations. 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, SO_2 and NH_3 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 NH_3 was captured on a citric acid-impregnated cellulose-fiber filter downstream of the QFF used for ions and OC/EC analysis. SO_2 was captured on a K_2CO_3- impregnated cellulose-fiber filter downstream of a QFF. The dilution sampler SO_2 results for Run 4 of are about an order of magnitude lower than the other three runs (Table 4-15); this run also had a negative filter weight for the TMF and it is possible that there was not sufficient material on the filter to provide a valid sample. Historical data of sulfur in the fuel (0.25 grains per hundred standard cubic feet (gr/100 scf)) accounts for approximately 0.5-0.6 lb/hr of S in the stack, which would equal approximately 1.7 lb/hr of $SO_4^=$ in the stack. This estimation is in good general agreement with the levels measured by the dilution sampler, except for the one outlier in Run 4.

Ambient levels of SO_2 from a monitoring station near the sampling 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 are 4.5 ppb, which is within the range measured by the local monitoring station.

Table 4-15. Inorganic Secondary PM Precursor Results (Site Bravo).

Parameter	Units	Value						
Run Number	-	Run 1 *(i)*	Run 2 *(i)*	Run 3 *(ii)*	Run 4 *(iii)*	Average	RSD	Ambient
Date	-	9/6/2001	9/7/2001	9/8/2001	9/9/2001		(%)	9/11/2001
Ammonia (DS)	mg/dscm	1.1E+0	1.1E+0	1.1E+0	9.3E-1	1.1E+0	8	2.5E-3
	ppm	1.5E+0	1.5E+0	1.6E+0	1.3E+0	1.5E+0	8	3.5E-3
	lb/hr	2.9E+0	2.9E+0	2.9E+0	2.2E+0	2.7E+0	12	n/a
Ammonia (BAAQMD ST-1B)	mg/dscm	1.1E+0	1.2E+0	1.1E+0	9.2E-1	1.1E+0	11	--
	ppm	1.6E+0	1.7E+0	1.6E+0	1.3E+0	1.5E+0	11	--
	lb/hr	3.1E+0	3.2E+0	2.8E+0	2.2E+0	2.9E+0	16	--
Sulfur Dioxide (DS)	mg/dscm	6.9E-1	8.5E-1	4.6E-1	6.2E-2	5.2E-1	66	1.2E-2
	ppm	2.6E-1	3.2E-1	1.7E-1	2.3E-2	1.9E-1	66	4.5E-3
	lb/hr	1.9E+0	2.3E+0	1.2E+0	1.5E-1	1.4E+0	69	n/a
NOx (as NO2) (CEMS)	mg/dscm	6.3E+0	5.7E+0	3.6E+0	2.2E+0	4.4E+0	43	n/a
	ppm	3.3E+0	3.0E+0	1.9E+0	1.1E+0	2.3E+0	43	n/a
	lb/hr	1.7E+1	1.6E+1	9.0E+0	5.1E+0	1.2E+1	48	n/a

CEMS - Continuous Emissions Monitoring System.
DS - Dilution Sampler
n/a- not applicable; only one run within detectable limits.
ND - Not Detected
RSD- Relative Standard Deviation
(i) Duct burners on.
(ii) Duct burners on for first 30 minutes of 360 minute test run.
(iii) Duct burners off.

NH_3 results from the dilution sampler agreed very well with those from the BAAQMD Method ST-1B impinger method. The average NH_3 concentration measured by both methods is 1.5 parts per million (volume) (ppmv), which is approximately consistent with previous measurements on this unit.

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

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 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. Emission factors based on only two test runs are reported for qualitative purposes only; in general, these have higher uncertainties and are not considered suitable for quantitative analysis.

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 (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.

As expected due to the small number of samples and the extremely low concentrations present in gas combustion exhaust, many of the reported emission factors derived from this test have high uncertainty. Run-to-run variability dominates random uncertainty, which in turn dominates total uncertainty in most cases. The high uncertainty in these tests is attributed to the very low pollutant concentrations present in the samples - at or near the ability of the methods to detect them - and to slightly different operating conditions for each test run. As expected, some of the highest uncertainties are associated with pollutants detected in fewer than all four test runs. Emission factors for substances detected in at least three valid test runs are considered to be the most reliable; those detected in fewer than three test runs are considered less reliable (not suitable for quantitative analysis) and are grouped separately in the tables. 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 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.

The large relative uncertainties of the dilution sampler results in these tests do not negate the value of the results, since the differences between results obtained with dilution and hot filter/iced impinger methods remain significant at the 95 percent confidence level and the results establish plausible upper bounds for emissions and species mass fractions.

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 (see table 3-1) employed, especially for PM2.5 speciation and precursor measurements. 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 operating conditions for each run varied with normal plant operation near full load, and included supplementary firing for some of the runs. Therefore, 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 considerable caution when using these results.

Although the authors consider the quality of these test data quality to be high, 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 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 reproduce 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 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 Emission Factors

Emission factors for primary particulate matter including PM2.5 mass, elements and ions were derived from the dilution sampling results (Table 5-1). Data from all valid runs were used to determine average results. Group 1 includes emission factors for substances detected in three or more valid test runs. These are considered the more reliable for this facility than are those in Group 2, albeit the relative uncertainties are high for the reasons discussed previously in Section 4. The high relative uncertainty in many of the results arises mainly from the high run-to-run variability, rather than analytical procedures, sample volume, dilution ratio, and other sources of uncertainty.

Table 5-1. Primary Emission Factors- Particulate Mass and Elements (Site Bravo).

Measurement Method	Substance		Emission Factor (lb/MMBtu)	Uncertainty at 95% Confidence Level (%) *(1)*	95% Confidence Upper Bound (lb/MMBtu) *(2)*	95th Percentile	5th Percentile	Number of Detected Runs
Dilution Method	**Group 1 *(3)***							
	PM2.5 mass	c	2.5E-4	260	7.0E-4	5.0E-4	6.3E-5	3
	Cl	c	1.4E-5	260	3.9E-5	2.8E-5	2.3E-6	3
	Cu	c	6.6E-7	340	2.2E-6	1.5E-6	7.5E-8	3
	Fe	c	8.5E-6	300	2.6E-5	1.8E-5	8.2E-7	3
	Mg	b,c	1.7E-6	250	4.5E-6	3.2E-6	2.6E-7	3
	Ni	c	2.5E-7	270	7.1E-7	5.1E-7	6.2E-8	3
	S	c	6.2E-6	290	1.8E-5	1.3E-5	1.6E-6	3
	Si	b,c	7.5E-6	350	2.5E-5	1.8E-5	7.0E-7	3
	Zn	c	7.9E-7	320	2.5E-6	1.8E-6	1.1E-7	3
	NO_3^-	c	2.2E-5	320	7.0E-5	5.0E-5	4.1E-6	3
	$SO_4^=$	c	1.8E-5	310	5.5E-5	3.9E-5	4.4E-6	3
	Cl^-	c	1.5E-5	250	4.0E-5	2.9E-5	4.4E-6	3
	Soluble Na	c	1.1E-6	360	4.4E-6	2.0E-6	5.1E-7	3
	Group 2 *(4)*							
	K	< c	1.8E-6	920	9.9E-6	2.9E-6	6.3E-7	2
	Al	< c	2.9E-6	880	1.6E-5	4.7E-6	1.1E-6	2
	Br	< c	7.0E-8	810	3.5E-7	1.1E-7	3.1E-8	2
	Ca	< c	4.1E-6	890	2.2E-5	6.6E-6	1.5E-6	2
	Co	<	4.7E-8	540	2.0E-7	6.1E-8	3.3E-8	2
	Mn	< c	2.4E-7	490	8.3E-7	3.2E-7	1.6E-7	2
	Pb	< c	1.5E-7	510	5.6E-7	2.1E-7	1.0E-7	2
	Ti	< c	5.5E-7	680	2.7E-6	8.0E-7	3.1E-7	2
	V	< c	2.3E-7	740	1.2E-6	3.4E-7	1.2E-7	2
Hot Filter/Iced Impinger Methods *(5)*	Total Filterable PM (Method PRE-4) *(7)*	<	6.0E-4	200	1.5E-3	1.5E-3	9.1E-5	4
	Filterable PM10 (Method PRE-4) *(7)*	<	2.9E-4	290	8.6E-4	5.8E-4	1.4E-5	3
	Inorganic CPM (Method 202)		2.7E-3	60	4.0E-3	3.8E-3	1.7E-3	4
	Total CPM (Method 202) *(6)*	<	3.0E-3	48	4.1E-3	3.9E-3	2.1E-3	4
	Total PM (Method PRE-4/202) *(6,7)*	<	3.6E-3	73	5.6E-3	4.1E-3	2.4E-3	4
	Total PM10 (Method PRE-4/202) *(6,7)*	<	3.3E-3	69	5.0E-3	3.9E-3	2.3E-3	4
	Total PM2.5 (Method PRE-4/202) *(6,7)*	<	3.1E-3	48	4.1E-3	3.9E-3	2.2E-3	4

< - detected in fewer than all valid test runs and/or sample fractions.
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 Ambient concentration.

(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 that the actual emissions differ from the reported emission factor value. Data users should exercise appropriate caution.
(2) 95% confidence upper bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% confidence upper bound provides a plausible upper bound (i.e., it is likely actual emissions are lower) for emissions.
(3) Substances detected in three or more samples are considered reliable for this test.
(4) Substances detected in two samples are considered qualitative, not suitable for quantitative analysis.

(5) Hot filter/iced impinger method results are subject to significant positive bias due to measurement artifacts; therefore, actual emissions are belived to be represented by dilution method results. The results are shown for reference only when comparing to other published emission factors.
(6) Total includes organic CPM, which was detected in only 1 run and therefore not reported separately.
(7) Total includes filterable PM2.5, which was detected in only 1 run and therefore not reported separately.
Duct burners were on for Runs 1 and 2, intermittent for Run 3 (total of approx. 30 minutes) and off for Run 4

The relative uncertainty for all the dilution sampler method results and the hot filter method results shown in Table 5-1 exceeds 100 percent. Because of this, the average results may not be significantly different from the respective concentrations in ambient air or zero. Blank results for Mg and Si are moderately high compared to the sample results. Although it is likely that such emission factors are unrepresentative, they are reported here to facilitate further analysis of

PM mass and speciation results in conjunction with results of other source tests conducted in this program. Data users should exercise considerable caution when applying these results.

The average emission factor for total PM2.5 (including CPM) measured using the hot filter/iced impinger train methods is more than ten times higher than the emission factor for PM2.5 determined from the dilution sampler results. This difference is attributed primarily to positive bias in the iced impinger method resulting from measurement artifacts, i.e., conversion of SO_2 to CPM in the impinger train (Wien, 2001) and excessive condensation of vapor species due to over-saturation of vapor phase species compared to the stack plume.

Uncertainty analysis enables an upper and lower bound for the actual emissions to be established at a known level of confidence. The 95 percent confidence upper bound for the dilution sampler results is less than the 95 percent confidence lower bound for the hot filter/iced impinger results. This indicates that the average results for the two methods are significantly different at the 95 percent confidence level. Despite the high *relative* uncertainty of the dilution sampler PM2.5 mass results, the *absolute* uncertainty (±0.00065 lb/MMBtu) is approximately half of the PM2.5 mass absolute uncertainty (±0.0014 lb/MMBtu) and one quarter of the total PM mass absolute uncertainty (±0.0026 lb/MMBtu) by the hot filter/iced impinger methods. Considering the aforementioned artifacts associated with the iced impinger CPM results and the absolute uncertainty of the results, the PM2.5 emission factor derived from dilution sampling is considered more representative of actual primary PM2.5 emissions.

The relative uncertainty of the dilution sampler mass results in this test is considerably greater than in the four previous tests of gas combustion sources with similar PM mass concentrations. The unusually high uncertainty was traced to a procedural error (over tightening of the filter cassettes) during the test that damaged the TMFs slightly. Therefore, the relative uncertainty of the mass results in this test is not considered representative of the dilution sampler's true capability. Further tests are needed to corroborate the emissions results and establish the performance of the dilution sampler method for this source category.

Particulate Carbon Emission Factors

Table 5-2 presents emission factors for particulate carbon (OC, EC, and total carbon) and particulate carbon species (SVOCs) derived from the dilution sampler measurements. Emission factors for almost all of the substances have very high uncertainties; all the related cautions in the previous paragraphs also apply. It is likely that emission factors with a relative uncertainty greater than 100 percent are unrepresentative, but they have been left on Table 5-2 because they are potentially important for use in source apportionment analysis, and to facilitate further analysis of PM mass and speciation results in conjunction with results of other source tests conducted in this program. Compounds with average emission factors less than the level in the field blank are excluded from the table.

It is very likely the OC results are positively biased due to a measurement artifact (i.e., adsorption of VOCs on the sampling media). The OC artifact appears to be 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. Back-up OC is a separate measurement used as an indicator of the potential OC artifact. The emission factors based on OC and back-up OC measurements are very similar, well within the uncertainties of the means, indicating the OC results are highly suspect. 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 OC artifact is not well understood, it is the current convention not to subtract the back-up OC from the primary result. The average EC emission factor, based on only two results that are barely above the method detection limits, is much lower than the OC emission factor and the relative uncertainty is very large. 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.

Speciated particulate carbon emission factors also are extremely low. Only six particulate carbon species were found in all four test runs, and only four of these - phenanthrene, 7-methylbenzo(a)pyrene, 2-methylphenanthrene, D-D-MePy/MeFl and anthrone - were found at average concentrations more than five times the field blank. Only one of these four compounds - 7-methylbenzo(a)pyrene - has uncertainty less than 100 percent.

Table 5-2. Primary Emission Factors- Particulate Carbon (Site Bravo).

Substance	Average (lb/MMBtu)	Uncertainty at 95% Confidence Level (%) *(1)*	95% Confidence Upper Bound (lb/MMBtu) *(2)*	95th Percentile	5th Percentile	Number of Detected Runs
Group 1 *(3)*						
Organic Carbon (OC) *(5)*	a b 2.0E-4	108	3.6E-4	2.7E-4	1.3E-4	3
OC Backup *(6)*	b 1.8E-4	60	2.6E-4	2.0E-4	1.6E-4	3
Total Carbon	a b 2.2E-4	112	3.8E-4	2.8E-4	1.4E-4	3
7-methylbenzo(a)pyrene	1.8E-7	63	2.7E-7	2.5E-7	1.2E-7	4
Anthrone	4.0E-8	100	7.4E-8	6.3E-8	2.6E-8	4
Group 2 *(4)*						
Elemental Carbon	< 1.9E-5	366	5.3E-5	2.3E-5	1.4E-5	2
1,4+1,5+2,3-dimethylnaphthalene	< c 2.5E-6	830	1.3E-5	3.9E-6	1.0E-6	2
2-methylnaphthalene	< c 1.1E-6	778	5.1E-6	1.6E-6	4.8E-7	2
1-methylnaphthalene	< c 5.8E-7	736	2.7E-6	8.7E-7	2.8E-7	2
Pyrene	< c 1.8E-7	810	9.0E-7	2.8E-7	7.7E-8	2
7-methylbenz(a)anthracene	< 7.5E-8	758	3.6E-7	1.1E-7	3.6E-8	2
E-trimethylnaphthalene	< c 4.8E-8	301	1.3E-7	5.7E-8	3.9E-8	2

< - detected in fewer than three valid runs.

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 Ambient concentration.

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

(3) Substances detected in three or more samples are considered reliable for this test.

(4) Substances detected in two samples are considered qualitative, not suitable for quantitative analysis.

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

Duct burners were on for Runs 1 and 2, intermittent for Run 3 (total of approx. 30 minutes) and off for Run 4

Thirteen compounds were detected in only two runs; the relative uncertainties associated with these emission factors are extremely high (average of approximately 500 percent) which reflects their sporadic appearance and extremely low concentrations. These results are considered qualitative and not suitable for quantitative analysis.

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, NH_3

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

Substance		Average (lb/MMBtu)	Uncertainty at 95% Confidence Level (%) (a)	95% Confidence Upper Bound (%) (b)	95th Percentile	5th Percentile	Number of Detected Runs
NH_3 (DS)		1.6E-3	30	2.0E-3	1.7E-3	1.5E-3	4
SO_2 (DS)		7.5E-4	109	1.4E-3	1.2E-3	1.9E-4	4
NOx (as NO_2) (CEMS)		6.5E-3	75	1.0E-2			4
VOC^{C}_{8+} (c):							
2,3,5-trimethylhexane		2.1E-4	46	3.0E-4	2.5E-4	1.6E-4	4
1-decene		2.0E-4	49	2.8E-4	2.4E-4	1.4E-4	4
Octanal		5.9E-5	77	9.3E-5	8.2E-5	3.9E-5	4
Styrene + heptanal		4.7E-5	91	8.1E-5	7.5E-5	3.1E-5	4
o-xylene		3.0E-5	98	5.3E-5	4.9E-5	1.7E-5	4
2,2,5-trimethylhexane		5.7E-6	39	7.7E-6	6.3E-6	4.8E-6	4
n-propylbenzene		5.2E-6	81	8.5E-6	7.7E-6	3.2E-6	4
1,2,3,4-trimethylbenzene		4.2E-6	47	5.9E-6	5.0E-6	3.3E-6	4
Octene-1		3.9E-6	85	6.5E-6	6.0E-6	2.3E-6	4
Limonene		3.8E-6	46	5.3E-6	4.4E-6	2.9E-6	4
2,6-dimethyloctane		3.3E-6	53	4.7E-6	4.0E-6	2.3E-6	4
1,3-diethylbenzene		3.3E-6	79	5.3E-6	4.4E-6	2.0E-6	4
C10 paraffin C	<	2.9E-6	90	4.8E-6	3.6E-6	2.1E-6	3
Isobutylbenzene		2.8E-6	84	4.6E-6	4.0E-6	1.7E-6	4
2,4,4-trimethyl-1-pentene		2.8E-6	42	3.8E-6	3.1E-6	2.3E-6	4
C11 paraffin B	<	2.7E-6	71	4.1E-6	3.2E-6	2.1E-6	3
3,6-dimethyloctane	<	2.5E-6	97	4.2E-6	3.1E-6	1.6E-6	3
Isopropylbenzene		2.4E-6	90	4.0E-6	3.6E-6	1.4E-6	4
2-propyltoluene		1.8E-6	97	3.1E-6	2.8E-6	9.1E-7	4
C9 olefin 1	< g	1.2E-6	90	2.0E-6	1.4E-6	9.0E-7	3
C9 paraffin 3	<	9.6E-7	93	1.6E-6	1.1E-6	6.4E-7	3
Total VOC^{C}_{8+} (c)	<	6.0E-4	58	8.8E-4	7.6E-4	4.2E-4	3+

DS - Dilution Sampler

CEMS - Continous Emissions Monitoring System.

(a) 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).

distribution.

(c) Sum of VOC with carbon number of 8 and greater.

g - mean is less than 5 times the MDL.

Duct burners were on for Runs 1 and 2, intermittent for Run 3 (total of approx. 30 minutes) and off for Run 4.

and VOC_{8+} are derived from the dilution sampler results (NH_3 results from the impinger train method are not significantly different). The VOC_{8+} emission factors are derived exclusively from the canister results, and due to the large number of compounds that were detected, emission factors are reported only for those with a relative uncertainty of 100 percent or smaller. 11 additional VOC_{8+} were measured in the Tenax® samples at concentrations greater than 5 times the Tenax® field blank; however, the uncertainty of the results is well above 100 percent so these are not reported. The carbonyl data quality from the dilution sampler and the Celanese method results is not considered adequate (see Section 4) for emission factor development due to poor method performance at the extremely low concentrations present in the samples

Other VOC Emission Factors

Emission factors for VOCs with a carbon number of seven or lower are presented in Table 5-4. All the results are derived from the canister samples. No results from the Tenax® samples were detected in two or more runs and at more than five times the level in the blanks.

PM2.5 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 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

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

Substance	Average (lb/MMBtu)	Uncertainty at 95% Confidence Level (%) (a)	95% Confidence Upper Bound (%) (b)	95th Percentile	5th Percentile	Number of Detected Runs
Toluene	1.7E-4	80	2.7E-4	2.5E-4	1.1E-4	4
Propane	1.2E-4	56	1.8E-4	1.4E-4	9.2E-5	4
Ethane	1.2E-4	55	1.7E-4	1.4E-4	9.1E-5	4
n-butane	5.0E-5	95	8.6E-5	7.5E-5	2.0E-5	4
Hexanal	4.8E-5	69	7.4E-5	6.1E-5	3.1E-5	4
Acetylene	4.3E-5	94	7.4E-5	6.4E-5	1.9E-5	4
Isobutane	2.6E-5	87	4.4E-5	3.9E-5	1.3E-5	4
Propene	2.5E-5	57	3.6E-5	2.9E-5	1.8E-5	4
Benzene	2.2E-5	91	3.7E-5	3.4E-5	1.3E-5	4
Iso-butene	1.1E-5	66	1.6E-5	1.3E-5	7.5E-6	4
Cyclopentane	4.7E-6	98	8.2E-6	7.0E-6	2.4E-6	4
Chlorobenzene	< 3.5E-6	90	5.8E-6	4.5E-6	2.7E-6	3
c-2-hexene	3.3E-6	51	4.7E-6	4.1E-6	2.8E-6	4
1-butene	3.2E-6	58	4.7E-6	3.7E-6	2.2E-6	4
Benzaldehyde	2.9E-6	67	4.4E-6	4.2E-6	1.7E-6	4
1,3-butadiene	1.9E-6	83	3.1E-6	2.7E-6	1.2E-6	4
Cyclopentene	1.5E-6	81	2.4E-6	2.2E-6	6.7E-7	4
t-2-butene	1.4E-6	60	2.1E-6	1.7E-6	9.6E-7	4
Cyclohexene	< 1.1E-6	47	1.5E-6	1.1E-6	1.1E-6	3
C7 olefin 2	< 9.4E-7	68	1.4E-6	1.1E-6	8.5E-7	3
2-methyl-2-butene	9.2E-7	67	1.4E-6	1.3E-6	6.2E-7	4
2-methyl-2-pentene	< 7.5E-7	80	1.2E-6	8.6E-7	5.9E-7	3

< - detected in fewer than all valid runs.

(a) 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 that the actual emissions differ from the reported emission factor value. Data users should exercise appropriate caution.

(b) 95% upper confidence bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% upper

g - mean is less than 5 times the MDL.

Duct burners were on for Runs 1 and 2, intermittent for Run 3 (total of approx. 30 minutes) and off for Run 4.

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, Na^+, Cl^-, fluoride, phosphate, Ca, magnesium), 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 agrees with the average measured PM2.5 mass to within 34 percent (dilution method results), which is within the uncertainty of the two results. It should be noted that although the reconstructed mass agrees well with the measured mass, there is considerable suspicion regarding the reliability of the OC mass that comprises most of the reconstructed mass (see Sections 4, 6 and 7 for additional discussion). The OC mass is multiplied by a factor of 1.082 to account for hydrocarbon speciation (based on the total carbon fraction of all the SVOCs detected in any run). It is assumed that elements are 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 were 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 not included in the reconstructed mass.

The speciation profile for PM2.5, based on dilution sampler results, is given in Table 5-5. This table includes all results from the ED-XRF analysis of the dilution sampler TMFs, the ion analysis of the dilution sampler QFFs and the OC/EC analysis of the dilution sampler QFFs.

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

Substance	Average Mass Fraction *(1)* *(2)* (%)		Uncertainty at 95% Confidence Level (%) *(3)*	95% Confidence Upper Bound (%) *(4)*	Count
Group 1 *(5)* :					
OC *(6)*	b	73	81	110	3
NO_3^-	c	5.1	230	13	3
$SO_4^=$	c	4.4	200	10	3
Cl^-	c	3.8	140	7.3	3
Si	b c	3.5	300	10	3
Fe	c	2.7	250	7.2	3
Soluble Na	c	0.72	230	2.3	3
Zn	c	0.27	250	0.71	3
Cu	c	0.18	280	0.53	3
Ni	c	0.10	240	0.27	3
Group 2 *(7)* :					
EC	< c	2.8	220	7.2	2
Ca	< c	1.0	310	3.2	2
Al	< c	0.77	300	2.4	2
K	< c	0.45	320	1.4	2
Ti	< c	0.13	630	0.94	2
Mn	< c	0.07	240	0.20	2
V	< c	0.06	630	0.41	2
Pb	< c	0.03	340	0.10	2
Co	<	0.02	430	0.09	2
Br	< c	0.01	340	0.05	2
Backup OC *(8)*		72	130	140	3

(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 excluded from speciation calculations. The average reconstructed PM2.5 mass is 34% greater than average measured PM2.5 mass; the difference is within the 95% confidence interval of the measurements.

(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) Substances detected in three or more samples are considered reliable for this test.

(6) OC measurements are subject to a potential positive bias from adsorption of VOC species. Refer to footnote *(8)* and Section 7 for further discussion.

(7) Substances detected in two samples are considered qualitative, not suitable for quantitative analysis.

(8) 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.

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 Ambient concentration.

Figure 5-1 presents the data presented in Table 5-5 graphically. 93 percent of the reconstructed mass is accounted for by substances measured in three or more test runs (Group 1), and 99 percent by those measured in at least 2 runs (Groups 1 and 2). The majority of the reconstructed mass (73 percent) is accounted for by OC, with NO_3^- being the next most abundant constituent (5.1 percent). The relative uncertainties associated with the species mass fractions are all larger than 200 percent except for OC and Cl^-, which is a consequence of the extremely low species concentrations present in the stack gas samples. Nevertheless, the 95 percent upper confidence bound can be used as an estimate of the likely upper bound for the mass fraction. The 95 percent upper confidence bound for the OC mass fraction is greater than 100 percent and should be ignored. Back-up OC, which represents a mass fraction of 72 percent, represents 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.

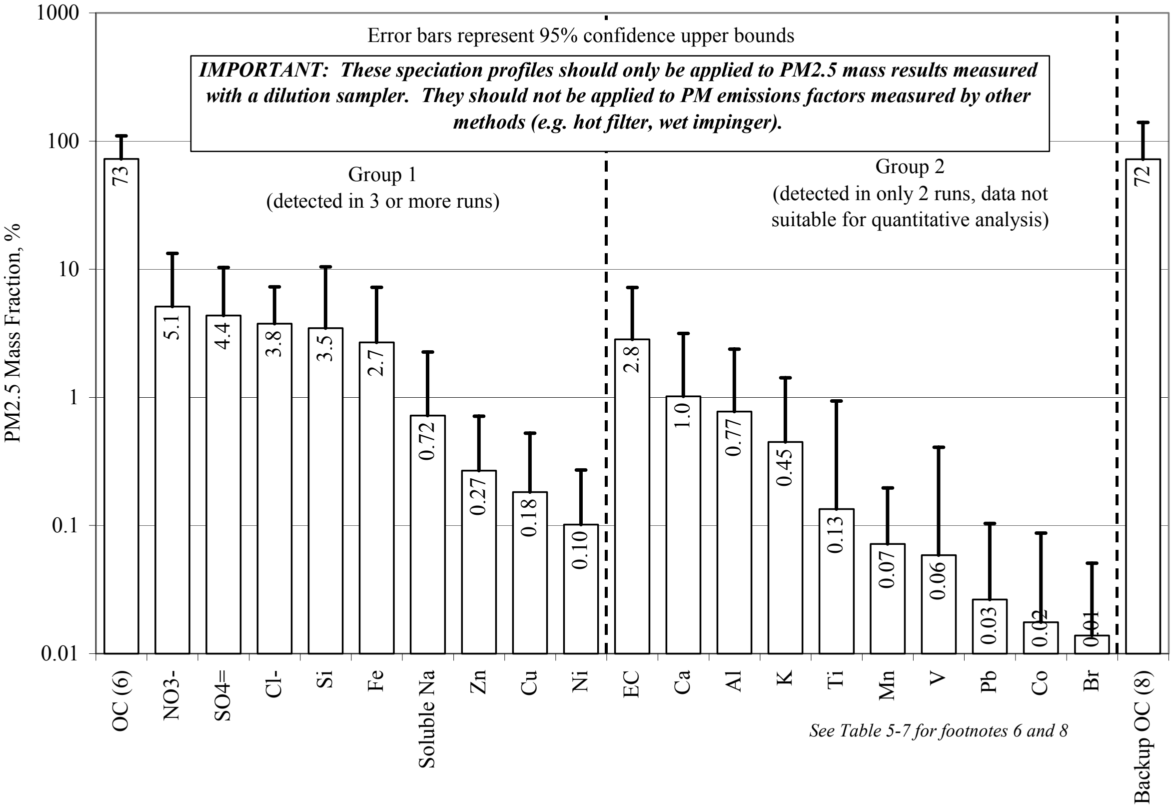


Figure 5-1. PM2.5 speciation profile, as measured by the dilution sampler, normalized by reconstructed PM2.5 mass (Site Bravo).

Particulate Carbon Speciation Profile (Dilution Sampler)

Table 5-6 and Figure 5-2 show the organic aerosol speciation profile, expressed as a mass fraction normalized by the OC mass measured by TOR on the QFFs. This mass fraction is determined by multiplying the species carbon fraction by the average species emission factor, then dividing by the average species emission factor for OC, both in units of lb/MMBtu. The speciated SVOCs do not account for a large fraction of the OC mass. This is typical of many other research studies. Two possible explanations are that there is a significant positive bias in the OC results (e.g., due to the VOC adsorption artifact as discussed elsewhere in this report) or that not all of the organic compounds were extractable or elutable by the analytical methods employed. Given the prominence of back-up OC in the results, the former argument seems more likely. Particulate carbon species detected in at least three runs (Group 1) account for approximately 0.5 percent of the OC mass. If Group 2 (detected in 2 runs) substances are added, the total accounts for 1.7 percent of the OC mass and if all substances detected are included, the total is 2.8 percent of the OC mass.

PM2.5 Mass Speciation Profile (Method PRE-4/202)

As noted previously, the dilution sampler results are considered the most representative of true PM2.5 emissions due to artifacts (i.e., conversion of gaseous SO_2 to $SO_4^=$, excessive condensation of vapors) associated with Method 202 that lead to positive bias in the $SO_4^=$ and mass results. *The speciation profile is presented here only to illustrate the differences between the two methods, and should not be used for source apportionment or source receptor analysis since they do not represent actual emissions*. Table 5-7 and Figure 5-3 present the speciation profile of the PM2.5 mass as measured by hot filter/iced impinger methods (Method PRE-4/202). The mass fraction is normalized using the reconstructed PM2.5 mass based on the organic CPM residue mass, filterable PM2.5 mass and individual inorganic CPM residue species measurements. Elements detected with inductively coupled plasma/mass spectrometry (ICP-MS) are assumed converted to the highest stable oxide during combustion, except for S and Cl for which the IC measurements were used. The reconstructed mass accounts for 98 percent of the measured total PM2.5 mass.

Table 5-6. OC Speciation Profile – Dilution Sampler Results (Site Bravo).

Substance		Average Mass Fraction *(1)* (%)	Uncertainty At 95% Confidence Level (%) *(2)*	95% Confidence Upper Bound (%) *(3)*	Count
Group 1 *(4)* :					
Phenanthrene	b c	0.33	184	0.75	4
7-methylbenzo(a)pyrene		0.07	99	0.13	4
2-methylphenanthrene	b c	0.05	278	0.15	4
Anthrone		0.02	125	0.04	4
Group 2 *(5)* :					
1,4+1,5+2,3-dimethylnaphthalene	< c	0.58	304	1.78	2
2-methylnaphthalene	< c	0.29	331	0.94	2
1-methylnaphthalene	< c	0.16	323	0.50	2
Xanthone	< b c	0.06	400	0.22	2
Pyrene	< c	0.04	299	0.13	2
Fluoranthene	<	0.04	218	0.09	2
A-trimethylnaphthalene	< b c	0.03	217	0.08	2
7-methylbenz(a)anthracene	<	0.02	329	0.07	2
B-trimethylnaphthalene	<	0.02	225	0.05	2
E-trimethylnaphthalene	< c	0.01	237	0.03	2
F-trimethylnaphthalene	<	0.01	224	0.03	2

n/a- not applicable; only one run within detectable limits.

(1) SVOC carbon mass expressed as a percent of organic carbon mass measured by TOR on quartz fiber filters; results less than 5 times field blank excluded.

(2) 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 the reported mass fraction is not representative of actual emissions. Data users should exercise appropriate caution.

(3) 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.

(4) Substances detected in three or more samples are considered reliable for this facility.

(5) Substances detected in two samples are considered qualitative, not suitable for quantitative analysis.

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 Ambient concentration.

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.

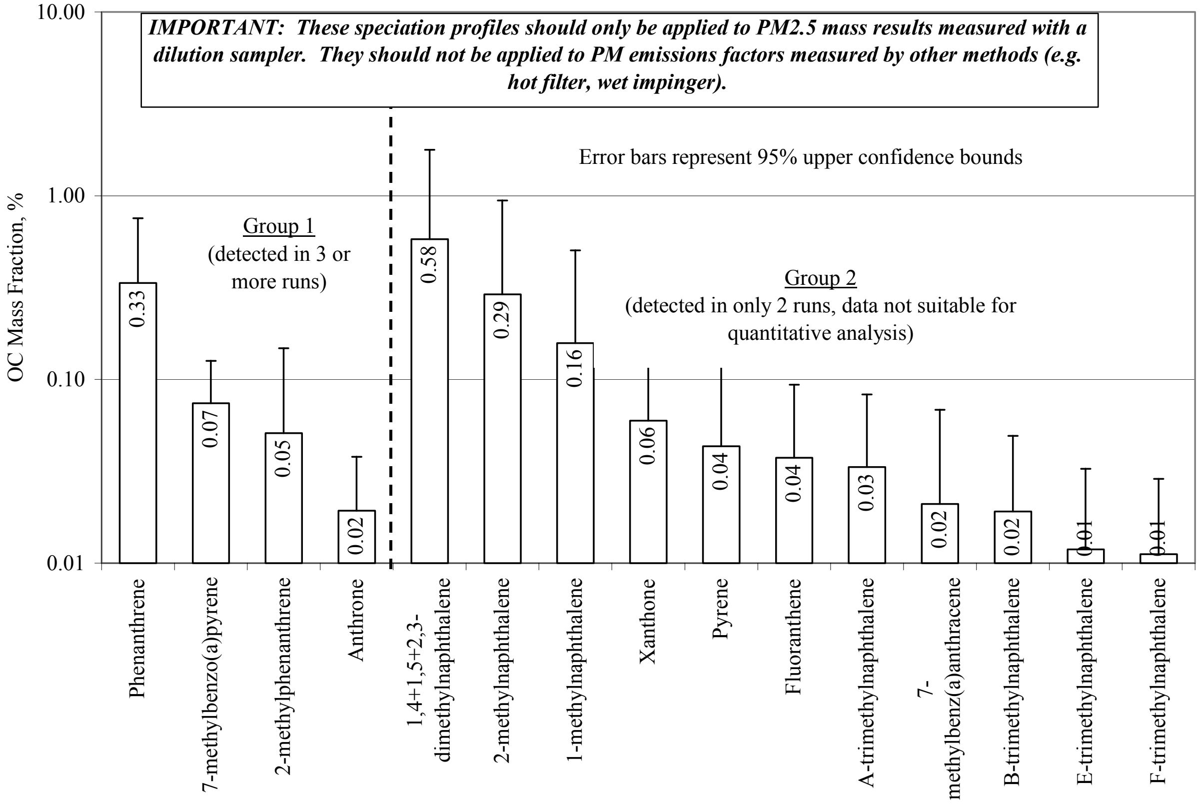


Figure 5-2. OC speciation profile, as measured by dilution sampler, normalized by measured OC mass (Site Bravo).

Nearly all of the PM2.5 mass comes from CPM (99 percent). Filterable PM2.5 mass, which is the mass collected from the filter and one cyclone rinse fraction, accounts for less than 4 percent of the total PM2.5 mass. However filterable PM2.5 mass was detected in only one run so the uncertainty is unknown. Of the substances detected in three or more test runs, $SO_4^=$ has the greatest abundance at 48 percent followed by NH_4^+ at 8.7 percent. Cl^- accounts for 17 percent of the mass, and organic CPM, which was detected in only one run and hence of unknown uncertainty, accounts for 19 percent of the average PM2.5 mass, respectively. Na accounts for 3.4 percent but was detected in only one run hence the uncertainty is unknown. The prominence of Cl^- could be indicative of the coastal location of this facility.

Table 5-7. PM2.5 Mass Speciation - Method PRE-4/202 Results (Site Bravo).

Substance	Average Mass Fraction (a) (%)	Uncertainty (%) (b)	95% Confidence Upper Bound (%) (c)	Count
Group 1 (d):				
$SO_4^=$	48	52	68	4
NH_4^+	8.7	156	19	4
Zn	0.22	111	0.40	4
Mn	0.031	159	0.068	4
Ba	0.0029	59	0.0041	4
Group 2 (e):				
Organic CPM (Method 202)	19	n/a	n/a	1
Cl^-	17	427	54	2
Na	3.4	n/a	n/a	1
Filterable PM2.5 (Method PRE-4)	3.0	n/a	n/a	1
Ca	0.45	n/a	n/a	1
Sr	0.019	266	0.044	2

(a) Mass fraction is normalized using reconstructed PM2.5 mass, which is 98% of measured PM2.5 mass.

(b) 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 the reported emission factor value is not representative of actual emissions. Data users should exercise appropriate caution.

(c) 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 emissions are lower) for emissions.

(d) Substances detected in three or more samples are considered reliable for this test.

(e) Substances detected in less than 3 samples are considered qualitative, not suitable for quantitative analysis.

n/a - not applicable; uncertainty cannot be calculated for single datum.

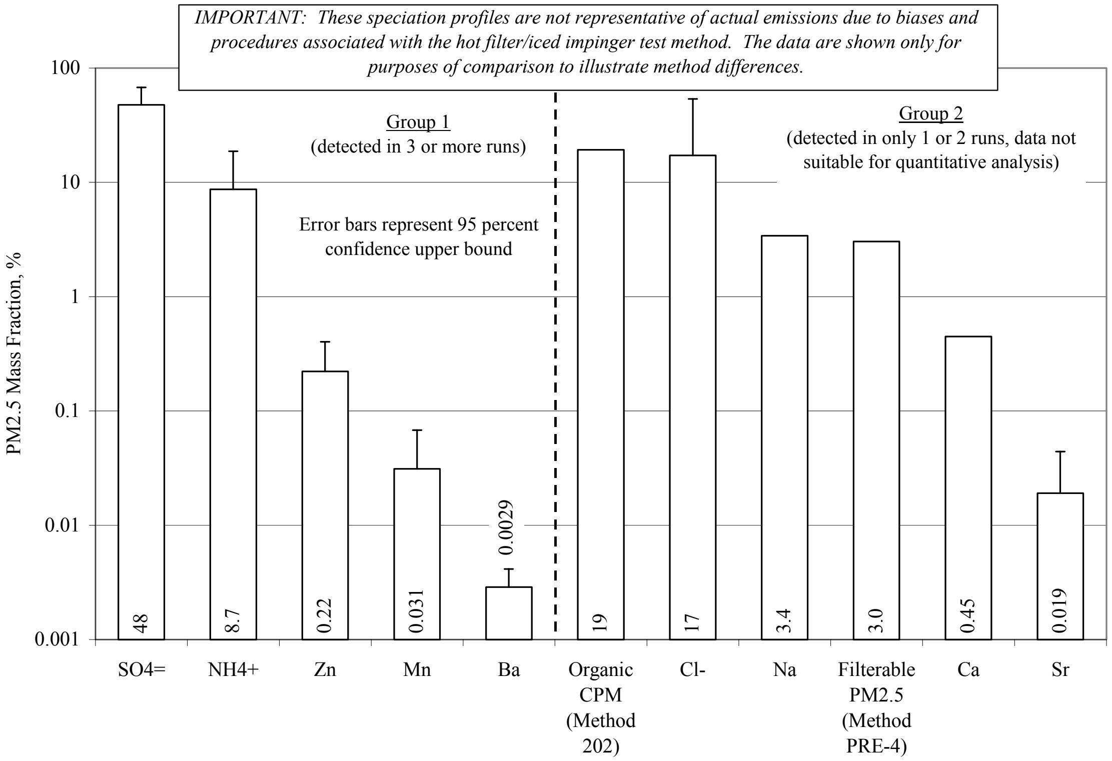


Figure 5-3. PM2.5 mass speciation profile - Method PRE-4/202 results (Site Bravo).

6. QUALITY ASSURANCE

SAMPLE STORAGE AND SHIPPING

All samples that required refrigeration were stored on-site in a refrigerator prior to shipment. Samples were shipped via overnight courier to their respective labs in an ice chest with blue ice. In-stack (Method PRE-4) and impinger filters (Method 202) were stored in a desiccator at ambient conditions prior to shipment. Upon receipt of samples at the lab, those requiring refrigeration were stored at 4 °C (nominal). Samples were packed, shipped and stored in a manner to prevent breakage.

METHOD 202 AND METHOD PRE-4 SAMPLES

QA/QC samples for Methods PRE-4, 8 and 202 which were collected and analyzed during the tests include the following:

- Reagent blanks. These are samples of the reagents or media used in the field for collecting samples. Reagent blanks are taken directly from the original container or bottle as received from the manufacturer (e.g. liquid reagents for absorbing pollutants in impingers), after any pre-test conditioning normally performed before a test (e.g., pre-fired QFFs). The results are used to assess the contribution of contamination or background levels of pollutants in the reagents. One reagent blank of each type was collected for the entire sampling campaign.

- Recovery blanks. These are samples of the rinse reagents used to recover samples. Recovery blanks are taken from the wash bottles used in the field to rinse the sample from the sampling equipment into the storage containers. The results are used to assess the contribution of contamination or background levels of pollutants in the rinse reagents including any contamination that may have been introduced in the field. One recovery blank of each type was collected for the entire sampling campaign.

- Field blanks. A field blank (also known as a dynamic blank) is involved in all aspects except for the actual collection of the sample. For example, Method PRE4/202 field blank consists of a complete sample train cleaned, charged, assembled, heated and leak-checked at the sampling location in the same manner as the trains used to collect samples. It remains at the sampling location for the duration of a test, then is recovered and analyzed in the same manner as the samples. The results are used to assess the cumulative effects of contamination and background levels of pollutants introduced with the reagents, sampling equipment and handling in the field and laboratory. Field blanks are the most complete indicators of the practical quantification limits of the overall method. One Method PRE-4/202 field blank was collected for the entire sampling campaign.

Gravimetric Analysis

The balance for the Method PRE-4 in-stack filters and acetone rinses was calibrated daily with two "S" type weights in the range of the media being weighed and the tare was set prior to weighing each batch of filters. If the results of these performance tests deviated by more than ±1 mg, the balance was recalibrated. Performance test results were within specifications, thus recalibration was not required. If consecutive sample weights deviated by more than ±0.5 mg, the sample was returned to the desiccator for at least 6 hours before reweighing. Pre- and post-weights, check weights and reweights (if required) were recorded on data sheets.

Table 6-1 presents the results of the dichloromethane reagent, water reagent and acetone recovery blanks. The acetone recovery blank values are used to correct the EPA Method PRE-4 results and the dichloromethane and water rinse blanks are used to correct Method 202 results. Results of the filter blank weights are also presented in Table 6-1.

The net QFF weights for all the in-stack samples are less than zero (-0.40 to –0.84 mg). The QFF in the field blank train also is negative (-0.20 mg). This is common when testing gas combustion sources. It is most likely due to loss of minute fiber fragments during sample handling or possibly loss of filter impurities (if present) during heating. All negative filter weights are treated as zeros in final calculations. The tolerance of the constant weight procedure according to Method PRE-4 is 0.5 mg (when two consecutive weights agree within 0.5 mg agree, the last weight is reported). The results show that the final two consecutive weights usually agree within near or less than 0.1 mg using a 5-place (0.01 mg resolution) balance, so the actual analytical precision is better than the tolerance.

Because particulate concentration in gas combustion stack gas is well below the range the method was originally intended for, the results of this test were used to assess the results relative to the limits of the method. As one measure of method performance, the MDL for the gravimetric analytical procedure was defined as 3 times the standard deviation of the pre-test and post-test filter weighings (two weights for each). For the filter weights, the MDL is approximately 0.32 mg and LQL, defined as 10 times the standard deviation, is 1.06 mg. These can be converted to in-stack MDL and LQL by dividing by the average sample gas volume, which was approximately 3.5 dscm (6-hour test runs) for these tests.

Table 6-1. Method PRE-4/202 Filter and Reagent Blank Results (Site Bravo).

Sample	Mass (mg)
Method 202 Water Reagent Blank (180 mL)	0.3
Method 202 Dichloromethane Reagent Blank (180 mL)	ND *(1)*
Acetone Recovery Blank (62 mL)	2.71
Method 8 IPA Reagent Blank (405 mL)	0.05
Method 202 Impinger Filter Field Blank	0.3
Method PRE-4 Filter Field Blank	-0.2
Dilution Sampler Filter Field Blank	-0.6 *(2)*
Dilution Sampler Filter Trip Blank	-0.01

(1) Detection limit = 1 mg
(2) Teflon® membrane separated from support ring causing damage to the filter

The MDL and LQL for a method as a whole may be defined using the standard deviation of a number of field (dynamic) blanks. For these tests, the standard deviation of the net filter weights for all four test runs can be used since all the measurements are close (within 5 times) to the blank level - "near zero" for practical purposes by this method. The overall method MDL and LQL defined this way are 0.61 mg and 2.02 mg, respectively. Because they are less than zero, all of the in-stack filter net weights fall below the MDL.

All the acetone rinse net weights also are within 5 times the net weight of the recovery blank. The MDL and LQL for the acetone rinse procedure can be estimated by using the results of the field blank and the acetone recovery blank (Table 6-2). The raw analytical results are corrected to 30 mL rinse volume, which is the approximate average rinse volume for all the stack samples. The resulting method MDL for the rinses including the acetone recovery blank is 1.71 mg and the LQL is 5.68 mg. 9 of the 12 net weights for the stack sample acetone rinses are below the MDL, and the rest are below the LQL. The acetone recovery blank weight is somewhat high compared to previous tests and much greater than the field blank rinses, indicating possible contamination of the acetone recovery blank. If the acetone recovery blank is excluded from the analysis, the method MDL and LQL are 1.07 mg and 3.57 mg, respectively. Compared to these levels, six of the stack samples are below the MDL and all but one of the rest is below the LQL.

Table 6-2. Method PRE-4 MDL and LQL Based on Acetone Rinse Field and Recovery Blank Weights (Site Bravo).

Sample Fraction	Volume (mL)	Mass (mg)	Mass @30 mL (mg)
Field Blank PM10 cyclone catch rinse	25	0.07	0.08
Field Blank PM2.5 cyclone catch rinse (2.5-10 µm)	32	0.19	0.18
Field Blank <PM2.5 rinse (<2.5 µm)	23	0.57	0.74
Acetone Recovery Blank	62	2.71	1.31
Standard Deviation	--	--	**0.57**
Standard Deviation, excluding recovery blank	--	--	**0.36**
MDL (3*standard deviation)	--	--	**1.71**
MDL (3*standard deviation) excluding recovery blank	--	--	**1.07**
LQL (10*standard deviation)	--	--	**5.68**
LQL (10*standard deviation) excluding recovery blank	--	--	**3.57**

The filterable PM2.5 result includes one acetone rinse fraction plus the filter. Therefore, the MDL and LQL for filterable PM2.5 are the sum of the fractions: 1.68 mg and 5.50 mg, respectively. Of the four PM2.5 stack samples, all are less than the total MDL. Therefore, the filterable PM2.5 results from Method PRE-4 should be considered qualitative. Similarly, the MDL and LQL for filterable PM10 and total FPM can be estimated by adding in the other acetone rinses (2 rinses included in PM10, 3 rinses included in total FPM). Based on these results, it is clear that Method PRE-4 (and by extension, similar methods such as EPA Methods 201A, 5 or 17) does not have sufficient sensitivity for determining actual filterable PM emissions from gas combustion.

Inorganic Residue Analysis

As described in Method 202, a water reagent blank was analyzed in the same manner as the field samples, including the extra analysis of the residue to determine ion and element concentrations. The equivalent in-stack concentrations in mg/dscm using the average stack sample gas volume (approximately 3.5 dscm) were calculated (Table 6-3). Compared to the stack sample results

Table 6-3. Method 202 Water Reagent Blank Results (Site Bravo).

Compound		Concentration (mg/dscm)
Fluoride		9.0E-3
Chloride		6.1E-2
Nitrate (as N)		1.9E-2
Sulfate (as $SO_4^{=}$)	<	5.2E-3
Al	<	9.6E-4
Ba	<	3.2E-5
Be	<	3.2E-5
B	<	3.2E-4
Cd	<	6.4E-5
Ca		3.2E-2
Cr	<	1.3E-4
Co	<	3.2E-4
Cu	<	1.9E-4
Fe	<	6.4E-4
Pb	<	6.4E-4
Mg		4.9E-3
Mn	<	1.6E-4
Mo	<	1.6E-4
Ni	<	6.4E-4
P	<	1.9E-3
K	<	3.2E-2
Si		1.8E-2
Ag	<	3.2E-4
Na		1.1E-1
Sr		1.2E-4
S		1.2E-2
Tl	<	1.9E-3
Sn	<	1.6E-3
Ti	<	3.2E-4
V	<	3.2E-4
Zn	<	3.2E-4
Zr	<	3.2E-4

< - below laboratory limit of quantification (Detection limit x 3.33)

presented in Section 4, Cl^-, $SO_4^{=}$, NH_4^+, Zn, S, Sr, and Mn are the only substances with average stack sample concentrations greater than 5 times their respective concentrations in the water reagent blank. The average sample concentrations of Be, Cd, Cr, Co, Fe, Pb, Mo, Ni, P, K, Si, Ag, Tl, Sn, Ti, V and Zr are all less than the concentrations in the reagent blank, with most having sample concentrations approximately equal to the reagent blank concentrations. Ortho-phosphate was not detected in the reagent blank or the stack samples.

DILUTION SAMPLER

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

- A DSB was collected at the field site after the emissions sampling campaign, before the dilution sampler was cleaned. The DSB was obtained by plugging the sample probe inlet and drawing air through the dilution air filters (HEPA and activated carbon) and the dilution sampler and collecting samples in the same manner as the stack samples. DSB results are an indication of cross-run contamination resulting from deposition of species on dilution sampler surfaces during sampling and/or dilution air purification system (HEPA/carbon filter) breakthrough. The only DSB collected in this test was for carbonyl samples.

- Field blanks were collected by setting up and breaking down the dilution sampler sampling equipment without drawing gas through the sampling media. Field blank results are an indication of contamination during the handling and transport of the sampling media plus any contamination in the reagents. Field blanks were collected for all sample types except canisters;

- Trip blanks are sampling media that are shipped from the lab to the test site and back but are not opened. Trip blank results are an indication of contamination during the transport of the sampling media plus any contamination in the reagents. The only trip blank that was collected in this test was for Tenax® samples;

- Ambient air samples were collected by drawing air directly through a PM2.5 separator and into the sampling media. When compared with the DSB results, the ambient air results provide a means of evaluating dilution air purification system breakthrough. It also provides an indication of the potential contribution of pollutants in the ambient air to stack emissions. Ambient air samples were collected for all sample types.

- The field blank and trip blank results are presented as in-stack equivalents using the average stack sample volumes and dilution factors. Ambient air sample results presented in Section 4 are as measured. The data quality is evaluated by comparing blank results to the 95 percent confidence lower bound of the average stack/ambient results presented in Section 4. The procedures used for calculating the confidence intervals are described in Section 5. If the blank or ambient level is greater than the 95 percent confidence lower bound, the data are flagged. Data that are so flagged should be used with caution because it is likely that they are not significantly different from the background levels in 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 relative humidity of 30 ±5 percent for a minimum of 24 hours prior to weighting. Weighing was performed on a Cahn 31 electro-microbalance with ±1 microgram sensitivity. The electrical charge on each filter was neutralized by exposure to a polonium source for 30 seconds prior to placing the filter 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 on the dilution sampler TMFs are 88, 300, and 29 µg for the valid runs (Runs 1, 2 and 3, respectively). Compared to the reported analytical uncertainty (2.684 µg), the stack sample weights are all above the analytical LOQ. The TMF net weight for Run 4 is less than zero. The large variability of the TMF results is unusual compared to previous tests using the same method, and was traced to a procedural error during this test (overtightening of the filter cassettes) that led to slight filter damage. The damage to the TMF for Run 4 was noticeable, with the polycarbonate ring visibly separated from the Teflon® membrane. The field blank filter net weight for the dilution sampler also is less than zero (Table 6-4); therefore, the result is reported as ND. The average PM2.5 mass in the stack sample is approximately 7 times the PM2.5 mass concentration in the ambient air; however, because of the variability of the stack results the 95 percent confidence lower bound of the average stack result is less than the ambient air concentration.

Table 6-4. Dilution Sampler PM2.5 Mass Blank Results (Site Bravo).

	mg/dscm
	FB
PM2.5 mass	ND

FB - Field Blank
ND - Not Detected

Ions and Secondary PM Gaseous Precursors Analysis

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 relative humidity (±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 micrograms per mL (µg/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) are 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 also were designated for reanalysis.

Table 6-5 lists the blank results for ions and the secondary PM gaseous precursors. None of the target ions was detected on the QFF or potassium carbonate-impregnated cellulose fiber filter field blanks. NH_3 was detected in the citric acid-impregnated cellulose fiber filter field blank; however, the level is well below the lower 95 percent confidence bound of the average stack result. The lower 95 percent confidence bounds of the average SO_2 and NH_3 stack concentrations are greater than their concentrations in the ambient air; those for Cl^-, NO_3^-, $SO_4^=$ and soluble Na^+ are not.

Table 6-5. Dilution Sampler PM Ion and Secondary PM Precursor Blank Results (Site Bravo).

	mg/dscm	
	DSB	FB
Cl^-	e	ND
NO_3^-	e	ND
$SO_4^=$	e	ND
NH_4^+	e	ND d
NH_3	e	1.0E-3
SO_2	e	ND
Soluble Na	e	ND

DSB - Dilution Sampler Blank
FB - Field Blank
d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.
e - QA/QC sample not collected

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. NIST standards are the definitive standard reference material (SRM), but are only available for the species Al, Ca, Co, Cu, Mn, and Si

(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 analytical laboratory's database.

Only Si, Mg and P were detected in the field blank (Table 6-6). The Si and Mg concentrations are not significant in the field blank but the stack concentration of P is to the blank concentration close (less than 5 times the field blank). 19 of the 24 elements detected in the stack also were detected at lower levels in the ambient air. All of the elements in the stack are present at concentrations 10 times greater than in the ambient air except for Na, S, Mg, Pb, and Br; however, none of the 95 percent confidence lower bounds exceeded the ambient air so the differences likely are not significant at this confidence level.

Organic and Elemental Carbon 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.

Known amounts of 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.

Table 6-6. Dilution Sampler Element Blank Results (Site Bravo).

	mg/dscm	
	FB	
Cl	ND	
Fe	ND	
Si	1.2E-04	a
Na	ND	
S	ND	
Ca	ND	
Al	ND	
K	ND	
Mg	1.1E-04	a
Ag	ND	c
Cr	ND	c
Zn	ND	
Cu	ND	
Ti	ND	
P	1.1E-04	c
Ni	ND	
Mn	ND	
V	ND	
Pb	ND	
Mo	ND	c
Sr	ND	c
Br	ND	
Zr	ND	c
Co	ND	

FB - Field Blank

ND - Not Detected

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

c - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

EC was not detected in the field blank or trip blank (Table 6-7). OC was detected in both blanks, slightly higher in the field blank than in the trip blank. The concentrations are greater than the 95 percent confidence lower bound of the average stack sample result; therefore, it is likely the stack sample and blank results are not significantly different. The average stack 95 percent confidence lower bound is greater than the ambient air concentration for OC, but not for EC.

Table 6-7. Dilution Sampler OC and EC Blank Results (Site Bravo).

	mg/dscm	
	FB	TB
OC*	9.3E-02 a	4.8E-2 b
EC	ND	ND
Backup Filter OC**	6.0E-02	4.7E-2 b

FB - Field Blank
ND - Not Detected
TB - Trip Blank
a - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.
b - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.
* OC measurements are subject to a potential positive bias from adsorption of VOC species. Refer to footnote ** and Sections 6 & 7 for further discussion.
** OC measured on a "backup" quartz fiber filter placed downstream of Teflon membrane filter. Refer to Sections 6 & 7 for further discussion.

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 placed downstream of the TMF, so that all the particles were removed prior to the backup QFF, was used to indicate the potential magnitude of the bias. High concentrations of OC (relative to the samples) were found on all of the backup QFFs. The backup OC is approximately 90 percent of the average OC measured in the stack samples. The ratios of backup OC to sample OC are 0.64, 0.98 and 0.36 for the field blank, trip blank and ambient sample, respectively. These results indicate the strong likelihood of a significant positive bias in the OC results (see Section 7 for additional discussion of implications).

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 acenapththene 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.

Fifteen of the 33 SVOCs detected in the stack samples also were detected in the field blank (Table 6-8). Of the 33 SVOCs, 14 were detected only in a single run and the uncertainty is unknown. Seven of the SVOCs in the stack were not present with a 95 percent confidence lower bound greater than the field blank. 7-Methylbenzo(a)pyrene, C-trimethylnaphthalene, 7-methylbenz(a)anthracene and anthrone are the only compounds with 95 percent confidence lower bounds above the field blank and ambient air concentrations, and with average concentrations greater than 5 times the field blank. Therefore, concentrations of the other 29 compounds in the stack sample are not likely to be significantly above their concentrations in the field blank and ambient air.

Table 6-8. Dilution Sampler PUF/ XAD® Tunnel and Field Blank Results (Site Bravo).

Compound	mg/dscm	
	FB	
1,4+1,5+2,3-dimethylnaphthalene	ND	
2-methylnaphthalene	ND	
Acenaphthene	5.3E-4	b
1,3+1,6+1,7-dimethylnaphthalene	ND	d
1+2-ethylnaphthalene	4.7E-4	b
Phenanthrene	1.4E-5	b
Dibenzofuran	ND	d
1-methylnaphthalene	ND	
2,6+2,7-dimethylnaphthalene	ND	d
E-dimethylphenanthrene	1.9E-4	d
Fluorene	ND	d
Biphenyl	ND	d
2,3,5+I-trimethylnaphthalene	9.6E-6	d
Xanthone	1.9E-5	b
C-methylphenanthrene	ND	d
C-dimethylphenanthrene	ND	d
Pyrene	ND	
7-methylbenzo(a)pyrene	ND	
Fluoranthene	1.0E-5	
A-trimethylnaphthalene	1.8E-5	b
C-trimethylnaphthalene	2.0E-5	
1-methylphenanthrene	ND	d
2-methylphenanthrene	8.0E-6	b
B-trimethylnaphthalene	6.4E-6	
7-methylbenz(a)anthracene	ND	
4-methylpyrene	ND	d
E-trimethylnaphthalene	ND	
F-trimethylnaphthalene	4.0E-6	
D-MePy/MeFl	9.6E-6	b
Anthrone	ND	
2,4,5-trimethylnaphthalene	ND	d
C-MePy/MeFl	1.0E-5	d
Anthracene	4.0E-6	d

FB - Field Blank

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

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

VOC Analysis

Calibration curves were performed weekly. Volatile organic compounds 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.

Of the 47 VOCs detected in the Tenax® samples, 20 were detected in the field blank (Table 6-9) and 43 were detected in the ambient air. Twenty-seven VOCs were detected in only a single run, therefore uncertainty is not known for these and these should be considered questionable results. Only nonanal, octanal and eicosane have 95 percent confidence lower bounds that are greater than the field blank and ambient air sample. However, the stack concentrations for these are close (with 5 times) to the field blank concentration and it is likely that they are not significantly different. Benzaldehyde, benzoic acid, hexadecanoic acid, phenol and acetophenone were detected in the Tenax® stack samples and field blank, but these should be disregarded because they are considered products of Tenax® degradation.

Carbonyls Analysis

Blanks collected in the field for the DNPH coated silica gel cartridges used to measure carbonyls included one field blank for every run and one DSB for the test campaign. Acetaldehyde and acetone are the only carbonyls detected in the field blanks (Table 6-10). The concentrations of these two compounds in all of the field samples are less than 5 times that in the average field blank, indicating sample concentrations may not be significantly above background levels of the test method. These plus formaldehyde, propionaldehyde and M-tolualdehyde also were detected in the DSB. Acetaldehyde, acetone, and formaldehyde also were detected in the ambient air, at levels higher than in the DSB, most likely signifying the possibility of significant breakthrough across the dilution air filtration system for these carbonyls. Comparing the ambient sample and

Table 6-9. Dilution Sampler Tenax® VOC Blank Results (Site Bravo).

	mg/dscm	
	FB	
Hexadecanoic acid	4.4E-2	b
Benzaldehyde	3.2E-2	b
Nonanal	ND	
Acetophenone	9.0E-3	b
Decanal	ND	
Styrene	7.2E-2	b
Pentadecane	2.8E-3	b
Heptadecane	ND	
Dodecane	3.6E-3	b
Tetradecane	1.6E-3	b
Phenol	8.4E-3	b
Cyclohexanone	ND	d
Hexadecane	ND	
Decane	1.2E-2	b
m & p-xylene	5.0E-3	b
Butyl acetate	ND	d
Octadecane	ND	
p-isopropyltoluene	1.7E-2	b
Octanal	ND	
1-undecene	ND	
Undecane	6.2E-3	b
Nonane	3.5E-3	b
1-nonene	ND	d
1-decene	ND	d
Biphenyl	3.2E-3	b
Tridecane	1.2E-3	b
Ethylbenzene	3.4E-3	b
Dodecene	ND	
o-xylene	2.8E-3	b
2-heptanone	ND	d
1,2,4-trimethylbenzene	1.2E-3	b
Nonadecane	ND	d
3-methyloctane	ND	
Eicosane	ND	
1,3-dichlorobenzene	ND	d
2,3-benzofuran	ND	d
m-ethyltoluene	1.3E-3	b
Naphthalene	ND	
2-methylnaphthalene	ND	d
Propylbenzene	ND	d
Dimethyloctane	ND	d
o-ethyltoluene	ND	d
1,3,5-trimethylbenzene	ND	d
(+/-)-limonene	1.6E-3	d
2-methyloctane	ND	d
p-ethyltoluene	ND	d
4-ethyl-o-xylene	ND	d

FB - Field Blank

ND - Not Detected

b - 95% Confidence Lower Bound of the Average concentr

d - Insufficient data to calculate 95% Confidence Lower B

Table 6-10. Dilution Sampler Carbonyl Blank Results (Site Bravo).

	mg/dscm			
	DSB		FB	
Formaldehyde	6.6E-2	a	ND	
Acetaldehyde	8.5E-2	a	3.5E-2	b
Acetone	2.4E-1	a	5.6E-2	b
MEK	ND	d	ND	d
Glyoxal	ND		ND	

DSB - Dilution Sampler Blank
FB - Field Blank (Average of all Field Blanks)
ND - Not Detected
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.
d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

DSB indicates that the dilution air filtration system removal efficiency is approximately 56 percent for formaldehyde, 49 percent for acetone, and 84 percent for acetaldehyde. The levels present in the DSB are large compared to the raw stack results. For example, approximately 50 to 130 percent of the formaldehyde measured in the stack samples could be accounted for by breakthrough across the dilution air filtration system. Concentrations of formaldehyde, acetaldehyde and acetone in the samples are less than 5 times the DSB. Only glyoxal, which was not detected in the DSB or field blanks, has a 95 percent confidence lower bound for the stack sample average that is greater than the concentration in the blanks and the ambient air sample.

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. 20 percent or greater of every carbonyl detected in the stack samples was measured in the second (back) cartridge (Table 6-11) indicating breakthrough potential. In the ambient sample, the back cartridge is significant only for glyoxol. The observation that breakthrough appears to be more of a problem with the stack samples than with the ambient samples may indicate a potential interference from other substances present in the stack sample. Because results for acetaldehyde and acetone may be biased by background levels in the test method, 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.

Table 6-11. Carbonyl Breakthrough for Series DNPH-Coated Silica Gel Cartridges.

	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	70	30	80	20	66	34	48	52	52	48	na	na	100	ND
Acetaldehyde	59	41	54	46	62	38	66	34	68	32	43	57	100	ND
Acetone	73	27	63	37	52	48	73	27	59	41	47	53	86	14
Propionaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	46	54	ND	ND	ND	ND
Crotonaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MEK	ND	ND	ND	ND	ND	ND	67	33	ND	ND	ND	ND	100	ND
Butyraldehyde	ND	ND	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	ND	ND
Glyoxal	100	ND	58	42	53	47	49	51	ND	ND	ND	ND	78	22
Valeraldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
M-Tolualdehyde	ND	ND	ND	ND	ND	ND	ND	ND	100	ND	ND	ND	ND	ND
Hexanaldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected.

7. DISCUSSION AND FINDINGS

COMPARISON OF DILUTION AND HOT FILTER/ICED IMPINGER METHODS

The emission factor for total PM2.5 (including CPM) derived from the hot filter/iced impinger train methods (0.0031 lb/MMBtu) is more than ten times higher than the emission factor for PM2.5 derived from the dilution sampler results (0.00025 lb/MMBtu). In this test and several other tests of gas combustion sources using dilution samplers, the dilution sampler consistently yields much lower PM2.5 mass concentration and markedly different PM2.5 chemical speciation results compared to those from the traditional hot filter/iced impinger methods. The 95 percent confidence upper bound for the dilution sampler results is less than the 95 percent confidence lower bound for the hot filter/iced impinger results. This indicates that the average results for the two methods are significantly different at the 95 percent confidence level. Despite the high *relative* uncertainty of the dilution sampler PM2.5 mass results, the *absolute* uncertainty (±0.00065 lb/MMBtu) is approximately one half of the PM2.5 mass absolute uncertainty (±0.0014 lb/MMBtu) and one quarter of the total PM mass absolute uncertainty (±0.0026 lb/MMBtu) of the hot filter/iced impinger method results.

Total uncertainty of a measurement includes both random uncertainty (precision or variability) and systematic uncertainty (bias or accuracy). The total uncertainties calculated for these test results are dominated by random uncertainty resulting from run-to-run variability with both methods. In this test, the dilution sampling method is the most *precise* (smaller random uncertainty) in absolute terms. There are known artifacts (i.e., gaseous SO_2 conversion to solid residue and excessive condensation) and other limitations (insufficient sensitivity and high blank levels for in-stack FPM concentrations) that also impart bias (systematic uncertainty) in the hot filter/iced impinger method results. Therefore, the dilution sampler results are considered the most *accurate* (least systematic uncertainty) for this test. This bias is not included in the calculation of total uncertainty for the hot filter/iced impinger results because it is not easily quantifiable for a specific test. The probable impacts of these artifacts and limitations on the results are discussed further later in this section. Based on these considerations, the PM2.5 mass and speciation emission factors derived from the dilution sampler results are considered the most representative of actual primary PM2.5 emissions during this test.

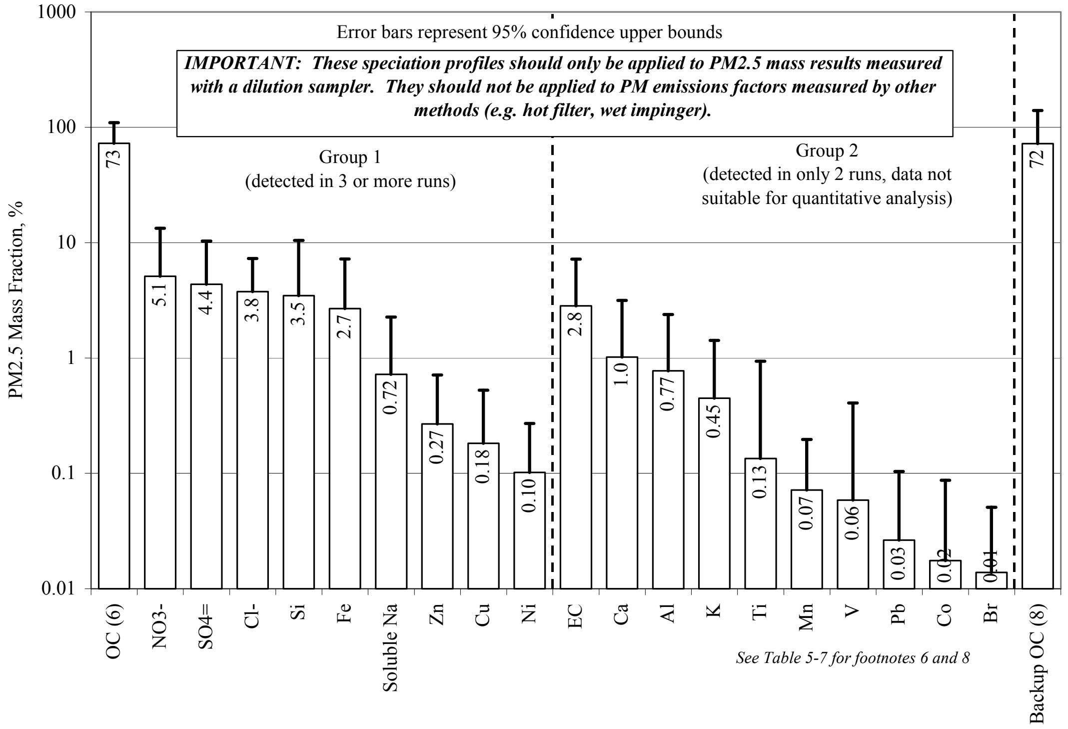
The valid PM2.5 mass results from the dilution sampler (29 to 300 μg) are well above the analytical lower quantification limit (15 μg) but the average has high relative uncertainty. This was traced to a procedural error (overtightening of the filter cassettes) that caused minor physical damage to some of the filters. This induced unusual variability (random uncertainty) in the gravimetric analysis results, including a negative net filter weight for one of the four runs. While this error adversely affects the uncertainty of the average PM2.5 mass result from the dilution sampler because the number of data points is reduced from 4 to 3 and because of the actual variation in filter weights that resulted, it does not affect the validity of other test results that do not depend on the gravimetric results. The relative uncertainty of the dilution sampler results is higher than expected based on previous tests of gas combustion sources using the same method. None of the prior tests using the dilution sampler resulted in negative net filter weights. This degree of variability is considered atypical of the dilution method's capability based on previous tests when proper procedures were followed.

Dilution sampling is designed to capture filterable matter and any aerosols that condense under simulated stack plume conditions. The sample gas was cooled from a stack temperature of approximately 229 °F (109 °C) to near ambient temperatures of 77 to 95 °F (25 to 35 °C) in this test as it mixed with dilution air in the dilution sampler. The effect of temperature variations within this range on the measurements is not known; however, no correlation between PM2.5 mass and sample temperature was found in this and prior tests (API 2001a, 2001b, 2001c). Therefore, sample temperature effects are not believed to be first order in these tests. Samples for analysis were then collected from the diluted sample. The conventional in-stack methods are intended to collect particles that are filterable at the filter temperature and those that condense downstream of the filter in a series of aqueous impingers placed in an ice bath. The gas temperature leaving the impingers was 60 to 63 °F (16 to 17 °C) in this test. The in-stack method cooled the sample without dilution by rapidly quenching the gas sample in water maintained at near freezing temperatures. Thus, both systems cooled the sample gas to similar final temperatures, yet the results are strikingly different. Since aerosol condensation and size distribution depends on temperature, concentration, residence time and other fundamental factors, it is not surprising that the results of the two methods differ. However, mechanistic variations alone seem unlikely to account for all of observed differences. Examining the speciation of the collected particulate matter provides additional insight into the observed differences.

Primary PM2.5 Emissions Speciation

The dilution and in-stack methods yielded very different speciation results compared to each other. Substantially all of the PM2.5 mass determined by Method PRE-4/202 - on average, 97 percent - was contained in the CPM fraction collected in the impingers, with the vast majority of this contained in the inorganic CPM fraction. This finding is qualitatively consistent with earlier tests of gas-fired combustion sources (API, 2001a, API, 2001b; API, 2001c, Wien et al., 2003) and other independent studies (e.g., Corio and Sherwell, 2000). The impinger residue comprising the CPM fraction was analyzed to understand better the reasons for the difference in results produced by this method and the dilution method. Using the results for filterable PM2.5, organic CPM, and inorganic CPM species presented earlier in Tables 4-5, 4-6 and 4-7, the reconstructed mass can be calculated and compared to the measured mass. $SO_4^=$, Cl^- and NH_4^+ account for most of the reconstructed inorganic CPM mass, with smaller contributions from Na, Ca, Zn, Mn, Sr and Ba (Figure 7-1b). Note the NH_4^+ probably originates from titrating the inorganic fraction with sodium hydroxide (NaOH) to stabilize any H_2SO_4 present in the sample during the inorganic fraction analysis (see Figure 3-3). $SO_4^=$ plus NH_4^+ account for 57 percent of the reconstructed mass, on average. The reconstructed mass for individual test runs accounts for 61 to 90 percent of the measured mass, and the sum of the average results for each substance accounts for approximately 98 percent of the measured mass. In other tests of gas-fired sources, $SO_4^=$ plus NH_4^+ accounted for 70-90 percent of the reconstructed mass (API, 2001a; API, 2001b; API, 2001c).

In striking contrast to the Method PRE4/202 speciation results, the dilution sampler results show $SO_4^=$ and Cl^- comprise only 7 percent of the reconstructed mass (Figure 7-1a); NH_4^+ was detected in only 1 run, results are considered not reliable and consequently not included on the figure. OC is the dominant component (73 percent) in these samples (see discussion of OC measurement artifacts later in this section).

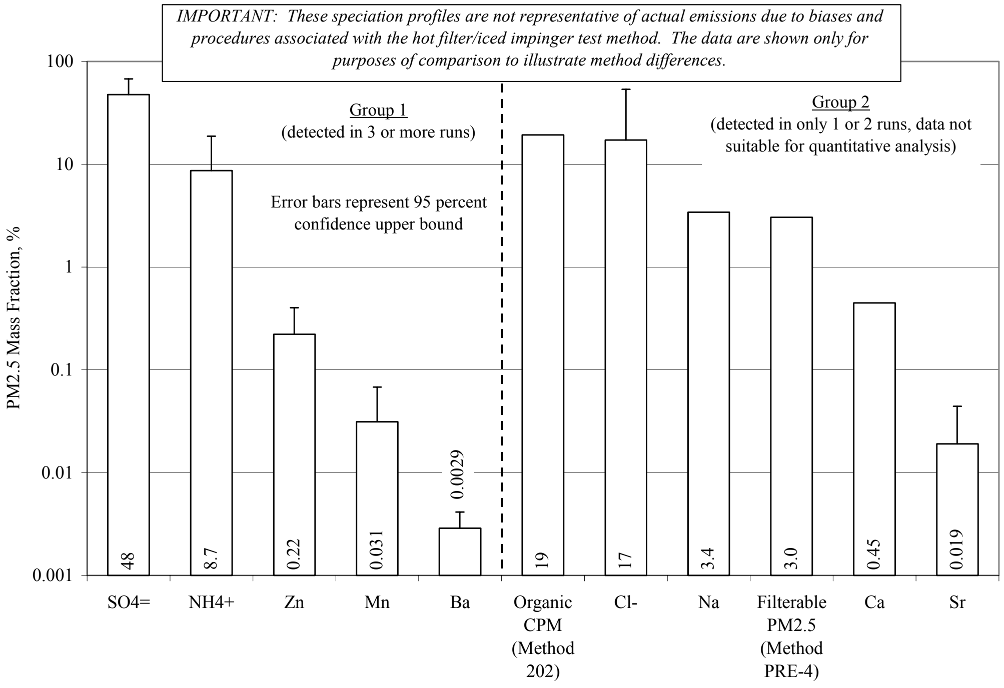


Error bars represent 95% confidence upper bounds

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).

See Table 5-7 for footnotes 6 and 8

(a) Primary PM2.5 speciation measured using dilution sampler.



IMPORTANT: These speciation profiles are not representative of actual emissions due to biases and procedures associated with the hot filter/iced impinger test method. The data are shown only for purposes of comparison to illustrate method differences.

Error bars represent 95 percent confidence upper bound

(b) CPM speciation measured using Method 202.

Figure 7-1. Comparison of PM2.5 speciation using different methods.

Sulfur Balance

Since sulfur is the dominant species in the CPM and not in the dilution samples, sulfur levels in other samples and in the fuel (expressed as in-stack $SO_4^=$ equivalent) were compared to validate the results. Sulfur is an easily measured element and hence fairly reliable as an indicator of mass balance. The $SO_4^=$ levels in the impinger aliquot from the Method 202 train and those from the Method 8 train compare well with each other despite the differences in impinger reagent (Table 7-1). The $SO_4^=$ measured in the Method 202 aliquot and the impinger residue are in good agreement with each other, indicating that the $SO_4^=$ in the inorganic CPM mass originated from the impinger sample rather than from sample contamination or other sources during analysis. The Method 202 $SO_4^=$ results are more than 100 times greater than the particulate $SO_4^=$ measured on the dilution sampler QFF, but is within a factor of 2 of the SO_2 (as measured on the K_2CO_3-impregnated cellulose-fiber filter) and total $SO_4^=$ measured in the dilution sampler. Due to the variability of the results, a two-fold difference is not significant at the 95 percent confidence level, but a 100-fold difference is significant. Run 4 of the dilution sampler SO_2 measurement is 1/10 of the other three samples, and is probably not representative of the actual concentration. Even if Run 4 is neglected, the difference between particulate $SO_4^=$ measured in the dilution sampler and Method 202 impingers remains substantial.

Table 7-1. Comparison of $SO_4^=$ Measurements (Site Bravo).

Units	mg/dscm (all expressed as in-stack $SO_4^=$ equivalent)				
Run number	Run 1	Run 2	Run 3	Run 4	Average
Fuel sulfur (based on typical fuel S value and actual stack conditions)	0.81	0.79	0.63	0.61	**0.71**
Impinger aliquot (M202)	1.1	1.1	0.76	0.99	0.99
Impinger residue (M202)	1.1	1.1	0.74	0.97	0.97
Impinger aliquot (mM8)	1.2	1.2	0.79	1.1	1.1
Dilution Sampler:					
QFF	0.0048	0.030	0.0027	NV	0.0088
K_2CO_3-impregnated cellulose fiber backup filter	0.69	0.86	0.48	0.06	0.52 0.68 (2)
Total (sum of QFF and K_2CO_3-impregnated filter)	0.69	0.86	0.48	0.06	0.52 0.69(2)
Ambient (1)	0.0021	--	--	--	0.0021

(1) One ambient sample taken on separate day.
(2) Excluding run 4 as outlier.

The expected $SO_4^=$ value based on fuel sulfur is in much better agreement with the dilution sampler results than with the iced impinger results. Historical data for sulfur in the natural gas supply for this plant shows a typical range from 0.25 to 0.30 grains/scf fuel (as S), which is equivalent to an in-stack average of approximately 0.71 mg/dscm of $SO_4^=$ at the stack conditions for this test. This expected sulfur concentration in the stack compares very well with the total gaseous plus particulate sulfur measured by the dilution sampler (excluding the dilution sampler SO_2 result for Run 4, which is an unexplained outlier). Particulate $SO_4^=$ (determined from the QFF) accounts for less than 2 percent of the total $SO_4^=$measured by the dilution sampler – stated another way, gaseous SO_2 (determined from the K_2CO_3-impregnated cellulose filter) accounts for more than 98 percent of the total $SO_4^=$. Thus, the dilution sampler and the iced impingers seem to be doing a reasonable job of capturing all the sulfur in the sample, but sulfur partitioning between the gas and particle phases appears to be very different.

Ambient air $SO_4^=$ data obtained from a local monitoring station showed an annual (2001) average of 4.5×10^{-3} mg/dscm, with an annual 24-hour maximum of 4.3×10^{-2} mg/dscm. The value measured during this test is approximately one half the annual average value but well within the 24-hour variation indicated by the 24-hour maximum. The particulate $SO_4^=$ in the ambient air is equivalent to approximately one fourth of the particulate $SO_4^=$ measured in the dilution sampler, but is negligible compared to the total gaseous plus particulate sulfur measured in the dilution sampler and the inorganic CPM. It is clear from the ambient air results that most of the sulfur measured in the stack sample by both sampling systems originates from the fuel rather than the ambient air.

Iced Impinger Method Artifacts

The formation of artifact $SO_4^=$ caused by oxidation of dissolved SO_2 in the aqueous solutions appears likely because the amount of $SO_4^=$ in the impingers greatly exceeds the amount of true particulate $SO_4^=$ determined by the dilution sampler. SO_2 and O_2 both are soluble in water (H_2O). The dissolved SO_2 can form hydrated SO_2 ($SO_2 \bullet H_2O$), bisulfite ion (HSO_3^-) and sulfite ion ($SO_3^=$) in aqueous solution. At the pH range of interest in this test, (potential of hydrogen (pH) = 2 to 7), HSO_3^- is the preferred state. The individual dissociations are very fast, so aqueous-phase equilibria are established instantaneously. The dissociation of dissolved SO_2

enhances its aqueous solubility so that the total amount of dissolved $SO_4^=$ always exceeds that predicted by Henry's Law for SO_2 alone. There are several pathways for $SO_4^=$ formation by reaction of these ions with dissolved O_2, ozone (O_3) and hydrogen peroxide (H_2O_2), and this can be catalyzed by many substances such as Fe and Mn (Seinfeld and Pandis, 1998). Free NH_3 in the samples can increase the amount of dissolved SO_2, and thereby increase artifact $SO_4^=$ formation, since it instantly reacts in aqueous solution forming ammonium sulfite/bisulfite ions and additional SO_2 must dissolve to maintain equilibrium.

EPA Methods 202 and 8 implicitly acknowledge the potential for conversion of SO_2 to $SO_4^=$ by requiring a post-test purge of the impingers immediately following the test to purge the impinger solutions of dissolved SO_2. Method 8 requires a 15-minute purge with air immediately following the test. Method 202 recommends purging the impingers with nitrogen (air also is permitted by the method) for one hour immediately following sample collection. Method 202 provides the option of omitting the post-test purge if the pH of the impingers is above 4.5. While the pH of the impingers met this criterion in this test, the nitrogen purge was performed anyway because the potential for the SO_2-to-$SO_4^=$ artifact was recognized.

The significance of the SO_2-to-$SO_4^=$ artifact in the iced impinger methods is documented in the literature for high SO_2 concentrations (DeWees et al, 1989; U.S. EPA, 1996; Filadelfia and McDannel, 1996). Earlier studies of systems having SO_2 levels of approximately 2000 ppm showed that the SO_2-to-$SO_4^=$ artifact occurs in spite of post-test purging and that it can account for up to 42 percent of the measured CPM (Filadelfia and McDannel, 1996).

Wien et al. (2001) evaluated the SO_2-to-$SO_4^=$ artifact in the laboratory at low SO_2 concentrations typical of gas combustion by passing pure compressed gas mixtures with representative amounts of O_2, carbon dioxide (CO_2), nitrogen gas (N_2), nitric oxide (NO) and SO_2 through two sets of paired Method 202 impinger trains. No particulate or condensable substances were added. Tests were performed for 1-hour and 6-hour sampling runs with mixtures containing 0, 1, and 10 ppm SO_2. One pair of trains was purged with nitrogen for one hour immediately following the tests, while the other was not. The samples were stored at 4 °C for approximately 2 weeks prior to analysis. Significant amounts of $SO_4^=$, approximately proportional to the SO_2 concentration in the gas, were present in impingers regardless of the post-test purge. While the post-test purge clearly reduced $SO_4^=$ concentration in the impingers, significant $SO_4^=$ still remained. Purging was less efficient at reducing $SO_4^=$ for the 6-hour runs than for the 1-hour runs, indicating that much of the SO_2 oxidation occurs within this period. Wien compared the laboratory data to field results from a gas-fired refinery boiler using unpurged sample trains and concluded that approximately 50 to 100 percent of the $SO_4^=$ in the field samples, which comprised more than 80 percent of the CPM in that field test, could be attributed to the SO_2-to-$SO_4^=$ artifact. Therefore, it seems likely that the SO_2-to-$SO_4^=$ artifact is significant in this test, especially considering the differences in gaseous and particulate $SO_4^=$ measurements discussed earlier in this section.

COMPARISON OF RESULTS TO OTHER STUDIES

PM Emission Factors.

Corio and Sherwell reviewed PM10 emissions data collected from fossil fuel fired units (including seven sets of data from four natural gas-fired combined cycle cogeneration units and a natural gas-fired boiler) by EPA Methods 201/201A and 202, and noted the potential significance of the SO_2-to-$SO_4^=$ artifact (Corio and Sherwell, 2000). API and Wien et al. reported results for gas-fired boilers and process heaters collected using the same methods used in this test (API, 2001a; API, 2001b; API, 2001c; Wien et al., 2003). None of the FPM results for natural gas fired units from these other tests is significantly different from the Site Bravo results, based on overlap of the 95 percent confidence bounds (Table 7-2). It is not surprising that these differences are not significant at the 95 percent confidence level because analysis of the Site Bravo results shows it is likely that FPM concentrations for gas-fired units are below the LQL of the hot filter methods (discussed later in this section). Some of the differences observed may be due to differences in test techniques used and method performance at each site (e.g., sample volume, analytical balance sensitivity, significance of acetone blanks, techniques affecting contamination and loss of filter fragments, treatment of blanks and negative net filter weights in the data reduction, etc.).

The data from the other tests show that, on average, CPM accounts for 80 percent of the total PM10 (CPM plus FPM10), with the middle half of the data falling between 73 and 91 percent

Table 7-2. Comparison of Data from Corio and Sherwell (2000) and Current Program.

						Makeup of CPM			
		Filterable PM10		Condensable PM		Inorganic Fraction		Organic Fraction	
Source[1]	Description	lb/ MMBtu	% of Total PM10	lb/ MMBtu	% of Total PM10	lb/ MMBtu	% of Total CPM	lb/ MMBtu	% of Total CPM
Lakewood Cogeneration	Natural Gas-fired Boiler	0.0019	46	0.0022	54	0.0015	66	0.00076	34
Lakewood Cogeneration – Unit #1	Natural Gas-fired Combined Cycle Unit with SCR	0.00021	14	0.0012	86	0.0010	81	0.00023	19
Lakewood Cogeneration – Unit #2	Natural Gas-fired Combined Cycle Unit with SCR	0.00052	33	0.0011	67	0.00084	78	0.00024	22
Kamine Milford[2]	Natural Gas-fired Combined Cycle Unit	0.0132	56	0.011	44	0.0045	43	0.006	57
Kamine Milford[3]	Natural Gas-fired Combined Cycle Unit	0.0015	12	0.011	88	0.0067	60	0.0045	40
Kamine Milford[4]	Natural Gas-fired Combined Cycle Unit with Supplementary Firing	0.0012	10	0.011	90	0.0079	74	0.0028	26
Kamine Milford[5]	Natural Gas-fired Combined Cycle Unit with Supplementary Firing	0.0014	12	0.010	88	0.0066	66	0.0034	34
Bristol-Myers Squibb Cogen	Natural Gas-fired Combined Cycle Unit with Supplementary Firing	0.0018	25	0.005	75	--	--	--	--
Site A (API, 2001a)	Refinery Gas-fired Boiler	0.00016	2	0.0097	98	0.0091	94	0.00064	6
Site B (API, 2001b)	Refinery Gas-fired Process Heater	0.00064	12	0.0046	88	0.0044	96(6)	0.00014	3(6)
Site C (API, 2001c)	Natural Gas-fired Steam Generator	0.00008	6	0.0012	94	0.00052	44(6)	0.00048	41(6)
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	0.00059	7	0.0078	93	0.0066	86(6)	0.0011	14(6)
Site Bravo [7]	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	0.00029	9	0.0030	91	0.0027	91(6)	0.00055	6(6)

[1] Lakewood, Kamine Milford and Bristol-Myers Squibb data collected with EPA Methods 201/201A and 202; data from Sites A, B, C, Alpha, and Bravo collected using EPA Methods PRE-4 and 202.

[2] Steam injection (SI) on, waste heat recovery boiler supplementary firing (WHRB-SF) off.

[3] SI off, WHRB-SF off.

[4] SI on, WHRB-SF on.

[5] SI off, WHRB-SF on.

[6] Remaining CPM mass accounted for by back-half filter and was not characterized.

[7] Duct burners were on for Runs 1 and 2, intermittent for Run 3 (total of approx. 30 minutes) and off for Run 4.

(25th to 75th percentile). The average Site Bravo result (91 percent) falls within the upper end of this range. The CPM emission factors from the other tests fall within a factor of approximately 2 to 4 of the average Site Bravo CPM result. The middle half of the other CPM data covers a wide range - 0.0019 to 0.010 lb/MMBtu (25th to 75th percentile) – illustrating the high variability of CPM measurements for gas-fired units. This variability probably results from many factors, including differences in specific measurement techniques and methods (e.g., uncontrolled factors affecting the significance of the SO_2-to-$SO_4^=$ artifact), fuel differences (e.g., sulfur content), process design and operation, air pollution control equipment, geographic location and ambient conditions, etc. Again, the average Site Bravo result (0.0030 lb/MMBtu) falls within this middle range for gas-fired units. On average, 73 percent of the CPM from the other tests is accounted for by the inorganic CPM fraction. The average inorganic CPM fraction for Site Bravo (91 percent) falls into the upper end of the range of the other data (87th percentile).

EPA's *Compilation of Air Pollutant Emission Factors*, known as AP-42, is the most frequently cited source of source emission factors (U.S. EPA, 2000a). The Site Bravo CPM emission factor (0.0030 lb/MMBtu) is lower, approximately one half, compared to those found in AP-42 for uncontrolled stationary gas turbines (0.0047 lb/MMBtu) and external gas combustion (0.0056 lb/MMBtu) (Table 7-3). The uncertainty associated with the published emission factors is not given in AP-42. The AP-42 CPM emission factors are slightly higher than the 95 percent upper confidence bounds of the average Site Bravo CPM emission factor. Assuming the AP-42 and Site Bravo emission factors have similar confidence bounds, the differences would not be considered significant at this confidence level.

The Site Bravo FPM emission factor is approximately one seventh of the AP-42 factors, which are identical for both types of sources. It should be noted that special techniques to reduce the LQL and variability for FPM were applied in this test (more sensitive analytical balance, long test runs, special handling techniques), which could account for much of this difference. In addition, the performance of hot filter methods in general, discussed later in this section, may not be adequate to accurately discern differences in FPM of this magnitude.

Note, the comparison of the Site Bravo results to the uncontrolled gas turbine emission factor in AP-42 is not strictly valid because the measurements in this test were performed downstream of the supplementary burners, oxidation catalyst and SCR system. Nevertheless, the semi-quantitative agreement of our results with those presented in the EPA database provides additional confidence in the validity of the results found here. It also suggests that since the AP-42 CPM emission factors are based on tests using similar iced impinger measurement methods, it is likely that the AP-42 CPM emission factor also contains positive bias due to the SO_2-to-$SO_4^=$ artifact and excessive condensation artifact.

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

Source	Unit Type	Total PM10	Filterable PM10		Condensable PM		PM2.5 *(2)*
		lb/MMBtu	lb/MMBtu	% of Total PM10	lb/MMBtu	% of Total PM10	lb/MMBtu
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)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	--	0.00048 *(3)*	--	--	--	--
Site Bravo (prior test, without duct burners)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	--	0.00120 *(3)*	--	--	--	--
Site Bravo *(5)* (this test)	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

(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 filterable and condensable 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) Duct burners were on for Runs 1 and 2, intermittent for Run 3 (total of approx. 30 minutes) and off for Run 4.

The average FPM result for this test is lower than previous test results for this plant (Table 7-3). This could be attributed to the improved test techniques used during this test to improve sensitivity, but the differences are not significant at the 95 percent confidence level. In the prior tests, all of the FPM filters had negative net weights and the reported FPM is derived solely from the acetone rinse results. The relatively high result reported in the prior tests without duct burners is due to a single high acetone rinse result for one of the runs, an outlier that is suspicious but no reason was found to exclude it. No prior CPM results were available.

Also shown in Table 7-3 are results of dilution sampler measurements for gas-fired process heaters, boilers steam generators, and natural gas-fired home appliances (Hildemann et al., 1991, API, 2001a; API, 2001b; API, 2001c; Wien et al., 2003). This comparison is relevant because:

(1) it illustrates that the difference between dilution sampling and hot filter/iced impinger test methods is not unique to this test or the type and configuration of gas-fired sources, thereby providing a degree of validation for these results; and (2) it illustrates that PM2.5 mass measured by the dilution sampler is much lower than the nearest corresponding AP-42 emission factors for all the gas-fired source types tested in this program, emphasizing the need for new emission factors for these source categories. Results from hot filter/iced impinger methods demonstrate the correspondence in results using these methods among the different tests and the striking difference between these and the dilution sampler results. The CPM and FPM10 results for Site Bravo agree well with the other results shown, as previously discussed. The average Bravo PM2.5 emission factor derived from the dilution sampler results compares well with the results from Hildemann and API Site A, and are higher than the results from API Sites B and C and Wien et al.'s Site Alpha. The reasons for large difference in PM2.5 concentration between these two groups of tests are not well understood. Additional tests are needed to corroborate all of the recent dilution sampler test results.

The Hildemann PM2.5 results for natural gas-fired home appliances are significant in this context because they were obtained using the original sampler upon which the 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 PM2.5 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 PM2.5 mass results for Site Bravo and Hildemann are remarkably similar.

In summary, the FPM, CPM and PM2.5 mass emission factors for Site Bravo are close to the levels expected based on previous tests and other results published in the open literature. The dilution sampler used in this test simulates the key fundamental conditions governing condensation (temperature, concentrations and time) that are found in actual stack plumes. In contrast impingers do not simulate these conditions, and it is likely that impinger results include significant positive bias due to the SO_2-to-$SO_4^=$ artifact. The sensitivity of the dilution sampler procedures used in this test is much greater than conventional hot filter methods for FPM. Based on these considerations, the emission factors for PM2.5 derived from the dilution sampler results are believed to be the most representative measurements of the true primary PM2.5 emissions from Site Bravo during this test.

Particulate Carbon

Particulate carbon – OC and EC – accounted for the vast majority of the reconstructed PM2.5 mass measured using the dilution sampler. The OC emission factor for Site Bravo (0.00014 lb/MMBtu) is approximately equal to the average OC emission factor (0.00011 lb/MMBtu) from four 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 low and results for all sites are within a factor of four of the average EC emission factor. The OC, EC and total SVOC emission factors for Site Bravo all fall within the middle half of the data for other sources (between the 25th and 75th percentile). The total VOC emission factor for Site Bravo is comparable to the other results, but in the upper fifth (81st percentile) of the range.

Table 7-4. Average Particulate Carbon and VOC Emission Factors (lb/MMBtu).

Source	Unit Type	Organic Carbon	Elemental Carbon	Total Carbon	All SVOCs	Sum of All VOCs
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	7.3E-6	7.5E-5	1.7E-5	7.6E-4 *
Hildemann et al., 1991	Natural Gas-fired Home Appliances	9.0E-5	7.1E-6	9.7E-5	--	--
Site Bravo *(1)*	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	2.0E-4	1.9E-5	2.2E-4	8.1E-6	5.6E-4 *

* Does not include VOCs from canister samples.

(1) Duct burners were on for Runs 1 and 2, intermittent for Run 3 (total of approx. 30 minutes) and off for Run 4.

Secondary Particle Precursor Emission Factors

Emission factors for secondary particle precursors - NH_3, SO_2, NO_X and VOC– generally compare favorably with independent literature values for similar gas combustion systems with and without post-combustion controls (U.S. EPA, 2000a; ARB, 2000) and prior test data from the plant (Table 7-5). NO_X emissions are lower than the AP-42 value because it has no emission factors for similar plants with post-combustion emission controls, which achieve a high degree of NO_X, CO and organic compound emissions reduction. The 1,3-butadiene concentration measured in this test is slightly higher than those values reported in the literature. This might be attributed to measurement using a dilution system, since this compound tends to decay rapidly in the presence of NO after sample collection and dilution could reasonably be expected to reduce such interference. The uncertainty of this measurement is fairly high (83 percent); hence, these results should be corroborated by further tests to determine if the emission factor is reliable.

METHOD PERFORMANCE

Hot Filter/Iced Impinger Methods Performance

Due to the low FPM concentrations found during this test, the particulate mass collected on the filters is at, or below, the practical limits of the method as practiced in this test. Figure 7-2 presents the gravimetric analysis results for all of the PM2.5 samples as measured (i.e., without adjustments for negative net weights or blanks). Blank-corrected sample results and blank results are shown such that the total height of each bar represents the raw uncorrected result for each test. The front half rinse blank represents the acetone recovery blank drawn in the field from the rinse bottle used to recover the in-stack cyclone samples. The filter blank represents a filter that was placed in the filter holder, performing all test preparation steps including a leak check, then recovering the filter in the same manner as the samples. The acetone recovery blank ranges from approximately 6 to 140 percent of the front-half rinse, averaging 48 percent. The proximity of the samples to the levels in the blanks – in one case, the blank is greater than the sample – implies low confidence in the absolute magnitude of the rinse results. Only a single acetone recovery blank is required by the method, hence the variability of the blank cannot be determined from these results alone.

Table 7-5. Comparison of Emission Factors for Gaseous Compounds from Site Bravo and Other Data.

	AP-42 (U.S. EPA, 2000a) *(1)*	CATEF (ARB, 2000) *(2)*	Site Bravo (Prior plant test results - w/o duct burners)	Site Bravo (Prior plant test results - w/ duct burners)	Site Bravo (This test) *(3)*
NO_X	9.9E-02	--	6.1E-03	1.1E-02	6.5E-03
NH_3		1.0E-02	5.5E-03	7.1E-04	1.6E-03
VOC	2.1E-03	2.1E-03	--	--	1.3E-03
SO_2	3.4E-03	--	--	--	7.5E-04
1,3-butadiene	< 4.3E-7	1.2E-07	--	--	1.9E-06
Benzene	1.2E-05	4.5E-05	--	<4.4 E-6	2.2E-05
Ethylbenzene	3.2E-05	6.0E-06	--	--	--
Formaldehyde	7.1E-04	3.3E-04	--	1.2E-05	--
Naphthalene	1.3E-06	8.3E-06	--	--	--
PAH/SVOC	2.2E-06	8.8E-06	--	<1.5 E-8	6.0E-06
Propylene Oxide	< 2.9 E-5	4.7E-05	--	--	--
Toluene	1.3E-04	5.2E-05	--	--	1.7E-04
Xylenes	6.4E-05	3.3E-04	--	--	--

(1) Natural Gas-Fired, Lean-Premix, no post-combustion controls

(2) With oxidation catalyst and selective catalytic reduction (SCR)

(3) Duct burners were on for Runs 1 and 2, intermittent for Run 3 (total of approx. 30 minutes) and off for Run 4.

< - not detected, one-half detection limit shown.

All of the sample filter net weights are negative. This is common when using QFFs, for example, the filter tends to stick to the filter holder gasket or filter support leaving behind small fragments when attempting to separate them that may not be completely recovered. In these tests the filter, gasket and support were weighed together in aluminum foil packets before and after the tests, in an attempt to minimize imprecision (following the concept of EPA Method 5I) and avoid negative net weights. The source of negative net weights was not conclusively identified in these tests, but since it occurred with all of the stack samples and with the field blank, it is believed to be intrinsic to the handling and weighing procedures, or possibly even the filter material itself. Since a negative filter weight has no physical significance with respect to actual emissions, such results conventionally are reported as zero rather than as a negative emission or in summing different fractions of the sampling train. However, this convention leads to an inaccurate picture of the MDL and LQL of the measurement method. The filter blank net weight in this test is negative and ranges from 24 to 51 percent of the sample filter net weights, which implies low confidence in the absolute magnitude of the filter results.

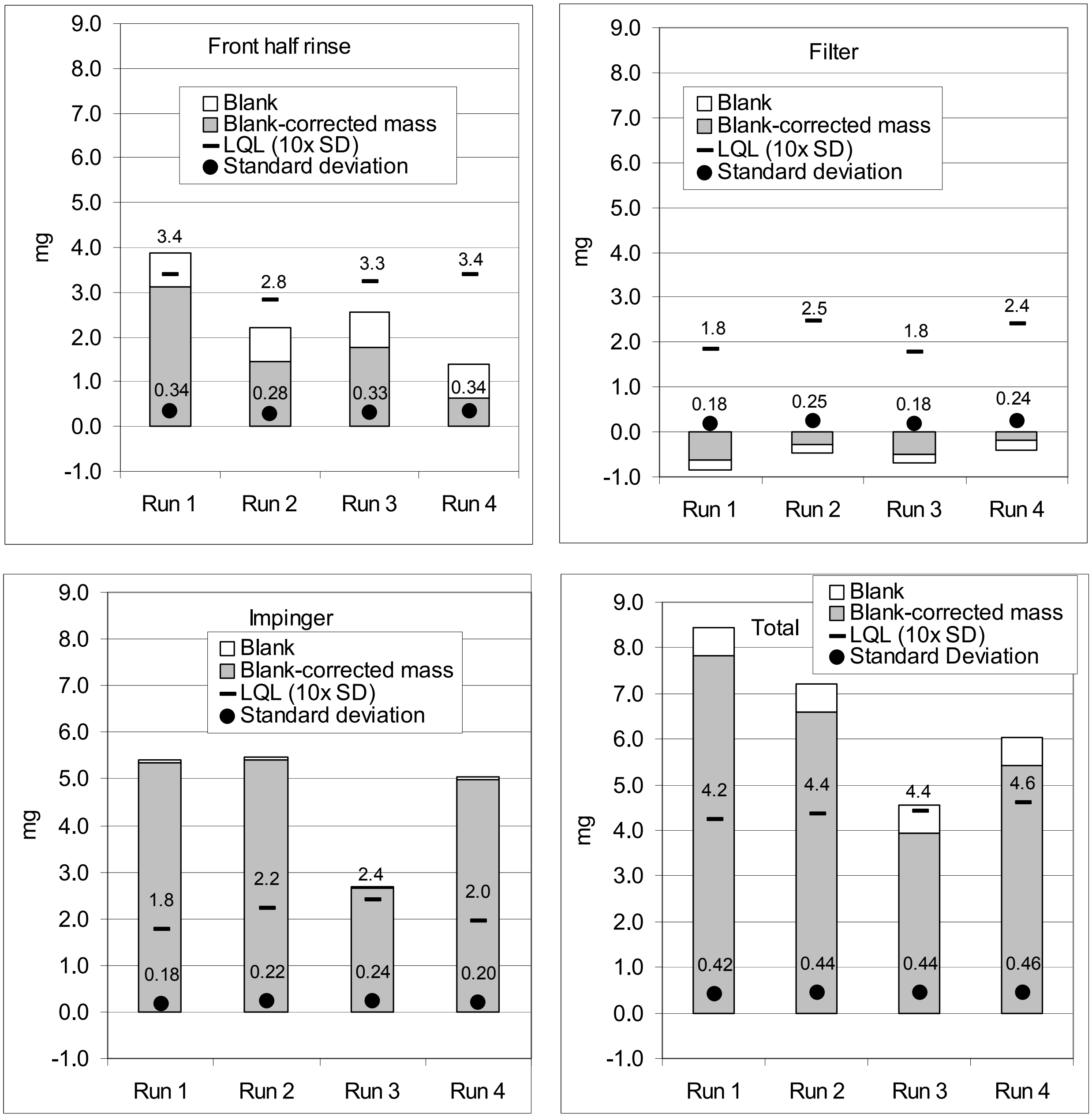


Figure 7-2. Gravimetric Analysis Results and LQL for EPA Method PRE-4/202 (Site Bravo; standard deviation and LQL values shown above symbols).

The gravimetric procedure given in Method PRE-4 (which references Method 5) calls weighing samples repeatedly until two weights agree within 0.5 mg and then reporting the final weight. In this test, the two final weights typically agree within 0.1 mg. For the results shown in Figure 7-2, the average of the duplicate pre-test tare weights and post-test sample weights were used rather than the final weight to facilitate error analysis. The standard deviation shown on the figure is the sum of the standard deviation of the duplicate pre- and post-test weighings. This data can be used as a guide for assessing the analytical MDL and LQL of the method (see Section 6). For example, MDL of an analytical method is often defined as three times the standard deviation of measurements near "zero" (Watson et al, 2001). The standard deviations for the acetone rinses and filter fractions are on the order of 0.2 to 0.4 mg, which corresponds to an MDL of approximately 0.6 to 1.2 mg. Clearly, the sample filter results are below the MDL, and the acetone results only slightly higher than the MDL.

Another definition of method performance is the LQL, defined as 10 times the standard deviation of measurements near zero (or approximately 3.33 times the minimum detection limit) (Watson et al, 2001). All of the filter and acetone rinse results fall below the LQL (Figure 7-2). The impinger results are well above both the MDL and the LQL, but as discussed previously are probably strongly biased by the SO_2-to-$SO_4^=$ artifact. Based on this analysis, it is apparent that these methods do not have sufficient sensitivity or selectivity for reliable particulate emissions measurements from gas-fired combustion sources.

Dilution Sampling Method Performance

Innovative tests were conducted at Site Bravo using a dilution sampling test method to conduct exploratory measurements of PM2.5 mass, particulate species, and gaseous fine particle precursor emissions. A broad range of chemical speciation and physical characterization methods was successfully applied to characterize the emissions. This test represents the first application of dilution sampling to an NGCC-SF of which the authors are aware. The performance of the specific dilution sampler design used in these tests is documented in this report and in several other publications. For example, Hildemann et al. (1989) extensively characterized particle losses in the sampler and the effects of dilution ratio and other factors on the results. The dilution sampling method is attractive because the sample collection media and analysis methods are identical to those used for ambient air sampling, thus the results are directly comparable with ambient air data. In addition, the dilution sampling method provides a representative sample of solid, liquid and condensable aerosol mass together on a single filter. 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.

With one exception, the overall method performance achieved with the dilution sampler in this test was considered satisfactory. During this test, a procedural error (overtightening of the TMF cassettes) produced high variability of the dilution sampler PM2.5 mass results compared to other tests using the same methods. One of the four filter net weights was less than zero for the same reason. This occurred despite written standard operating procedures (SOP) developed over the course of the past few years, but this aspect was not addressed in the SOP and the field sampling team did not recognize it as important. This error has been documented to prevent its occurrence in future tests and will be included in future revisions of the SOP. This highlights the need for written standards and procedures and adequate personnel training for conducting these measurements.

The three valid PM2.5 mass gravimetric results (88, 300, and 29 μg) exceed the reported analytical uncertainty for these test results (3 μg) and the tolerance established for duplicate analyses (15 μg) by a comfortable margin. Thus, the analytical sensitivity of the method is considered sufficient for this application. As discussed previously in Section 6, blank results were significant for several of the species measurements, especially for organic compounds. Although the absolute level of the blanks is low and typical of that considered acceptable for ambient air tests, some results are significant relative to the low concentrations of species in the stack samples. The significance of blanks could probably be reduced by testing for longer sampling periods to achieve larger sample volumes. However, this was not considered practical during this test since the equipment is not fully automated and cannot run unattended, and since cost limitations precluded running double shifts during the test. Further method evaluation tests are needed to establish dilution method performance specifications (e.g., random and systematic uncertainty) for gas-fired sources and other applications.

The stack results for many substances were near ambient air levels. A DSB collected for selected substances showed the potential for breakthrough of substances across the dilution air purification system. For future tests, DSBs should be collected to further document dilution air purification system performance and establish the level of bias in stack samples for all target substances.

Particulate Carbon Measurement Performance. OC is the largest component of the PM2.5 measured by the dilution sampler. There is currently heightened interest in particulate carbon from combustion sources due to PM10 and PM2.5 NAAQS, the new Regional Haze rule and existing Visibility rules. Some states already have initiated development of PM2.5 State Implementation Plans in preparation for implementation of the 1997 PM2.5 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, $SO_4^=$ and NO_3^- aerosols, and coarse (PM10-2.5) and fine (PM2.5) 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 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 7-6 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 ranged from 74 to 126 percent of the primary OC. 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 also reinforce the need for caution when using the OC results.

Table 7-6. OC and Backup Filter OC Results for Site Bravo (mg/dscm).

	Run 1	Run 2	Run 3	Run 4	Average	FB	Ambient
OC	0.193	0.153	0.079	NV	0.142	0.093	0.0088
Backup Filter OC	0.143	0.139	0.100	NV	0.127	0.060	0.0031
OC (Corrected for Backup)	0.050	0.014	-0.021	NV	0.014	0.033	0.0056
Backup OC/OC	74	91	126	NV	97	64	36

NV – not valid

Figure 7-3 shows stack OC with two different corrections to illustrate the potential impact of the artifact and the field blank: subtracting the field blank from the sample (wide bars), and subtracting the backup OC from the sample (thin bars). Although the ambient air OC result appears to be elevated above the stack samples, the data are presented in mass per sample and the OC results from the stack sample results have not been corrected for dilution ratio in this graph. The high blank and high backup OC levels indicate the possibility of a significant positive bias in the OC measurement. In Runs 2 and 3, the field blank-corrected OC result is below the analytical MDL. This result indicates that the true particulate carbon emission factor is probably less than measured result and that it is too low to measure with high confidence, even when using these state-of-the art techniques. Therefore, the OC emission factor for Site Bravo should be considered as an upper bound for the potential OC emissions, with significant uncertainty beyond the reported values.

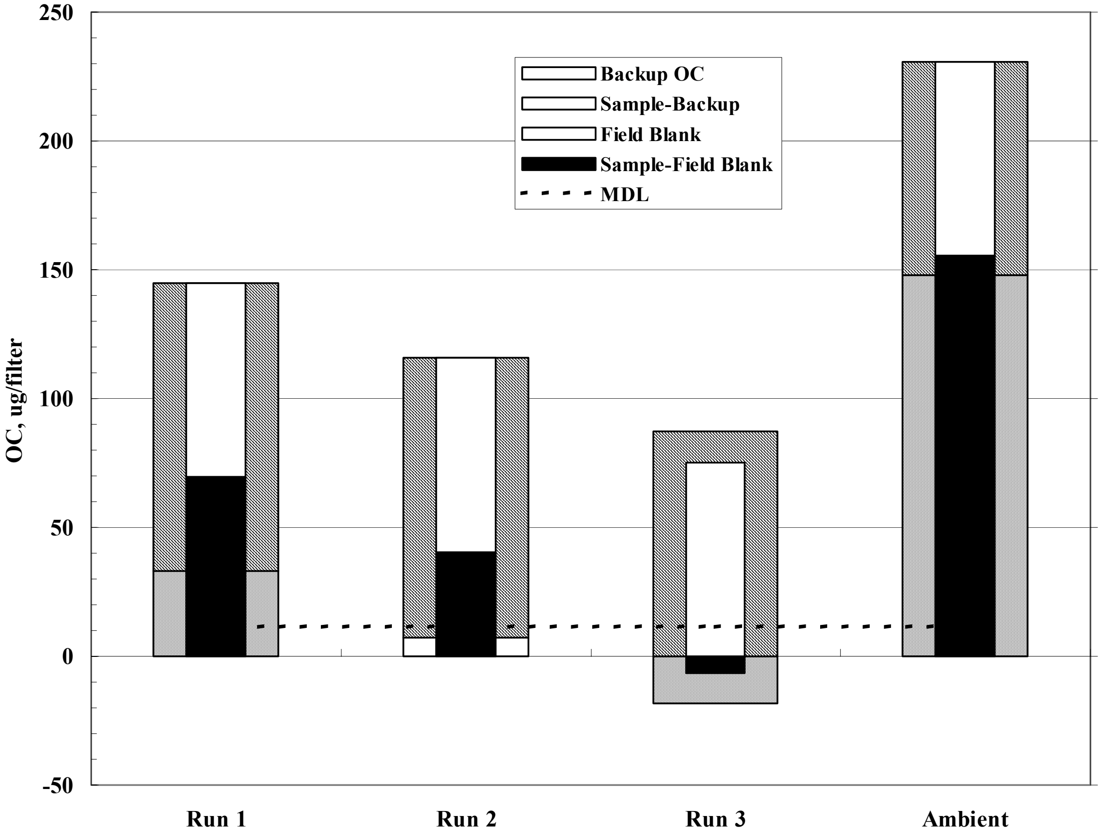


Figure 7-3. Site Bravo OC Results.

PROCESS OPERATION PARAMETRIC EFFECTS

The operating conditions during this test enabled evaluation of the impact of load and duct burner operation on emissions from Site Bravo. Runs 1 and 2 were performed with duct burners on throughout the runs. Runs 3 and 4 were performed with the duct burners off (except for a brief period during Run 3 when the were on). The gas turbine load also was approximately 7 to

15 percent lower for Runs 3 and 4 compared to Runs 1 and 2. It is likely that these differences in operation contributed to the variability of the test results.

Due to the very limited amount of data for each condition and changes in more than one parameter from test to test, any findings with respect to parametric effects are necessarily preliminary and qualitative. A larger number of samples is needed to quantify parametric effects in future tests. It is clear, however, from the results presented earlier in Section 4 that duct burner operation does not have a large impact on PM and inorganic emissions measured during this test. Any effect on PM mass is below the ability of Method PRE-4/202 to discern with high confidence, although the CPM result for Run 3 is somewhat lower than the other 3 runs indicating the possibility of a small effect (Figure 7-2). Dilution sampler results (Table 4-7) also do not reveal a major effect of duct burner operation on PM2.5 emissions, although Run 3 results also are slightly lower than Runs 1 and 2 (Run 4 is not valid). This is somewhat consistent with the Method PRE-4/202 results. The uncertainty associated with each pair of measurements is too large to conclude with high confidence that duct burner operation has a significant impact on particulate emissions. However, it seems safe to say that any effect is smaller than the uncertainty of these results.

It was noted previously in Section 4 that there was a significant increase in SVOC detection frequency and a slight increase in VOC detection frequency for Runs 1 and 2 compared to Runs 3 and 4, but that any effect on concentrations was not observable at levels significantly different from the field blanks or ambient air. Particulate carbon for Runs 1 and 2 is approximately twice that of the single measurement for Runs 3 and 4, but this is not significantly greater than the uncertainty of the results. Formaldehyde emissions were measured using a standard ambient air method (DNPH-coated silica gel cartridges, EPA Method TO-11A) with the dilution sampler. While this method is not the current regulatory method for measuring stationary source formaldehyde emissions and its use with dilution sampling is still considered exploratory, it was thought to be adequate for a qualitative assessment of parametric effects. The absolute concentrations of formaldehyde measured are very low – likely less than 60 ppb in the stack gas.

The formaldehyde results indicate a potentially discernable effect of duct burner operation. This observation is clouded by the presence of formaldehyde in quality assurance blanks. Field blanks were collected for each stack run. A dilution sampler "system" blank, which sampled only the purified dilution air in the dilution sampler, also was collected. Although the field blanks did not contain any detectable amounts of formaldehyde, the dilution sampler blank did (see Section 6 for additional discussion). Comparing the dilution sampler blank to the ambient air result (Figure 7-4) indicates significant breakthrough of formaldehyde in the ambient air across the dilution air purification system. In the figure, the dilution sampler blank result is subtracted from the stack sample results. All of the raw (uncorrected) stack results are well above the analytical MDL. For Runs 3 and 4, the formaldehyde concentration in the stack samples is lower than the dilution sampler blank concentration, causing the corrected result to be below the in-stack analytical MDL (the corrected results are less than zero). For Runs 1 and 2, the corrected formaldehyde concentration is greater than the MDL but is less than 5 times the dilution sampler blank.

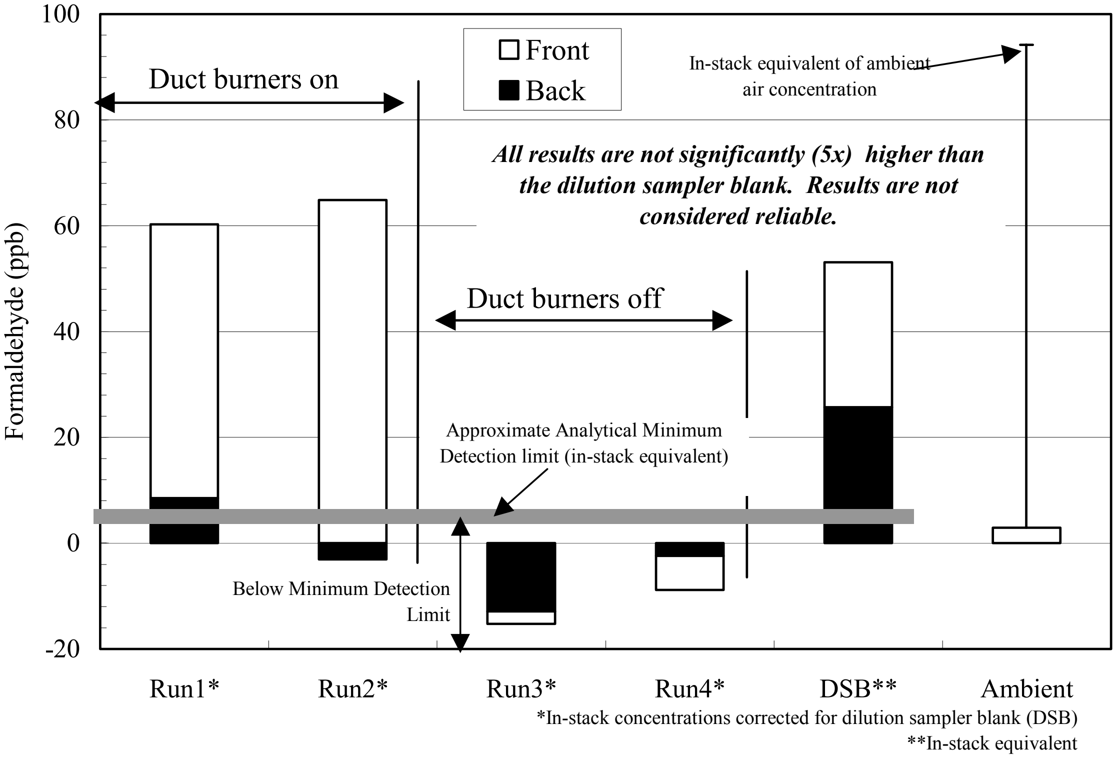


Figure 7-4. Tunnel Blank-Corrected Formaldehyde Concentrations, as Measured by the Dilution Sampler (Site Bravo).

Despite these observations, the data user is reminded that the data set is very limited and the quantitative formaldehyde stack results using this method are questionable because they are close (within 5 times) to the dilution sampler blank. More tests are needed to assess dilution air filter breakthrough, concentrations in blanks, and the method LQL (which is a more important indicator of measurement reliability based on blank results). Also, because of supplementary firing (duct burners) and the catalytic emissions controls in the HRSG that can potentially reduce and/or contribute to emissions, we remind the data user that Runs 1 and 2 with duct burners operating and results for Runs 3 and 4 without duct burners operating do not represent emissions from the gas turbine alone.

POTENTIAL EMISSIONS MARKER SPECIES

The results obtained using the dilution sampler are believed to provide the best representation of the chemical species present in the stack gas emissions. Ions, carbon, and other elements were detected in both stack and ambient air samples. A comparison of the observed concentrations of these species in ambient and stack samples can provide an indication of which species are considered good markers of natural gas combustion for this source.

Concentrations of all detected species have a higher in-stack average concentration than their concentrations in the ambient air sample (Figure 7-5), however not all of the differences are significant enough to distinguish ambient from stack concentrations with high confidence. The average concentrations of Br, Cl, K, Mg, Na, Pb, S, Cl^-, NO_3^-, and $SO_4^=$ are within a factor of ten of their respective ambient air concentrations. OC, EC and Co are species with higher concentrations that are more than an order of magnitude greater than the ambient concentrations, and might be potential marker species; however, OC is not unique to natural gas combustion and therefore unlikely to serve as a good marker. The lack of metals as marker species for natural gas combustion is consistent with a GRI report that found no significant levels of trace metals in natural gas samples (Chao et al., 1999). However, some species cannot reliably be distinguished because their in-stack concentrations are within a factor of ten from the minimum method detection limits (Figure 7-6); these include: Ag, Br, Co, Mn, Mo, P, Pb, Sr, Ti, V, Zr, Cl^-, NO_3^-, $SO_4^=$, NH_4^+, and EC. The above two criteria leaves OC as a potential marker species.

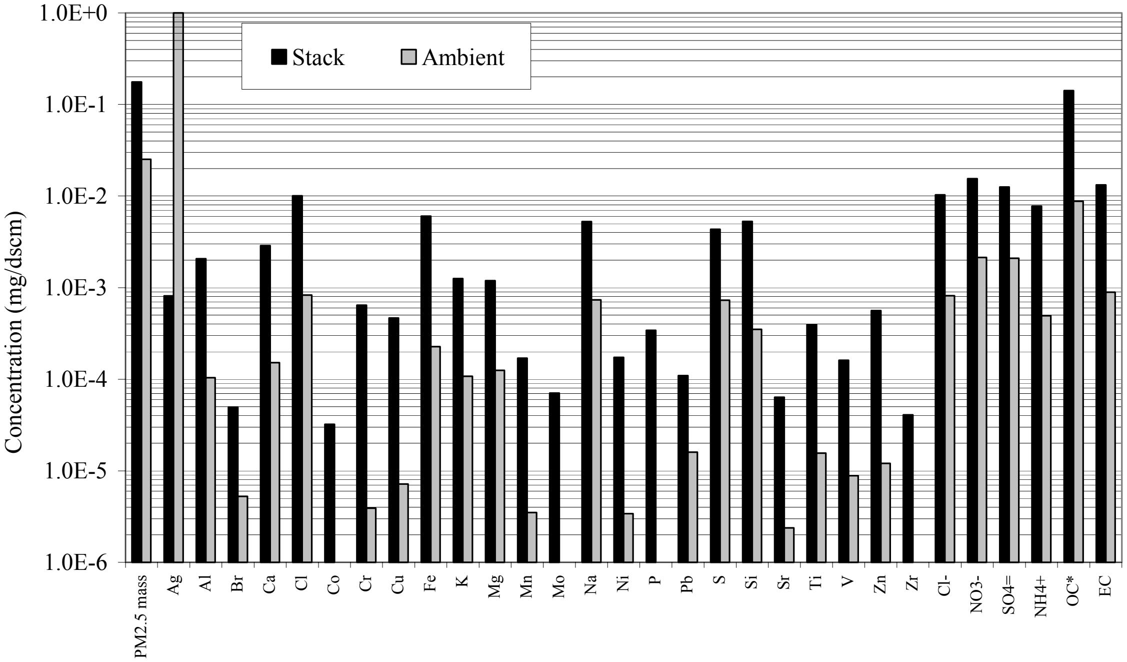


Figure 7-5. Mass Speciation for Dilution Sampler Ambient and Stack Samples (Site Bravo).

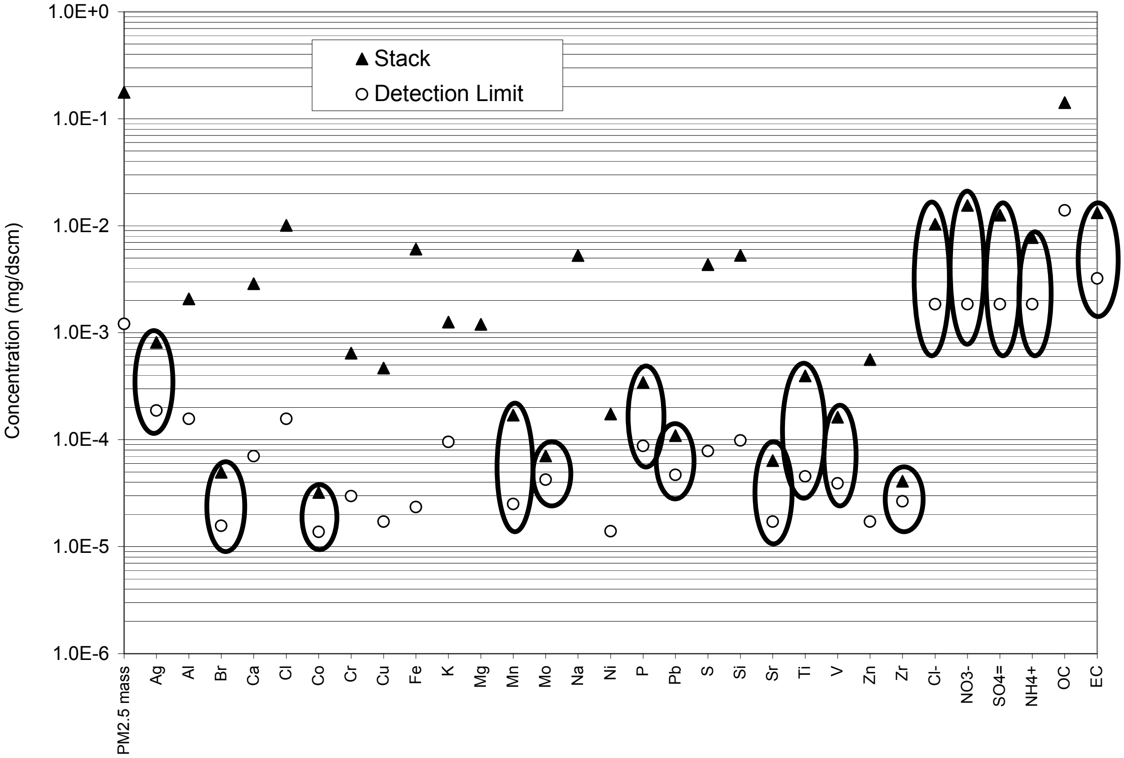
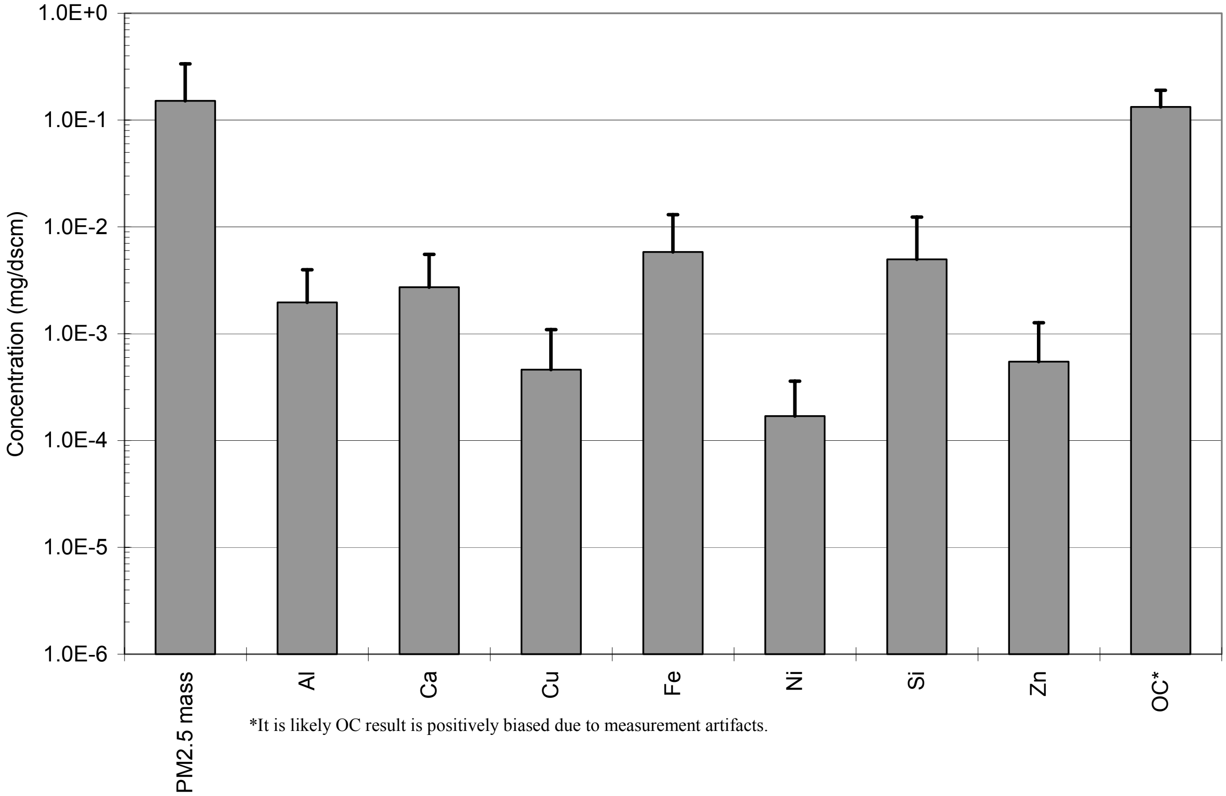


Figure 7-6. Comparison of Average Sample Concentration and Detection Limits (Site Bravo).

Subtraction of the ambient from in-stack concentrations provides an indication of which species may be considered as emissions markers. Ignoring species found near detection limits, the resulting emissions profile is presented in Figure 7-7. The error bars represent the standard deviations of the detected results. The reconstructed mass based on the results shown in Figure 7-7 is comparable to the PM2.5 mass. The uncertainty of several of these values is large, as reflected in the high standard deviations, indicating the average results may not be representative. Data users should exercise caution when using these as an emissions marker. Additional data is needed to provide a more robust analysis and greater confidence in any findings.



*It is likely OC result is positively biased due to measurement artifacts.

Figure 7-7. Stack Concentrations of Potential Gas Combustion Markers (Site Bravo).

Another potentially useful marker for source emissions is the organic species profile. All of the SVOCs detected were present at concentrations that are generally too low to serve as reliable markers for gas combustion. Only 11 SVOCs were detected in three or more test runs; only one of these – 7-methylbenzo(a)pyrene - is significantly (95 percent confidence lower bound greater than, or more than 5 times) higher than the blank and ambient air samples but is still fairly close - within a factor of 10 - to the MDL. Total SVOCs account for less than 4 percent of the OC measured by the dilution sampler.

Particulate carbon speciation can be a useful marker for source types (e.g., Zheng et al., 2002). For Site Bravo, 1,4+1,5+2,3-dimethylnaphthalene, xanthone, D-MePy/MeFl, E-dimethylphenanthrene, 4-methylpyrene, 7-methylbenz(a)anthracene, and 7-methylbenzo(a)pyrene are present at levels significantly above (greater than two standard deviations) their ambient concentrations, and might serve as potential marker species. However, motor vehicles are also predominant sources of dimethylnaphthalenes and methylnaphthalenes, and the sampling location was present within 2 miles of a major highway. Because the ambient air was sampled on only one day, it is possible that elevated levels of these compounds were present in the ambient air during source sampling that were not present when the ambient sample was taken. In addition, the relative concentrations of these compounds may not be unique enough to clearly distinguish this source from other (e.g., mobile internal combustion) sources.

There is a high degree of uncertainty associated with all of the organic data collected during the Site Bravo test. The low levels create a high degree of variability among the runs, which contributes to the high uncertainties. More comparisons to existing speciation profiles is necessary to gauge the uniqueness of the profile produced by this test. In addition, further testing of similar sources is recommended to provide a more robust basis for the emission factors and speciation profiles described herein.

EMISSION FACTOR QUALITY

Many of the emission factors developed from this test have large relative uncertainties. This was expected, due to the extremely low concentrations of pollutants in gas combustion exhaust and the limited number of tests. The large relative uncertainties of the dilution sampler results do not negate the value of the tests, since the results can be used to establish upper bounds for emissions and species mass fractions. The 95 percent upper confidence bound presented with the emission factors provides a plausible upper bound to emissions (i.e., the actual emission factor is very likely to be lower) based on these test results. As described earlier in this section, the observed differences between the hot filter/iced impinger and dilution methods remain significant at the 95 percent confidence level. The absolute uncertainty of the dilution sampler results is smaller than hot filter/iced impinger method results despite having high relative uncertainty. The dilution method results are not subject to positive bias resulting from the SO_2-to-$SO_4^=$ artifact. The sensitivity of the dilution method is better than the hot filter/iced impinger results. Standard ambient air sample collection and analysis methods were used with the dilution sampler to determine particulate mass, species and precursor concentrations. For these reasons, the data quality of the dilution sampler results is considered superior to the hot filter/iced impinger methods for this application.

Nevertheless, it should be noted that emission factors with an uncertainty greater than 100 percent must be considered potentially unrepresentative. In addition, this test represents the first application of this dilution sampler and sample collection methods to this type of source, and the results have not been corroborated by other independent tests. Data users should apply appropriate caution when using these results.

The data quality is well documented in this report. 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 or poor because the emission factors are based on a single test unit. The 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 such plants because of the wide range of designs, configurations, emission controls, ambient PM2.5 concentrations, weather conditions, fuel compositions, etc. that exist. This 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 LQLs of the state-of-the-art methods employed. Longer sampling times or measurements that are more sensitive may alleviate the proximity to LQLs but this would reduce the method's practicality. Widely accepted, standardized procedures for dilution sampling do not currently exist, and the reproducibility of the test results has been verified only qualitatively by comparison to other gas combustion sources tested within this program. Efforts are currently underway to develop standards for stationary source dilution sampling. 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 operating conditions for each run varied with normal plant operation near full load, and included supplementary firing for some of the runs. Therefore, 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:

- Particulate mass emissions from the NGCC-SF (including supplementary firing and post-combustion emission controls) were 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 large relative uncertainties in the emission factors derived from these test results.

- Average PM2.5 mass emission results obtained using two different methods of determining the emission factor for primary PM2.5 mass differ by more than a factor of ten: 0.00025 pounds of pollutant per million British thermal units of gas fired (lb/MMBtu) using the dilution sampler[4]; and 0.0031 lb/MMBtu using traditional hot filter/iced impinger methods for filterable and condensable particulate matter. Despite high relative uncertainty associated with the average results, the difference is significant at the 95 percent confidence level.

- Both the PM2.5 mass and the speciated mass fractions measured using dilution sampling are substantially different from those measured by hot filter/iced impinger methods. Because of significant measurement artifacts (conversion of gaseous SO_2 to solid $SO_4^=$ residue in the impingers, excessive condensation of vapors that would not occur under ambient conditions) and other limitations (inadequate sensitivity of the hot filter method, high blanks) of the hot filter/iced impinger methods, dilution sampling results are considered the most representative of actual primary PM2.5 emissions during this test.

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[4] Subsequent tests at Site Echo (England et al., 2004; England, 2004) showed that background PM2.5 in the dilution air was large in relation to stack PM2.5, and that stack PM2.5 was indistinguishable from the ambient air PM2.5 concentration. Therefore, it is likely that Site Bravo PM2.5 results are biased high and also may be indistinguishable from ambient air PM2.5 concentration.

- CPM and FPM10 emission factors derived from tests using conventional EPA methods are qualitatively consistent with published emission factors for external combustion of natural gas and natural gas-fired combustion turbines (U. S. EPA, 2000a). Most of the CPM, which dominates total PM10 emissions, is attributed to $SO_4^=$ compounds. Other studies (Wien et al., 2001) showed that a measurement artifact (SO_2-to-$SO_4^=$ conversion) can produce a relatively large positive bias in CPM as measured by iced impinger methods when applied to gas combustion. The SO_2-to-$SO_4^=$ conversion artifact can explain much of the observed difference between the dilution sampler and hot filter/iced impinger method results.

- OC and EC comprise approximately 73 and 2.9 percent of the average reconstructed PM2.5 mass, respectively, as measured using the dilution sampler. However, it is likely that the OC results are biased high due to an VOC adsorption artifact on the QFFs, which is more pronounced for clean sources such as gas combustion. Back-up filter results indicate that 74 to 126 percent of the measured OC may be due to this artifact. Further research is needed to improve the reliability of OC measurements.

- $SO_4^=$, Cl^-, NO_3^- and soluble Na together account for approximately 14 percent of the reconstructed PM2.5 mass derived from the dilution sampler results; $SO_4^=$ alone accounts for approximately 4 percent.

- Fe, Si, Ca, Al, and K account for approximately 8 percent of the reconstructed PM2.5 mass derived from the dilution sampler results. Smaller amounts of 16 other detected elements comprise another 5 percent.

- The measured PM2.5 mass and the reconstructed PM2.5 mass based on the sum of all measured chemical species derived from the dilution sampler results agreed within 34 percent. The difference between reconstructed and measured mass is not significant at the 95 percent confidence level.

- Most elements are not present at levels significantly above the background levels in the ambient air or the minimum detection limits of the test methods.

- Most organic compounds were not detected at levels significantly above background levels in the ambient air or field blanks. Most organic compounds are present at extremely low levels qualitatively consistent with gaseous fuel combustion based on published emission factors, other literature, and previous plant test results.

- Emission factors for secondary particle precursors are low and approximately consistent with published emission factors for gaseous fuel combustion, other literature, and previous plant test results.

- Because of the high relative uncertainty of the emission factors derived from this test, additional tests on other similar sources are needed 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.

- Further refinement and testing of the dilution sampling equipment and procedures is needed to minimize procedural errors and establish acceptable levels of method performance. Due to the proximity of many of the stack results to ambient air levels, a DSB for all measurements is recommended for future tests to verify that substances detected in the ambient air are not present in the dilution air.

The data in this report were developed using an experimental dilution test method applied to one source operating under several 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.

REFERENCES

40CFR60, App. A. Appendix A, Test Methods, in U.S. Code of Federal Regulations, Title 40, Part 60.

ASME. 1998. Test Uncertainty. ANSI/ASME PTC 19.1-1998, American Society of Mechanical Engineers, New York, NY.

API. 2001a. Gas-Fired Boiler – Test Report Site A: Characterization of Fine Particulate Emission Factors and Speciation Profiles from Stationary Petroleum Industry Combustion Sources. Publication No. 4703. American Petroleum Institute, Washington, D.C.

API. 2001b. Gas-Fired Heater – Test Report Site B: Characterization of Fine Particulate Emission Factors and Speciation Profiles from Stationary Petroleum Industry Combustion Sources. Publication No. 4704. American Petroleum Institute, Washington, D.C.

API. 2001c. Gas-Fired Steam Generator – Test Report Site C: Characterization of Fine Particulate Emission Factors and Speciation Profiles from Stationary Petroleum Industry Combustion Sources. Publication No. 4712. American Petroleum Institute, Washington, D.C.

ARB. 2000. California Air Toxics Emission Factors. California Air Resources Board, Sacramento, CA. http://www.arb.ca.gov/emisinv/catef/catef.htm, accessed November 26, 2003.

BAAQMD. 1982. *Source Test Procedure ST-1B: Integrated Ammonia Sampling*. Bay Area Air Quality Management District. San Francisco, CA. http://www.baaqmd.gov/mop/vol4/v4index.htm

Chao, S., Crippen, K., and Janos, A.. 1999. Analysis of Trace Level Compounds in Natural Gas. Gas Research Institute, Final Report, GRI-99/0111.

Chow, J. and J. Watson. 1998. Guideline to Speciated Particulate Monitoring. Prepared for Office of Air Quality Planning and Standards, U.S EPA. Draft 3, August 1998.

Corio, L.A. and J. Sherwell. 2000. In-stack condensible particulate matter measurements and issues. *J. Air & Waste Manage. Assoc.* 50:207-218.

Cui, W., D.J. Eatough and N.L.. Eatough. 1998. "Fine Particulate Organic Material in the Los Angeles Basin - I: Assessment of the High-Volume Brigham Young University Organic Sampling System, BIG BOSS," *J. Air & Waste Manage. Assoc.* 48:1024-1037

DeWees. W.G., S.C. Steinsberger, G.M. Plummer, L.T. Lay, G.D. McAlister and R.T. Shigehara. 1989. Laboratory and Field Evaluation of the EPA Method 5 Impinger Catch for Measuring Condensible Matter from Stationary Sources. *Proceedings of the 1989 EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants*, Air & Waste Management Association, Pittsburgh, PA.

DRI. 2000. DRI Standard Operating Procedure, Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples. DRI SOP #2-204.6, Revised June, 2000. http://vista.cira.colostate.edu/improve/Publications/SOPs/drisop.asp accessed November 26, 2003.

Eatough, D.J., D.A. Eatough, and E.A. Lewis. 1996. “Fine Particulate Chemical Composition and Extinction Apportionment at Canyonlands National Park Using Organic Particulate Material Concentrations Obtained with a Multi-System, Multichannel Diffusion Denuder Sampler,” J. Geophys. Res. 1996, 101(D14), 19515-19531.

England, G. C., B. Toby, and B. Zielinska. 1998. Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles. Publication No. 344, Health and Environmental Affairs Department, American Petroleum Institute, Washington, D.C.

England, G.C., B. Zielinska, K. Loos, et al. 2000. Characterizing PM2.5 emission profiles for stationary sources: comparison of traditional and dilution sampling techniques. *Fuel Proc. Technol.* 65-66:177-188.

England, G.C. 2004. “Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Impact Of Operating Parameters On Fine Particulate Emissions From Natural Gas-Fired Combined Cycle and Cogeneration Power Plants,” prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

England, G.C., S. Wien, T.P. McGrath, and D. Hernandez. 2004. “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,” prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

Filadelfia, E. J. and McDannel, M. D. 1996. Evaluation of False Positive Interferences Associated with the Use of EPA Method 202. Air and Waste Management Association 89th Annual Meeting and Exhibition, Nashville, Tennessee, June 1996.

Grosjean, D., and J.H. Seinfeld (1989). "Parameterization of the formation potential of secondary organic aerosols." *Atmos. Environ.* 23:1733-1747.

Hildemann, L.M., G.R. Cass, and G.R. Markowski. 1989. A dilution stack sampler for organic aerosol emissions: Design, characterization, and field tests. *Aerosol Sci. & Technol.* 10:193-204.

Hildemann, L.M., G.R. Markowski and G.R. Cass. 1991. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* 24(4):744-759.

Hildemann, L. M., Klinedinst, D. B., Klouda, G. A., Currie, L. A. and Cass, G. R., 1994. Sources of urban contemporary carbon aerosol. *Environ. Sci. Technol.* 28(9):1565:1576.

Hodan, W. 2002. *Updates and Improvements to the SPECIATE Data and Program*. SPECIATE Expert Panel Meeting, Charlotte, NC. October 10, 2002. http://www.epa.gov/ttn/chief/conference/ei12/poster/hodan.pdf

Johnson, D.A. and D.H.F. Atkins. 1975. An Airborne System for the Sampling and Analysis of Sulfur Dioxide and Atmospheric Aerosols. *Atmos. Environ.* 9:825-829.

Kirshstetter, T.W., C.E. Corrigan and T. Novakov. 2001. Laboratory and Field Investigation of the Adsorption of Gaseous Organic Compounds onto Quartz Filters. *Atmos. Environ.* 35:1663-1671.

May, K.R. 1967. Physical Aspects of Sampling Airborne Microbes, in Gregory, P.H. and Monteith, J.L. (Eds.) Airborne Microbes, Cambridge Univ. Press, Cambridge.

Mazurek,M.A., Hildemann,L.M., Cass,G.R., Simoneit,B.R.T., Rogge,W.F. 1993. Methods of analysis for complex organic aerosol mixtures from urban emission sources of particulate carbon. In *Sampling and Analysis of Airborne Pollutants*, Winegar,E.D. and Keith,L.H., Eds. Lewis Publishers, Boca Raton, FL, pp. 177-190.

McDonald, J., Zielinska, B., Fujita, E., Chow, J., Watson, J., Sagebiel, J., Hayes, T., Sheetz, L. and Batie, S. 1998. Chemical Speciation of PM2.5 Emissions from Residential Wood Combustion and Meat Cooking. Air and Waste Management Association Specialty Conference on PM2.5: A Fine Particulate Standard, Long Beach, CA, January 1998.

NRC. 1999. Research Priorities for Airborne Particulate Matter, II: Evaluation Research Progress and Updating the Portfolio. National Research Council. National Academy Press, Washington. D.C.

Rubenstein, G. 2001. "Sources of Uncertainty When Measuring Particulate Matter Emissions from Natural Gas-Fired Combustion Turbines," Annual Meeting of the West Coast Section, Air and Waste Management Association, San Diego, California (March 30, 2001).

Ryan, R. 2002. Speciation Profiles and Assignment Files Located on EMCH. Memorandum, U.S. EPA, Emission Factor and Inventory Group, Research Triangle Park, NC, March 8, 2002. http://www.epa.gov/ttn/chief/emch/speciation/emch_speciation_profile.pdf

Seinfeld, J.H. and Pandis, S.N., 1998. *Atmospheric Chemistry and Physics from Air Pollution to Climate Change*, John Wiley & Sons, New York, NY.

Turpin, B.J., J.J. Huntzinger and S.V. Hering. 1994. Investigation of Organic Aerosol Sampling Artifacts in the Los Angeles Basin. *Atmos. Environ.* 28, 3061-3071.

U.S. EPA. 1996. *Method 202 – Determination of Condensable Particulate Emissions from Stationary Sources*. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC. http://www.epa.gov/ttnemc01/promgate.

U.S. EPA. 1997b. Procedures For Preparing Emission Factor Documents (Revised). EPA-454/R-95-015, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 (November 1997).

U.S. EPA. 1999a. *Particulate Matter (PM2.5) Speciation Guidance Document*. Draft Guidance Document. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. pp. 97-108.

U.S. EPA. 1999b. *EPA Preliminary Method PRE-4 – Draft Method for Determination of PM10/PM2.5*. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC. http://www.epa.gov/ttn/emc/prelim.html accessed November 26, 2003.

U.S. EPA. 1999c. *Compendium Method TO-11A – Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]*, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. U.S. Environmental Protection Agency. Office of Research and Development. Washington, D.C. January 1999; EPA/625/R-96/010b.

U.S. EPA. 1999d. *Compendium Method TO-13A – Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS),* Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. U.S. Environmental Protection Agency. Office of Research and Development. Washington, D.C. January 1999; EPA/625/R-96/010b.

U.S. EPA. 1999e. *Compendium Method TO-15 – Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS),* Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. U.S. Environmental Protection Agency. Office of Research and Development. Washington, D.C. January 1999; EPA/625/R-96/010b..

U.S. EPA. 1999f. Method IO-3.3. *Determination of Metals in Ambient Particulate Matter,* Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, EPA/625/R-96/010a, Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1999g. *Using X-Ray Fluorescence (XRF) Spectroscopy*, Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, EPA/625/R-96/010a, Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C.

U. S. EPA. 2000a. Supplement F to the Fifth Edition of AP-42. *Compilation of Air Pollutant Emission Factors Volume I: Stationary Point and Area Sources*, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U. S. EPA. 2001. *Conditional Test Method 37 – Measurement of Formaldehyde Emissions From Natural Gas-Fired Stationary Sources - Acetyl Acetone Derivitization Method*, U.S.

Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. http://www.epa.gov/ttnemc01/ctm/ctm-037.pdf.

U.S. EPA. 2002a. SPECIATE v3.2 Intro and User's Guide. November 1, 2002. http://www.epa.gov/ttn/chief/software/speciate/spec32_user_guide.txt.

U.S. EPA. 2002b. SPECIATE v3.2 Release Notes. November 1, 2002. http://www.epa.gov/ttn/chief/software/speciate/spec32_rel_notes.txt.

Watson, J.G., N.F. Robinson, C. Lewis and T. Coulter. 1997. Chemical Mass Balance Receptor Model Version 8 (CMB8) User's Manual. Desert Research Institute Document No. 1808.1D1 December, 1997.

Watson, J.G., B.J. Turpin, J.C. Chow. 2001. The Measurement Process: Precision, Accuracy and Validity. In *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*; 9th Edition; Cohen, B.S. and C.S. McCammon Jr.; CGIH Worldwide, Cincinnati, OH, 201-216.

Watson, J.G. and J. Chow. 2002. *Considerations in Identifying and Compiling PM and VOC Source Profiles for the SPECIATE Data Base*. SPECIATE Expert Panel Meeting, Charlotte, NC. October 10, 2002. http://www.epa.gov/ttn/chief/software/speciate/panel_minutes.zip.

Wien, S.E., G.C. England, K.R. Loos, K. Ritter. 2001. Investigation of Artifacts in Condensible Particulate Measurements for Stationary Combustion Sources. Paper #536. Air and Waste Management Association, 94th Annual Conference and Exhibition, Orlando, Florida, 25-27 June 2001.

Wien, S., England, G.C. and Chang, M.C. 2003. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-Fired Combustion Systems, Topical Report: Test Results for a Gas-Fired Process Heater (Site Alpha)," U.S. Department of Energy, Pittsburgh, PA.

Zheng, M., G.R. Cass, J.J. Schauer, E.S. Edgerton. 2002. Source Apportionment of PM2.5 in the Southeastern United States Using Solvent-Extractable Organic Compounds as Tracers. *Environ. Sci. Technol.* 36:2361-2371.

Zielinska, B., J. Sagebiel, G. Harshfield, A.W. Gertler and W.R. Pierson. 1996. Volatile Organic Compounds in the C2-C20 Range Emitted from Motor Vehicles: Measurement Methods. *Atmos. Environ.* 30:2269-2286.

APPENDIX A LIST OF ABBREVIATIONS

<	upper estimate of true emission
°C	degrees Celsius
°F	degrees Fahrenheit
µg	micrograms
µg/cm^2	micrograms per square centimeter
µg/mL	micrograms per milliliter
µm	micrometers
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
Btu	British thermal units
C_2	carbon number of 2
Ca	calcium
Cd	cadmium
CEC	California Energy Commission
CEMS	continuous emissions monitoring system
cfm	cubic feet per minute
Cl^-	chloride ion
Cl	chlorine
CO	carbon monoxide
Co	cobalt
CO_2	carbon dioxide
CPM	condensible particulate matter
Cr	chromium
Cu	copper
DI	distilled deionized
DNPH	2,4-dinitrophenylhydrazine
DOE	United States Department of Energy
DRI	Desert Research Institute
DSB	dilution system blank
dscm	dry standard cubic meters
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 volts
FB	field blank
Fe	iron
FID	flame ionization detection
FPM	filterable particulate matter
FTIR	Fourier transform infrared detection
Ga	gallium
GC	gas chromatography
GC/IRD/MSD	gas chromatography/infrared detector/mass selective detector
GC/MS	gas chromatography/mass spectrometry
GE	General Electric
GE EER	General Electric Energy and Environmental Research Corporation
gr/100 scf	grains per hundred standard cubic feet
GRI	Gas Research Institute
H_2O	water
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
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
HSO_3-	bisulfite ion
IC	ion chromatography
ICP/MS	inductively coupled plasma/mass spectrometry
In	indium
IPA	isopropanol
K_2CO_3	potassium carbonate
K	potassium
keV	kilo electron volts
km	kilometers
KHP	potassium hydrogen phthalate
La	lanthanum
lb/hr	pounds per hour
lb/MMBtu	pounds of pollutant per million British thermal units of gas fired
L/m	liters per minute
LOQ	limits of quantification
LQL	lower quantification limits
MDL	method detection limit
MEK	methylethylketone
Mg	magnesium
mg	milligram

mg/dscm	milligrams per dry standard cubic meter
MID	multiple ion detection
mL	milliliter
mL/min	milliliter s per minute
mm	millimeter
MMBtu/hr	million British thermal units per hour
Mn	manganese
Mo	molybdenum
MSD	mass selective detector
MSD/FTIR	mass selective detector/Fourier transform infrared detection
MW	megawatt
N_2	nitrogen gas
Na	sodium
Na^+	sodium ion
NAAQS	National Ambient Air Quality Standards
NaOH	sodium hydroxide
ND	not detected
NETL	National Energy Technology Laboratory
ng/µ	nanograms per microliter
NGCC-SF	natural gas-fired combined cycle power plant
NH_3	ammonia
NH_4^+	ammonium ion
NH_4OH	ammonium hydroxide
Ni	nickel
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO_3^-	nitrate ion
NO_x	oxides of nitrogen
NPS	National Park Service
NRC	National Research Council
NV	not valid
NYSERDA	New York State Energy Research and Development Authority
O_2	molecular oxygen
O_3	ozone
OC	organic carbon
P	phosphorus
PAH	polycyclic aromatic hydrocarbon
Pb	lead
Pd	palladium
pH	potential of hydrogen
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 micrometers
PM2.5	particulate with aerodynamic diameter less than 2.5 micrometers
ppb	parts per billion
ppmv	parts per million (volume)
PUF	polyurethane foam

QA	quality assurance
QFF	quartz fiber filter
Rb	rubidium
RH	relative humidity
RSD	relative standard deviation
S	sulfur
Sb	antimony
scf	standard cubic feet
SCR	selective catalytic reduction
Se	selenium
Si	silicon
SI	Système Internationale
sL/min	standard liters per minute
Sn	tin
SO_2	sulfur dioxide
$SO_3^=$	sulfite ion
$SO_4^=$	sulfate ion
SOP	standard operating procedures
Sr	strontium
SRM	standard reference material
SS	stainless steel
SVOC	semivolatile organic compound
TC	total carbon
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
XAD®-4	Amberlite® sorbent resin (trademark)
XRF	x-ray fluorescence
Y	yttrium
Zn	zinc
Zr	zirconium

APPENDIX B SI CONVERSION FACTORS

	English (US) units	X	Factor	=	SI units
Area:	1 ft^2	x	9.29×10^{-2}	=	m^2
	1 in^2	x	6.45	=	cm^2
Flow Rate:	1 gal/min	x	6.31×10^{-5}	=	m^3/s
	1 gal/min	x	6.31×10^{-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	4.54×10^{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	3.785×10^{-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