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

TOPICAL REPORT: TEST RESULTS FOR A COGENERATION PLANT WITH SUPPLEMENTARY FIRING, OXIDATION CATALYST AND SCR AT SITE GOLF

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TOPICAL REPORT: TEST RESULTS FOR A COGENERATION PLANT WITH SUPPLEMENTARY FIRING, OXIDATION CATALYST AND SCR AT SITE GOLF

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This report presents test results obtained on one source measured at one nominal operating condition 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.

<p style="text-align:center">SITE GOLF OPERATING CONDITIONS [a]</p>

	Run 1	Run 2	Run 3
GT (Load) (%)	99	99	99
Duct Burner	ON	ON	ON
SCR	ON	ON	ON
Oxidation Catalyst	ON	ON	ON

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

ACKNOWLEDGEMENTS

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 μm (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;

- Identify and characterize PM2.5 precursor compound emissions that can be used in source-receptor and source apportionment analysis.

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

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EXECUTIVE SUMMARY

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 to form solid or liquid aerosols as the exhaust plume mixes and cools to near-ambient temperature immediately after the stack discharge. These techniques have been widely used in recent research studies. For example, Hildemann et al. (1994) and McDonald et al. (1998) used filtered ambient air to dilute the stack gas sample followed by 80-90 seconds residence time to allow aerosol formation and growth to stabilize prior to sample collection and analysis. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source-receptor and source apportionment analysis for PM2.5 National Ambient Air Quality Standards (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 cogeneration plant (Cogen-SF) employing an aeroderivative gas turbine, supplementary firing and post-combustion emission controls. The gas turbine is equipped with a lean premix combustion system for oxides of nitrogen (NO_x) emissions control. The heat recovery steam generator (HRSG) is equipped with natural gas-fired duct burners for additional steam production, an oxidation catalyst for reduction of CO emissions followed by a selective catalytic reduction (SCR) 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 an innovative dilution sampling protocol. The flue gas temperature at the stack measurement location was approximately 408 degrees Fahrenheit (°F) during the tests.

The dilution sampler design used in these tests is a compact version of the well-characterized Hildemann et al. (1989) design. The compact sampler was developed in a separate task of this program (Chang and England, 2004) to address issues of size and weight in the original design that preclude its use on many stationary sources. Comparability of results against the original

design was established in other tests (England et al, 2004; Hernandez et al., 2004). 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 particulate with aerodynamic diameter less than 10 μm (PM10) emission standards or permit limits. Widely accepted, standardized procedures for dilution sampling do not currently exist.

Three six-hour test runs were performed at the stack on separate, consecutive days under approximately constant operating conditions near full load. 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 source-specific 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

In summary, the main findings of this test are:

- Particulate mass emissions from this Cogen-SF (including post-combustion emission controls) are extremely low, qualitatively consistent with levels expected for gaseous fuel combustion based on published emission factors and other independent tests. The low particulate and related pollutant concentrations in the exhaust from the plant contribute to moderate uncertainties in most of the emission factors derived from these test results.

- The average source-specific PM2.5 mass emission factor obtained using dilution sampling at this Cogen-SF plant is 0.00029 pounds of pollutant per million British thermal units of gas fired (lb/MMBtu). Historical test results at this site for both

filterable and condensable particulate matter using traditional EPA test methods were not available for direct comparison. Although published emission factors for the same plant configuration could not be found, data for other types of gas-fired systems using traditional hot filter/iced impinger methods are available in EPA AP-42. To illustrate the approximate differences between these methods, the average dilution sampler result is approximately 1/22 of the published AP-42 total particulate matter (filterable plus condensable) emission factor for natural gas-fired stationary combustion turbines and 1/25 of that for natural gas combustion in external combustion equipment (boilers, heaters, etc.). This difference is qualitatively consistent with other tests of stationary gas-fired sources using both dilution and traditional EPA methods. Previous reports suggest the observed difference is largely due to measurement artifacts and other limitations associated with the traditional hot filter/iced impinger test methods (conversion of gaseous sulfur dioxide (SO_2) to solid sulfate ion ($SO_4^=$) residue in the iced impinge method, excessive condensation of vapors that would not occur under ambient conditions, inadequate sensitivity and high blanks in the hot filter method, etc.).

- Organic carbon (OC) and elemental carbon (EC) comprise approximately 50 and 5.4 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 organic adsorption artifact on the quartz fiber filters (QFFs), which is more pronounced for clean sources such as gas combustion. Back-up filter results indicate that 78 to 91 percent of the measured OC may be due to this artifact. Further research is needed to improve the reliability of OC measurements.

- $SO_4^=$, chloride ion (Cl^-), nitrate ion (NO_3^-), ammonium ion (NH_4^+) and soluble sodium (Na) together account for approximately 41 percent of the reconstructed PM2.5 mass. $SO_4^=$ alone accounts for approximately 27 percent.

- The reconstructed PM2.5 mass based on the sum of all measured chemical species is 2.3 times higher than the measured PM2.5 mass. The difference lends further support to the likelihood of a positive bias due to measurement artifacts in the OC measurement.

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

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

- Additional tests on other similar sources are recommended to corroborate the results and findings from this test and verify dilution sampling method performance. The results of this test provide a plausible upper bound for the measured emissions.

- Exploratory measurements using a commercial laser photometer to measure real-time PM2.5 trends in the diluted sample and ambient air were made to determine if the technique could be used to optimize the filter mass loadings in the dilution sampler and to determine if any correlation with stack PM2.5 could be established. Some correspondence between the laser photometer response and PM2.5 mass measured on filters was found, but further evaluation of the technique is needed to assess whether it can be useful in this type of application.

- Exploratory measurements were made using a scanning mobility particle sizer to determine if the technique is viable in the field stack sampling environment for characterizing ultrafine particle size distribution. The results for two test runs showed peak number concentrations at approximately 20 nanometers and peak mass concentrations at approximately 130 to170 nanometers. The total mass of particles between 5 and 300 nanometers is approximately one-third of the total PM2.5 mass measured on filters; however, the procedures and instrumentation are still developmental in this application so no firm conclusions may be drawn from the results.

- Further refinement and testing of the dilution sampling equipment and procedures is needed to minimize procedural errors and improve knowledge of method precision and accuracy. Future tests should include collection of field blanks and dilution sampler blanks to add to the current method performance metrology database. Improved procedures are needed for recovering deposits from the probe and venturi to reduce the significance of blanks in both the dilution method and in traditional EPA methods for very low concentrations in exhaust from sources such as gas-fired Cogen-SF plants. Improvements to reduce background levels in the dilution air also are needed for such sources.

The data in this report were developed using an experimental dilution test method applied to one source operating under one nominal condition 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 dilution and cooling 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 48 megawatt (MW) natural gas- and refinery gas-fired cogeneration plant unit with supplementary firing (Cogen-SF), oxidation catalyst and selective catalytic reduction (SCR) at Site Golf from October 15 to October 17, 2003. 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) 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 research program are 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.

PROJECT OBJECTIVES

The specific objectives of this test were to:

- Obtain PM2.5 mass and speciation results using a dilution sampler system;

- Characterize sulfate, nitrate, ammonium, inorganic elements, elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media in the dilution sampler;

- Develop mass and species emission factors and speciation profiles for PM2.5;

- Compare emission factors obtained from the test with similar emission factors from other tests and published literature.

TEST OVERVIEW

The scope of testing is summarized in Table 1-1. A dilution sampler, described in Section 3, was used to collect all emission samples except carbon monoxide (CO) and oxides of nitrogen (NOx), which were measured using existing plant instrumentation. All emission samples were collected from the exhaust stack downstream of combustion processes and post-combustion emission control equipment. The dilution sampler design used in these tests is a compact version of the well-characterized Hildemann et al. (1989) design. The compact sampler was developed in a separate task of this program (Chang and England, 2004) to address issues of size and weight in the original design that preclude its use on many stationary sources. Comparability of results against the original design was established in other tests (England et al, 2004; Hernandez et al., 2004). The samples were analyzed for the substances listed in Table 1-2. Process data and fuel gas samples were collected during the tests to document operating conditions.

Table 1-1. Test Matrix for Site Golf.

Sampling Location	No. of Test Runs (Total)	Sample Type/ Parameter	Sampling/ Test Method	Equipment	Sample Run Time (min)	Analytical Method/ Principle
Unit Stack	3	Flue Gas/ PM2.5 (mass)	DS (TMF)	DS	360	Gravimetry
		Flue Gas/ PM2.5 (elements)	DS (TMF)	DS	360	XRF
		Flue Gas/ PM2.5 (ions)	DS (Quartz Filter)	DS	360	IC
		Flue Gas/ PM2.5 (OC/EC)	DS (Quartz Filter)	DS	360	TOR
		Flue Gas/ PM2.5 (particle size distribution)	DS (SMPS)	DS	360	SMPS
		Flue Gas/ NH$_3$	DS (citric acid-impregnated cellulose fiber filter)	DS	360	Colorimetry
		Flue Gas/ Velocity, Flowrate	EPA Method 1, 2 (40CFR60 Appendix A)	Pitot tube	10*	Water Manometer
		Flue Gas/ Moisture	EPA Method 4 (40CFR60 Appendix A)	Iced impinger train	30	Gravimetric
		Flue Gas/ O2, CO, NOx	40CFR60 Appendix B	Plant CEMS	360	Paramagnetism, NDIR, Chemiluminesence
Fuel Gas Feed Line	3	Fuel Gas/ Sulfur & HC speciation, heating value	Stainless Steel Canisters (silica coated)	Stainless Steel Canisters	Grab samples	ASTM D5291; ASTM D6228-98; ASTM D3588-98.

* Velocity measured pre- and post-dilution sampler operation   SMPS: scanning mobility particle sizer

DS: dilution sampler   TMF = Teflon® membrane filter

IC: ion chromatography   TOR: thermal-optical reflectance

NDIR: Non-Dispersive Infrared Spectrosopy   XRF: x-ray fluorescence

CEMS: continuous emission monitoring system

Table 1-2. Summary of Analytical Targets.

Parameters	In-Stack		Dilution Sampler						Fuel Gas
	Impingers	Gases	Quartz Filter	TMF	Citric acid Filter	SMPS	Gases	DustTrak	Canister
PM2.5 mass				X				X	
PM2.5 mass PSD						X			
Sulfate			X						
Chloride			X						
Ammonium			X						
Nitrate			X						
Soluble Sodium			X						
Elements				X					
Organic carbon			X						
Elemental carbon			X						
Ammonia (gaseous)					X				
NO_x		X							
CO		X							
O_2		X							
Moisture or relative humidity	X						X		
Velocity		X							
Temperature		X					X		
Hydrocarbon gases									X
Non-hydrocarbon gases									X
Sulfur compounds									X
Gross heating value									X

PSD: particulate size distribution

SMPS: scanning mobility particulate sizer

TMF = Teflon[®] membrane filter

Source Level (Undiluted Exhaust Gas) Samples

Direct extractive integrated sampling for moisture content was performed using a traditional wet impingement method. Molecular oxygen (O_2), CO and NO_X were measured using the existing plant continuous emission monitoring system (CEMS).

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 28:1 with ambient air purified by passing through a high efficiency particulate air (HEPA) filter and activated carbon. Because PM2.5 behaves aerodynamically almost like a gas at typical stack conditions, the samples were extracted non-isokinetically from a single sampling point. After bypassing a portion of the mixed and diluted

sample, the sample was conveyed to a residence time chamber where it resided for approximately 10 seconds to allow time for low-concentration aerosols, especially organics, to condense and grow. The diluted and aged sample was extracted from the aging section through a cyclone separator to remove particles larger than 2.5 μm and conveyed to a sample manifold, to which the following sampling media were attached for sample collection:

- Teflon$^®$ membrane (TMF) for PM2.5 mass and elements;

- High-purity quartz for particulate ions and carbon speciation;

- Citric acid-impregnated cellulose fiber for gaseous ammonia.

Two instrumental analyzers also were attached to the dilution sampler to obtain physical size characteristics and evaluate emission trends:

- Laser photometer (DustTrak) for PM2.5 concentration;

- Scanning mobility particle sizer (SMPS) for ultrafine particle size distribution.

Three 6-hour test runs near full load (100 percent of base load) with duct burners on were performed on three separate test days. A field blank and a trip blank were collected to establish background concentrations of measured substances.

Process Samples

Fuel gas grab samples were collected on each day of the test series and analyzed for specific gravity, gross heating value, sulfur content, hydrocarbon gases and non-hydrocarbon gases. Gross heating value based on continuous on-line natural gas analysis was recorded by the plant data system.

KEY PERSONNEL

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

- Glenn England (GE EER) – Program Manager (949) 859-8851 ext. 136

- Stephanie Wien (GE EER) – Project Engineer (949) 859-8851 ext. 155

- Bob Zimperman (GE EER) – Field Team Leader (949) 552-1803

- Neal Conroy (GE Mostardi Platt Associates (GE MPA)) – Dilution Tunnel Sampling Leader (949) 552-1803

- Aaron McGushion (GE EER) – Engineer (949) 859-8851 ext. 113

- Judith Chow, John Watson, and Barbara Zielinska (Desert Research Institute (DRI)) – Consulting and Laboratory Analysis (775) 674-7050

- Karl Loos (Shell Global Solutions U.S.) – API Work Group Chairman (281) 544-7268

- Karin Ritter (API) – API Project Officer (202) 682-8472

- Paul Drayton (GRI) – GRI Project Manager (847) 768-0694

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- Kathy Stirling (DOE/NETL) – DOE Contracting Officer Representative (918) 699-2008

- Barry Liebowitz (NYSERDA) – NYSERDA Project Manager (518) 862-1090 ext. 3248

2. PROCESS DESCRIPTION

PROCESS DESCRIPTION

Tests were performed on a natural and refinery fuel gas-fired cogeneration plant unit with water spray intercooling in the combustion turbine compressor and supplementary firing in the heat recovery steam generator (Cogen-SF) (Figure 2-1). The unit provides power and process steam for refinery operations. The combustion turbine/generator's rated capacity is 48 MW. The unit is also equipped with natural gas and/or refinery fuel gas-fired duct burners that can be fired alone using fresh air or as supplementary firing with gas turbine exhaust. During these tests, the unit fired 100 percent refinery fuel gas through both the combustion turbine and duct burners during all test runs.

POLLUTION CONTROL EQUIPMENT DESCRIPTION

The combustion turbine employs water spray injection into the annular combustor to suppress peak combustion temperatures and thereby reduce NOx formation. The heat recovery steam generator is equipped with an oxidation catalyst for control of CO emissions followed by a SCR system for control of NOx emissions. The SCR reagent (ammonia) is injected immediately upstream of the SCR catalyst. The stack is equipped with a CEMS for CO, O_2 and NOx.

SAMPLING LOCATIONS

Flue Gas Sampling Locations

The cogeneration unit exhausts through a vertical, cylindrical stack. Emissions sampling was conducted at this stack, which has an inside diameter of 10 feet (120 inches) and has three ports. There were two 6-inch diameter flanged ports positioned at 90 degrees to each other. The sampling locations exceeded the minimum EPA Method 1 requirements for upstream and downstream disturbances. The ports were at least 30 feet (3 stack diameters) downstream of the nearest disturbance and more than 10 feet (1 diameter) upstream from the top of the stack. An additional 2-inch port was located between the two 6-inch ports. All ports were accessed from a

single circular platform that is accessed by ladders. Absence of cyclonic flow and stratification was established from previous testing at this unit. A preliminary velocity check was performed prior to the tests to determine the point of average velocity. Sampling was performed with the probe located near a point of average velocity.
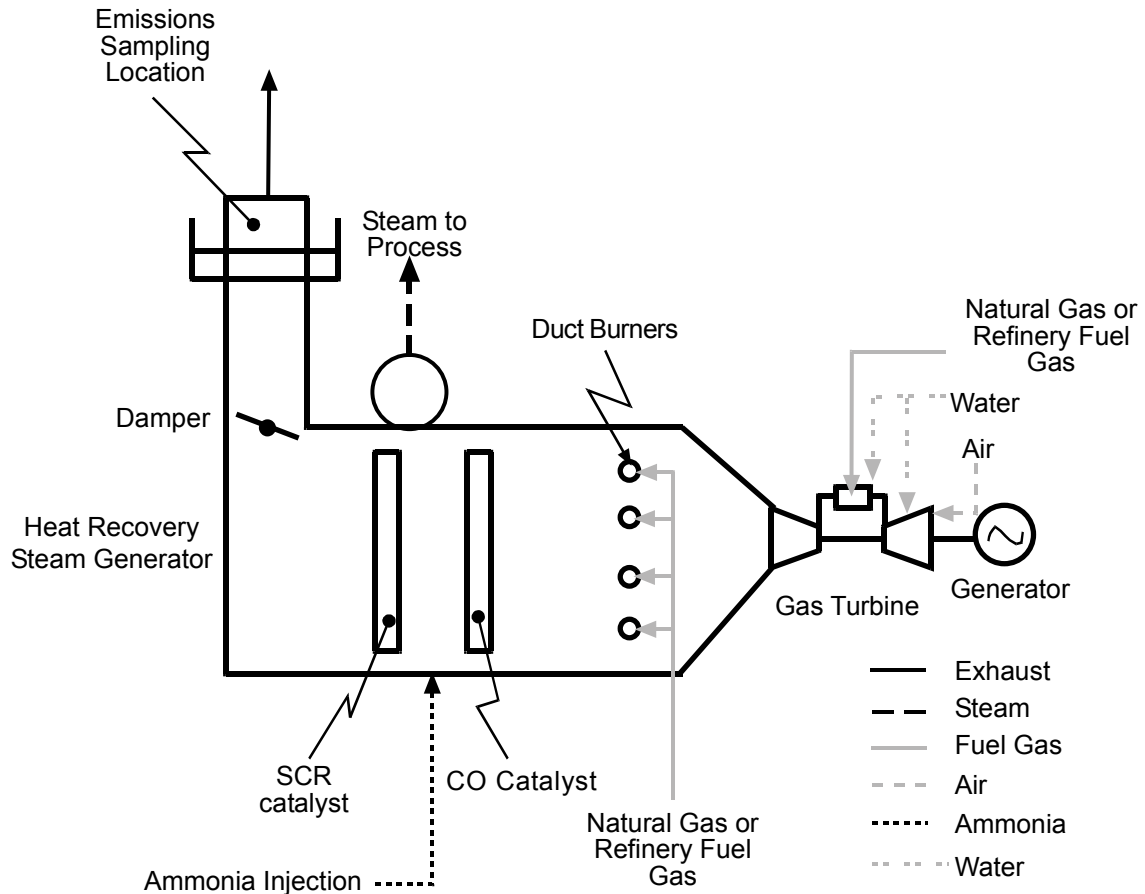
Figure 2-1. Site Golf Process Overview.

3. TEST PROCEDURES

An overview of the sampling and analysis procedures is given in Table 3-1. Figure 3-1 shows the testing chronology for the dilution sampler and in-stack methods. The time of day for the start and finish of each measurement run is shown on the figure. For example, Run 1 began at 12:00 hours and finished at 16:00 hours on Wednesday, October 15. All samples were collected at points of average flow. A sample run time of six hours was chosen as the longest practical sampling time in a single test day, so that sufficient material would be collected to exceed detection limits.

STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

An S-type Pitot tube (EPA Method 2) was used to determine the average stack gas velocity and volumetric flow rate. Stack gas molecular weight was calculated in accordance with EPA Method 3. Moisture content of the sample was determined based on weight gain in an impinger train according to EPA Method 4. A full velocity traverse of the stack was performed before and after Runs 1 and 2 and before Run 3 to determine total stack gas flow rate.

UNDILUTED EXHAUST GAS TEST METHODS

O_2, CO, and NO_x

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

DILUTION SAMPLING METHOD

PM2.5 mass and chemical speciation in the stack gas were determined using a dilution sampling method.

Table 3-1. Sampling and Analysis Procedures (Site Golf).

Sampling Location	Sample Type/Measurements	Sampling Approach	Analytical Principle	Reference
Exhaust Duct	Undiluted exhaust gas/velocity and temperature	S-type pitot and thermocouple	S-type pitot and thermocouple	U. S. EPA Method 2
	Undiluted exhaust gas/O_2, CO, NO_X	Continous emissions monitors	Paramagnetism, NDIR, Chemiluminesence	40 CFR 60 App B
	Diluted Exhaust Gas/PM2.5 mass, elements	Dilution sampler and Teflon® filter	Gravimetry and XRF	U.S. EPA, 1999a; Hildemann et al., 1989
	Diluted Exhaust Gas/PM2.5 OC/EC	Dilution sampler and Quartz filter	TOR	U.S. EPA, 1999a; Hildemann et al., 1989
	Diluted Exhaust Gas/PM2.5 ions: sulfate, nitrate, chloride, ammonium, soluble Na	Dilution sampler and Quartz filter	IC	U.S. EPA, 1999a; Hildemann et al., 1989
	Diluted Exhaust Gas/Gaseous PM2.5 precursors - Ammonia	Dilution sampler and K2CO3- impregnated cellulose-fiber filter	IC	Chow and Watson, 1998
	Diluted Exhaust Gas/Ultrafine PM size distribution	Dilution sampler and SMPS		

IC: ion chromatography
OC/EC: organic carbon/elemental carbon
PM2.5: PM with aerodynamic diameter < 2.5 microns
SMPS: scanning mobility particle sizer
TOR: thermal/optical reflectance
XRF: x-ray fluorescence

Dilution Sampler

The dilution sampler design used in these tests is a compact version of the well-characterized Hildemann et al. (1989) design. The compact sampler was developed in a separate task of this program (Chang and England, 2004) to address issues of size and weight in the original design that preclude its use on many stationary sources. Comparability of results against the original design was established in other tests (England et al, 2004; Hernandez et al., 2004).

		Cogen Exhaust Stack				Trip Blank	Field Blank
	Time	Velocity	CEM	Dilution Sampler	Moisture	Dilution Sampling Media	Dilution Sampling Media
15-Oct-03 Wed.	11:00		Run 1	Run 1	Run 1		
	12:00		12:00	12:00			
	13:00						
	14:00						
	15:00				14:55 - 3:25		
	16:00						
	17:00						
	18:00		18:00	18:00			
	19:00						
16-Oct-03 Thurs.	9:00		Run 2	Run 2	Run 2		
	10:00		10:00	10:00			
	11:00						
	12:00						
	13:00						
	14:00				14:24 - 14:54		
	15:00						
	16:00		16:00	16:00			
	17:00						
17-Oct-03 Fri.	8:00		Run 3	Run 3	Run 3		
	9:00		9:15	9:15			
	10:00				10:00 - 10:30		
	11:00						
	12:00						
	13:00						
	14:00						
	15:00		15:15	15:15			
	16:00						

Figure 3-1. Testing Chronology for Site Golf

PM2.5 mass and chemical speciation in the stack gas was determined using a dilution sampler (Figure 3-2). A stainless steel probe with a buttonhook nozzle was used to withdraw the stack gas sample at a rate of approximately 25 liters per minute (L/min). The sample was transported from the probe into the dilution sampler. The sample was mixed in the sampler with purified ambient air using a mixing plate and turbulent flow conditions to cool and dilute the sample to near-ambient conditions. The ambient air used for dilution was purified using a HEPA filter to remove particulate matter (PM) and an activated carbon bed to remove gaseous organic

compounds. The dilution air temperature and relative humidity (RH) were measured but not controlled. After mixing, the sample aged for approximately 10 to 15 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.

The sample flow rate through the probe and the dilution air flow rate were monitored using venturi flow meters and thermocouples. The venturi velocity heads were 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.
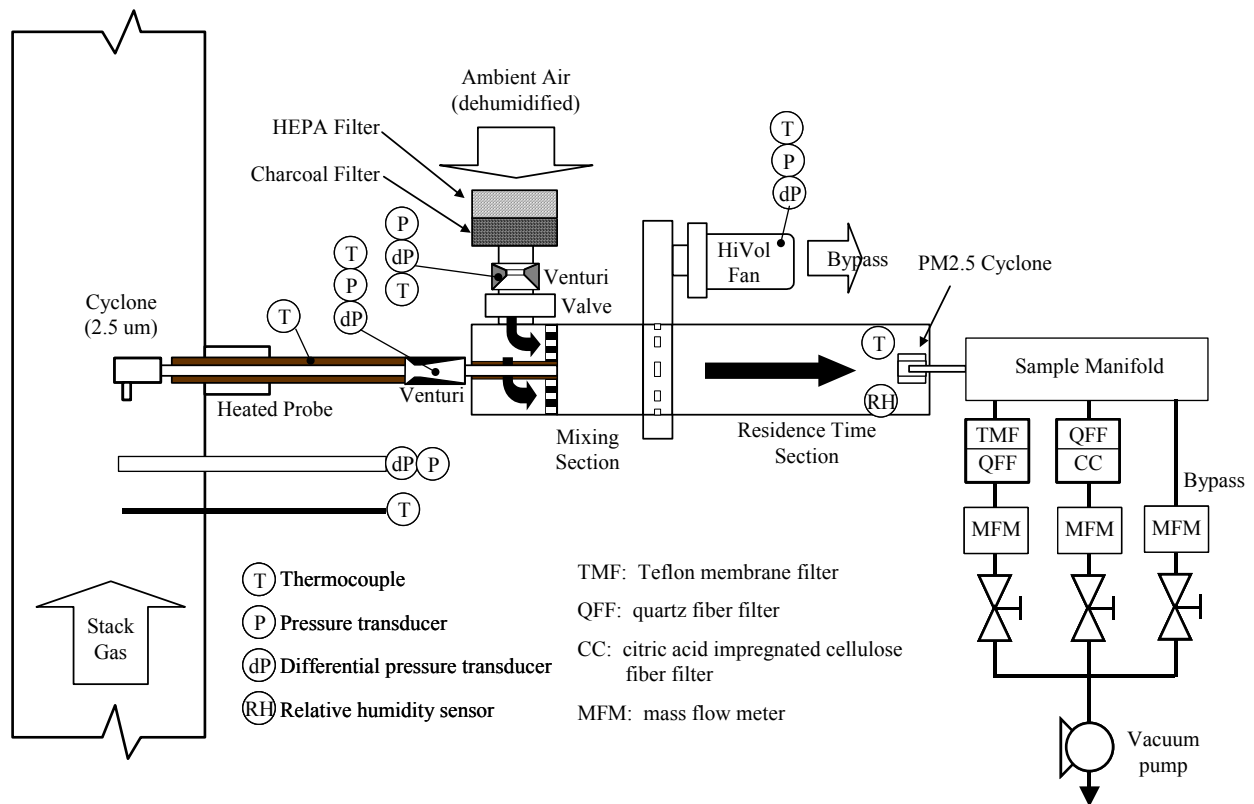
Figure 3-2. Dilution Sampler (Site Golf).

The nominal target dilution ratio based on work by Hildemann et al. (1989) was 30:1 (dilution air:sample). 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 (dry) ranged from 24:1 to 31:1 during the stack runs (Table 3-2), which resulted in average diluted sample temperatures of 25 to 31 degrees Celsius (^{o}C). Diluted sample temperatures are within 4 ^{o}C of the ambient air temperature. The calculated RH of the diluted sample—based on measured ambient air RH, dilution ratio, measured stack gas moisture content and sample temperature—ranges from 44 to 53 percent. These values are in good agreement (with 4 percent RH) with the RH measured by a sensor in the residence time chamber. Since the RH of the fully diluted sample was well below 70 percent for all tests, aerosol growth due to moisture in the sample is assumed negligible (Hinds, 1998).

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

Parameter	Units	Golf-Run 1 15-Oct-03	Golf-Run 2 16-Oct-03	Golf-Run 3 17-Oct-03	Average
Ambient Air Temp.	^{o}C	21.3	24.6	26.2	24.0
Ambient RH	%	41.8	43.0	47.3	44.0
Dilution Chamber Temp.	^{o}C	24.5	28.3	27.9	26.9
Dilution Chamber RH	%	44.7	43.6	53.0	47.1
Stack Sample Flow Rate (dry)	slpm	14.8	15.6	16.5	15.6
Dilution Air Flow Rate (dry)*	slpm	463	443	389	432
HiVol Bypass Flow Rate (wet)	slpm	413	401	356	390
Dilution Ratio (wet)*	L/L	28.1	25.5	21.3	25.0
Dilution Ratio (dry)*	L/L	31.3	28.4	23.6	27.7
Teflon Filter Flow Rate (dry) (mass, elements)	dry slpm	35.4	35.1	35.1	35.2
Quartz Filter Flow Rate (dry) (ions, OC/EC)	dry slpm	35.5	35.2	35.2	35.3
Citric Acid Filter Flow Rate (dry) (NH3)	dry slpm	35.5	35.2	35.2	35.3
Cyclone Bypass Flow Rate (dry)	dry slpm	40.0	40.1	40.1	40.1

*Based on dilution air venturi flow rate.

PM2.5 Mass

Samples for PM2.5 mass measurements were collected on a 47-millimeter (mm) diameter polymethylpentane ringed, 2.0-µm pore size, TMF (Gelman No. RPJ047) placed in a Teflon$^®$ filter holder. The filter packs were equipped with quick release connectors to ensure that no

handling of the filters is required in the field. The flow rate through the filter was monitored during sampling by a mass flow meter at a sampling rate of approximately 35 standard liters per minute (sL/min). Weighing was performed on a Cahn 31 electro-microbalance with ±1 microgram sensitivity. In addition to the filter mass, the sample probe and venturi were recovered after each test run using acetone, then the rinses were evaporated and weighed, following EPA Method 5 procedures (40CFR60, App. A).

Elements

Sample collected on the TMF was also analyzed by energy dispersive x-ray fluorescence (ED-XRF) analysis for the following 40 elements: aluminum (Al), silver (Ag), arsenic (As), gold (Au), barium (Ba), bromine (Br), calcium (Ca), cadmium (Cd), chlorine (Cl), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium (Ga), mercury (Hg), indium (In), potassium (K), lanthanum (La), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), palladium (Pd), rubidium (Rb), 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 ED-XRF analyzer with a side-window, liquid-cooled, 60 kiloelectron volts (keV), 3.3 milliamp rhodium anode x-ray tube and secondary fluorescers was used. The silicon detector had an active area of 30 square 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 x-ray fluorescence (XRF) analyses were conducted on each sample to optimize the detection limits for the specified elements. The filters were removed from their petri slides and placed with their deposit sides downward into polycarbonate filter cassettes. A polycarbonate retainer ring kept the filter flat against the bottom of the cassette. The cassettes were loaded into a carousel in the x-ray chamber. The sample chamber was evacuated to 10^{-3} Torr. A computer program controlled the positioning of the samples and the excitation conditions. Complete analysis at five excitation conditions required approximately 5 hours for each sample.

Sulfate, Nitrate, Chloride, Ammonium, and Soluble Na

Samples for determining water-soluble chloride ion (Cl^-), nitrate (NO_3^-), sulfate ($SO_4^=$), ammonium (NH_4^+), and soluble sodium (Na^+) were collected on quartz fiber filters (QFFs). The flow rate through the filter was monitored during sampling by a mass flow meter at a sample flow rate of approximately 35 sL/min.

Each QFF was cut in half, and one filter half was placed in a polystyrene extraction vial with 15 milliliter (ml) of distilled deionized (DI) water. The extraction vials were capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material. After extraction, these solutions were stored under refrigeration prior to analysis. Cl^-, NO_3^-, and $SO_4^=$, NH_4^+, and Na^+ were measured with a Dionex 2020i ion chromatograph (IC). Approximately 2 ml of the filter extract is injected into the ion chromatograph.

Organic and Elemental Carbon

47 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 35 sL/min. A ½-inch punch from the QFF was taken 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. The TOR carbon analyzer consists of a thermal system and an optical system. Reflected light is continuously monitored throughout the analysis cycle. The negative change in reflectance is proportional to the degree of pyrolytic conversion of carbon that takes place during OC analysis. After oxygen is introduced, 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.

<u>Ammonia (NH$_3$)</u>

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 flow rate through the filter was monitored during sampling by a mass flow meter at a target sample flow rate of approximately 35 sL/min. These filters were extracted with DI water and then analyzed using automated colorimetry.

<u>Continuous PM2.5 Mass Concentration</u>

Aerosol concentration in the diluted sample was measured instrumentally using a laser photometer (Thermo Scientific Corporation (TSI) DustTrak, Model 8250). The instrument provided real-time indicators of aerosol concentrations in the size range of approximately 0.1 to 2.5 μm. The measurements were intended primarily for trend analysis rather than absolute measurements, since the instrument could not be calibrated for the specific aerosol characteristics of this test.

Light scattering is the basic principle of operation. An aerosol sample is continuously drawn through a cyclone to remove particles larger than 2.5 μm, then into the sensing chamber (Figure 3-5). One section of the aerosol stream is illuminated with a small beam of laser light. Particles in the aerosol stream scatter light in all directions. A lens at 90° to both the aerosol stream and laser beam collects some of the scattered light and focuses it onto a photodetector. The detection circuitry converts the light into a voltage. This voltage is proportional to the amount of light scattered which is, in-turn, proportional to the volume concentration of the aerosol. Based on the wavelength of the laser (780 nanometers (nm)) and the sensitivity of the photodiode, the minimum particle size that can be measured is approximately 0.1 μm. The actual response depends on the aerosol size distribution, physical properties and optical properties. Each laser photometer was factory calibrated against a gravimetric reference using the respirable fraction of standard International Organization for Standardization (ISO) 12103-1, A1 test dust (Arizona Test Dust). This test dust has a wide size distribution covering the entire size range of the laser photometer and is representative of a wide variety of ambient aerosols. The wide range of particle sizes averages the effect of particle size dependence on the measured signal. However,

the accuracy of the reading depends on the actual physical and optical properties of the aerosol being measured.
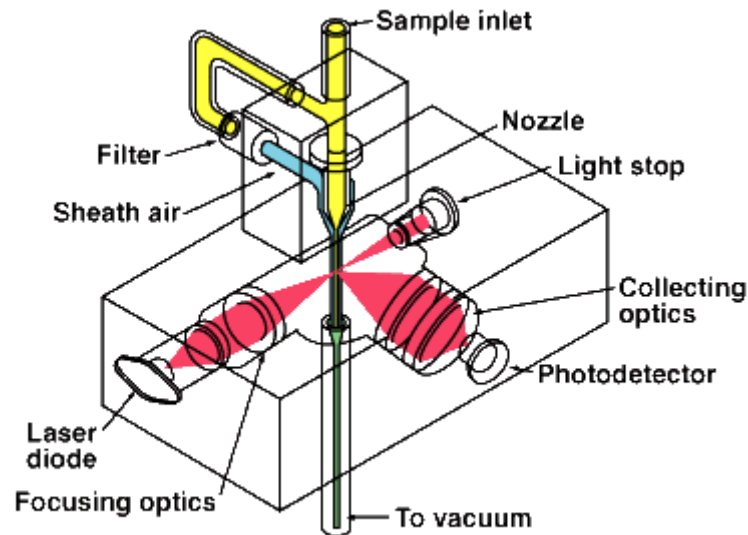
Figure 3-5. Laser Photometer (DustTrak Model 8250, TSI Inc., Shoreview, Minnesota).

A ¼-inch Tygon® sample line approximately four feet in length was used to connect the laser photometer to a metal sample port on the dilution sampler manifold. The port to which the Tygon® line was attached was grounded through the sample manifold legs, but with the line itself being nonconductive there may be potential for some particle losses due to electrostatic charge. The instrument was warmed up for at least 30 minutes prior to use. Prior to testing, a filter was temporarily attached to each sample inlet to verify the instrument zero. Sampling rate was 1.7 L/min. Instrument response during each test was recorded using the internal data logger and later transferred to a computer for data reduction.

Ultrafine Particle Size Distribution

The size and number concentration of particles in the range of 5 to 500 nanometers was measured using a scanning mobility sizer (Wide-Range Particle Spectrometer Model 1000XP, Configuration B, MSP Corporation, Shoreview, Minnesota). The scanning mobility sizer (SMS)

consists of a differential mobility analyzer (DMA) in series with a condensation nuclei counter (CNC) (Figure 3-6). An impactor containing a Po-210 strip is placed before the DMA to remove particles larger than 0.5 μm and neutralize particle charge. In the DMA, an electrical field is generated by applying a voltage to the center electrode, which classifies particles in different size ranges according to their electrical mobility. By varying the DMA voltage and operating conditions, particles of different sizes can be extracted. The DMA voltage was stepped incrementally to obtain a scan of the full particle size range. The particles extracted by the DMA are counted in the CNC. The CNC saturates the sample stream with butyl alcohol, which condenses on the particles and grows them large enough to be counted optically. The sample then passes through laser photometer, which counts the particles.

This test represented the first use of a brand new instrument in a somewhat adverse field sampling situation and the measurements are considered exploratory. Prior to the field test, the instrument was set up in the laboratory and checked for proper functional operation. The SMS was then packed and transported to the field. The butyl alcohol reservoir was drained prior to shipment and the instrument was retained in a vertical orientation to avoid internal spillage of any remaining alcohol. At the stack location following functional checks, the SMS was attached to the dilution sampler manifold using a 1/4-inch Tygon® sampling line approximately 4 feet long. Sample flow rate was set to 0.3 L/min. Prior to each test run, a zero check was performed by attaching a filter to the SMS inlet while sampling and verifying that the readings dropped to near zero. After the zero check, the instrument was operated for the duration of the test run. The operation was configured to sample particles in 48 or 96 size bins, with total scan times of 144 and 240 seconds, respectively (see Section 4 for operating details).
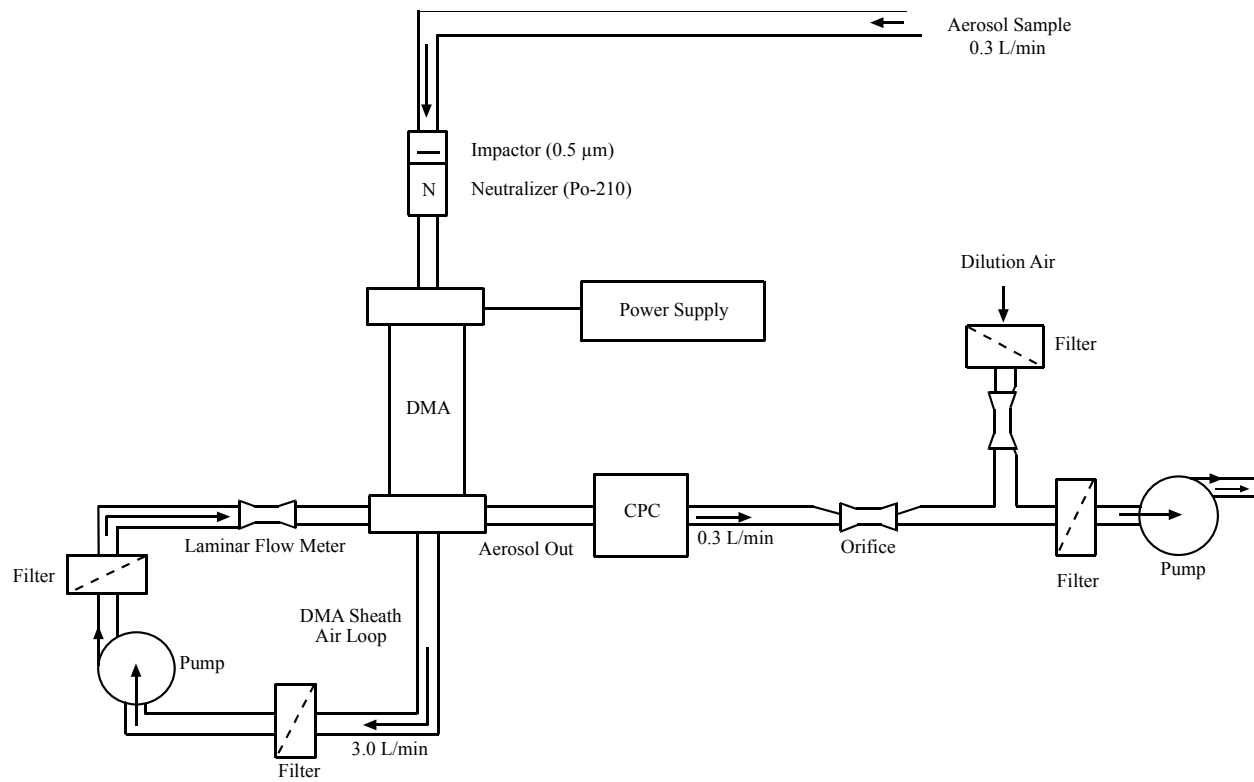
Figure 3-6. Scanning Mobility Sizer.

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 (MDLs) 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.

PROCESS OPERATING CONDITIONS

The Cogen-SF operating conditions were relatively constant during testing and the average results from run to run are very consistent (Table 4-2).

The average gross heat input to the unit during the tests was calculated from the fuel flow rate and fuel higher (gross) heating value (HHV) as measured by plant instrumentation. The average gross heat input was used to convert in-stack emission rates (lb/hr) to emission factors pounds of pollutant per million British thermal units of gas fired (lb/MMBtu), which are presented in Section 5.

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

Substance	Dilution Sampler (mg/dscm)	Substance	Dilution Sampler (mg/dscm)	Substance	Dilution Sampler (mg/dscm)
PM2.5 mass	2.3E-3	K	4.1E-5	Tl	1.7E-5
Ag	8.2E-5	La	4.4E-4	U	1.6E-5
Al	6.9E-5	Mn	1.1E-5	V	1.7E-5
As	1.1E-5	Mo	1.8E-5	Y	9.0E-6
Au	2.1E-5	Ni	6.0E-6	Zn	7.4E-6
Ba	3.6E-4	P	3.8E-5	Zr	1.2E-5
Br	6.9E-6	Pb	2.1E-5	Cl-	3.4E-3
Ca	3.0E-5	Pd	7.4E-5	Nitrate (NO3-)	3.4E-3
Cd	8.2E-5	Rb	6.6E-6	SO4=	3.4E-3
Cl	7.1E-5	S	3.3E-5	NH4+	3.4E-3
Co	6.0E-6	Sb	1.2E-4	Soluble Na	3.4E-4
Cr	1.3E-5	Se	8.5E-6	Soluble K	6.9E-4
Cu	7.4E-6	Si	3.8E-5	Organic Carbon (OC)	2.6E-2
Fe	1.0E-5	Sn	1.2E-4	Elemental Carbon (EC)	6.0E-3
Ga	1.3E-5	Sr	7.7E-6	Backup Filter OC	2.6E-2
Hg	1.8E-5	Ti	2.0E-5	NH3	9.2E-4
In	9.3E-5				

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

Parameter	Units	Golf-Run 1	Golf-Run 2	Golf-Run 3	Average	RSD (%)
Date	dd-mmm-yr	15-Oct-03	16-Oct-03	17-Oct-03		
Start Time	hh:mm	12:00	10:00	9:15		
End Time	hh:mm	18:00	16:00	15:15		
Gross Heat Input to Gas Turbine	MMBtu/hr	443.3	444.1	441.2	442.9	0.34
Gross Heat Input to Duct Burners*	MMBtu/hr	86.1	82.6	77.0	81.9	5.6
Total Gross Heat Input	MMBtu/hr	529.4	526.7	518.2	524.8	1.1
Generator Electrical Output	MW	47.6	47.7	47.6	47.6	0.12
Fuel Flow Rate to Gas Turbine	scfm	6,500	6,500	6,600	6,533	0.88
Fuel Flow Rate to Duct Burners**	scfm	789	741	667	732.2	8.4
NH3 to SCR Injection Rate	lb/hr	125.4	119.9	113.3	119.5	5.1
NOx Water Injection Rate	gpm	41.2	41.5	41.2	41.3	0.42
Interstage Water Injection Rate	gpm	6.6	6.8	7.2	6.9	4.4
NOx Concentration (dry, 15% O2)	ppmv	1.4	1.5	1.5	1.5	3.9
CO Concentration	%, dry	3.2	3.4	3.7	3.4	7.3
O_2 Concentration (dry, 15% O2)	ppmv	13.5	13.6	13.7	13.6	0.74
Barometric Pressure	in Hg	29.99	30.1	30.1	30.1	0.21
Ambient Temperature***	F	70	76	79	75	5.9
Ambient Relative Humidity***	%	41.8	43.0	47.3	44.0	6.7

* Includes 31 MMBtu/hr fired in continuous pilot.

** Excludes fuel flow to pilot.

*** Based on measurements by GE EER at the stack sampling location.

Fuel gas analyses indicate an average total sulfur level of 25 to 29 (parts per million (volume) (ppmv), as elemental sulfur (Table 4-3). Assuming an average refinery fuel gas HHV of 1065 British thermal units/standard cubic feet (Btu/scf), these correspond to a sulfur level in the fuel gas of approximately 0.0019 to 0.0023 lb/MMBtu. Expressed as sulfur dioxide (SO_2), these values correspond to levels of 0.0039 to 0.0045 lb/MMBtu. Note, the HHV of the grab samples collected during the test are approximately 10 percent lower than the HHV reported by the plant based on plant continuous gas analysis instruments. The samples contained approximately six percent nitrogen, which if not included in the heating value calculation would account for most of the difference. While no definitive explanation for this discrepancy was found, it was speculated that the field sample lines used to collect natural gas samples may have had a small amount of nitrogen remaining from purging the lines prior to sampling.

PRELIMINARY TESTS

Preliminary tests with an S-type Pitot probe were conducted to establish a single point of average velocity through each of the sampling ports for sample collection.

STACK GAS CONDITIONS AND FLOW RATE

A summary of the stack conditions during testing is presented in Table 4-4. Stack traverses with an S-type Pitot probe before and after test Runs 1 and 2 were used to determine the average stack gas velocity for flow rate calculations. For test Run 3, one pre-test velocity traverse was performed. Stack gas temperature during the tests ranged from 407 to 409°F.

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.

Table 4-3. Refinery Fuel Gas Analysis Results (Site Golf).

	Units	Golf-Run1	Golf-Run2	Golf-Run3	Average	RSD (%)
Non-Hydrocarbon Gases						
Nitrogen	% v/v	6.24	6.06	5.68	5.99	5
Oxygen/Argon	% v/v	0.09	0.07	0.07	0.08	15
Carbon Dioxide	% v/v	1.21	1.16	1.11	1.16	4
Carbon Monoxide	% v/v	1.11	1.13	1.07	1.10	3
Hydrogen	% v/v	29.5	29.2	29.8	29.5	1
Helium	% v/v	<0.01	<0.01	<0.01	<0.01	n/a
Hydrocarbons						
Methane	% v/v	32.30	32.10	31.60	32.0	1
Ethane	% v/v	11.4	11.6	11.4	11.5	1
Ethene	% v/v	6.63	6.56	6.32	6.50	2
Ethyne	% v/v	ND	ND	ND	ND	n/a
Propane	% v/v	2.47	2.64	2.95	2.69	9
Propene	% v/v	5.42	5.93	6.09	5.81	6
Propadiene	% v/v	ND	ND	ND	ND	n/a
Propyne	% v/v	0.025	0.030	0.029	0.028	9
i-Butane	% v/v	0.651	0.653	0.694	0.666	4
n-Butane	% v/v	0.685	0.729	0.728	0.714	4
1-Butene	% v/v	0.158	0.180	0.204	0.181	13
i-Butene	% v/v	0.151	0.170	0.199	0.173	14
trans-2-Butene	% v/v	0.108	0.118	0.149	0.125	17
cis-2-Butene	% v/v	0.070	0.075	0.095	0.080	17
1,3-Butadiene	% v/v	ND	ND	ND	ND	n/a
i-Pentane	% v/v	0.843	0.762	0.810	0.805	5
n-Pentane	% v/v	0.306	0.288	0.320	0.305	5
neo-Pentane	% v/v	ND	ND	ND	ND	n/a
Pentenes	% v/v	0.224	0.119	0.289	0.211	41
Hexanes +	% v/v	0.447	0.394	0.403	0.415	7
Hydrogen Sulfide	% v/v	ND	ND	ND	ND	n/a
Carbonyl Sulfide	% v/v	ND	ND	ND	ND	n/a
Calculated Elemental Composition						
Carbon	% w/w	68.60	68.99	69.63	69.07	1
Hydrogen	% w/w	19.40	19.41	19.51	19.44	0
Oxygen	% w/w	3.04	2.93	2.78	2.92	4
Nitrogen	% w/w	8.96	8.67	8.08	8.57	5
Sulfur	ppmv	26.0	29.3	24.6	26.6	9
Helium	% w/w	<0.01	<0.01	<0.01	<0.01	n/a
Heat of Combustion % Physical Properties*						
Lower Heating Value	Btu/scf	964	974	988	975	1
Higher Heating Value	Btu/scf	1,060	1,069	1,066	1,065	0
Higher Heating Value	Btu/lb	20,642	20,719	20,523	20,628	0
Specfic Gravity	vs dry/normal air	0.674	0.677	0.682	0.678	1

n/a - not applicable

ND - Not Detected.

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

Parameter	Units	Golf-Run 1	Golf-Run 2	Golf-Run 3
Date	dd-mmm-yr	15-Oct-03	16-Oct-03	17-Oct-03
Temperature	F	407	408	409
Moisture	% v	11.1	11.3	11.2
Velocity	ft/s	95.5	96.0	98.9
	m/s	29.1	29.3	30.1
Flowrate	acfm	462,000	464,000	478,000
	dscfm	246,000	247,000	255,000
	dscmm	6,970	7,010	7,220

PM2.5 mass concentration and emission rate averages 0.16 mg/dscm and 0.15 lb/hr, respectively, with a relative standard deviation of 23 percent, based on TMF weight (Table 4-5). PM2.5 was not detected in the field and trip blanks samples (see Section 6 for additional discussion of blanks).

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

Run Number	Units	Results				RSD	MDL
	-	Golf-Run 1	Golf-Run 2	Golf-Run 3	Average	(%)	(1)
Date	-	14-Oct-99	15-Oct-99	16-Oct-99			
PM2.5	mg/dscm	1.2E-1	1.8E-1	1.9E-1	1.6E-1	23	2.3E-3
	lb/hr	1.1E-1	1.7E-1	1.8E-1	1.5E-1	25	

(1) MDL for average dilution ratio.
MDL- Method Detection Limit
RSD- Relative Standard Deviation

One developmental aspect of the dilution sampling protocol is recovery of deposits on the surfaces of the sampler upstream of the filters. Hildemann (1989) demonstrated that losses of monodisperse ammonium fluoroscein particles between 1.3 and 6.2 μm occur mainly in the probe and venturi. Approximately 5 to 20 percent of particles smaller than 2.5 μm were deposited in the sample inlet line and sample venturi. Losses in the tunnel section and aging chamber account for less than 1.5 to 3 percent of all particles from 1.3 to 6.2 μm. Therefore, quantitative recovery in this test focused on the probe and sample venturi. These sections were rinsed with acetone following each test run, following similar procedures given in EPA Method 5 (40CFR60, App. A). This produced two rinse samples for the dilution sampler (probe and

sample venturi) for each test run. A single acetone recovery blank (from the recovery bottle) was collected for the test campaign.

In general, the levels measured in the probe rinses (Table 4-6) are significant compared to the TMF results. For example, the average total mass found in the Run 1 dilution sampler rinses (corrected for acetone recovery blank) is 0.20 mg/dscm, compared to an average TMF result of 0.12 mg/dscm. This is strongly inconsistent with Hildemann's earlier results. Examining the acetone recovery blank results adds further insight. The acetone (wash) recovery blank mass is approximately 0.3 percent of the acetone rinse weight. EPA Method 5 (40CFR60, App. .A) limits the recovery (wash) blank concentration to 0.001 percent of the sample acetone weight. Clearly, the acetone recovery blank levels are high. In addition, the blank represents a significant number compared to the three TMF results, 0.06 mg/dscm compared to 0.12, 0.18, and 0.19 mg/dscm, respectively, and the average rinse sample results (on average, the blank levels equal approximately 29 percent of the blank-corrected rinse results). It should be noted that these blank levels are very low, far below the upper limit of ≤ 0.001 weight percent (10 ppm) residue specified for acetone reagent in EPA Method 5 (equivalent to approximately 1.2 mg for the volume of the recovery blank in this test) and typical reagent manufacturer's specifications for ACS grade (10 ppm) or HPLC-UV grade (5 ppm). Since the recovery blank is well below the reagent manufacturer's specification even for the highest grade of acetone available, it does not appear that field contamination is the source of the background but more likely the reagent itself. Further, based on an EPA study that showed a standard deviation of 0.36 mg for 22 sample train blanks performed in the laboratory using glass probes (Shigehara, 1996), approximately 70 percent of the rinse results are below the LQL (ten times standard deviation or 3.6 mg) of the acetone rinse procedure.

It is clear from these considerations that apparent background levels in the acetone prevent quantification of the deposits in the sample probe and venturi. Considering this and the earlier work of Hildemann et al. (1989), it is likely that the acetone rinses significantly overstate the actual mass of deposits. Therefore, the rinse results are not added to the TMF results for determining total PM2.5 mass.

Table 4-6. Dilution Sampler Probe and Venturi Rinse Results (Site Golf).

	Units	Golf-Run 1	Golf-Run 2	Golf-Run 3
Rinse mass - probe	mg	0.46	0.65	*1.56*
Rinse volume	mL	113	144	170
Rinse mass - venturi	mg	1.27	2.06	2.22
Rinse volume - venturi	mL	110	75	68
Rinse Mass (total, corrected for RB)	mg	1.2	2.2	3.2
Rinse Mass (total, corrected for RB, in-stack equivalent)	mg/dscm	0.20	0.34	0.48
Acetone recovery blank mass	mg	0.37		
Acetone recovery blank volume	mL	153		
Acetone recovery blank (in-stack equivalent)	mg/dscm	0.062	0.058	0.055

RB = Acetone recovery blank

These results indicate that the acetone rinse procedure does not have the required sensitivity for these low concentrations. An improved or alternative method of recovering deposits from the probe and venturi is needed for gas combustion sources. This could include use of Type I water or other high purity organic solvents and/or modifications to the analytical procedures. The use of glass-lined sample probes also has been suggested to minimize blanks (Shigehara, 1996). Use of constant acetone rinse volumes for blanks and samples (e.g., bringing all sample volumes to 200 mL prior to storage and analysis) may help reduce variability of the results somewhat. Based on Hildemann's earlier results, these deposits are expected to account for less than 20 percent of the total PM2.5, and more probably less than 5 percent. Further tests are needed to assess particle losses in the probe and venturi at these low concentrations.

Laser Photometer Measurements

Exploratory measurements using a commercial laser photometer to measure real-time PM2.5 trends in the diluted sample and ambient air were made to determine if the technique could be used to optimize the filter mass loadings in the dilution sampler and to determine if any correlation between stack PM2.5 trends and other measurements could be established. Laser photometer measurements were made during Run 2 and Run 3 show variations in the stack

samples laser photometer response (Figures 4-1 and 4-2). The average laser photometer responses during each test run agree fairly well with the filter results. The average PM2.5 mass concentration measured by the laser photometer was approximately 0.20 mg/dscm (compared to 0.18 mg/dscm for the dilution sampler PM2.5 mass measurements) and about 0.25 mg/dscm (compared to 0.19 mg/dscm for the dilution sampler PM2.5 mass measurements). The differences are not significant at the 95 percent confidence level considering the variation in the laser photometer response. The apparent difference between the laser photometer and the filter results may indicate that the aerosol properties in the stack samples are significantly different from those of the calibration aerosol (see Section 3). The unsteady trends shown in the figures are surprising given the relatively steady process conditions indicated by other readings. The correspondence between laser photometer response and TMF results is promising, but the number of tests and range of concentrations is too small to draw firm conclusions. Further assessment of the technique based on these results is needed to determine the usefulness of this measurement technique in this application.

Ultrafine Particle Size Distribution

Exploratory measurements using the SMS were made to determine if the technique is viable in the field stack sampling environment for characterizing ultrafine particle size distribution. The SMS was operated during the three days of testing at the site Golf on October 15 through 17, 2003. Testing at site Golf was the first field measurement performed with the SMS instrument. A representative of the manufacturer (MSP Corporation) was present on site on October 15, 2004 for spectrometer shakedown.

Throughout the first day of testing (October 15, 2004), large spurious particle count readings were observed. These were attributed to electric arcing at high intensity of electric field within the DMA cell. The voltage applied across the DMA cell is varied between approximately 0 and 10,000 volts to allow classification of aerosol particles ranging in size from 10 to 500 nm, with the higher voltages corresponding to larger particles. One possible reason for the observed arcing is ambient moisture condensation within the SMS instrument during overnight storage. Condensed moisture can cause electric arcing when high voltages are applied across the DMA
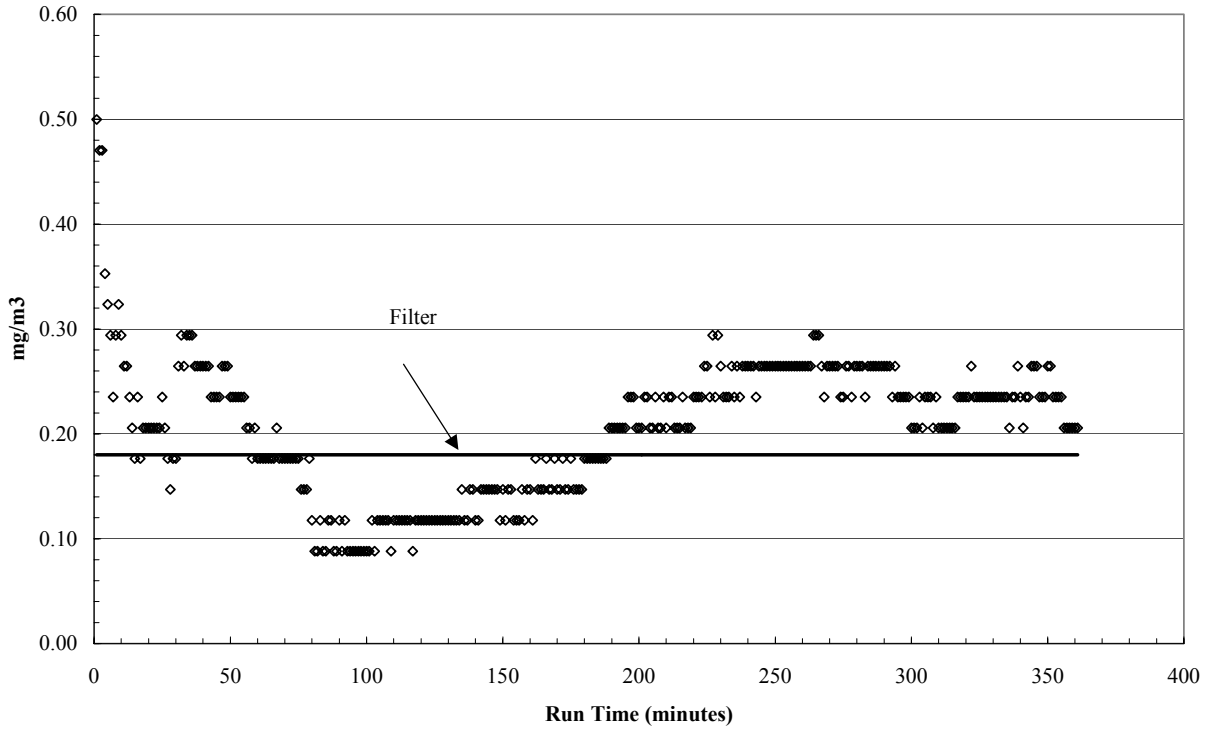
Figure 4-1. Run 2 Laser Photometer Results (Site Golf).
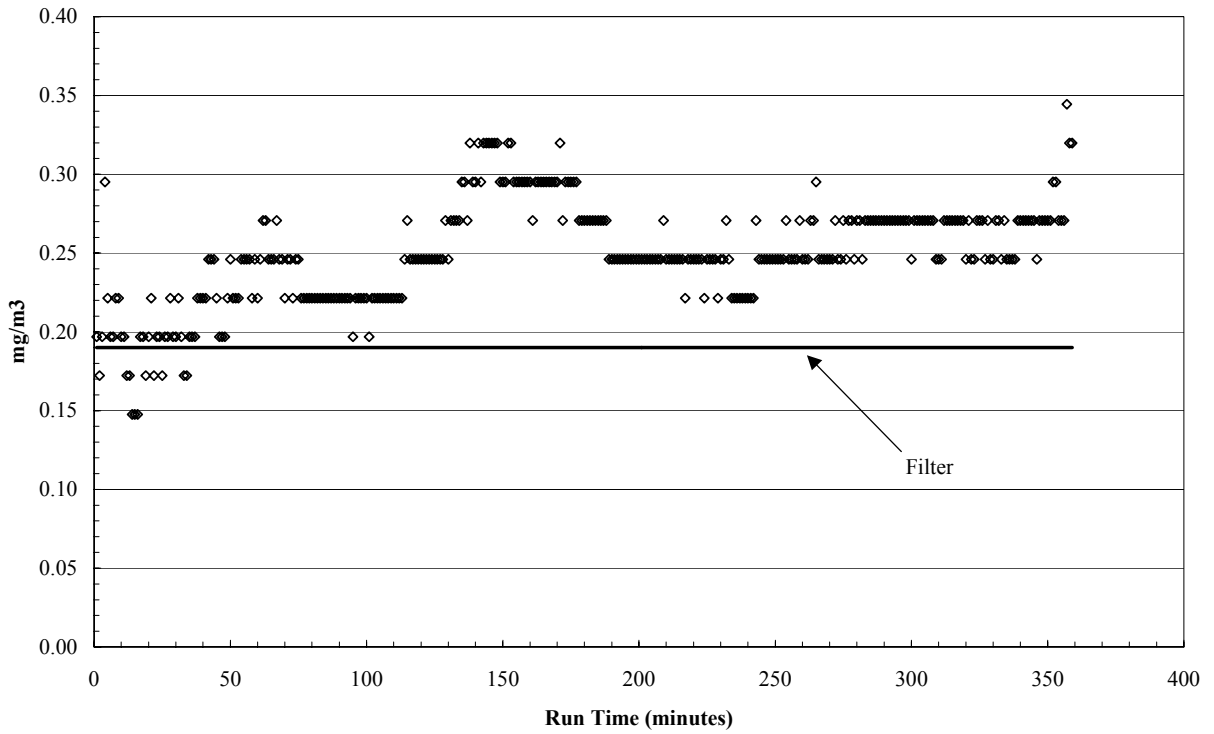
Figure 4-2. Run 3 Laser Photometer Results (Site Golf).

cell. A short-term solution to the electric arcing problem was to decrease the upper voltage limit used by DMA cell. Such voltage restriction results in a cut-off of measured particle diameters. During the first day of testing (October 15) at Site Golf, no particles of size greater than 300 nm were observed. During testing on October 16, the upper particle size limit was set at 400 nm, allowing restriction of the voltage across the DMA cell to below 7,000 volts. Again, no particles of size greater than 300 nm were observed. For tests on October 17, the upper particle size limit was set at 300 nm, restricting the voltage across the DMA cell to below 5,000 volts. No arcing was observed during October 16 and 17 tests. A long-term solution to moisture condensation within the instrument includes overnight instrument would be to purge with de-humidified air (by inserting a silica gel cartridge in the sample line to the instrument and allowing it to run overnight). The instrument purge was added after completion of testing at Site Golf and worked reliably during later tests at a different site. Test data for October 15 was compromised by instrument malfunction due to arcing and is not reported here.

During October 16, 2003, the SMS data were collected from approximately 12:45 p.m. to 3:58 p.m. A total of 75 individual 2.5-min SMS spectra were collected. Individual spectra were averaged to obtain particle size distribution and total number and mass concentrations. A spike in reported DMA cell pressure was observed at approximately 2:40 p.m. Post-test data analysis showed that the detected particle distribution changed significantly after this pressure spike. It is believed that the sampling line integrity was compromised during the pressure spike, resulting in mixing of sample gas with ambient air. Therefore, the data obtained after 2:40 p.m. were excluded from averaging. In addition, three sample spectra recorded in the beginning of the test displayed a transient character due to stabilization of the instrument response and were excluded from averaging. Only spectra recorded between 12:52 p.m. and 2:27 p.m. were used for data reduction. The peak particle number concentration occurs at approximately 20 nm, while the peak mass concentration occurs in the range of approximately 130 to 170 nm (Figure 4-3). A particle density of 0.8 g/cc was used for calculating particle mass. The ragged peak in the mass distribution reflects low particle counts at the high end of the size range.

During October 17, 2003, the SMS data were collected from approximately 9:43 a.m. to 3:15 p.m. A total of 74 individual 4-min SMS spectra were collected. Again, individual spectra were averaged to obtain particle size distribution and total number and mass concentrations. DMA cell

10/16/2003 - Golf Run #2
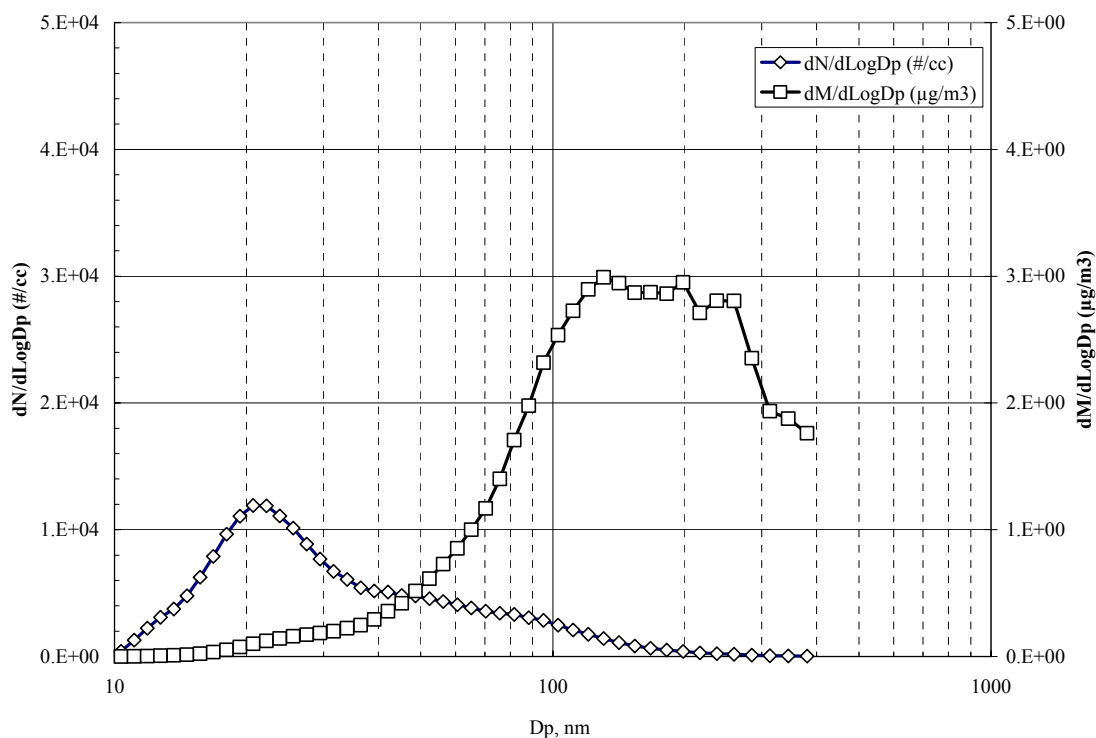
Figure 4-3. Particle Number Size Distribution During Run 2 (not corrected for dilution ratio; Site Golf).

pressure was observed to decrease from about 683 mm Hg in the beginning of the test to about 616 mm Hg at the end of the test. During post-test data analysis, the MSP Corporation representative suggested that variable cell pressure can be observed when high sample inlet pressures result in unsteady operation of pumps used to maintain sample and sheath flows within the WPS instrument. WPS data analysis software automatically corrects data for varying cell pressure. However, the data recorded between 9:43 a.m. and 11:09 a.m. were excluded from averaging due to variability caused by changing cell pressure. Only spectra recorded between 11:09 p.m. and 3:06 p.m. were used for data reduction. The peak particle number concentration occurs at approximately 20 nm. The peak mass concentration occurs at approximately 170 nm, with a slight secondary peak evident at approximately 20 nm (Figure 4-4).

The scan-to-scan variation in measured number counts within a test run is large. Average particle count distribution and the variation observed during October 17, 2003 tests are shown in Figure 4-5. Particles are counted in 48 channels (size bins), covering particle sizes between 10
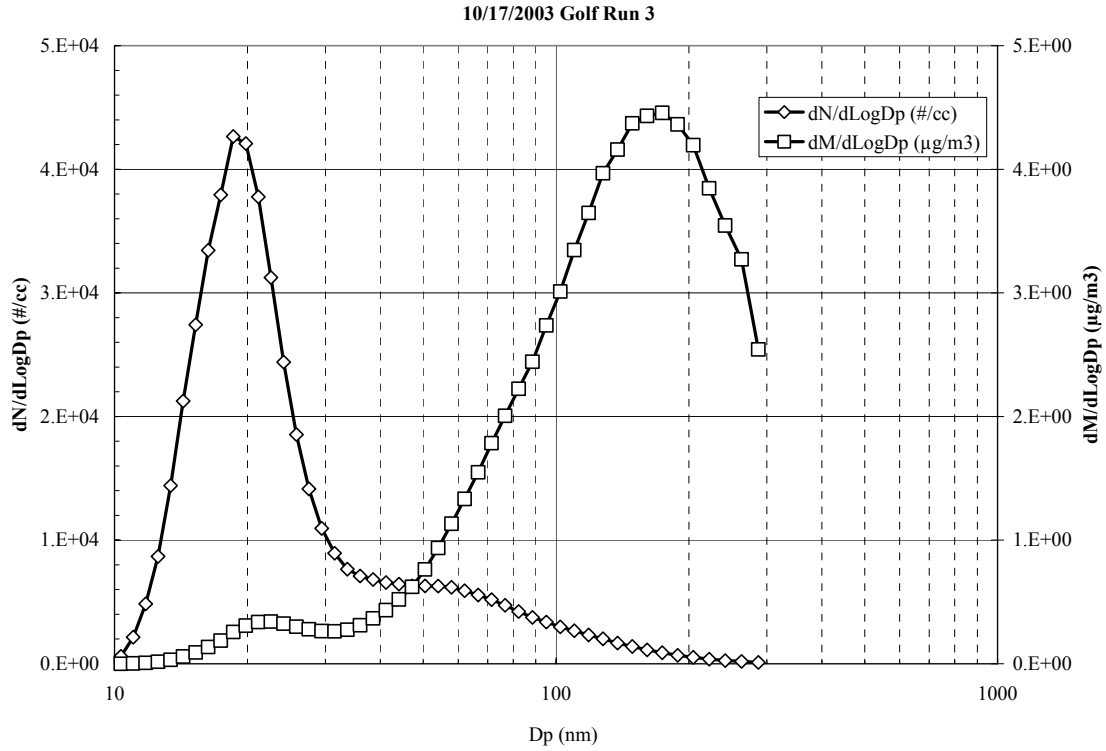
Figure 4-4. Particle Number and Mass Size Distribution During Run 3 (not corrected for dilution ratio; Site Golf).
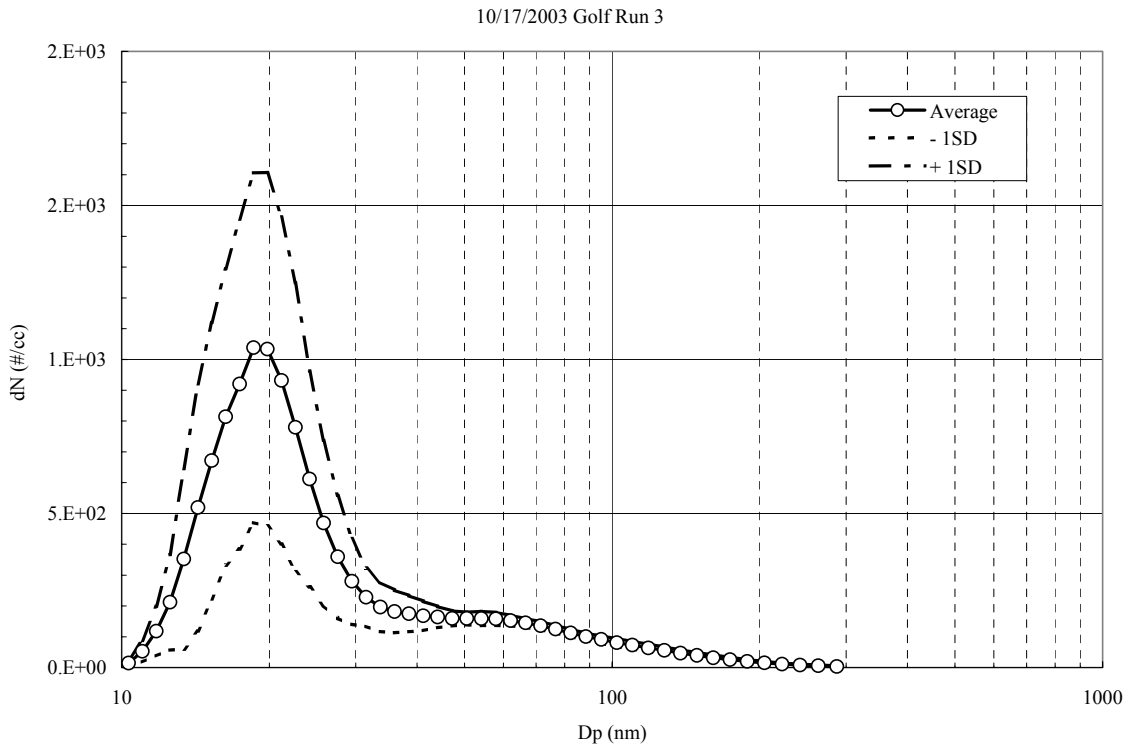
Figure 4-5. Variability of Particle Number Counts (not corrected for dilution ratio; Site Golf, Run 2).

and 300 nm. The average particle count distribution is obtained by averaging the observed number of particles within each size bin. Standard deviations are calculated individually for each bin. Curves marked "– 1 SD" and "+ 1 SD" represent one standard deviation from the average. It should be noted that low particle counts recorded for each particle size bin are probably the main source of the significant data variability evident in the large standard deviations. Another possible reason is that the tests at site Golf were the first in operation of the WPS spectrometer, and sampling and operational procedures were still developmental. Observed standard deviations of particle size distributions were considerably lower during subsequent tests at other sites, suggesting that the variation may be reduced with more experience.

Table 4-7 summarizes the total particle number and mass concentrations based on the integrated particle number concentration measurements during the October 16 and 17 tests. The results are corrected for dilution ratio, to equivalent in-stack concentrations. A particle density of 0.8 g/cc was assumed for calculating total mass. The total mass measured by the SMS is almost the same on the two days of testing. The average SMS results for Runs 2 and 3 (0.061 mg/dscm) are approximately one-third of the average PM2.5 mass from the TMF measurements for Runs 2 and 3 (0.17 mg/dscm). This difference may be due to a relatively small number of particles larger than 300 nm that are present in the TMF samples; however, given the small number of tests and newness of the SMS in this application, it is premature to draw any strong conclusions in this regard.

Table 4-7. Total Particle Number and Mass Concentrations – SMS Results (corrected for dilution; Site Golf).

	Units	10/16	10/17
Number	particles/cm^3	1.79E+05	3.49E+05
Mass	mg/m^3	0.061	0.062

*Assumes density of 0.8 mg/cm^3

Lessons learned with respect to the SMS measurements during testing at site Golf included:

- Electric arcing in DMA cell can be avoided by overnight instrument purge with de-humidified air and restriction of upper particle size limit;

Excess sample inlet pressure leads to unsteady DMA cell pressure and unstable instrument response and must be avoided.

Sulfate, Nitrate, Chloride, Ammonium and Soluble Sodium

QFFs were analyzed for $SO_4^=$, Cl^-, NO_3^-, NH_4^+ and Na^+ ion. Of these, $SO_4^=$ is highest in average concentration at 0.10 mg/dscm, followed by NH_4^+ at 0.036 mg/dscm (Table 4-8). Relative standard deviations for the ions ranged from 7 to 55 percent. Cl^- and Na^+ were detected in the field and trip blanks at significant levels (greater than 95 percent confidence lower bound of the average stack results); the other ions were not detected in the blanks (see Section 6 for additional discussion of blanks).

Table 4-8. Dilution Sampler Sulfate, Nitrate, Chloride Ammonium and Soluble Sodium Results (Site Golf).

Parameter	Units	Value					RSD	MDL
Run Number	-	Golf-Run 1	Golf-Run 2	Golf-Run 3	Average		(%)	(1)
Date	-	14-Oct-99	15-Oct-99	16-Oct-99				
Sulfate	mg/dscm	7.5E-2	1.2E-1	1.1E-1	1.0E-1		22	3.4E-3
	lb/hr	6.9E-2	1.1E-1	1.0E-1	9.4E-2		23	
Nitrate	mg/dscm	6.6E-3	9.6E-3	1.1E-2	9.0E-3		24	3.4E-3
	lb/hr	6.1E-3	8.9E-3	1.0E-2	8.5E-3		26	
Ammonium	mg/dscm	2.6E-2	4.1E-2	4.0E-2	3.6E-2		25	3.4E-3
	lb/hr	2.4E-2	3.8E-2	3.8E-2	3.3E-2		26	
Soluble Na	mg/dscm	3.2E-3	1.8E-3	1.0E-3	2.0E-3	b c	55	3.4E-4
	lb/hr	3.0E-3	1.7E-3	9.7E-4	1.9E-3		54	
Chloride	mg/dscm	4.5E-3	4.1E-3	ND	< 4.3E-3	b c	7	3.4E-3
	lb/hr	4.2E-3	3.8E-3	ND	< 4.0E-3		7	

Shaded area represents substances detected in fewer than three valid test runs. Not considered suitable for quantitative analysis.
(1) MDL for average dilution ratio.
MDL- Method Detection Limit
ND - Not Detected
RSD- Relative Standard Deviation
< - detected in fewer than all 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 Trip Blank concentration.

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 excellent 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.

<u>Particulate Carbon</u>

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 0.14 to 0.20 mg/dscm with a relative standard deviation of 19 percent (Table 4-9). EC concentration ranged from 0.012 to 0.033 mg/dscm with a relative standard deviation of 53 percent. OC accounts for approximately 85 percent of the total carbon mass. OC was detected in the field and trip blanks, EC was not detected in the blanks (see Sections 6 and 7 for additional discussion of results).

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

Parameter	Units	Value				RSD	MDL
Run Number	-	Golf-Run 1	Golf-Run 2	Golf-Run 3	Average		
Date	-	14-Oct-99	15-Oct-99	16-Oct-99		(%)	(1)
Organic Carbon (OC) **	mg/dscm	1.9E-1	2.0E-1	1.4E-1	1.7E-1	19	2.6E-2
	lb/hr	1.8E-1	1.8E-1	1.3E-1	1.6E-1	17	
Elemental Carbon (EC)	mg/dscm	1.2E-2	3.3E-2	1.7E-2	2.1E-2	53	6.0E-3
	lb/hr	1.1E-2	3.1E-2	1.6E-2	1.9E-2	52	
Total Carbon (TC)*	mg/dscm	2.0E-1	2.3E-1	1.5E-1	2.0E-1	19	6.0E-3
	lb/hr	1.9E-1	2.1E-1	1.5E-1	1.8E-1	18	
Backup Filter OC ***	mg/dscm	1.7E-1	1.5E-1	1.2E-1	1.5E-1	17	2.6E-2
	lb/hr	1.6E-1	1.4E-1	1.2E-1	1.4E-1	15	

* TC = OC + EC; TC Average calculated as average of TC runs, not OC Average + EC Average; TC MDL is lesser of OC MDL and EC MDL.
** OC measurements are subject to a potential positive bias from adsorption of VOC species. 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.
(1) MDL for average dilution ratio.
MDL- Method Detection Limit
ND - Not Detected
RSD- Relative Standard Deviation

The QFFs used for OC/EC analysis have the potential for positive OC bias due to adsorption of volatile organic compounds (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. Therefore, the magnitude of any bias in the OC result is potentially significant, and may be the same magnitude as the measured value. Supporting this observation is the fact that the total PM2.5 mass is less than half the reconstructed mass, and on average OC comprises 50 percent of the reconstructed mass. The OC

artifact is the subject of ongoing studies (Turpin et al., 1991, 1994, 2000; Kirshstetter et al., 2001), and because the artifact is not well understood, it is the current convention not to subtract the backup OC from the primary result. However, the similarity of the primary and backup OC results indicates the need for caution when using these results.

Elements

Element concentrations were measured by 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. All elements except Na were below MDL in the field and trip blanks (see Section 6).

Thirteen elements were detected and nine elements – Ca, Cu, Fe, K, Mg, Ni, S, Si, and Zn - were found in all three valid test runs (Table 4-10) (excluding Na and Mg). S is the most abundant element present. The elements stack concentrations are generally low; only Fe, S, and Si have average concentrations greater than five times the MDL. 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 $SO_4^=$. Ag, As, Au, Ba, Cd, Cl, Co, Cr, Ga, Hg, In, La, P, Pb, Pd, Rb, Sb, Se, Sn, Sr, Tl, U, Y, and Zn are below detectable levels for all sample runs.

Inorganic Fine Particle Precursors

NO_X 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. NH_3 concentration ranged from 3.2 to 4.1 mg/dscm (4.5 to 5.7 ppm by volume) with a relative standard deviation of 12 percent (Table 4-11). The measured ammonia concentrations are consistent with typical SCR performance at this site. NO_X concentration was steady at 3.4 mg/dscm for all three runs. NH_3 was detected in the field and trip blanks at levels over two orders of magnitude less than the sample levels (refer to section 6 for further discussion).

Table 4-10. Elements, as Measured by the Dilution Sampler (Site Golf).

Parameter	Value						%	
Units	mg/dscm						%	
Run	Golf-Run 1	Golf-Run 2	Golf-Run 3	Average			RSD	MDL
Date	14-Oct-99	15-Oct-99	16-Oct-99					(2)
S	2.7E-02	3.8E-2	4.1E-2	3.5E-2			21	3.3E-5
Si	5.9E-03	2.5E-3	2.1E-3	3.5E-3	b	c	60	3.8E-5
Na	7.2E-04	1.9E-3	2.2E-3	1.6E-3	b	c	49	(1)
Fe	1.4E-03	1.6E-3	1.5E-3	1.5E-3			7	1.0E-5
Ca	4.0E-04	8.6E-4	6.3E-4	6.3E-4			36	3.0E-5
K	3.5E-04	7.2E-4	7.7E-4	6.1E-4			37	4.1E-5
Mg	7.1E-04	6.9E-4	2.3E-4	5.4E-4			50	(1)
Al	2.8E-04	5.8E-4	4.6E-4	4.4E-4			35	6.9E-5
Zn	1.4E-04	1.9E-4	9.1E-5	1.4E-4			35	7.4E-6
Cu	1.8E-04	1.1E-4	5.3E-5	1.1E-4			54	7.4E-6
Mo	1.7E-04	6.8E-5	4.4E-5	9.4E-5	b	c	71	1.8E-5
Br	4.1E-05	2.8E-5	4.5E-5	3.8E-5			24	6.9E-6
Ni	3.1E-05	4.4E-5	2.7E-5	3.4E-5			25	6.0E-6
La	ND	ND	7.4E-4	<	7.4E-4	e	n/a	4.4E-4
Ba	5.1E-04	ND	ND	<	5.1E-4	e	n/a	3.6E-4
Ti	ND	1.1E-4	ND	<	1.1E-4	e	n/a	2.0E-5
V	ND	6.3E-5	ND	<	6.3E-5	e	n/a	1.7E-5
Mn	ND	4.8E-5	4.6E-5	<	4.7E-5		4	1.1E-5
Cr	ND	2.1E-5	ND	<	2.1E-5	e	n/a	1.3E-5
Co	9.2E-06	ND	ND	<	9.2E-6	e	n/a	6.0E-6
Sr	9.7E-06	ND	7.9E-6	<	8.8E-6	b	14	7.7E-6

Shaded area represents substances detected in fewer than three valid test runs. Not considered suitable for quantitative analysis.

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

(2) MDL for average dilution ratio.

MDL- minimum detection limit

n/a- not applicable

ND - not detected

RSD- relative standard deviation

< - detected in fewer than all 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 trip blank concentration.

e - Insufficient data to calculate 95% confidence lower bound of the average concentration (i.e. zero or one valid run).

Table 4-11. Inorganic Secondary PM Precursor Results (Site Golf).

Parameter	Units	Value				RSD	MDL
Run Number	-	Golf-Run 1	Golf-Run 2	Golf-Run 3	Average	RSD	MDL
Date	-	14-Oct-99	15-Oct-99	16-Oct-99		(%)	(1)
Ammonia (DS)	mg/dscm	4.1E+0	3.6E+0	3.2E+0	3.6E+0	12	9.2E-4
	ppm	5.7E+0	5.1E+0	4.5E+0	5.1E+0	12	
	lb/hr	3.7E+0	3.3E+0	3.0E+0	3.4E+0	11	
Nitrigen Oxides (NOx as NO2) (CEMS)	mg/dscm	3.4E+0	3.4E+0	3.4E+0	3.4E+0	0	
	ppm	1.8E+0	1.8E+0	1.8E+0	1.8E+0	0	
	lb/hr	3.1E+0	3.2E+0	3.2E+0	3.2E+0	2	

CEMS - Continuous Emissions Monitoring System.

DS - Dilution Sampler

(1) MDL for average dilution ratio.

MDL- Method Detection Limit

ND - Not Detected

RSD- Relative Standard Deviation

5. EMISSION FACTORS AND SPECIATION PROFILES

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

EMISSION FACTOR DEVELOPMENT

Source-specific emission factors were determined by dividing the emission rate, in lb/hr, by the measured heat input, in million British thermal units per hour (MMBtu/hr), to give pounds per million British thermal units (lb/MMBtu) for each test run. Heat input is the product of the measured fuel flow rate and the average fuel heating value, obtained from the plant process data. Average emission factors were determined by taking the arithmetic mean of the detected data for valid test runs. Undetected data were excluded from calculations. This treatment of undetected data differs from the procedure used by EPA for development of emission factor documents (U.S. EPA, 1997b), in which one-half of the MDL is substituted for undetected data and used in sums and averaged data. The approach used in this report was chosen to avoid ambiguity when using the results for source apportionment analysis. Because one-half the detection limit is not included in the average results, and uncertainty cannot be determined based on a single datum, emission factors are reported for only those substances detected in at least two of the three test runs. Emission factors based on data detected in at least three test runs are considered the most reliable.

<u>Speciation Profiles</u>

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

<u>Uncertainty and Representativeness</u>

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

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

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

bound represents a plausible upper bound for emissions (i.e., it is likely that the actual emissions are below the upper bound). The reported uncertainty does not include the potential uncertainty associated with different plant configurations, operating conditions, geographical locations, fuel variations, etc.

Quality Assurance Samples

Two types of blanks for the dilution sampler measurements were collected in the field during these tests to assess sampling bias: a field blank and a trip blank. The blanks were analyzed for all substances measured in the stack samples. The average and lower 95 percent confidence bound of the stack sample results were compared to the maximum blank value for screening purposes as follows:

- If the average stack sample result is less than the highest blank, the emission factor is excluded.

- If the lower 95 percent confidence bound of the average stack result is less than the highest field blank or trip blank result, the emission factor is flagged with a footnote "b" or "c", respectively.

- For organic carbon, if the average stack sample result is less than five times the highest blank result, the emission factor is flagged with a footnote "B".

- If a substance was not detected in any of the valid test run samples, the emission factor is flagged with the symbol "<".

Refer to Section 6 for presentation of blank results.

Emission Factor Quality

This test represents one of the first applications of dilution sampling to this type of source and in many cases, the extremely low concentrations of particulate matter and other pollutants challenged the limits of the state-of-the-art methods employed. In addition, because all of the emission measurements were made at the stack downstream of supplementary burners and post-combustion air pollution controls, the results do not represent emissions from the gas turbine alone. The resulting emission factors are not considered representative of any particular

operating condition at this plant, but rather are the average of the operating conditions during this test. Consequently, data users should apply considerable caution when using these results.

Emission factors derived from a test of a single unit should be used with considerable caution. Such results do not necessarily represent results from a random sample of an entire source category population due to differences in design, configuration, emission controls, maintenance condition, operating conditions, geographic location, fuel compositions, ambient/weather conditions and other factors. The source-specific emission factors derived from this test should not be considered representative of all refinery gas-fired Cogen plants.

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

EMISSION FACTORS

Primary PM2.5 Mass, Elements, Ions, and Particulate Carbon Emission Factors

Emission factors for primary PM2.5 mass, elements, ions, and particulate carbon were derived from the dilution sampling results (Table 5-1). The highest elements emission factors are S and Fe at 6.2E10-5 and 2.6E10-6 lb/MMBtu, respectively. The particulate carbon is primarily OC (3.1E10-4 lb/MMBtu), about an order of magnitude greater than EC (3.7E10-5 lb/MMBtu). $SO_4^=$ is the highest ion emission factor at 1.8E10-4 lb/MMBtu. Soluble Na and EC have uncertainties greater than 100 percent indicating it is likely that actual emissions are different from the reported value, and they cannot be distinguished from zero or the MDL with high

confidence. These substances are presented because they may be of special interest for source apportionment or data analysis; however, data users should use appropriate caution with these data.

Table 5-1. Primary Emission Factors – Particulate Mass, Elements, Ions, and Particulate Carbon (Site Golf).

Substance		Emission Factor (lb/MMBtu)		Uncertainty at 95% Confidence Level (%) *(1)*	95% Confidence Upper Bound (%) *(2)*	95th Percentile (lb/MMBtu)	5th Percentile (lb/MMBtu)	Number of Detected Runs
Particulate Mass	PM2.5 mass	2.9E-4		60	4.2E-4	3.5E-4	2.2E-4	3
Elements	Br	6.8E-8		62	9.7E-8	8.2E-8	5.1E-8	3
	Ca	1.1E-6		92	1.8E-6	1.5E-6	7.4E-7	3
	Fe	2.6E-6		22	3.1E-6	2.8E-6	2.4E-6	3
	K	1.1E-6		93	1.8E-6	1.4E-6	6.8E-7	3
	Ni	6.1E-8		65	8.9E-8	7.5E-8	5.1E-8	3
	S	6.2E-5		54	8.6E-5	7.4E-5	4.8E-5	3
	Zn	2.5E-7		87	4.0E-7	3.2E-7	1.8E-7	3
	Mn	< 8.5E-8		46	1.1E-7	8.5E-8	8.4E-8	2
	NO_3^-	1.6E-5		64	2.4E-5	2.0E-5	1.2E-5	3
	$SO_4^=$	1.8E-4		56	2.5E-4	2.0E-4	1.4E-4	3
	NH_4^+	6.4E-5		68	9.6E-5	7.4E-5	4.7E-5	3
Particulate Carbon	OC	3.1E-4	B	49	4.2E-4	3.4E-4	2.6E-4	3
	EC	3.7E-5		133	7.1E-5	5.5E-5	2.2E-5	3
	OC Backup	2.7E-4	B	44	3.5E-4	3.0E-4	2.3E-4	3

Shading indicates substances not detected in at least 3 valid test runs. Data not suitable for quantitative analysis.

< - detected in fewer than all test runs

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

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

B - Stack average is less than five times the field blank or reagent blank (as applicable).

As noted in Section 4, it is very likely the OC results are positively biased due to adsorption of VOCs on the sampling media. This artifact is significant in these tests because of the extremely low OC concentrations present in the exhaust. Backup filter OC (also shown on Table 5-1) is a separate measurement used as an indicator of the potential artifact. The emission factors based on OC and backup filter 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 artifact is not well understood, it is the current convention not to subtract the backup filter OC from the primary result. Despite these limitations of the test

results, it is clear from the results that particulate carbon emissions from this refinery gas-fired Cogen are extremely low. Data users should apply appropriate caution when using these results.

Secondary Particle Precursor Emission Factors

Emissions of NO_X and NH_3 are considered secondary fine particle precursors (Table 5-2). The emission factor for NO_X is derived from the plant's continuous emission monitoring results. The emission factor for NH_3 is derived from the dilution sampler results. Note, the NH_3 emission factor does not include particulate NH_4^+ measured separately on the QFF, since the objectives of the test were to determine PM2.5 species and PM2.5 precursors separately.

Table 5-2. Secondary Particle Precursor Emission Factors (Site Golf).

Substance	Average (lb/MMBtu)	Uncertainty at 95% Confidence Level (%) (1)	95% Confidence Upper Bound (%) (2)	95th Percentile	5th Percentile	Number of Detected Runs
NH3	6.4E-3	34	8.0E-3	7.0E-3	5.9E-3	3
NOx as NO2 (CEMS)	6.0E-3	16	7.0E-3	6.2E-3	5.9E-3	3

DS - Dilution Sampler
CEMS - Continous Emissions Monitoring System.
(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% in

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

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 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 (sulfate and nitrate at a minimum, preferably also ammonium, potassium, sodium, chloride, fluoride, phosphate, calcium, 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 PM2.5 mass measured by the dilution sampler in these tests, it is considered more appropriate to normalize the PM2.5 speciation profile using the reconstructed PM2.5 mass. The reconstructed PM2.5 mass is determined from the individual species measurements with adjustments for assumed oxidation state and hydrocarbon speciation. The average reconstructed PM2.5 mass is greater than the measured PM2.5 mass by a factor of

1.8 to 2.9. There is considerable suspicion regarding the reliability of the OC mass that comprises most of the reconstructed mass and this probably accounts for most of the discrepancy (see Sections 4, 6 and 7 for additional discussion). The OC mass was multiplied by a factor of 1.08 to account for hydrocarbon speciation (based on historical data: the total carbon fraction of all detected semivolatile organic compound (SVOCs) from similar sources). Elements are generally converted to the highest stable oxide form during combustion, except for S, Cl and fixed nitrogen, which are assumed to be present as $SO_4^=$, Cl^-, NO_3^- and NH_4^+. Mg is not included in the reconstructed mass because the ED-XRF analysis is semi-quantitative for this element, and only soluble Na is included for the same reason. Undetected target substances are included as zeros in the reconstructed mass and for uncertainty calculations. Soluble Na and EC have uncertainties greater than 100 percent indicating it is likely that actual emissions are different from the reported value, and they cannot be distinguished from zero or the MDL with high confidence. These substances are presented because they may be of special interest for source apportionment or data analysis; however, data users should use appropriate caution with these data.

The speciation profile is dominated by OC and $SO_4^=$ (Table 5-3 and Figure 5-1). Fifty percent of the reconstructed mass is accounted for by OC, with $SO_4^=$ plus NH_4^+ accounting for 37 percent of the remainder. Backup filter OC, which represents a mass fraction of 44 percent, indicates the potential magnitude of positive bias in the OC result due to the VOC adsorption artifact (discussed elsewhere in this report). This simply underscores that data users need to apply appropriate caution when using the OC and other species mass fraction results.

Table 5-3. Speciation Profile for Primary Emissions- Dilution Sampler Results (Site Golf).

Substance	Average Mass Fraction *(1) (2)* (%)	Uncertainty at 95% Confidence Level (%) *(3)*	95% Confidence Upper Bound (%) *(4)*	Number of Detected Runs
OC *(5)*	50	37	63	3
$SO_4^=$	27	52	36	3
NH_4^+	9.5	66	14	3
EC	5.4	101	9.1	3
NO_3^-	2.4	73	3.7	3
Si	2.0	160	4.2	3
Soluble Na	b 1.3	148	2.6	3
Fe	0.57	23	0.66	3
Ca	0.30	70	0.44	3
K	0.30	96	0.49	3
Al	0.22	74	0.33	3
Zn	0.06	60	0.08	3
Mo	0.04	190	0.09	3
Cu	0.04	142	0.07	3
Br	0.01	85	0.02	3
Ni	0.01	31	0.02	3
Cl-	0.74	228	1.92	2
Mn	0.02	221	0.04	2
Backup Filter OC **	43	46	57.33	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 included as zeros in speciation calculations. The average reconstructed PM2.5 mass is 2.8 times greater than average measured PM2.5 mass, OC results are probably biased high.

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

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

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

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

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

< - not detected in all valid tests.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.
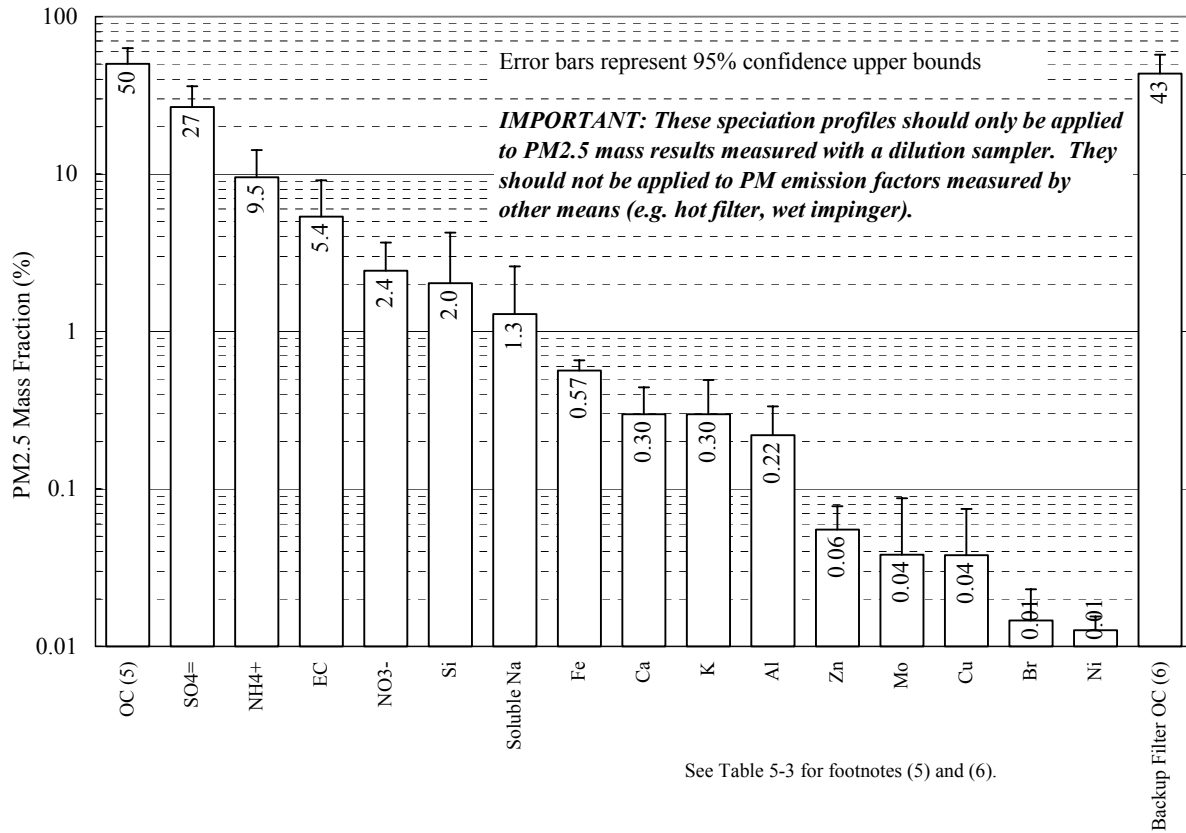
Figure 5-1. PM2.5 speciation profile, as measured by the dilution sampler, normalized by reconstructed PM2.5 mass (Site Golf).

6. QUALITY ASSURANCE

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

SAMPLE STORAGE AND SHIPPING

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

DILUTION SAMPLER SAMPLES

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

- Field blanks (FB) provide an indication of contamination during the handling and transport of the sampling media plus any contamination in the reagents. A single FB was collected for the test campaign by setting up and breaking down the dilution sampler sampling equipment without drawing gas through the sampling media. FBs were collected for all sample types. The FB results are presented as in-stack equivalents by applying the FB analytical results to the average sample volumes and dilution ratios;

- Trip blanks (TB) provide an indication of contamination during the transport of the sampling media plus any contamination in the reagents. TBs are sampling media that are shipped from the lab to the test site and back but are not opened. A single TB was collected for each sample type. The TB results are presented as in-stack equivalents by applying the TB analytical results to the average sample volumes and dilution ratios.

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

Gravimetric Analysis

Prior to testing, unused filters were stored for at least one month in a controlled environment, followed by one week of equilibration in the weighing environment, to achieve stable filter tare weights. New and used filters were equilibrated at 20±5°C and a 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 (µg) sensitivity. The electrical charge on each filter was neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance was calibrated with a 20 milligram (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.

All of the net weights for the dilution sampler stack sample TMFs were positive and range from 47 to 97 µg. Compared to the reported analytical uncertainty (2.4 µg), the stack sample weights are greater than the analytical limit of quantification (LOQ).

PM2.5 was not detected in the FB or the TB (Table 6-1).

Table 6-1. PM2.5 Dilution Sampler PM2.5 Mass Blank Results (Site Golf).

	mg/dscm	
	Golf-FB	Golf-TB
PM2.5 mass	ND	ND

FB - Field Blank
TB - Trip Blank
ND - Not Detected

<u>Ions and Inorganic Secondary PM Precursors Analysis</u>

The primary standard solutions were prepared with reagent grade salts, that were dried in an oven at 105 °C for one hour and then brought to room temperature in a desiccator. These anhydrous salts were weighed to the nearest 0.10 mg on a routinely calibrated analytical balance under controlled temperature (approximately 20 °C) and 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 milliliter (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) were traceable to National Institute of Standards and Technology (NIST) simulated rainwater standards. If the values obtained for these standards did not coincide within a pre-specified uncertainty level (typically three standard deviations of the baseline level or ±5 percent), the samples between that standard and the previous calibration standards were reanalyzed.

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

Table 6-2 lists the blanks concentrations for ions and the secondary PM gaseous precursors. Cl⁻, NH₃, and soluble Na were detected in the TB and FB indicating probable laboratory or reagent

contamination for these substances. Cl⁻ and soluble Na were detected in the blanks at levels greater than the respective 95 percent confidence lower bounds of the stack sample average results; therefore, stack sample results for these substances are probably biased high and should be used with caution.

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

	mg/dscm			
	Golf-FB		Golf-TB	
Cl-	3.8E-3	b	6.0E-3	c
NO3-	ND		ND	
SO4=	ND		ND	
NH4+	ND		ND	
NH3	8.0E-3		9.4E-3	
Soluble Na	3.8E-4	b	4.4E-4	c

FB - Field Blank
TB - Trip Blank
ND - Not Detected
b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.
c - 95% Confidence Lower Bound of the Average concentration is less than the TB concentration.
    or one valid run).

Elemental (XRF) Analysis

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

A quality control standard and a replicate from a previous batch were analyzed with each set of samples. When a quality control value differed from specifications by more than ±5 percent or when a replicate concentration differed from the original value (when values exceed 10 times the

detection limits) by more than ±10 percent, the samples were reanalyzed. If further tests of standards showed that the system calibration had changed by more than ±2 percent, the instrument was recalibrated as described above. All XRF results were entered directly into the DRI databases.

Only Na was detected in either the FB or TB (Table 6-3). All other elements were ND in both the FB and the TB. The Na FB and TB concentrations were greater than the 95 percent confidence lower bound of the Na stack sample results. It should be noted that Na and Mg are not reliably determined by XRF analysis due to interferences.

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

EC was not detected in the TB or FB while OC was detected in both blanks (Table 6-4). The OC levels found in both blanks were less than the 95 percent confidence lower bound of the average stack results. The QFFs used for OC/EC analysis have the potential for positive OC bias due to adsorption of VOCs on the filter. A backup QFF sampled behind the TMF to indicate the potential magnitude of the bias caused by this artifact showed high concentrations of OC that are significant in all the samples. The average OC concentration measured in the backup filters is about 90 percent to the average OC measured in the field samples (Table 4-7). Therefore, the OC results are highly uncertain and should be used with extreme caution.

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

Element	mg/dscm			
	Golf-FB		Golf-TB	
Al	ND		ND	
Br	ND		ND	
Ca	ND		ND	
Cu	ND		ND	
Fe	ND		ND	
K	ND		ND	
Mg	ND		ND	
Mn	ND	e	ND	e
Mo	ND	e	ND	e
Na	1.9E-3	b	2.5E-4	c
Ni	ND		ND	
S	ND		ND	
Si	ND		ND	
Ti	ND	e	ND	e
Zn	ND		ND	

FB - Field Blank

TB - Trip Blank

ND - Not Detected

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

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

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

Table 6-4. Dilution Sampler OC and EC Blank Results (Site Golf).

	mg/dscm	
	Golf-FB	Golf-TB
OC*	6.4E-2	8.7E-2
EC	ND	ND
Backup Filter OC**	6.0E-2	7.6E-2

FB - Field Blank

TB - Trip Blank

ND - Not Detected

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

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

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

* 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.

Lower Quantification Limit

The MDL of an analytical method is often defined as three times the standard deviation of measurements near "zero", e.g., in a blank sample media of a given sample type (Watson et al, 2001). This reflects the performance of the method under ideal circumstances. A more meaningful measure of method performance is the lower quantification limit (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). This is frequently defined using multiple sets of field blank results. In this test, few of the target substances were detected in the single field blank. Hence, it is not possible to rigorously define the LQL based on the single field blank collected in this test. In previous tests at other field sites within this program, field blanks and dilution sampler blanks (DSBs) were collected. An analysis of these results will be included in a separate report to make a preliminary assessment of the method LQL for various substances. As more tests are conducted, it is recommended that both field blanks and DSBs be collected to add to the current database of method performance metrology.

7. DISCUSSION AND FINDINGS

DILUTION METHOD PERFORMANCE

Accuracy

The accuracy of the dilution sampling method has been generally established based on the work of Hildemann et al. (1989), as discussed above. Based on the Hildemann particle loss experiments (the equivalent of analyte spiking), the most conservative PM2.5 mass accuracy using only the TMF results (ignoring sampling losses upstream of the TMF) can be expected to be in the range of approximately ±10 to ±20 percent (i.e., losses of 1.3 and 2.4 μm particles upstream of the filter were 7 and 21 percent, respectively). Hildemann's experiments and theoretical analysis show that losses decrease with decreasing particle size, so the average accuracy for a distribution of particle sizes below 2.5 μm is expected to be closer to the ±10 percent range. Sampling bias in the PM2.5 mass concentration measurement is approximately 5 percent, based on typical performance criteria for the equipment used (reported accuracy of flow meters, temperature sensors, pressure transducers, etc.).

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

Precision

Precision can be assessed by calculating relative standard deviation for the dilution sampler results. From Table 4-5, the relative standard deviation of the PM2.5 mass concentration results

including all runs is 23 percent. This precision is comparable to recent tests at Site Echo (relative standard deviation (RSD) = 41 percent) and Site Delta Gas-Fired Operation (RSD = 20 percent). Generally, PM2.5 mass measurement precision has improved with dilution sampler operating experience. Precisions for Site Charlie (RSD = 84 percent) and Site Bravo (RSD = 104 percent) (recall that the sites have been tested in alphabetical order) were considerably higher although the precision for Site Alpha was low (RSD = 15 percent).

Fuel Sulfur and Sulfate Measurements

The sulfur levels in the refinery fuel gas were about 2 to 20 times higher than typical sulfur levels in natural gas (Perry et al., 1984). Sulfur is oxidized during combustion should be conserved in both the process and the measurement system, i.e.,

$$S_{fuel} \text{ [MMBtu/hr]} = S_{SO2} \text{ [MMBtu/hr]}/2 + S_{SO4} \text{ [MMBtu/hr]}/3$$

Where S_{fuel} is the fuel total sulfur content, S_{SO2} is the stack gas SO_2 concentration, and S_{SO4} is the stack gas particulate sulfate content. Factors of 1/2 are applied to S_{SO2} and 1/3 to S_{SO4} to account for differences in molecular weight when comparing to fuel sulfur. Stack SO_2 was not measured during these tests. The S in the measured stack $SO_4^=$ as a fraction of the fuel sulfur was 2.1 percent, 2.9 percent, and 3.5 percent for Runs 1, 2, and 3, respectively. Thus, by difference, the majority – 96.5 to 97.9 percent - of the sulfur found in the stack is expected to be gaseous SO_2. These $SO_4^=/SO_2$ fractions are typical of gas-fired sources.

Particulate Carbon Measurements

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 kilometer (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. Quartz fiber filters (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 filter 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 7-1 presents the data from the backup and primary QFFs used in this test. The corrected OC concentration - i.e., the OC mass measured on the backup QFF subtracted from the OC mass measured on the primary QFF – also is presented to illustrate the potential significance of the VOC artifact. For this test, the backup OC ranges from 78 to 91 percent and averages 86 percent of the primary OC stack results. These results are qualitatively similar to the independent results of Hildemann et al. (1991), who determined speciated PM emissions from natural gas-fired home appliances using methods identical to those used in this program. Hildemann found that OC accounted for 84.9 percent of PM mass and that the backup OC accounts for 73 percent of the measured OC emissions, on average. Hildemann's data are incorporated into EPA's SPECIATE database, and are currently the only PM speciation data widely available for gas-combustion. Thus, Hildemann's results provide validation of the OC results measured in this study, and reinforce the need for caution when using the OC results.

Table 7-1. OC and Backup Filter OC Results for Site Golf (mg/dscm).

	Run 1	Run 2	Run 3	Average	FB	TB
OC	0.191	0.195	0.137	0.174	0.064	0.0870
Artifact OC	0.173	0.153	0.124	0.150	0.060	0.076
OC - corrected for artifact	0.018	0.042	0.013	0.025	0.027	0.011
Artifact OC/OC (%)	91	78	90	86	85	87

FB - Field Blank

TB - Trip blank

Dilution Ratio Measurements

During these tests the dilution ratio (DR) was measured directly using a dilution air venturi flow meter (Q_{DA}) and a sample gas venturi flow meter (Q_S); DR = Q_{DA}/Q_S. The DR can also be determined indirectly from the Q_S, the sum of all the sample media flow meter flows (Q_{TS}), and the dilution sampler exhaust flow (Q_{EX}) measured by an orifice meter downstream of the vacuum pump motor; DR = ($Q_{EX} + Q_{TS} - Q_S$)/Q_S. The dilution air venturi is a recent addition to the dilution sampler; for previous tests, the DR was measured using the indirect method. Table 7-2 compares DR for the three tests measured directly and indirectly. Agreement between the two methods is good; with an average difference less than 10 percent, providing confidence in the measurements. The direct method is considered more reliable and used for emissions calculations. It is considered more reliable because it uses less measurements that can contribute to measurement error, the Q_{EX} differential pressure measurement and exhaust flow can be interfered by external air flows (wind), and the Q_{DA} flow meter is more appropriately sized for the application that the Q_{EX} flow meter; Q_{EX} flows are at the low end of the flow meter range whereas the Q_{DA} flows are near the middle of the flow meter calibration range.

Table 7-2. Comparison of Dilution Ratios Measured by Direct and Indirect Methods: Site Golf

	Run 1	Run 2	Run 3	Average
DR - direct flows measurement*	31.3	28.4	23.6	27.7
DR - indirect flows measurement**	34.0	31.2	26.8	30.6
DR Direct/DR Indirect (%)	92	91	88	91

DR: dilution ratio = dilution air flow/sample probe flow

* Sample probe flow and dilution air flow measured directly by calibrated ventures.

** Sample probe flow measured directly by calibrated venturi; dilution air flow measured indirectly as: DS exhaust flow + sum of sample media flows - sample probe flow. All measured with calibrated flowmeters.

Dilution Sampler Equipment and Method Improvements

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

- Blanks/Contamination. Due to budget constraints, DSB samples and ambient air samples were not collected for the Site Golf tests. A review of results from previous tests shows that, although PM2.5 mass measurements are generally not significantly affected by contamination, DSB results are significant relative to many of the species measurements in the stack. Generally, both DSB and stack results reflect extremely low concentrations, so it is not entirely surprising that the DSB results are significant. It has not been possible to differentiate the source of the DSB contamination from the dilution air or residual contamination on the surfaces of the samplers. For most substances, field blanks are lower than the DSBs, which indicate that sample handling is probably not the contamination source. It is recommended that future tests include at least one DSB for all measured substances, and that the performance of the dilution air purification system (HEPA and activated carbon filters) is evaluated for low concentration measurements. Procedural precautions to ensure adequate cleaning of the sampler and prevention of contamination should continue to receive special attention for gas-fired combustion sources. More DSB and other blank results also are recommended to improve knowledge of method LQLs.

- Sample Probe and Venturi PM Recovery. The PM2.5 collected in the sample probe and venturi may be a significant portion of the total PM2.5 collected in the dilution system. Rinses of the sample probe and venturi using acetone were used to recover this material; however, PM residue levels measured in acetone blanks were significant relative to the very low PM2.5 concentrations emitted from the gas-fired source and it was not possible to determine the source of the PM2.5 collected from the sample probe and venturi – the process or the acetone. It is recommended possible improvements to the sample probe and venturi rinse procedure be evaluated. This investigation may include multiple reagent blanks analyses to determine the range and precision of the residue levels, multiple recoveries to assess recovery efficiency, determining the impact of rinse volume on residue mass, alternative (lower residue) rinse liquids, and modified procedures to reduce the volume of recovery liquid.

- Precision and Accuracy. After addressing the interference and contamination issues, further evaluation is recommended for a more rigorous assessment of precision and accuracy. Statistical tests (paired sample t-test and F-test) are conventionally used evaluating method performance. A larger number (than the three samples collected for this test program) of valid samples is recommended. Typically, 12 simultaneous paired samples under a single operating condition are considered sufficient for establishing method performance. This was not feasible in the present test program due to the long run times (6 hours) needed for speciated measurements. However, a future test program

could consider shorter runs for PM2.5 mass only. Paired sampling trains could include two dilution samplers with analyte spiking for evaluating bias.

COMPARISON TO OTHER STUDIES

PM2.5 Emission Factors

Table 7-3 compares results of dilution sampler measurements for gas-fired process heaters, boilers, steam generators, combined cycle power plants, and natural gas-fired home appliances (Hildemann et al., 1991, API, 2001a; 2001b; 2001c; Wien et al., 2003; Wein et al., 2004a, 2004b, 2004c, England et al., 2004). The average Golf PM2.5 emission factor derived from the dilution sampler results are at the near the middle of the range measured in other tests. The reasons for differences in PM2.5 concentration among the various dilution sampler tests are not well understood. Additional tests are needed to corroborate all of the recent dilution sampler test results.

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

Source	Unit Type	PM2.5 *(1)* lb/MMBtu
Hildemann et al. (1991)	Natural gas-fired home appliances	0.00011
Site A (API, 2001a)	Refinery Gas-fired Boiler	0.00036
Site B (API, 2001b)	Refinery Gas-fired Process Heater	0.000054
Site C (API, 2001c)	Natural Gas-fired Steam Generator	0.000056
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	0.000052
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	0.00025
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	0.00016
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Commercial Boiler (Nat. Gas)	0.00053 (2)
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	0.00015
Site Golf (this test)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR	0.00029

(1) Data collected using dilution sampler method; data presented is for PM<2.5 microns and includes filterable and condensable PM.
(2) High blank levels indicate results may be biased high.
 DS - Dilution Sampler

The Hildemann PM2.5 results for natural gas-fired home appliances 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. The recent results obtained in this program highlight the variability inherent in the reported emission factors, which should be considered when applying the results to source apportionment studies.

Particulate Carbon and Precursor Emission Factors

Particulate carbon – OC and EC – accounted for the majority of the reconstructed PM2.5 mass measured using the dilution sampler. It is believed, however, that the OC results are subject to positive bias from measurement artifacts (see discussion earlier in this section). The OC emission factor for Site Golf (0.00031 lb/MMBtu) is approximately equal to the average OC emission factor (0.00018 lb/MMBtu) from seven previous tests by the authors and one independent test of gas-fired sources (Table 7-4). With the exception of Site B, all the OC results are within a factor of three 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 five of the average EC emission factor. The EC emission factor for Site Golf falls within the middle half of the data for other sources (between the 25th and 75th percentile), while the OC emission factor falls into the upper quartile.

Emission factors for PM2.5 precursors NH_3 and NO_x are listed in Table 7-5 with emission factors from previous studies. As expected, NO_x emissions from combustion systems equipped with SCR are lower than unequipped combustors and NH_3 emissions tend to be higher from SCR units. NH_3 emissions from Site Golf are higher than average NH_3 emissions from SCR equipped units while NOx emissions from Site Golf are lower than average NO_x emissions from SCR equipped units

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

Source	Unit Type	OC	Backup OC	EC	TC
Hildemann et al. (1991)	Natural gas-fired home appliances	9.0E-5	6.7E-5	7.1E-6	9.7E-5
Site A (API, 2001a)	Refinery Gas-fired Boiler	1.5E-4	--	9.4E-5	2.5E-4
Site B (API, 2001b)	Refinery Gas-fired Process Heater	2.8E-5	--	1.9E-5	3.4E-5
Site C (API, 2001c)	Natural Gas-fired Steam Generator	2.3E-4	--	9.2E-6	2.4E-4
Site Alpha (Wein, et al., 2003)	Refinery Gas-fired Process Heater	6.7E-5	9.7E-5	7.3E-6	7.5E-5
Site Bravo (Wein, et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	2.0E-4	1.8E-4	1.9E-5	2.2E-4
Site Charlie (Wien, et al., 2004b	Natural Gas-fired Process Heater with SCR	1.9E-4	1.3E-4	3.6E-5	2.2E-4
Site Echo (England, et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	2.3E-4	2.3E-4	1.3E-5	2.4E-4
Site Golf (this test)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR	3.1E-4	2.7E-4	3.7E-5	3.5E-4

EMISSION FACTOR QUALITY

The source-specific emission factors developed from this test (Table 5-1) generally have relative uncertainties above 50 percent but below 100 percent (except for EC and Soluble Na - presented because they may be of special interest for source apportionment or data analysis). Factors driving the uncertainties are the three test runs data set (greater numbers of runs reduce the t-statistic) and the fact that many species were detected at concentrations near the MDL or blank levels. The data sets are normally distributed, with some exceptions, so the arithmetic mean and uncertainty bounds are a reasonable representation of the data central tendency and distribution observed in this test. The 95 percent upper confidence bounds presented with the emission factors provides plausible upper bounds to emissions (i.e., the actual emission factor is very likely to be lower). The dilution sampling method has been validated in the peer-reviewed scientific literature (Hildemann et al., 1989), and the ambient air sample collection and analysis methods are well documented in published EPA test methods and/or guidelines. The data quality is well documented throughout this report, and sufficient details are provided for others to reproduce the tests. However, the data quality for certain species (i.e., NH_3, OC, EC, Cl-, Si, soluble Na and Na, Ca, K, Mg, Al, Br and Ni) is fair to poor due to background levels in the purified dilution air, as discussed earlier in this section. 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. At this time, the method remains developmental for stationary sources. Widely recognized standard methods for stationary source dilution sampling do not presently exist. In a separate task of this program, efforts to develop a consensus standard method through ASTM International are underway at this writing.

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

Uncertainty is presented with all emission factor and mass fraction results; the uncertainty calculation includes analytical, sample volume, and dilution ratio uncertainties. The emission factor quality is necessarily considered below average because they are source-specific emission factors based on a single test. Further, the data quality for certain species (i.e., NH_3, OC, EC, Cl-, Si, soluble Na and Na, Ca, K, Mg, Al, Br and Ni) is fair to poor due to background levels in the purified dilution air, as discussed earlier in this section. The results from this limited set of test data should not be interpreted as representative of the entire population of Cogen-SFs because of the wide range of designs, configurations, emission controls, operating conditions, ambient PM2.5 concentrations, weather conditions, fuel compositions, etc. that exist. In addition, because all of the emission measurements were made at the stack downstream of post-combustion air pollution controls, the results do not represent emissions from the gas turbine alone. The operating conditions for each run varied with normal plant operation near full load. 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 this Cogen-SF (including post-combustion emission controls) are extremely low, qualitatively consistent with levels expected for gaseous fuel combustion based on published emission factors and other independent tests. The low particulate and related pollutant concentrations in the exhaust from the plant contribute to moderate uncertainties in most of the emission factors derived from these test results.

- The average source-specific PM2.5 mass emission factor obtained using dilution sampling at this Cogen-SF plant is 0.00029 lb/MMBtu. Historical test results at this site for both filterable and condensable particulate matter using traditional EPA test methods were not available for direct comparison. Although published emission factors for the same plant configuration could not be found, data for other types of gas-fired systems using traditional hot filter/iced impinger methods are available in EPA AP-42. To illustrate the approximate differences between these methods, the average dilution sampler result is approximately 1/22 of the published AP-42 total particulate matter (filterable plus condensable) emission factor for natural gas-fired stationary combustion turbines and 1/25 of that for natural gas combustion in external combustion equipment (boilers, heaters, etc.). This difference is qualitatively consistent with other tests of stationary gas-fired sources using both dilution and traditional EPA methods. Previous reports suggest the observed difference is largely due to measurement artifacts and other limitations associated with the traditional hot filter/iced impinger test methods (conversion of gaseous SO_2 to solid $SO_4^=$ residue in the iced impinge method, excessive condensation of vapors that would not occur under ambient conditions, inadequate sensitivity and high blanks in the hot filter method, etc.).

- OC and EC comprise approximately 50 and 5.4 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 organic adsorption artifact on the QFFs, which is more pronounced for clean sources such as gas combustion. Back-up filter results indicate that 78 to 91 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^- $NH_4^+$and soluble Na together account for approximately 41 percent of the reconstructed PM2.5 mass. $SO_4^=$ alone accounts for approximately 27 percent.

- The reconstructed PM2.5 mass based on the sum of all measured chemical species is 2.3 times higher than the measured PM2.5 mass. The difference lends further support to the likelihood of a positive bias due to measurement artifacts in the OC measurement.

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

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

- Additional tests on other similar sources are recommended to corroborate the results and findings from this test and verify dilution sampling method performance. The results of this test provide a plausible upper bound for the measured emissions.

- Exploratory measurements using a commercial laser photometer to measure real-time PM2.5 trends in the diluted sample and ambient air were made to determine if the technique could be used to optimize the filter mass loadings in the dilution sampler and to determine if any correlation with stack PM2.5 could be established. Some correspondence between the laser photometer response and PM2.5 mass measured on filters was found, but further evaluation of the technique is needed to assess whether it can be useful in this type of application.

- Exploratory measurements were made using a scanning mobility particle sizer to determine if the technique is viable in the field stack sampling environment for characterizing ultrafine particle size distribution. The results for two test runs showed peak number concentrations at approximately 20 nanometers and peak mass concentrations at approximately 130 to170 nanometers. The total mass of particles between 5 and 300 nanometers is approximately one-third of the total PM2.5 mass measured on filters; however, the procedures and instrumentation are still developmental in this application so no firm conclusions may be drawn from the results.

- Further refinement and testing of the dilution sampling equipment and procedures is needed to minimize procedural errors and improve knowledge of method precision and accuracy. Future tests should include collection of field blanks and dilution sampler blanks to add to the current method performance metrology database. Improved procedures are needed for recovering deposits from the probe and venturi to reduce the significance of blanks in both the dilution method and in traditional EPA methods for very low concentrations in exhaust from sources such as gas-fired Cogen-SF plants. Improvements to reduce background levels in the dilution air also are needed for such sources.

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

for future refinement and validation of the experimental dilution method for specific applications so that it may be applied in future tests to develop more robust emission factors.

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APPENDIX A. LIST OF ABBREVIATIONS

<	upper estimate of the true emission
°C	degrees Celsius
°F	degrees Fahrenheit
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
Br	bromine
Btu/scf	British thermal unit per standard cubic foot
Ca	calcium
Cd	cadmium
CEC	California Energy Commission
CEMS	continuous emissions monitoring system
Cl	chlorine
Cl^-	chloride ion
cm^3	cubic centimeters
CNC	condensation nuclei counter
CO	carbon monoxide
Co	cobalt
Cogen-SF	supplementary firing
Cr	chromium
Cu	copper
DI	distilled deionized
DMA	differential mobility analyzer
DOE/NETL	United States Department of Energy National Energy Technology Laboratory
DR	dilution ratio
DRI	Desert Research Institute
DSB	dilution sampler blank
DT	dilution tunnel
EC	elemental carbon
ED-XRF	energy dispersive x-ray fluorescence
EPA	Environmental Protection Agency
ERA	Environmental Research Associates
eV	electron volts
FB	field blank

Fe	iron
FID	flame ionization detection
Ga	gallium
GE	General Electric
GE EER	General Electric Energy and Environmental Research Corporation
GE MPA	GE Mostardi Platt Associates
gpm	gallons per minute
GRI	Gas Research Institute
HEPA	high efficiency particulate air
Hg	mercury
HHV	higher heating value
HRSG	heat recovery steam generator
IC	ion chromatography
In	indium
ISO	International Organization for Standardization
K	potassium
keV	kiloelectron volts
KHP	potassium hydrogen phthalate
km	kilometer
L/min	liters per minute
La	lanthanum
lb/hr	pounds per hour
lb/MMBtu	pounds of pollutant per million British thermal units of gas fired
LOL	lower quantification limit
LOQ	limit of quantification
MDL	minimum in-stack detection limit
Mg	magnesium
mg	milligram
mg/dscm	milligrams per dry standard cubic meter
ml	milliliter
mm	millimeter
MMBtu/hr	million British thermal units per hour
Mn	manganese
Mo	molybdenum
MW	megawatt
Na	sodium
Na^+	sodium ion
NAAQS	National Ambient Air Quality Standards
ND	not detected
NH_3	ammonia
NH_4^+	ammonium ion
Ni	nickel
NIST	National Institute of Standards and Technology
nm	nanometer
NMHC	non-methane hydrocarbon
NO_3^-	nitrate ion

NO_x	oxides of nitrogen
NYSERDA	New York State Energy Research and Development Authority
O_2	molecular oxygen
OC	organic carbon
P	phosphorus
Pb	lead
Pd	palladium
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 micrometers
PM2.5	particulate with aerodynamic diameter less than 2.5 micrometers
ppmv	parts per million (volume)
QA	quality assurance
QFF	quartz fiber filter
Rb	rubidium
RH	relative humidity
RSD	relative standard deviation
S	sulfur
Sb	antimony
scf	standard cubic feet
scfm	standard cubic feet per minute
SCR	selective catalytic reduction
Se	selenium
SI	Système Internationale
Si	silicon
sL/min	standard liters per minutes
SMPS	scanning mobility particle sizer
SMS	scanning mobility sizer
Sn	tin
SO_2	sulfur dioxide
$SO_4^=$	sulfate ion
Sr	strontium
SRM	standard reference material
SVOC	semivolatile organic compound
TB	trip blank
TC	total carbon
Ti	titanium
Tl	thallium
TMF	Teflon-membrane filter
TOR	thermal/optical reflectance
TSI	Thermo Scientific Incorporated
U	uranium
V	vanadium
VOC	volatile organic compound
WPS	wide range particle spectrometer
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