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

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This report presents test results obtained on one source measured at several operating conditions 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.

The emission factors developed from this test are source-specific for the time and conditions of this test; therefore, they do not necessarily represent emission factors for typical operation of this specific source or the general population of similar sources. 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.

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FOREWORD

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM2.5). PM2.5 in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and/or incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. These deficiencies in the current methods can have significant impacts on regulatory decision-making. The current program was jointly funded by the U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) to provide improved measurement methods and reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM2.5 concentrations. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source apportionment and source receptor analysis for PM2.5 NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

The goals of this program were to:

- Develop improved dilution sampling technology and test methods for PM2.5 mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.
- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source-receptor and source apportionment analysis;
- 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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BACKGROUND

In 1997, the United States Environmental Protection Agency promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (μm) referred to as PM2.5. PM2.5 in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. Primary aerosol includes both filterable particles that are solid or liquid aerosols at stack temperature plus those that form as the stack gases cool through mixing and dilution processes in the plume downwind of the source. These deficiencies in the current methods can have significant impacts on regulatory decision-making. PM2.5 measurement issues were extensively reviewed by the American Petroleum Institute (England et al., 1998), and it was concluded that dilution sampling techniques are more appropriate for obtaining a representative particulate matter sample from combustion systems for determining PM2.5 emission rate and chemical speciation. Dilution sampling is intended to collect 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 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 backup generator Diesel engine employing a Caterpillar 3406C engine rated at 500 horsepower. The tests were performed in collaboration with a more comprehensive test program undertaken by University of California at Riverside (UCR) for the California Energy Commission. The engine and test bed were located at the UCR Bourns College of Engineering Center for Environmental Research and Technology. Tests were performed with and without a post-combustion catalytic Diesel particulate filter (DPF) over a wide range of operating load. The results of other measurements performed by UCR, including comprehensive chemical characterization of particulate matter and particle size, are reported elsewhere. The specific goal of the tests described in this report was to compare several different methods and equipment for measuring PM2.5 emissions. Particulate emission measurements were made in the exhaust duct downstream of the engine and DPF using four different dilution sampling technologies and with a hot filter/iced impinger method typically used for stationary source emissions testing. The flue gas temperature at the stack measurement location was approximately 385 to 440°F during the tests.

The primary objective of these tests was to compare results from two different dilution sampling systems. The Desert Research Institute dilution sampler used in these tests follows the well-characterized Hildemann et al. (1989) benchmark design. The dilution sampler simulates the cooling and dilution processes that occur in the plume downwind of a combustion source, so that organic compounds and other substances that condense 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. This system is referred to as the "Alpha" sampler throughout this report. The second sampling system was a new compact design developed by GE Energy and Environmental Research Corporation (GE EER) based on the Hildemann concept but with faster mixing, shorter residence time, lower weight and smaller dimensions. This system is referred to as the "Beta" sampler throughout this report. 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. In addition, UCR made measurements with a standard mobile source dilution system based on International Organization for Standardization (ISO) Method 8178, an automated dilution sampler (Sierra Instruments BG-2) and a standard hot filter/iced impinger train (California Air Resources Board (ARB) Method 5). UCR's measurements were made on different days than the GE EER measurements, but under identical engine operating conditions. Multiple test runs were performed at two different loads, with and without the DPF installed.

FINDINGS

The main findings of this test are:

- PM2.5 mass emissions measured using a new, more compact dilution sampler are in good agreement (within 7 percent, on average) with the benchmark sampler design originally developed by Hildemann et al. in terms of accuracy and precision. The bias is not significant at the 95 percent confidence level, and precision of both samplers is similar. This provides preliminary validation of the design criteria used to modify the original Hildemann concept into a smaller, lighter sampler that is more practical for routine stationary source emission testing. More rigorous validation tests using paired sampling trains and a larger number of test runs are recommended.

- Particle deposits in the sample nozzle, probe and venturi were found to be significant and should be recovered separately in every run of future tests. When probe deposits are taken into account, the results from two research dilution samplers agree well with results from an ISO 8178 constant volume dilution sampler[1] under high particulate loading conditions but appear to be biased low by approximately 25 percent under low particulate loading conditions. Further evaluation of the research sampler designs is recommended to address these differences.

- Elemental carbon accounts for approximately 78 percent of particulate carbon under baseline conditions (for 50 and 75 percent load combined, without DPF) and 81 to 85 percent of particulate carbon with the DPF (for 75 and 50 percent load, respectively).

- PM2.5 mass concentration in the exhaust was the same at 50 and 75 percent load under baseline conditions (without DPF), but decreased with increasing load with the DPF installed. It is likely that higher exhaust temperature at 75 percent load results in higher DPF efficiency.

- The DPF PM2.5 mass reduction efficiency was approximately 83 percent at 50 percent load and 87 percent at 75 percent load. It is likely that part of this reduction efficiency is due to lower fuel sulfur content with the DPF.

- Sulfate and nitrate were detected at concentrations near the detection limits under some conditions. They contributed less than 2 percent to total PM2.5 mass. Chloride, ammonium and other ions were not detected in the samples.

- Based on backup filter organic carbon measurements, organic carbon results are probably biased high due to volatile organic compound adsorption artifacts associated with the quartz fiber filters. The results suggest bias may account for most or all of the measured organic carbon. Further development of organic carbon measurement procedures is needed for reliable organic carbon results.

- Number concentration of ultrafine particles peaked at approximately 65 to 75 nanometers. The size mode was similar with and without the DPF installed.

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[1] Total engine exhaust volume was collected, therefore there was no sample probe. ISO 8178 specifies the design must minimize deposits upstream of the filter. Recovery of deposits from the dilution tunnel is not specified in the method.

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 National Ambient Air Quality Standards (NAAQS) implementation and streamline the environmental assessment of oil, gas and power production facilities.

More recent pilot-scale tests have been performed on a furnace fired to simulate different combustion unit types to refine the original dilution sampler design in order to make the instrument more portable without sacrificing accuracy. These tests have resulted in a smaller design with a shorter residence time and more rapid mixing. The dilution sampling protocol was used to collect PM emissions data from a Diesel-fired Caterpillar 3406C engine at Site Foxtrot on April 2-3, 2003 (Baseline Test – engine operated without any pollution control) and April 22-23, 2002 (DPF Tests – engine operated after installation of a Diesel particulate filter, DPF), using both the old dilution sampler design (Alpha Sampler) and the new design (Beta Sampler). Emissions data were also obtained from conventional sampling methods. The U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) jointly funded the current tests. These tests were performed in conjunction with a CEC-funded program being undertaken by the University of California at Riverside (UCR). This test program is designed to provide reliable source emissions data for use in assessing the contribution of oil, gas, power generation and other industrial combustion sources to ambient PM2.5 concentrations.

The goals of this program were to:

- Develop improved dilution sampling technology and test methods for PM2.5 mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.
- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, that are useful for source-receptor and source apportionment analysis; and
- Identify and characterize PM2.5 precursor compound emissions that are useful for source-receptor and source apportionment analysis.

PROJECT OBJECTIVES

The overall goal of this test was to compare results obtained using different dilution sampling methods and to determine PM2.5 emissions from a Diesel engine. In addition, parametric testing was performed to determine the effect of engine load and emission control equipment on emissions. Two dilution samplers based on a design developed at the California Institute of Technology (CIT) in the late 1980's (Hildemann et al., 1989) were used. The unique feature of the Hildemann design is a long residence time after dilution so that organic compounds and other substances that condense under ambient conditions will be collected as particulate matter. One of the dilution samplers was developed by the Desert Research Institute (DRI), derived directly from the Hildemann design and similar in size and weight (the "Alpha sampler"). The other dilution sampler was developed in a separate task of this program and is much more compact and lightweight (the "Beta sampler"). The two dilution samplers differ in nominal air-to-flue gas sample dilution ratios, mixing rates, and residence times. In addition, measurements using two different dilution samplers typically employed for mobile source tests and with a hot filter/iced impinger sampling train were made by the UCR team (details of these measurements are reported elsewhere).

The specific objectives of this test were:

- Compare PM2.5 mass, organic carbon (OC) and elemental carbon (EC) measured by the Alpha and Beta samplers;
- Compare PM and PM2.5 mass obtained from California Air Resources Board (ARB) Method 5 (hot filter/iced impinger), the two CIT-type dilution sampling systems, an International Organization for Standardization (ISO) method 8178 constant volume system, and a proportional volume micro-dilution system test stand;
- Compare PM2.5 mass, OC, and EC emissions at 75 percent and 50 percent load;
- Determine the effects of a catalytic DPF on PM2.5 mass, OC, and EC emissions, and on ultrafine particle number concentration and size distribution;
- Determine the effect of load on emissions with and without a DPF.
- Characterize sulfate, nitrate, ammonium, and OC/EC in particulate matter collected on filter media in the dilution sampler;
- Develop emission factors for PM2.5;

- Compare emission factors obtained from this test program with similar emission factors currently available.

TEST OVERVIEW

Test Matrix

The tests were conducted in two tests series (Table 1-1): Baseline (without a particulate control device and with California low-sulfur – <500 parts per million, ppm – Diesel fuel) and DPF (with a particulate control device and with ultra-low sulfur – <15 ppm – Diesel fuel). During each test series, measurements were conducted at two engine loads: 75 and 50 percent.

In addition to the measurements made by GE Energy and Environmental Research Corporation (GE EER), UCR also performed other tests and measurements (Table 1-2) including ISO test method 8178 at five engine loads: 100, 75, 50, 25, and 10 percent. Three runs were conducted for each load, totaling 15 runs. The samples collected using Method ISO 8178 were analyzed for particulate matter (PM) mass, particle size distribution (PSD), OC/EC, semi-volatile organic compound (SVOC) and carbonyls. A Sierra Instruments model BG-2 mini-diluter test stand was used to measure PM mass at five engine loads: 100, 75, 50, 25, and 10 percent. Three runs were conducted for each load, totaling 15 runs.

Source Level (Undiluted Exhaust Gas) Samples

Measurements also were made using California ARB Method 5 at three loads of 100, 75, and 50 percent to measure filterable PM mass, OC/EC, and organic and inorganic condensable particulate matter (CPM) mass. There were three Method 5 runs per load, totaling nine runs.

Diluted Exhaust Gas Samples

Dilution sampling was used to characterize PM2.5 including aerosols formed in the near-field plume. GE EER employed two different dilution samplers: DRI's original dilution sampler design (Alpha Sampler) and a new dilution sampler design developed by GE EER (Beta Sampler). The Beta Sampler design is described in more detail elsewhere (Chang and England, 2004). The dilution samplers extracted a sample stream from the stack into a mixing chamber,

Table 1-1. Test Matrix — Data Collected by GE EER (Site Foxtrot).

Phase	Load, %	Dilution Sampler	No. of Runs	Sampling Time, min.	Sample Parameter	Sampling Method	Analytical Principle	Analytical Lab
Baseline (Fuel S < 500 ppm)	75	Alpha	3	20	PM2.5 Mass PM2.5 PSD Ions OC/EC/TC	TMF SMPS Quartz Filter Quartz Filter	Gravimetric SMPS IC TOR	DRI, Quantum UCR DRI DRI
Baseline (Fuel S < 500 ppm)	50	Alpha	3	20	PM2.5 Mass PM2.5 PSD Ions OC/EC/TC	TMF SMPS Quartz Filter Quartz Filter	Gravimetric SMPS IC TOR	DRI, Quantum UCR DRI DRI
Baseline (Fuel S < 500 ppm)	75	Beta	3	20	PM2.5 Mass PM2.5 PSD Ions OC/EC/TC	TMF SMPS Quartz Filter Quartz Filter	Gravimetric SMPS IC TOR	DRI, Quantum UCR DRI DRI
Baseline (Fuel S < 500 ppm)	50	Beta	3	20	PM2.5 Mass PM2.5 PSD Ions OC/EC/TC	TMF SMPS Quartz Filter Quartz Filter	Gravimetric SMPS IC TOR	DRI, Quantum UCR DRI DRI
DPF (Fuel S < 15 ppm)	75	Alpha	3	120	PM2.5 Mass PM2.5 PSD Ions OC/EC/TC	TMF SMPS Quartz Filter Quartz Filter	Gravimetric SMPS IC TOR	DRI, Quantum UCR DRI DRI
DPF (Fuel S < 15 ppm)	50	Alpha	3	120	PM2.5 Mass PM2.5 PSD Ions OC/EC/TC	TMF SMPS Quartz Filter Quartz Filter	Gravimetric SMPS IC TOR	DRI, Quantum UCR DRI DRI
DPF (Fuel S < 15 ppm)	75	Beta	3	120	PM2.5 Mass PM2.5 PSD Ions OC/EC/TC	TMF SMPS Quartz Filter Quartz Filter	Gravimetric SMPS IC TOR	DRI, Quantum UCR DRI DRI
DPF (Fuel S < 15 ppm)	50	Beta	3	120	PM2.5 Mass PM2.5 PSD Ions OC/EC/TC	TMF SMPS Quartz Filter Quartz Filter	Gravimetric SMPS IC TOR	DRI, Quantum UCR DRI DRI

IC: Ion Chromatography
PSD: Particle Size Distribution
SMPS: Scanning Mobility Particle Sizer
TMF: Teflon Membrane Filter
TOR: Thermal-Optical Relectance
OC/EC: Organic Carbon/Elemental Carbon

Table 1-2. Test Matrix– Other Data Collected by UCR (Site Foxtrot).

Sampling/Test Method	Load Conditions	No. of Test Runs (Total)	Analytes
ISO 8178	100, 75*, 50*, 25, 10	15	PM mass*, PSD, OC/EC, SVOCs, carbonyls
BG-2 Mini-diluter	100, 75, 50, 25, 10	15	PM mass
CARB Method 5	100, 75, 50	9	PM mass, OC/EC, organic & inorganic CPM

PM = particulate matter; PSD = particle size distribution; OC = organic carbon; EC = elemental carbon; SVOC = semi-volatile organic compounds.
*Only these results are reported here. Other results will be reported elsewhere.

where it was diluted with purified ambient air approximately 40:1 for the Alpha Sampler and 30:1 for the Beta Sampler. The target dilution ratio for the Alpha Sampler was 40:1 because that is the nominal recommendation by Hildemann et al. (1989) for this design. The Beta Sampler was designed for a dilution ratio of 20:1 based on prior work (Chang and England, 2004); however, a target of 30:1 was selected for this test to avoid overloading the filters while allowing for a reasonable sampling duration. Because PM2.5 behaves aerodynamically approximately like a gas at typical duct exhaust conditions, the samples were extracted non-isokinetically. A slipstream of the mixed and diluted sample was extracted into a residence time chamber where it was aged for approximately 70 seconds for the Alpha Sampler and 10 seconds for the Beta Sampler to allow time for low-concentration aerosols, especially organics, to condense and grow. The diluted and aged samples then passed through cyclone separators sized to remove particles larger than 2.5 µm, after which samples were collected on various media: high-purity quartz fiber filters (QFF) for ions—water-soluble ammonium (NH_4^+), chloride (Cl^-), nitrate (NO_3^-), sulfate ($SO_4^=$), and sodium (Na^+)—and carbon speciation, and Teflon® membrane filters (TMF) for PM2.5 mass. The UCR Bourns College of Engineering Center for Environmental Research and Technology (CE-CERT) staff operated a scanning mobility particle sizer (SMPS) to measure particle size distribution from the Beta Sampler.

Three separate runs were performed at each load using both the Alpha and Beta samplers. Sampling times were selected to produce acceptable filter loadings based on anticipated PM concentrations. For the baseline tests, the sampling time was 20 minutes. The sampling time for the DPF runs was 120 minutes. For each run: (1) PM2.5 mass was sampled on a TMF and analyzed gravimetrically, (2) ultrafine PSD was characterized using a SMPS, (3) ions concentrations were determined via ion chromatography (IC) analysis of PM collected on a QFF and (4) OC/EC concentrations were measured via thermal-optical analysis on a QFF. The measurement and analytical techniques are described in more detail in Section 3.

Process Samples

A sample of the Diesel fuel burned in the engine was collected on each day of source testing and analyzed for sulfur content, ash, moisture, heating value, viscosity, API gravity, asphaltenes, ash elemental composition, mercury, and carbon, hydrogen, oxygen, and nitrogen.

Process Parameters

Table 1-3 shows process parameters recorded by the host site. The measured data included electrical output load, exhaust temperature and concentrations of carbon dioxide (CO_2), carbon monoxide (CO), and nitrogen oxides (NO_x). Exhaust gas flow was determined by direct measurement of the total exhaust.

Table 1-3. Process Operating Data Collected during Test Runs (Site Foxtrot).

Parameter	Units	Frequency
Load bank output	kW	Every minute
Exhaust temperature	°C	Every minute
Exhaust CO_2	%	Every minute
Exhaust NOx	ppm	Every minute
Exhaust CO	ppm	Every minute

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- Karl Loos (Shell Global Solutions U.S.) – API Work Group Chairman
- Karin Ritter (API) – API Project Officer
- Paul Drayton (GRI) – GRI Project Manager
- Marla Mueller (CEC) – CEC Project Manager

- Kathy Stirling (DOE) – DOE Contracting Officer Representative
- Barry Liebowitz (NYSERDA) – NYSERDA Project Manager
- Wayne Miller, Bill Welch and Kent Johnson (UCR) – UCR program team

2. PROCESS DESCRIPTION

Site Foxtrot's tests were performed on a six-cylinder, 4-stroke compression ignition Caterpillar 3406C engine (Figure 2-1) at CE-CERT. The engine's output at 100 percent load was approximately 350 kilowatts (kW). The unit fired California ARB Diesel with a typical sulfur content from 75-150 ppm when the unit was not fitted with any pollution controls (Baseline tests). The unit was retrofitted with a Johnson Matthey DPF for the DPF tests. The DPF employs a passive noble metal catalyst system that destroys soot in two steps. The first step uses a platinum oxidation catalyst designed to oxidize a portion of the nitric oxide (NO) to nitrogen dioxide (NO_2). The catalyst also oxidizes CO and unburned hydrocarbons. In the second step, the soot is trapped on a ceramic filter where it is oxidized in the presence of NO_2. The DPF was tested using ultra-low sulfur (less than 15 ppm) Diesel although the manufacturer claims the DPF can tolerate up to 50 ppm. Hot engine exhaust gases were channeled through a vertical, cylindrical stack or a horizontal duct depending on the sampling requirements.

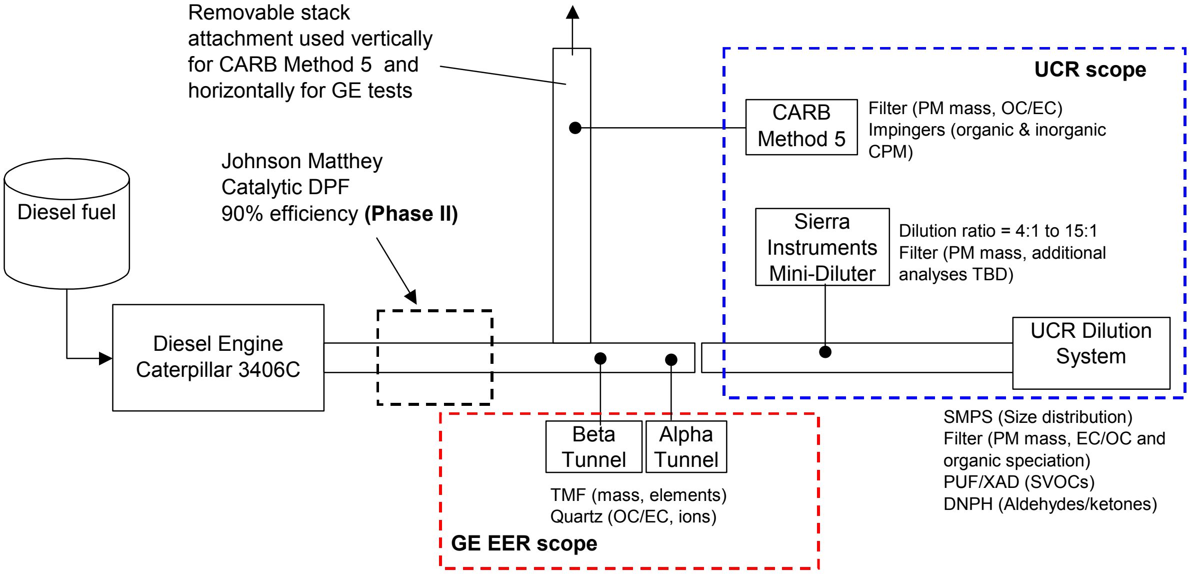

Figure 2-1. Site Foxtrot Process Overview.

SAMPLING LOCATIONS

Flue Gas Sampling Locations

The duct used during GE EER's testing was positioned horizontally approximately 40 inches above ground level. The duct had an inside diameter of 6 inches and two 3-inch diameter ports positioned at 90 degrees (°) to each other (Figure 2-2). During the Baseline tests, the two 3-inch sample ports were positioned at 180° to one another, with one being approximately 36 inches downstream from the other. The upstream port was approximately one- duct diameter downstream of a second 90° bend. The configuration was changed for the DPF tests. A new port was added directly opposite to the downstream port from the Baseline series, so that the probes from the two dilution samplers could be co-located in the duct through opposing ports.

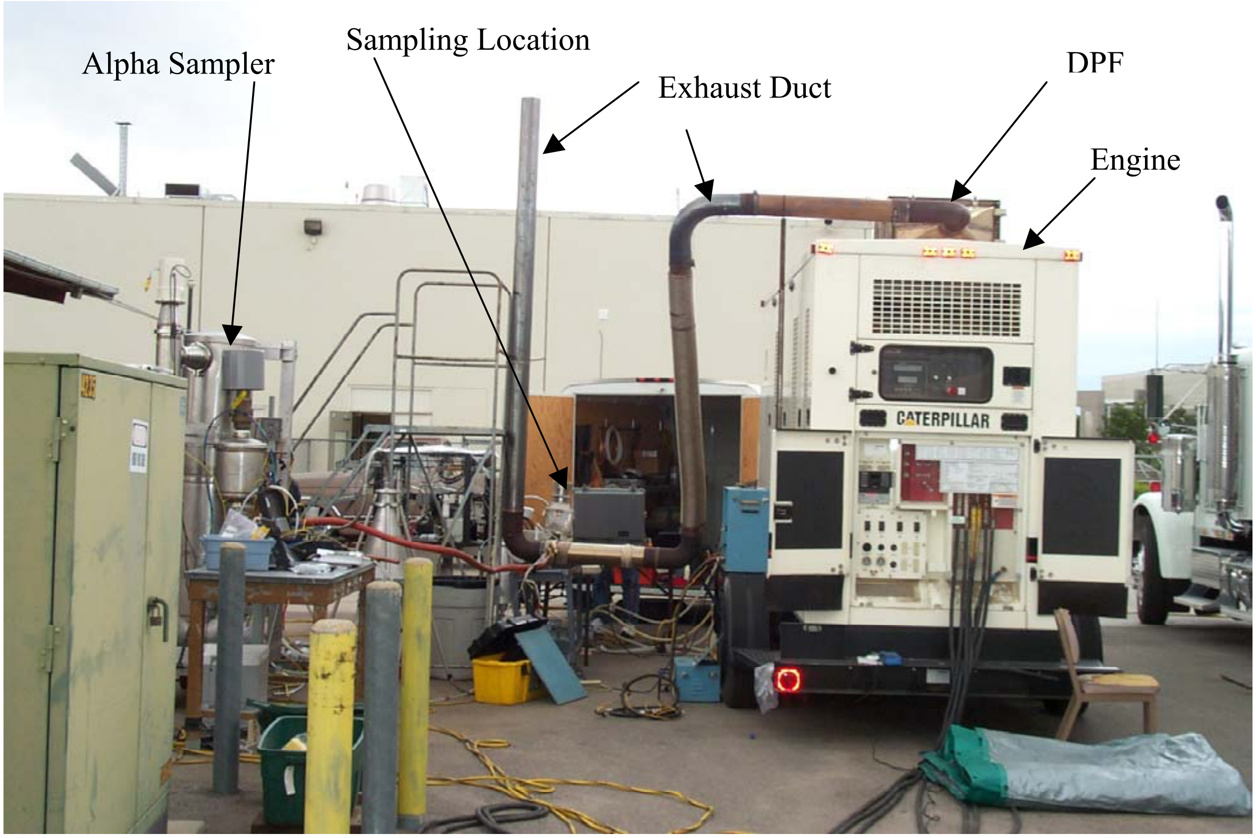

Figure 2-2. Photograph of Exhaust Duct Indicating Sampling Location.

3. TEST PROCEDURES

An overview of the sampling and analysis procedures is given in Table 3-1. Figure 3-1 shows the testing chronology for the dilution samplers and undiluted exhaust gas methods. The time of day for the start and finish of each measurement run is shown on the figure. The two dilution samplers were run concurrently. All samples were collected at points of average velocity through their respective ports.

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

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	EPA Methods 1 and 2
	Undiluted exhaust gas/ CO_2, CO, NOx	Continuous emissions monitoring	Electrochemical cell	EPA Methods 3A and 7E
	Diluted exhaust gas/ PM2.5 mass	Dilution Sampler and Teflon filter	Gravimetry	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	Dilution Sampler and Quartz filter	IC	U.S EPA, 1999a; Hildemann et. al., 1989
	Diluted exhaust gas/ Ultrafine PSD	SMPS	SMPS	TSI

IC: Ion Chromatography
PM2.5: Particulate matter with aerodynamic diamter less than 2.5 microns
PSD: Particle Size Distribution
SMPS: Scanning Mobility Particle Sizer
TOR: Thermal-Optical Relectance
OC/EC: Organic Carbon/Elemental Carbon

STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

Stack gas flow rate was measured by UCR directly using a calibrated venturi flow meter within the total volume ISO 8178 dilution system. Exhaust flow rates are corrected for a small amount of air in-leakage that occurred through the sampling ports. An S-type Pitot tube (EPA Method 2) was used to determine the average stack gas velocity to provide a check on the direct stack gas volumetric flow rate measurement. Stack gas molecular weight was calculated in accordance with EPA Method 3. Moisture content of the sample was determined based on weight gain of the impingers used in the controlled condensation train according to EPA Method 4. A single point Pitot tube was continuously monitored during all sampling to verify operating conditions and exhaust gas flow rates had not changed.

		Engine Exhaust Duct				Dilution Systems Blanks	
	Time	Velocity	CEM	Alpha Dilution Sampler	Beta Dilution Sampler	Alpha Dilution Sampler	Beta Dilution Sampler
02-Apr-03	12:40						
Wed.	13:10					System Blank	System Blank
	13:40					13:40	13:40
	14:10						
	14:40						
	15:10					15:00	15:00
	15:40						
	16:10						
03-Apr-03	10:00	8:00 - 8:30	75% - Run 1	75% - Run 1	75% - Run 1		
Thurs.	10:10		10:13	10:13	10:13		
	10:20		10:33	10:33	10:33		
	10:30						
	10:40		75% - Run 2	75% - Run 2	75% - Run 2		
	10:50		10:50	10:50	10:50		
	11:00		11:10	11:10	11:10		
	11:10						
	11:20						
	11:30		75% - Run 3	75% - Run 3	75% - Run 3		
	11:40		11:35	11:35	11:35		
	11:50		11:55	11:55	11:55		
	12:00						
	13:30		50% - Run 1	50% - Run 1	50% - Run 1		
	13:40		13:40	13:40	13:40		
	13:50		14:00	14:00	14:00		
	14:00		50% - Run 2	50% - Run 2	50% - Run 2		
	14:10		14:10	14:10	14:11		
	14:20		14:30	14:30	14:31		
	14:30		50% - Run 3	50% - Run 3	50% - Run 3		
	14:40		14:40	14:40	14:42		
	14:50		15:00	15:00	15:02		
	15:00						
	15:10						

Figure 3-1a. Chronology for (Baseline) Engine Tests without Emissions Controls (Site Foxtrot).

	Time	Engine Exhaust Duct				Dilution Systems Blanks	
		Velocity	CEM	Alpha Dilution Sampler	Beta Dilution Sampler	Alpha Dilution Sampler	Beta Dilution Sampler
21-Apr-03	13:00					System Blank	System Blank
Mon.	13:20					13:25	13:25
	13:40						
	14:00						
	14:20						
	14:40						
	15:00						
	15:20					15:25	15:25
22-Apr-03		8:00 - 8:30	DPF-75% - Run 1	DPF-75% - Run 1	DPF-75% - Run 1		
Tues.	9:40		9:40	9:40	9:40		
	10:00						
	10:20						
	10:40						
	11:00						
	11:20		11:40	11:40	11:40		
	11:40						
	12:00		DPF-75% - Run 2	DPF-75% - Run 2	DPF-75% - Run 2		
	12:20		12:15	12:15	12:15		
	12:40						
	13:00						
	13:20						
	13:40						
	14:00		14:15	14:15	14:15		
	14:20		DPF-75% - Run 3	DPF-75% - Run 3	DPF-75% - Run 3		
	14:20		14:20	14:20	14:20		
	14:40						
	15:00						
	15:20						
	15:40						
	16:00		16:20	16:20	16:20		
	16:20						
23-Apr-03	7:20	8:00 - 8:30	DPF-50% - Run 1	DPF-50% - Run 1	DPF-50% - Run 1		
Wed.	7:40		7:40	7:40	7:40		
	8:00						
	8:20						
	8:40						
	9:00						
	9:20		9:40	9:40	9:40		
	9:40		DPF-50% - Run 2	DPF-50% - Run 2	DPF-50% - Run 2		
	9:40		9:45	9:45	9:45		
	10:00						
	10:20						
	10:40						
	11:00						
	11:20		11:45	11:45	11:45		
	11:40		DPF-50% - Run 3	DPF-50% - Run 3	DPF-50% - Run 3		
	12:00		11:50	11:50	11:50		
	12:20						
	12:40						
	13:00						
	13:20						
	13:40		13:50	13:50	13:50		
	14:00						
	14:20						

Figure 3-1b. Chronology for Engine Tests with DPF Emissions Control (Site Foxtrot).

UNDILUTED EXHAUST GAS TEST METHODS

CO_2, CO, and NO_x

CO_2, CO, and NO_x concentrations in undiluted exhaust gas samples were measured on-site by the UCR continuous emissions monitoring system (CEMS). The instrumentation and sampling system is analogous to EPA methods 3A, 7E and 10.

DILUTION SAMPLER TESTS

Alpha Sampler

PM2.5 mass and chemical speciation in the stack gas was determined using the DRI dilution sampler (Figure 3-2). A stainless steel probe with a buttonhook nozzle was used to withdraw isokinetically the stack gas sample at a rate of approximately 25 liters per minute (L/min). The sample was transported from the probe through a heated copper line into the dilution sampler. The sample was mixed in the sampler with purified ambient air under turbulent flow conditions to cool and dilute the sample to near-ambient conditions. The ambient air used for dilution was purified using a high efficiency particulate arrest (HEPA) filter to remove PM and an activated carbon bed to remove gaseous organic compounds. After passing through a length equal to 10 diameters, approximately 50 percent of the diluted sample was withdrawn into a large chamber, where the sample aged for and average of approximately 70 seconds (bulk mean gas residence time) to allow low-concentration aerosols (especially organic aerosols) to fully form. After aging, the sample was withdrawn through a manifold of three cyclone separators to remove particles larger than 2.5 µm into a sample manifold which distributed the diluted and aged sample to the sample collection media (TMF, QFF).

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

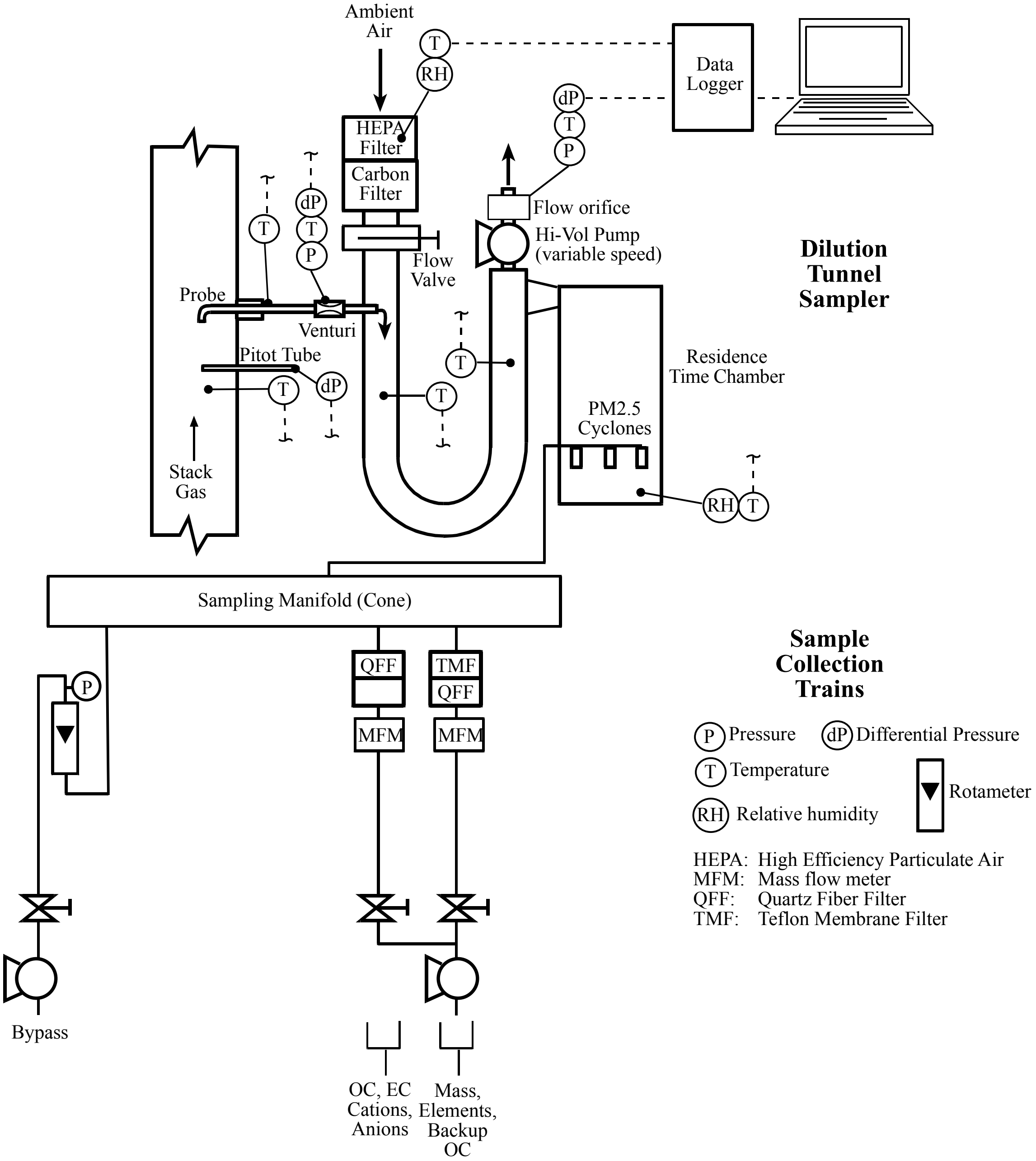

Figure 3-2. Alpha (DRI) Dilution Sampler System (Site Foxtrot).

The sample flow rate through the probe was monitored using a heated (150 ºC) venturi flow meter and thermocouple. The venturi velocity head was measured continuously during the test using a pressure transducer. An S-type Pitot tube with electronic pressure transducer and thermocouple were used to monitor the velocity head and temperature at a single point in the stack during the test. The thermocouples and pressure transducers were connected to a laptop computer data acquisition system. Total sampling time for each Baseline test run was 20 minutes and the total sampling time for each DPF test run was two hours.

The dilution air flow slide valve and HiVol fan speed were adjusted to maintain the target dilution ratio and sample flow rates. Hildemann et al. (1989) recommended a minimum dilution ratio of 40:1 and noted that mixing between the sample and the dilution air begins to degrade below a dilution ratio of approximately 20:1. For these tests, the nominal target dilution ratio was approximately 39:1 for each baseline test run and 36:1 for each DPF test run, which resulted in average diluted sample (chamber) temperatures of 16 to 27 °C (Table 3-2). These dilution ratios were selected to achieve low in-stack detection limits while allowing for collection of sufficient material for analysis. The diluted sample temperatures are within approximately 5 °C of the ambient air temperature.

A relative humidity (RH) sensor in the residence time chamber malfunctioned during the test. Calculated RH of the diluted sample based on measured ambient air RH, dilution ratio, measured stack gas moisture content and diluted sample temperature ranged from 32 to 61 percent. Aerosol growth due to moisture condensation is expected to be negligible below a RH of approximately 70 percent (Hinds, 1998).

Hildemann et al. (1989) extensively characterized particle losses as a function of particle size, and found that losses of particles in the sample line and venturi were in the range of 7 to 18 percent for particles smaller than 2.5 µm, depending on particle size. At the end of each series of tests, the probe, nozzle, sample venturi, and connecting sample line (Alpha sampler only) were quantitatively rinsed with acetone to recover any deposited particulate matter. For baseline tests, this was performed twice, once at the end of the 50 percent load tests and again at the end of the 75 percent load tests. For the DPF tests, the probe was recovered once, resulting in a single

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

(a) Alpha Sampler, Baseline 50% Load.

Parameter	Units	50%-Base-R1 03-Apr-03	50%-Base-R2 03-Apr-03	50%-Base-R3 03-Apr-03	Average
Ambient Air Temp.	^{o}C	18.9	17.6	18.2	18.2
Ambient RH	%	30.6	33.7	34.0	32.8
Dilution Chamber Temperature	^{o}C	22.2	18.9	19.8	20.3
Dilution Chamber RH*	%	30.5	38.5	37.6	35.5
Stack Sample Flow Rate (dry)	slpm	16.9	18.1	17.6	17.5
Dilution Air Flow Rate (dry)	slpm	681	696	693	690
HiVol Bypass Flow Rate (dry)	slpm	477	492	489	486
Dilution Ratio (wet)	slpm/slpm	40.2	38.5	39.4	39.4
Dilution Ratio (dry)	slpm/slpm	43.0	41.2	42.1	42.1
Teflon Filter Flow Rate (dry) (mass, elements)	slpm	34.8	34.9	34.8	34.8
Quartz Filter Flow Rate (dry) (ions, OC/EC)	slpm	34.8	34.8	34.8	34.8
Cyclone Bypass Flow Rate (dry)	slpm	142	142	142	142

(b) Alpha Sampler, Baseline, 75% Load.

Parameter	Units	50%-Base-R1 03-Apr-03	50%-Base-R2 03-Apr-03	50%-Base-R3 03-Apr-03	Average
Ambient Air Temp.	^{o}C	16.7	17.7	17.9	17.4
Ambient RH	%	38.1	31.7	29.8	33.2
Dilution Chamber Temperature	^{o}C	19.7	17.5	20.1	19.1
Dilution Chamber RH*	%	37.5	39.8	32.2	36.5
Stack Sample Flow Rate (dry)	slpm	15.2	16.2	16.1	15.8
Dilution Air Flow Rate (dry)	slpm	663	678	678	673
HiVol Bypass Flow Rate (dry)	slpm	456	472	471	466
Dilution Ratio (wet)	slpm/slpm	43.7	42.0	42.0	42.6
Dilution Ratio (dry)	slpm/slpm	46.8	44.9	45.0	45.6
Teflon Filter Flow Rate (dry) (mass, elements)	slpm	34.7	34.9	34.8	34.8
Quartz Filter Flow Rate (dry) (ions, OC/EC)	slpm	34.6	35.0	35.1	34.9
Cyclone Bypass Flow Rate (dry)	slpm	143	143	143	143

(c) Alpha Sampler, DPF, 50% Load.

Parameter	Units	50%-DPF-R1 23-Apr-03	50%-DPF-R2 23-Apr-03	50%-DPF-R3 23-Apr-03	Average
Ambient Air Temp.	^{o}C	14.2	17.8	20.9	17.6
Ambient RH	%	60.8	44.2	34.8	46.6
Dilution Chamber Temperature	^{o}C	16.3	22.8	27.0	22.0
Dilution Chamber RH*	%	61.3	37.6	28.1	42.3
Stack Sample Flow Rate (dry)	slpm	17.4	17.1	17.0	17.1
Dilution Air Flow Rate (dry)	slpm	694	680	670	681
HiVol Bypass Flow Rate (dry)	slpm	487	474	465	475
Dilution Ratio (wet)	slpm/slpm	40.0	39.8	39.5	39.8
Dilution Ratio (dry)	slpm/slpm	42.7	42.6	42.2	42.5
Teflon Filter Flow Rate (dry) (mass, elements)	slpm	34.6	34.7	34.6	34.6
Quartz Filter Flow Rate (dry) (ions, OC/EC)	slpm	34.6	34.6	34.7	34.6
Cyclone Bypass Flow Rate (dry)	slpm	155	154	153	154

(d) Alpha Sampler, DPF, 75% Load.

Parameter	Units	75%-DPF-R1 22-Apr-03	75%-DPF-R2 22-Apr-03	75%-DPF-R3 22-Apr-03	Average
Ambient Air Temp.	^{o}C	16.2	17.1	22.5	18.6
Ambient RH	%	37.9	35.5	28.6	34.0
Dilution Chamber Temperature	^{o}C	21.3	20.2	21.7	21.1
Dilution Chamber RH*	%	32.4	34.5	35.3	34.1
Stack Sample Flow Rate (dry)	slpm	17.5	17.5	17.5	17.5
Dilution Air Flow Rate (dry)	slpm	675	683	676	678
HiVol Bypass Flow Rate (dry)	slpm	471	479	472	474
Dilution Ratio (wet)	slpm/slpm	38.6	39.0	38.7	38.7

probe/venturi wash for the DPF test series. A single acetone reagent blank (from the primary reagent container) was collected for each of the baseline and DPF test campaigns.

Two dilution sampler blank (DSB) samples also were collected with the Alpha sampler. Filtered dilution air was drawn into the module without sample gas flow for a sampling period of two hours. For both the ambient air sample and the DSB samples, the same sampling media were used as described below and in Figure 3-2. Tables 3-2a-d list the sample gas conditions and flow rates for the Alpha Sampler dilution samples.

Beta Sampler

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

- The heated sample line between the probe and venturi was removed;
- The mixing section was shortened by adding a mixing plate to allow for more rapid dilution of the sample gas; and
- The residence time was shortened to approximately 10 to 15 seconds by eliminating the large residence chamber.
- The sample path through the dilution sampler is linear rather than convoluted.

Table 3-3 presents the Beta Sampler operating conditions and flow rates during the tests. Conditions are generally similar to those for the Alpha sampler, commensurate with the lower dilution ratios achieved during the tests. Dilution sampler operating conditions were generally consistent for each three run test series. For all test runs, the dilution chamber relative humidity was below the 70 percent threshold where it can impact particulate growth.

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 two-stage Savillex filter holder with Teflon® ring supports inside. The filter packs were plugged directly into the bottom of the sampling module to ensure that no handling of the filters was required in the field. The flow rate through the filter was set prior to sample collection at a target rate of 35 standard liters per minute (sLpm) with a needle valve and monitored during sampling using a Thermo Scientific Incorporated (TSI) mass flow meter (Model 4043). A rotameter was used on the mass filter of the Beta sampler during the baseline tests because one of the TSI flow meters was damaged. Weighing was performed on a Cahn 31 electro-microbalance with a ±1 microgram sensitivity.

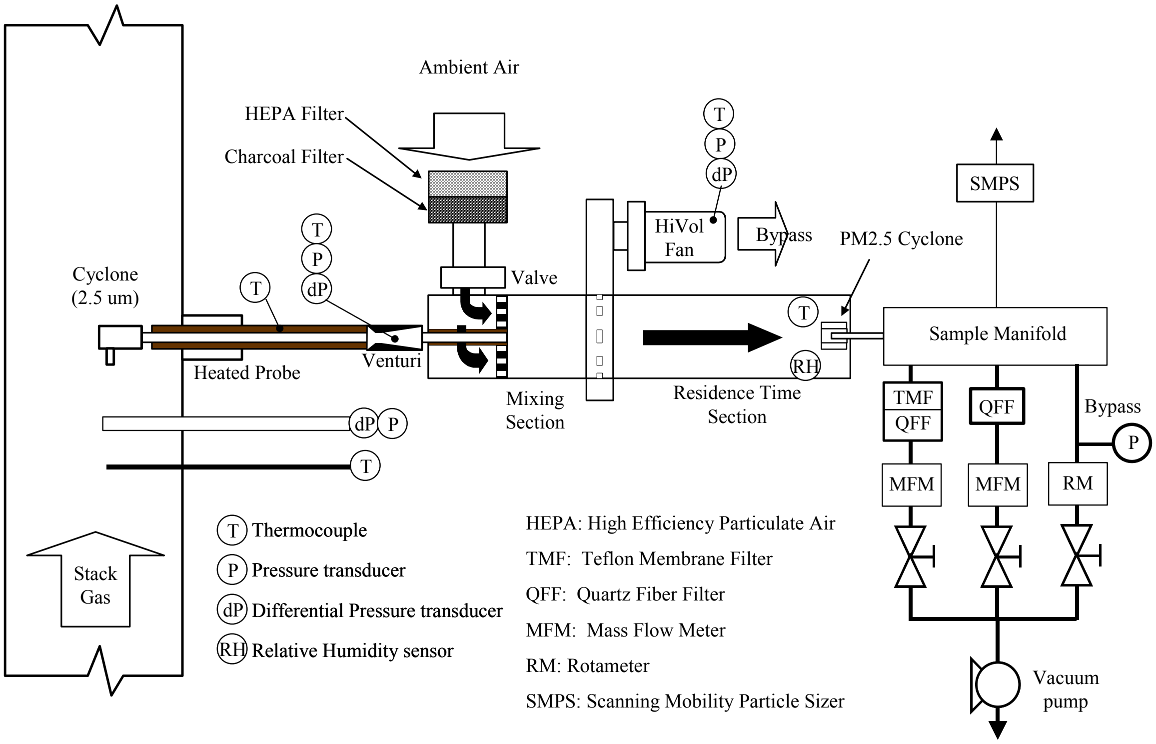

Figure 3-3. Beta (EER) Dilution Sampler (Site Foxtrot).

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

(a) Beta Sampler, Baseline, 50% Load.

Parameter	Units	50%-Base-R1 3-Apr-03	50%-Base-R2 3-Apr-03	50%-Base-R3 3-Apr-03	Average
Ambient Air Temp.	°C	18.9	17.6	18.2	18.2
Ambient RH	%	30.6	33.7	34.0	32.8
Dilution Chamber Temperature*	°C	21.9	20.6	21.2	21.2
Dilution Chamber RH**	%	33.1	36.5	36.3	35.3
Stack Sample Flow Rate (dry)	slpm	17.9	18.2	17.9	18.0
Dilution Air Flow Rate (dry)	slpm	540	539	533	538
HiVol Bypass Flow Rate (dry)	slpm	452	451	444	449
Dilution Ratio (wet)	slpm/slpm	30.2	29.6	29.7	29.8
Dilution Ratio (dry)	slpm/slpm	32.3	31.6	31.8	31.9
Teflon Filter Flow Rate (dry) (mass, elements)	slpm	34.7	34.8	34.8	34.8
Quartz Filter Flow Rate (dry) (ions, OC/EC)	slpm	34.5	34.5	34.5	34.5
Cyclone Bypass Flow Rate (dry)	slpm	37.2	37.3	37.9	37.5

(b) Beta Sampler, Baseline, 75% Load.

Parameter	Units	75%-Base-R1 3-Apr-03	75%-Base-R2 3-Apr-03	75%-Base-R3 3-Apr-03	Average
Ambient Air Temp.	°C	16.7	17.7	17.9	17.4
Ambient RH	%	38.1	31.7	29.8	33.2
Dilution Chamber Temperature*	°C	19.7	20.7	20.9	20.4
Dilution Chamber RH**	%	40.2	34.1	32.5	35.6
Stack Sample Flow Rate (dry)	slpm	18.5	17.9	16.2	17.5
Dilution Air Flow Rate (dry)	slpm	562	575	524	554
HiVol Bypass Flow Rate (dry)	slpm	472	485	432	463
Dilution Ratio (wet)	slpm/slpm	30.5	32.1	32.3	31.6
Dilution Ratio (dry)	slpm/slpm	32.6	34.4	34.6	33.8
Teflon Filter Flow Rate (dry) (mass, elements)	slpm	34.8	34.7	34.7	34.7
Quartz Filter Flow Rate (dry) (ions, OC/EC)	slpm	34.5	34.5	34.5	34.5
Cyclone Bypass Flow Rate (dry)	slpm	39.0	39.0	39.0	39.0

(c) Beta Sampler, DPF, 50% Load.

Parameter	Units	50%-DPF-R1 23-Apr-03	50%-DPF-R2 23-Apr-03	50%-DPF-R3 23-Apr-03	Average
Ambient Air Temp.	°C	14.2	17.8	20.9	17.6
Ambient RH	%	60.8	44.2	34.8	46.6
Dilution Chamber Temperature*	°C	17.2	20.8	23.9	20.6
Dilution Chamber RH**	%	59.4	44.4	35.4	46.4
Stack Sample Flow Rate (dry)	slpm	18.6	18.9	18.9	18.8
Dilution Air Flow Rate (dry)	slpm	600	597	594	597
HiVol Bypass Flow Rate (dry)	slpm	510	507	505	507
Dilution Ratio (wet)	slpm/slpm	32.3	31.6	31.4	31.7
Dilution Ratio (dry)	slpm/slpm	34.4	33.7	33.6	33.9
Teflon Filter Flow Rate (dry) (mass, elements)	slpm	34.6	34.6	34.6	34.6
Quartz Filter Flow Rate (dry) (ions, OC/EC)	slpm	34.6	34.6	34.6	34.6
Cyclone Bypass Flow Rate (dry)	slpm	40	40	39	40

(d) Beta Sampler, DPF, 75% Load.

Parameter	Units	75%-DPF-R1 22-Apr-03	75%-DPF-R2 22-Apr-03	75%-DPF-R3 22-Apr-03	Average
Ambient Air Temp.	°C	16.2	17.1	22.5	18.6
Ambient RH	%	37.9	35.5	28.6	34.0
Dilution Chamber Temperature*	°C	19.2	20.1	25.2	21.5
Dilution Chamber RH**	%	40.3	36.2	29.3	35.3
Stack Sample Flow Rate (dry)	slpm	24.1	17.4	17.5	19.7
Dilution Air Flow Rate (dry)	slpm	609	540	540	563
HiVol Bypass Flow Rate (dry)	slpm	524	449	450	474
Dilution Ratio (wet)	slpm/slpm	25.3	31.0	30.8	29.1
Dilution Ratio (dry)	slpm/slpm	26.7	32.8	32.5	30.7
Teflon Filter Flow Rate (dry) (mass, elements)	slpm	34.6	34.7	34.7	34.7
Quartz Filter Flow Rate (dry) (ions, OC/EC)	slpm	34.6	34.7	34.7	34.7
Cyclone Bypass Flow Rate (dry)	slpm	40	39	39	39

* Sensor failed, estimated at Ambient Air Temp plus 3 degrees C based on historical data.

**Estimated based on ambient air RH, dilution ratio, stack gas moisture content, and dilution chamber temperature.

$SO_4^=$, NO_3^-, and Cl^-

Samples for determining water-soluble Cl^-, NO_3^-, and $SO_4^=$, were collected on QFFs (Pallflex Tissuequartz 2500QAT-UP-47 mm). The flow rate through the filter was set prior to sample collection at a target rate of 35 sLpm with a needle valve and monitored during sampling using a TSI mass flow meter (Model 4043).

For analysis, each quartz-fiber filter was cut in half. One half was placed in a polystyrene extraction vial with 15 milliliter (mL) of distilled DI water while the other half was used for determination of OC and EC as described below. The extraction vials were capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material. After extraction, these solutions were stored under refrigeration prior to analysis. Cl^-, NO_3^-, and $SO_4^=$ were measured with a Dionex 2020i ion chromatograph. Approximately 2 ml of the filter extract was injected into the ion chromatograph.

Organic and Elemental Carbon

Forty-seven mm QFFs (Pallflex Tissuequartz 2500QAT-UP-47 mm) were used to collect samples for determination of OC and EC mass. The filters were heated in air for at least three hours at approximately 900 °C prior to use. The flow rate through the filter was monitored during sampling by a mass flow controller at a sample flow rate of approximately 37 L/min. These samples were collected with the Alpha and Beta samplers simultaneously. A ½-inch diameter punch was taken from each QFF for analysis.

The thermal/optical reflectance (TOR) method was used to determine OC and EC on the QFFs. The TOR method is based on the principle that different types of carbon-containing particles are converted to gases under different temperature and oxidation conditions. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments; 2) converting these compounds to CO_2 by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO_2); 3) reduction of CO_2 to methane (CH_4) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantification of CH_4 equivalents by a flame ionization detector (FID).

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

Ultrafine Particle Size Distribution

An SMPS was used for characterizing particle number distribution over the 0.01-0.4 μm size range. The SMPS consisted of two main components: a TSI Model 3071 differential mobility analyzer (DMA), which classifies particles according to size; and a TSI Model 3025 condensation particle counter (CPC), which counts particles leaving the DMA. The SMPS was assembled and software developed by personnel at UCR. The DMA included a radioactive Kr-85 charge neutralizer, which produces bipolar ions that apply an equilibrium charge distribution to the aerosol. The DMA extracts particles according to their electrical mobility, which is inversely related to particle size. The classified particles entered the condensation particle counter (CPC), where supersaturated alcohol vapor condensed onto the particles, causing them to grow larger. The particles were detected and counted by a simple diode laser light source and photodetector. By continuously varying the electrical field in the DMA, the particle size leaving the DMA was varied in a known manner enabling the particle size distribution to be determined. SMPS samples were withdrawn from the dilution sampler at 5-minute average intervals from each sampling locations. The SMPS measurements were repeated several times for each test and the average results were calculated for each test condition.

4. TEST RESULTS

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 and a standard pressure of 29.92 inches of mercury unless otherwise indicated. Substances that were not detected in any of the three 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. Section 6 and Section 7 provide additional analyses of these results. The approximate minimum in-stack detection limits achieved for all measured substances are given in Table 4-1.

Table 4-1. In-Stack Detection Limits for the Site Foxtrot Tests.

Parameters	Baseline Tests		DPF Tests	
	ug/dscm	mg/dscm	ug/dscm	mg/dscm
Organic Carbon (OC)	716.803	0.7168	116.519	0.1165
Elemental Carbon (EC)	164.928	0.1649	26.810	0.0268
PM2.5 mass	63.434	0.0634	10.311	0.0103
Cl^-	95.447	0.0954	15.466	0.0155
Nitrate (NO_3^-)	95.447	0.0954	15.466	0.0155
$SO_4^=$	95.447	0.0954	15.466	0.0155
NH_4^+	95.447	0.0954	15.466	0.0155
Organic Carbon (OC)	719.038	0.7190	116.509	0.1165
Elemental Carbon (EC)	165.442	0.1654	26.807	0.0268

PROCESS OPERATING CONDITIONS

The engine operated at approximately 75 and 50 percent of full capacity during the two phases of the test program. UCR monitored and recorded the engine operating data including exhaust flow rates that were used to determine emission factors. Samples of the engine fuel also were collected during the tests, but results were not available at this writing. A typical fuel analysis, shown in Table 4-2, was used in calculations to convert in-stack emission rates (lb/hr) to emission factors (pounds per million British thermal units, lb/MMBtu), which are presented in Section 5.

Table 4-2. Typical Diesel Fuel Analysis (Site Foxtrot).

Elements	Units	Values
C	wt. %	87.1
H	wt. %	12.6
N	wt. %	0.006
S*	wt. %	0.22
O	wt. %	0.04
Cl	wt. %	0
Ash	wt. %	0.01
H_2O	wt. %	0
Total	wt. %	100
Higher Heating Value	Btu/lb	19,613
Specific Gravity		0.86

*Not representative of fuel used in these tests.

A summary of the engine data recorded during the baseline tests is presented in Table 4-3. The 262.7 kW load corresponded to 75 percent of engine full capacity, while the 172.1 kW corresponded to 50 percent capacity. The exhaust flows shown on the table are corrected for leaks caused by GE EER's sampling setup. The correction factors are 0.99 and 0.94 for 75 and 50 percent load capacity, respectively. Gas concentrations, which were determined using a grab sampling technique, are presented on an "as measured" dry basis. Exhaust CO_2 averages 6.80 and 7.47 percent, respectively, for 50 and 75 percent load. Exhaust CO averages approximately 190 ppm at both loads. The calculated excess molecular oxygen (O_2) is 11.9 and 11.0 percent for 50 and 75 percent load, respectively. UCR did not provide engine data for the DPF tests, so conditions are assumed the same.

PRELIMINARY TEST RESULTS

Preliminary tests were conducted to establish single points of near-average velocity in the exhaust duct for collection of samples. A velocity profile was developed by traversing the exhaust duct with the Pitot probe for each test series. However, due to the small dimensions of the duct and varying velocity head pressures, the accuracy of the velocity measurements was considered questionable for exhaust flow determination. The flue gas flow data collected by the host site's instrumentations were used in the emissions calculations.

Table 4-3. Process Operating Data for Baseline Tests (Site Foxtrot).

Load - Run		75% - R1	75% - R2	75% - R3	Avg	RSD	50% - R1	50% - R2	50% - R3	Avg	RSD
Test Date		3-Apr-03	3-Apr-03	3-Apr-03			3-Apr-03	3-Apr-03	3-Apr-03		
Test Start Time		10:13	10:50	11:35			13:40	14:10	14:40		
Fuel	--	Diesel	Diesel	Diesel			Diesel	Diesel	Diesel		
THC	ppm	33	NA	31	32	5	39	NA	39	39	0
CO	ppm	193	NA	196	195	1	187	NA	186	187	0
NOx	ppm	1,010	NA	1,020	1,015	1	940	NA	930	935	1
CO_2	%	7.5	NA	7.5	7	0	6.8	NA	6.8	7	0
Ambient Temp.	°C	13.9	14.8	15.1	15	4	17.0	16.5	17.0	17	2
Ambient Press.	mmHg	741	741	741	741	0	740	740	740	740	0
Relative Humidity	%	43%	38%	34%	0	12	33%	35%	35%	0	4
H_2O	%	0.690%	0.641%	0.591%	0	8	0.642%	0.658%	0.690%	0	4
H_2O exhaust	%	7.1%	NA	7.1%	0	1	6.5%	NA	6.6%	0	1
kH	fact	0.896	0.891	0.887	1	1	0.891	0.893	0.896	1	0
Cycle Duration	sec	900	900	900	900	0	900	900	900	900	0
Exhaust Flow	scfm	805	807	801	805	0	614	616	614	615	0
Exhaust Flow	scmh	1,370	1,370	1,360	1,367	0	1,040	1,050	1,040	1,043	1
Exhaust Temp.	°C	437	436	440	438	0	385	385	385	385	0
Generator Load	kW	263	263	263	263	0	172	172	172	172	0

Notes:

1. Measured exhaust flow corrected for leak rate due to EER sampling set up
(exhaust flow at 75% multiplied by 0.99; exhaust flow at 50% multiplied by 0.94)
2. Concentrations and Water estimated from CERT Bag data not EER modal data.
3. Water in exhaust estimated from CO_2 and exhaust flow from UCR bag data not EER modal data.

NA - not available
RSD - relative standard deviation (%)
THC - total hydrocarbons

DILUTION SAMPLER RESULTS

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 in the dilution sampler. The dilution sampler determines only the PM2.5 fraction of PM emissions.

PM2.5 Mass – Alpha Sampler

The mean PM2.5 mass concentration measured on the TMF at 50 and 75 percent load is nearly the same, for both baseline and DPF conditions (Table 4-4). The Alpha and Beta dilution samplers extracted exhaust samples at an approximately the same rate of 20 L/min and dilution ratio was approximately the same for all tests. Because sampling rate was not proportional to flue gas flow rate, relatively constant filter weights reflects relatively constant concentration in the exhaust. This differs from constant volume sampling, where the entire exhaust flow is captured and filter weights would vary in proportion to load if concentration were the same.

The consistency of the results is quite good, showing a variability of less than 10 percent relative standard deviation (RSD) except for the baseline 75 percent load condition, which is somewhat higher (29 percent RSD).

Table 4-4. Dilution System Results – PM2.5 Alpha Sampler (Site Foxtrot).

	Units	Results (mg.dscm)			Average (mg/dscm)	RSD (%)
Run Number	-	Alpha-Base-50-R1	Alpha-Base-50-R2	Alpha-Base-50-R3	--	--
Date	-	03-Apr-03	03-Apr-03	03-Apr-03	--	--
Filter	mg/dscm	2.0E+1	2.3E+1	2.2E+1	2.2E+1	7.1
Filter	lb/hr	4.3E-2	4.9E-2	4.8E-2	4.6E-2	7.3
Probe/Venturi	mg/dscm	--	--	--	5.3E+0	n/a
Total	mg/dscm	--	--	--	2.7E+1	n/a
Total	lb/hr	--	--	--	5.8E-2	n/a
Run Number	-	Alpha-Base-75-R1	Alpha-Base-75-R2	Alpha-Base-75-R3	--	--
Date	-	03-Apr-03	03-Apr-03	03-Apr-03	--	--
Filter	mg/dscm	3.0E+1	1.7E+1	2.1E+1	2.3E+1	29
Filter	lb/hr	8.4E-2	4.9E-2	5.7E-2	6.3E-2	29
Probe/Venturi	mg/dscm	--	--	--	1.1E+1	n/a
Total	mg/dscm	--	--	--	3.4E+1	n/a
Total	lb/hr	--	--	--	9.4E-2	n/a
Run Number	-	Alpha-DPF-50-R1	Alpha-DPF-50-R2	Alpha-DPF-50-R3	--	--
Date	-	23-Apr-03	23-Apr-03	23-Apr-03	--	--
Filter	mg/dscm	3.7E+0	3.6E+0	3.6E+0	3.6E+0	1.5
Filter	lb/hr	7.9E-3	7.7E-3	7.8E-3	7.8E-3	1.2
Probe/Venturi*	mg/dscm	--	--	--	3.8E-1	n/a
Total	mg/dscm	--	--	--	4.0E+0	n/a
Total	lb/hr	--	--	--	8.6E-3	n/a
Run Number	-	Alpha-DPF-75-R1	Alpha-DPF-75-R2	Alpha-DPF-75-R3	--	--
Date	-	22-Apr-03	22-Apr-03	22-Apr-03	--	--
Filter	mg/dscm	2.9E+0	2.9E+0	2.8E+0	2.9E+0	2.5
Filter	lb/hr	8.2E-3	8.0E-3	7.8E-3	8.0E-3	2.7
Probe/Venturi*	mg/dscm	--	--	--	3.8E-1	n/a
Total	mg/dscm	--	--	--	3.3E+0	n/a
Total	lb/hr	--	--	--	9.1E-3	n/a

RSD- Relative standard deviation

*Average for both 50 and 75 percent load conditions.

At baseline conditions, average particle deposits in the sample probe and venturi are significant, accounting for 20 to 32 percent of the sum of the filter plus probe/venturi deposits. This is somewhat greater than was expected for PM2.5 based on the previous results of Hildemann, et al. (1989). Increased deposits in the probe may suggest the presence of coarse (2.5 to 10 µm) and large (greater than 10 µm) particles in the exhaust, greater probe losses due to high sample temperature (increasing probe losses due to thermophoresis), or inertial losses in the flexible sample line. Since an in-stack cyclone was not used for these tests, the probe/venturi deposits cannot be rigorously attributed to a specific size fraction; however, prior data for Diesel engines suggests that the vast majority of the particles by number and mass are much smaller than 2.5 µm (ARB, 1997; Kittelson et al., 2002). Therefore, the probe/venturi deposits are included in the total PM2.5 mass concentration and emission rates. Note, since probe/venturi rinses were not performed for every run, the RSD of the total results cannot be determined. Because of the significance of the deposits to the total PM2.5 mass, it is recommended that the sample nozzle, probe and venturi be recovered after every test run to better assess measurement precision.

PM2.5 mass concentration with the DPF is much lower compared to baseline, reflecting a high particle destruction and removal efficiency of the DPF. The probe/venturi deposits are much less significant for the DPF tests, comprising only 9 to 12 percent of the sum of filter plus probe/venturi deposits. Variability of the PM2.5 mass results for the DPF tests was very good, less than five percent RSD.

PM2.5 Mass – Beta Sampler

Average PM2.5 mass measured by the Beta sampler with the DPF configuration was 3.8 and 3.3 mg/dscm for 50 and 75 percent load, respectively, including the probe and venturi rinse (Table 4-5). PM2.5 Beta sampler PM2.5 mass results were invalid for baseline conditions. During baseline tests, the mass flow meter used to measure sample flow through the TMF/QFF filter pack in the Beta sampler failed. The mass flow meter was replaced in the field with a temporary rotameter; however, due to an installation error, there was an undetected leak between the rotameter and the filter leading to a large low bias in the reported particulate mass concentration. For this reason, the Beta sampler PM2.5 mass, element and backup OC results derived from the

TMF/QFF filter pack for baseline conditions are invalid. This problem also had a small negative bias effect on the calculated dilution ratio for baseline tests, but does not otherwise impact the Beta sampler OC and ion results.

Table 4-5. Dilution System Results – PM2.5 Beta Sampler (Site Foxtrot).

	Units	Results (mg/dscm)			Average (mg/dscm)	RSD (%)
Run Number	-	Beta-Base-50-R1*	Beta-Base-50-R2*	Beta-Base-50-R3*	--	--
Date	-	03-Apr-03	03-Apr-03	03-Apr-03	--	--
Filter	mg/dscm	1.0E+1	1.1E+1	1.0E+1	1.0E+1	0.7
Filter	lb/hr	2.2E-2	2.3E-2	2.2E-2	2.2E-2	0.9
Probe/Venturi**	mg/dscm	--	--	--	1.4E+1	n/a
Total	mg/dscm	--	--	--	2.5E+1	n/a
Total	lb/hr	--	--	--	5.3E-2	n/a
Run Number	-	Beta-Base-75-R1*	Beta-Base-75-R2*	Beta-Base-75-R3*	--	--
Date	-	03-Apr-03	03-Apr-03	03-Apr-03	--	--
Filter	mg/dscm	1.0E+1	1.0E+1	9.5E+0	1.0E+1	4.6
Filter	lb/hr	2.8E-2	2.9E-2	2.7E-2	2.8E-2	5.0
Probe/Venturi**	mg/dscm	--	--	--	1.4E+1	n/a
Total	mg/dscm	--	--	--	2.4E+1	n/a
Total	lb/hr	--	--	--	6.7E-2	n/a
Run Number	-	Beta-DPF-50-R1	Beta-DPF-50-R2	Beta-DPF-50-R3	--	--
Date	-	23-Apr-03	23-Apr-03	23-Apr-03	--	--
Filter	mg/dscm	3.1E+0	3.7E+0	3.9E+0	3.6E+0	12
Filter	lb/hr	6.7E-3	8.0E-3	8.4E-3	7.7E-3	12
Probe/Venturi**	mg/dscm	--	--	--	2.8E-1	n/a
Total	mg/dscm	--	--	--	3.8E+0	n/a
Total	lb/hr	--	--	--	8.3E-3	n/a
Run Number	-	Beta-DPF-75-R1	Beta-DPF-75-R2	Beta-DPF-75-R3	--	--
Date	-	22-Apr-03	22-Apr-03	22-Apr-03	--	--
Filter	mg/dscm	3.2E+0	2.9E+0	2.9E+0	3.0E+0	6.8
Filter	lb/hr	9.0E-3	8.0E-3	8.1E-3	8.4E-3	6.8
Probe/Venturi**	mg/dscm	--	--	--	2.8E-1	n/a
Total	mg/dscm	--	--	--	3.3E+0	n/a
Total	lb/hr	--	--	--	9.2E-3	n/a

RSD- Relative standard deviation

*Baseline PM2.5 measurements results are invalid due to a flow measurement error. Results are shown for information only.

**Average for both 50 and 75 percent load conditions.

Shaded area represents invalid measurements.

The sample probe/venturi deposit results are not affected by the above flow measurement error. Surprisingly, the average Beta sampler probe/venturi deposits for baseline conditions appear to be nearly twice as high as the average Alpha sampler results, despite the shorter and linear sample path. A single probe/venturi rinse for the 50 and 75 percent load conditions together was performed as a quality assurance check instead of separate rinses for each load because the deposits were not expected to be significant based on the results of Hildemann et al. (1989) showing that probe/venturi deposits of particles less than 1.4 µm should be less than 5 percent of the total and because 80 to 95 percent of the particle mass was expected to be smaller than 1 µm (Kittelson et al., 2002). Since only a single rinse was collected for the 50 and 75 percent load conditions together, it is not possible to determine if this is due to a single event or if it is truly representative of the average probe/venturi deposits during these tests, nor is it possible to determine the uncertainty associated with the result. Therefore, the baseline probe rinse results should be viewed with caution, both because of the single sample and because of the unexpectedly high result. Because of the significance of the deposits to the total PM2.5 mass, it is recommended that the sample nozzle, probe and venturi be recovered after every test run to better assess measurement precision.

The aforementioned mass flow meter was repaired prior to the DPF test series. PM2.5 mass concentrations measured by the Beta sampler with the DPF are similar at 50 and 75 percent load. The RSD of the average TMF results is very good, less that 12 percent. The single probe/venturi rinse result for the two load conditions accounts for 7 to 9 percent of the average total PM2.5 mass concentration for each condition. The TMF and probe/venturi deposit results from the Beta and Alpha samplers are in excellent overall agreement for the DPF test conditions.

OC/EC – Alpha Sampler

Table 4-6 summarizes the OC/EC results for the Alpha sampler. For baseline conditions, OC concentration ranges from 3.9 to 5.7 mg/dscm and EC concentration ranges from 15 to 27 mg/dscm. The variability is greater for the baseline 75 percent load results, but the mean concentrations for 50 and 75 percent loads are very similar. EC accounts for approximately 80 percent of the total carbon mass.

Table 4-6. Dilution System OC/EC Results for Alpha Tunnel (Site Foxtrot).

Parameter	Units	Value				
Run Number	-	Alpha-Base-50-R1	Alpha-Base-50-R2	Alpha-Base-50-R3	Average*	RSD
Date	-	03-Apr-03	03-Apr-03	03-Apr-03		(%)
Organic Carbon (OC)**	mg/dscm	4.5E+0	4.5E+0	4.1E+0	4.4E+0	5.4
	lb/hr	9.7E-3	9.7E-3	8.8E-3	9.4E-3	5.5
Elemental Carbon (EC)	mg/dscm	1.6E+1	1.7E+1	1.7E+1	1.6E+1	3.0
	lb/hr	3.4E-2	3.6E-2	3.6E-2	3.5E-2	3.1
Total Carbon (TC)	mg/dscm	2.0E+1	2.1E+1	2.1E+1	2.1E+1	1.5
	lb/hr	4.4E-2	4.5E-2	4.5E-2	4.5E-2	1.7
Backup Filter OC ***	mg/dscm	1.6E+0	2.0E+0	2.7E+0	2.1E+0	26
	lb/hr	3.5E-3	4.4E-3	5.9E-3	4.6E-3	26
Run Number	-	Alpha-Base-75-R1	Alpha-Base-75-R2	Alpha-Base-75-R3	Average*	RSD
Date	-	03-Apr-03	03-Apr-03	03-Apr-03		(%)
Organic Carbon (OC)**	mg/dscm	5.7E+0	4.0E+0	3.9E+0	4.5E+0	22
	lb/hr	1.6E-2	1.1E-2	1.1E-2	1.3E-2	22
Elemental Carbon (EC)	mg/dscm	2.7E+1	1.5E+1	1.6E+1	1.9E+1	35
	lb/hr	7.4E-2	4.1E-2	4.4E-2	5.3E-2	35
Total Carbon (TC)	mg/dscm	3.2E+1	1.9E+1	2.0E+1	2.4E+1	32
	lb/hr	9.0E-2	5.3E-2	5.5E-2	6.6E-2	32
Backup Filter OC ***	mg/dscm	3.1E+0	1.6E+0	1.9E+0	2.2E+0	36
	lb/hr	8.7E-3	4.6E-3	5.2E-3	6.1E-3	36
Run Number	-	Alpha-DPF-50-R1	Alpha-DPF-50-R2	Alpha-DPF-50-R3	Average*	RSD
Date	-	23-Apr-03	23-Apr-03	23-Apr-03		(%)
Organic Carbon (OC)**	mg/dscm	5.6E-1	4.2E-1	5.3E-1	5.0E-1	15
	lb/hr	1.2E-3	9.0E-4	1.1E-3	1.1E-3	15
Elemental Carbon (EC)	mg/dscm	3.8E+0	3.8E+0	3.7E+0	3.8E+0	2.4
	lb/hr	8.2E-3	8.3E-3	7.9E-3	8.1E-3	2.5
Total Carbon (TC)	mg/dscm	4.4E+0	4.2E+0	4.2E+0	4.3E+0	2.0
	lb/hr	9.4E-3	9.2E-3	9.0E-3	9.2E-3	1.9
Backup Filter OC ***	mg/dscm	2.2E-1	2.1E-1	1.8E-1	2.0E-1	12
	lb/hr	6.3E-4	5.8E-4	4.9E-4	5.7E-4	12
Run Number	-	Alpha-DPF-75-R1	Alpha-DPF-75-R2	Alpha-DPF-75-R3	Average*	RSD
Date	-	22-Apr-03	22-Apr-03	22-Apr-03		(%)
Organic Carbon (OC)**	mg/dscm	5.8E-1	5.6E-1	3.7E-1	5.0E-1	22
	lb/hr	1.6E-3	1.6E-3	1.0E-3	1.4E-3	22
Elemental Carbon (EC)	mg/dscm	3.0E+0	2.8E+0	2.8E+0	2.9E+0	3.6
	lb/hr	8.4E-3	7.9E-3	7.9E-3	8.0E-3	3.5
Total Carbon (TC)	mg/dscm	3.6E+0	3.4E+0	3.2E+0	3.4E+0	5.3
	lb/hr	1.0E-2	9.4E-3	8.9E-3	9.5E-3	5.5
Backup Filter OC ***	mg/dscm	1.9E-1	1.7E-1	1.8E-1	1.8E-1	6.3
	lb/hr	5.4E-4	4.7E-4	5.0E-4	5.0E-4	6.2

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

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

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

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

With the DPF installed, the concentrations of OC are approximately one tenth and EC concentrations are approximately one-fourth of their respective concentrations for baseline operation. The OC results tend to be somewhat more variable than the EC results under these conditions but still within reasonable bounds (22 percent or much less).

The QFFs used for OC/EC analysis have the potential for positive OC bias due to adsorption of VOCs on the media and the collected sample. A backup QFF placed directly behind the TMF was used to evaluate the potential magnitude of the absorptive bias on the clean media. The average OC concentrations on the backup filter are in general about half those on the primary filter. Therefore, the magnitude of any bias in the OC result is potentially significant, and may be on the same magnitude as the measured value. 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. This issue is further discussed in Section 6 and Section 7.

The sample nozzle, probe, venturi and transfer line rinses could not be analyzed for carbon content. Because the particle losses in the probe/venturi appear to be significant, and since the magnitude of the EC results is comparable to the PM2.5 mass results, it is likely the EC results are biased low. It is recommended that further characterization of these losses be undertaken in future studies to evaluate the magnitude of the potential bias. As a rough estimate, the magnitude of EC losses may be assumed proportional to PM2.5 mass losses.

<u>OC/EC – Beta Sampler</u>

Table 4-7 summarizes the OC/EC results for the Beta sampler. OC concentration ranges from 6.0 to 14 mg/dscm and EC concentration ranges from 18 to 22 mg/dscm for baseline conditions. The EC fraction accounts for approximately 61 to 77 percent of the total carbon mass, and averages 73 percent for baseline conditions. The EC fraction is slightly greater for 50 percent load than for 75 percent load. OC and EC concentrations with the DPF installed are approximately one-tenth and one-sixth of their respective baseline concentrations, and the EC fraction of total carbon mass is slightly greater. The variability of the EC results is quite good, 11 percent relative standard deviation or less for all test conditions. Note, although the primary QFF results

Table 4-7. Dilution System OC/EC Results for Beta Tunnel (Site Foxtrot).

Parameter	Units	Value				
Run Number	-	Beta-Base-50-R1	Beta-Base-50-R2	Beta-Base-50-R3	Average*	RSD
Date	-	03-Apr-03	03-Apr-03	03-Apr-03		(%)
Organic Carbon (OC)**	mg/dscm	6.5E+0	6.3E+0	6.0E+0	6.2E+0	4.6
	lb/hr	1.4E-2	1.4E-2	1.3E-2	1.3E-2	4.6
Elemental Carbon (EC)	mg/dscm	2.1E+1	1.8E+1	2.0E+1	2.0E+1	6.1
	lb/hr	4.5E-2	4.0E-2	4.3E-2	4.2E-2	5.9
Total Carbon (TC)	mg/dscm	2.7E+1	2.5E+1	2.6E+1	2.6E+1	5.1
	lb/hr	5.9E-2	5.3E-2	5.6E-2	5.6E-2	4.9
Backup Filter OC*** (a)	mg/dscm	2.5E+0	2.0E+0	2.5E+0	2.4E+0	12
	lb/hr	5.5E-3	4.4E-3	5.4E-3	5.1E-3	12
Run Number	-	Beta-Base-75-R1	Beta-Base-75-R2	Beta-Base-75-R3	Average*	RSD
Date	-	03-Apr-03	03-Apr-03	03-Apr-03		(%)
Organic Carbon (OC)**	mg/dscm	1.4E+1	8.8E+0	6.3E+0	9.9E+0	42
	lb/hr	4.0E-2	2.5E-2	1.8E-2	2.8E-2	42
Elemental Carbon (EC)	mg/dscm	2.2E+1	2.2E+1	2.0E+1	2.1E+1	7.1
	lb/hr	6.2E-2	6.2E-2	5.5E-2	6.0E-2	7.4
Total Carbon (TC)	mg/dscm	3.7E+1	3.1E+1	2.6E+1	3.1E+1	17
	lb/hr	1.0E-1	8.7E-2	7.2E-2	8.8E-2	17
Backup Filter OC*** (a)	mg/dscm	2.6E+0	2.6E+0	2.8E+0	2.6E+0	3.8
	lb/hr	7.2E-3	7.4E-3	7.7E-3	7.4E-3	3.6
Run Number	-	Beta-DPF-50-R1	Beta-DPF-50-R2	Beta-DPF-50-R3	Average*	RSD
Date	-	23-Apr-03	23-Apr-03	23-Apr-03		(%)
Organic Carbon (OC)**	mg/dscm	5.2E-1	4.9E-1	4.5E-1	4.9E-1	6.4
	lb/hr	1.1E-3	1.1E-3	9.7E-4	1.0E-3	6.4
Elemental Carbon (EC)	mg/dscm	2.8E+0	3.4E+0	3.1E+0	3.1E+0	10
	lb/hr	5.9E-3	7.3E-3	6.7E-3	6.7E-3	10
Total Carbon (TC)	mg/dscm	3.3E+0	3.9E+0	3.6E+0	3.6E+0	8.4
	lb/hr	7.1E-3	8.4E-3	7.7E-3	7.7E-3	8.7
Backup Filter OC***	mg/dscm	1.8E-1	2.0E-1	1.7E-1	1.9E-1	7.3
	lb/hr	3.9E-4	4.3E-4	3.7E-4	4.0E-4	7.5
Run Number	-	Beta-DPF-75-R1	Beta-DPF-75-R2	Beta-DPF-75-R3	Average*	RSD
Date	-	22-Apr-03	22-Apr-03	22-Apr-03		(%)
Organic Carbon (OC)**	mg/dscm	6.8E-1	5.2E-1	4.4E-1	5.5E-1	23
	lb/hr	1.9E-3	1.5E-3	1.2E-3	1.5E-3	23
Elemental Carbon (EC)	mg/dscm	2.1E+0	2.4E+0	2.6E+0	2.4E+0	11
	lb/hr	5.9E-3	6.7E-3	7.3E-3	6.7E-3	11
Total Carbon (TC)	mg/dscm	2.8E+0	2.9E+0	3.1E+0	2.9E+0	4.7
	lb/hr	7.9E-3	8.1E-3	8.6E-3	8.2E-3	4.4
Backup Filter OC***	mg/dscm	3.3E-1	1.8E-1	2.1E-1	2.4E-1	34
	lb/hr	9.3E-4	5.1E-4	5.8E-4	6.7E-4	34

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

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

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

a. Baseline Backup Filter OC measurements are biased low due to a flow measurement error. Results are shown for information only.

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

are not directly affected by the TMF flow measurement error discussed earlier, they are probably marginally biased low, probably by less than 6 percent (the TMF flow normally represents approximately 6 percent of the flows used to calculate dilution ratio, therefore the leak results in a small low bias in the dilution ratio and resulting in-stack concentration).

Backup OC in the Beta sampler is equivalent to approximately 40 percent of the primary QFF OC. It should be noted that this percentage is probably biased low by the same amount as PM2.5 mass because of the aforementioned sample flow measurement error (the backup QFF was in the same filter pack as the TMF). Nevertheless, the results clearly indicate the potential for significant positive bias in the OC measurement.

$SO_4^=$, Cl^-, and NO_3^- ions – Alpha Sampler

Table 4-8 shows ion results for the Alpha sampler. Ion concentrations during the baseline runs are below the minimum detection limits due to the very short sampling runs (20 minutes). With the DPF, longer test runs were conducted (two hours). $SO_4^=$ and NO_3^- concentrations average 0.019 and 0.045 mg/dscm at 50 percent load. At 75 percent load, $SO_4^=$ was not detected and NO_3^- concentration averaged 0.033 mg/dscm. Compared to in-stack detection limits shown previously in Table 4-1, the average results are very near, within a factor of three, the minimum detection limits. A slightly elevated NO_3^- concentration with the DPF installed is consistent with the operating principle of the DPF, which relies on oxidation of NO to promote particulate destruction. However, the results are too near the detection limits to be conclusive. Cl^- was not detected in any of the runs.

It should be noted that DPF tests were conducted with ultra-low sulfur Diesel (< 15 ppm sulfur (S)) and the baseline tests were conducted with California low sulfur Diesel fuel (< 500 ppm S). Therefore, one might expect to see a difference in the $SO_4^=$ content between the baseline and DPF tests. However, because the sampling times were very different for baseline (20 minutes) and DPF (120 minutes) tests, the $SO_4^=$ method detection limit (MDL) is much higher for the baseline tests. This masked any differences in measured $SO_4^=$ resulting from fuel S content. Since this measurement was not a main objective of these tests, it does not affect the overall success of the test.

Table 4-8. Dilution System Ion Results for Alpha Sampler (Site Foxtrot).

Parameter	Units	Value				
Run Number	-	Alpha-Base-50-R1	Alpha-Base-50-R2	Alpha-Base-50-R3	Average	RSD
Date	-	03-Apr-03	03-Apr-03	03-Apr-03		(%)
Sulfate	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Nitrate	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Chloride	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Run Number	-	Alpha-Base-75-R1	Alpha-Base-75-R2	Alpha-Base-75-R3	Average	RSD
Date	-	03-Apr-03	03-Apr-03	03-Apr-03		(%)
Sulfate	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Nitrate	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Chloride	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Run Number	-	Alpha-DPF-50-R1	Alpha-DPF-50-R2	Alpha-DPF-50-R3	Average	RSD
Date	-	23-Apr-03	23-Apr-03	23-Apr-03		(%)
Sulfate	mg/dscm	2.0E-2	1.6E-2	2.0E-2	1.9E-2	10
	lb/hr	4.3E-5	3.5E-5	4.2E-5	4.0E-5	10
Nitrate	mg/dscm	8.1E-2	3.0E-2	2.5E-2	4.5E-2	68
	lb/hr	1.7E-4	6.5E-5	5.4E-5	9.7E-5	68
Chloride	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Run Number	-	Alpha-DPF-75-R1	Alpha-DPF-75-R2	Alpha-DPF-75-R3	Average	RSD
Date	-	22-Apr-03	22-Apr-03	22-Apr-03		(%)
Sulfate	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Nitrate	mg/dscm	2.6E-2	3.6E-2	3.8E-2	3.3E-2	20
	lb/hr	7.2E-5	1.0E-4	1.1E-4	9.3E-5	20
Chloride	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a

n/a - not applicable
ND - not detected
RSD- Relative standard deviation

$SO_4^=$, Cl^-, and NO_3^- ions – Beta Sampler

Table 4-9 shows ion results for the Beta sampler. Ion concentrations during the baseline runs are below detection limits, except for Run 1 at 75 percent load. During the DPF runs, $SO_4^=$ was not detected at 50 percent load, while NO_3^- concentration averages 0.088 mg/dscm. At 75 percent load, $SO_4^=$ and NO_3^- concentrations averaged 0.028 and 0.058 mg/dscm, respectively.

Table 4-9. Dilution System Ion Results for Beta Sampler (Site Foxtrot).

Parameter	Units	Value				
Run Number	-	Beta-Base-50-R1	Beta-Base-50-R2	Beta-Base-50-R3	Average	RSD
Date	-	03-Apr-03	03-Apr-03	03-Apr-03		(%)
Sulfate	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Nitrate	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Chloride	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Run Number	-	Beta-Base-75-R1	Beta-Base-75-R2	Beta-Base-75-R3	Average	RSD
Date	-	03-Apr-03	03-Apr-03	03-Apr-03		(%)
Sulfate	mg/dscm	1.1E-1	ND	ND	1.1E-1	n/a
	lb/hr	3.0E-4	ND	ND	3.0E-4	n/a
Nitrate	mg/dscm	7.8E-2	ND	ND	7.8E-2	n/a
	lb/hr	2.2E-4	ND	ND	2.2E-4	n/a
Chloride	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Run Number	-	Beta-DPF-50-R1	Beta-DPF-50-R2	Beta-DPF-50-R3	Average	RSD
Date	-	23-Apr-03	23-Apr-03	23-Apr-03		(%)
Sulfate	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Nitrate	mg/dscm	6.0E-2	1.0E-1	1.0E-1	8.8E-2	28
	lb/hr	1.3E-4	2.2E-4	2.2E-4	1.9E-4	28
Chloride	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a
Run Number	-	Beta-DPF-75-R1	Beta-DPF-75-R2	Beta-DPF-75-R3	Average	RSD
Date	-	22-Apr-03	22-Apr-03	22-Apr-03		(%)
Sulfate	mg/dscm	1.0E-2	2.8E-2	4.6E-2	2.8E-2	64
	lb/hr	2.8E-5	7.9E-5	1.3E-4	7.8E-5	63
Nitrate	mg/dscm	4.7E-2	7.3E-2	5.3E-2	5.8E-2	24
	lb/hr	1.3E-4	2.1E-4	1.5E-4	1.6E-4	24
Chloride	mg/dscm	ND	ND	ND	ND	n/a
	lb/hr	ND	ND	ND	ND	n/a

n/a - not applicable
ND - not detected
RSD- Relative standard deviation

Ultrafine Particle Size Distribution

An SMPS was used to determine the number concentration and size distribution of ultrafine particles (smaller than 0.1 um). The SMPS results were reduced using an inversion routine and are expressed as dN/dLog(Dp), called number concentration as a function of particle aerodynamic diameter (Dp), and as dM/dLog(Dp), called mass concentration as a function of particle aerodynamic diameter.

Average SMPS results for each baseline test run are presented in Figure 4-1. Each run average is the mean of 11 individual scans during each 20-minute baseline test run. For baseline conditions, the particle number size mode is 65 to 75 nm and the peak number concentrations are slightly lower for 75 percent load (2.1x10^5 to 2.4x10^5) compared to 50 percent load (2.6x10^5 to 3.5x10^5). Size mode appears to shift slightly lower for 75 percent load compared to 50 percent load. There is more variability among the 50 percent load runs than for the 75 percent load runs. The mass concentrations peak at approximately 300 nm and larger. The range of the SMPS instrument as configured by UCR staff during these tests was approximately 30 to 500 nm (0.03 to 0.5 µm), and, as expected, particles larger than 500 nm are the most significant contributors to mass. Note, the data scatter apparent at the low and high end of the instrument size range reflects low particle counts in those size bins.

Particle number concentrations are much lower than baseline with the DPF installed, however the size mode is approximately the same (55 to 75 nm) (Figure 4-2). Peak number concentrations at 50 percent load (5.5x10^4 to 6.2x10^4) are greater than at 75 percent load (1.7x10^4 to 4.7x10^4). Mass concentration peaks at approximately 300 nm and larger.

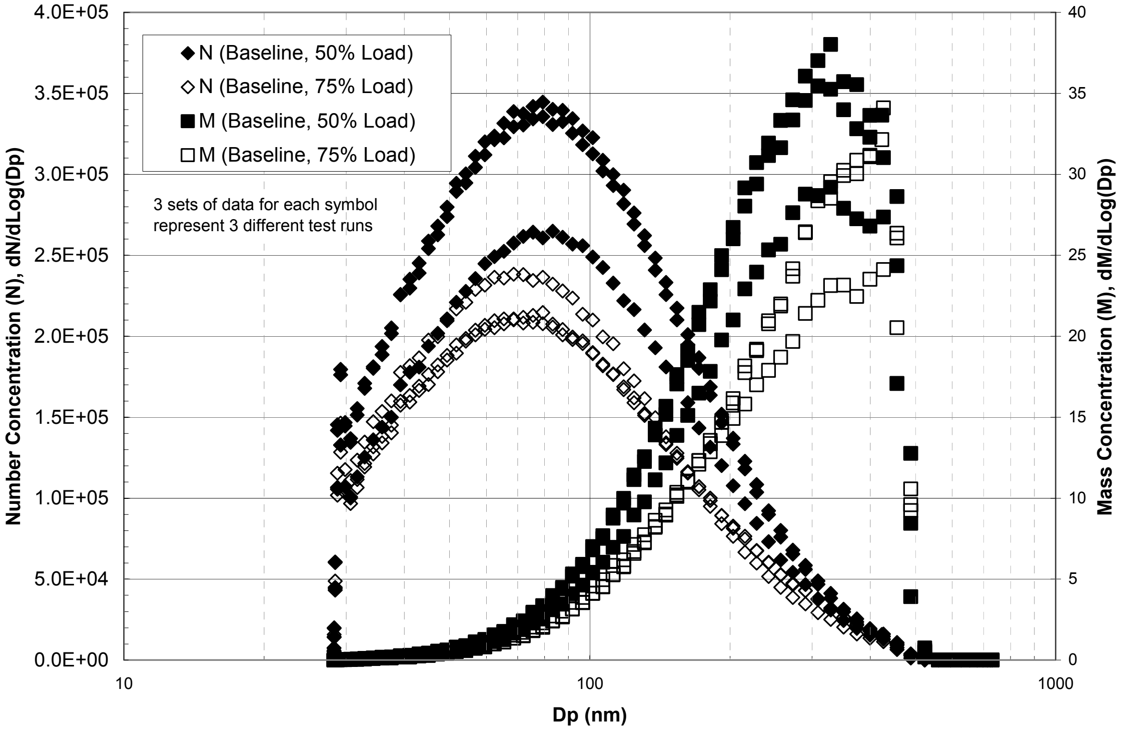

Figure 4-1. PM Number and Mass Size Distributions for 50 percent and 75 percent Load Baseline Tests (Site Foxtrot).

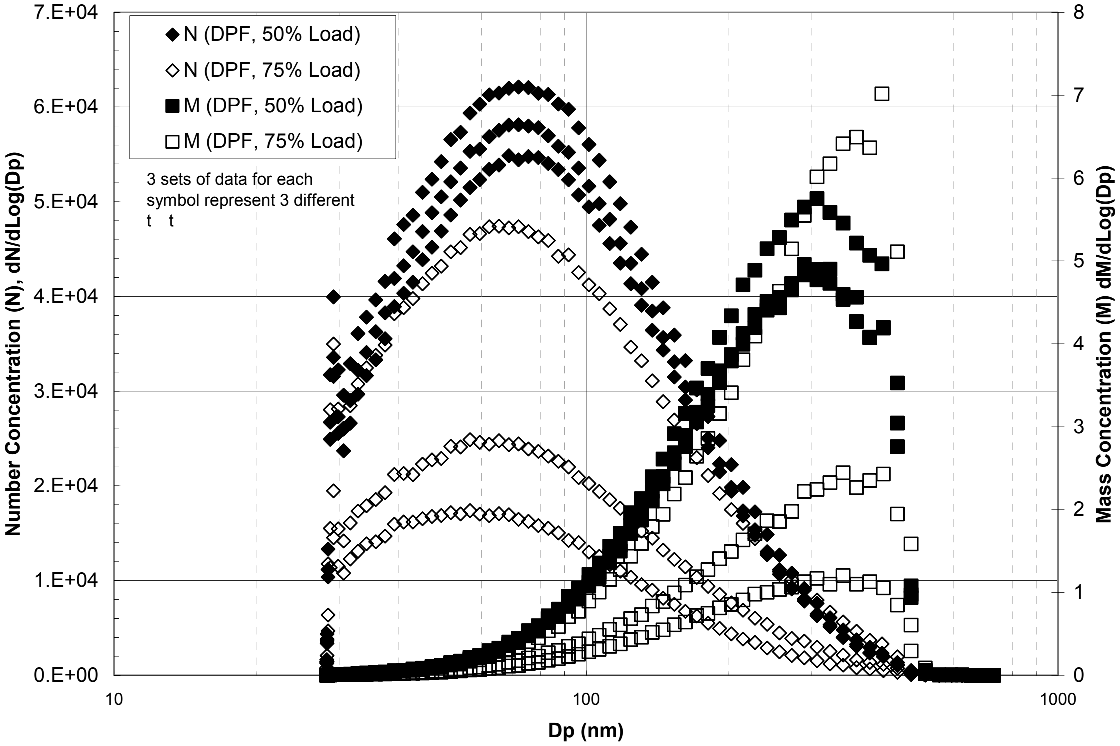

Figure 4-2. Ultrafine Particle Number and Mass Size Distributions for 50 percent and 75 percent Load DPF Tests (Site Foxtrot).

<u>ISO 8178 Dilution Sampler Results</u>

Measurements were made on separate days by the UCR team using a constant volume dilution sampling system following ISO 8178 requirements. Preliminary results of those measurements were provided by UCR for this report. The average results and relative standard deviation are presented in Table 4-10. Further details will be presented elsewhere (UCR's report was not complete at this writing).

Table 4-10. ISO 8178 Dilution Sampler Results

	ISO 8178		RPD, %		
	Average, mg/dscm	RSD, %	Alpha*	Beta*	Alpha & Beta*
Baseline, 50% Load	29.5	3.6	-9%	n/a	-9%
Basline, 75% Load	30.0	2.1	12%	n/a	12%
DPF, 50% Load	5.30	3.7	-24%	-33%	-26%
DPF, 75% Load	4.33	5.8	-25%	-31%	-25%

*Includes probe, sample line and venturi rinses.
RSD = relative standard deviation
RPD = relative percent difference of mean results

5. EMISSION FACTORS AND SPECIATION PROFILES

Emission factors derived from tests of several similar sources 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 from the results of this single test were determined by dividing the emission rate, in lb/hr, by the measured heat input, in pounds of pollutant per British thermal unit (MMBtu/hr), to give pounds per million British thermal units (lb/MMBtu) for each test run (since one horse power-hour (hp-hr) is equal to 7,000 Btu, multiply lb/MMBtu by 0.007 to convert lb/MMBtu to lb/hp-hr). Heat input values were calculated by personnel at Site Foxtrot and were based on fuel heating values and flow rates. 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 test runs. Emission factors based on data detected in at least three test runs are considered the most reliable.

Speciation Profiles

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

Uncertainty and Representativeness

As a measure of emission factor reliability, the bias (accuracy or systematic uncertainty) and precision (variability or random uncertainty) of the results, the total relative uncertainty (at the 95 percent confidence level) and 95 percent confidence upper bound were calculated for each emission factor and mass fraction using standard error analysis procedures (ASME, 1990).

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 test run; therefore, emission factors are not reported for these substances.

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

Blanks and Ambient Air Samples

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

- At each operating condition (baseline or DPF and 50 percent or 75 percent load) results were compared to the highest result measured in the two relevant DSBs (from the Alpha and Beta samplers). These DSBs represent a "clean" system at the beginning of the test before any stack samples were collected.
- At each operating condition (baseline or DPF) results were compared to the highest result measured in the baseline operation FB and the DSB operation FB and trip blank.
- If the average stack sample result is less than the highest blank, the emission factor is excluded.
- If the lower 95 percent confidence bound of the average stack result is less than the highest DSB or FB result, the emission factor is flagged with a footnote "a" or "b", respectively.
- If a substance was not detected in all 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 the Alpha and Beta dilution samplers to this type of source. The resulting emission factors are not considered representative of any particular operating condition for this engine, but rather are the average of the operating conditions during the tests. Consequently, data users should apply caution when using these results.

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

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

Widely recognized standard methods for stationary source dilution sampling do not presently exist. Recently, EPA published a conditional test method (CTM-039) for stationary source dilution sampling and conducted limited tests on coal- and oil-fired boilers (U.S. EPA, 2003a). EPA proposed the method as an alternative for testing needed to develop PM2.5 emission inventories (U.S. EPA, 2003b). While the equipment and procedures specified in the method differ from those used in this program, it indicates such methods may become more generally accepted in the future.

The quality of the source-specific emission factors derived from this test should not be considered high because the emission factors from a single test or a single unit may not be representative of the entire source category population or range of operating conditions. This does not mean that these test results are not of value or high quality, but rather indicates that more tests are needed to corroborate the results before they are widely applied. As noted above, the emission factors derived from these test results may best be used in conjunction with test results from other units within the source category population to develop more robust, reliable emission factors.

EMISSION FACTORS

Emission factors for primary PM2.5 mass, OC, EC and ions were derived from the dilution sampling results. For baseline conditions, only the Alpha sampler results are presented because the Beta sampler PM2.5 mass, elements and backup OC results are not valid (due to the TMF flow measurement error discussed in Section 4) for those conditions. The baseline results for 50 and 75 percent load are combined because the PM2.5 mass results are not significantly different based on the statistical t-test (see Section 7 for further discussion). For DPF tests, the Alpha and Beta sampler results are combined since PM2.5 mass results are not significantly different; however, 50 and 75 percent load results are not combined since those results appear to be significantly different based on t-test results (see Section 7 for discussion of method performance).

PM2.5 Mass Emissions Factors

Tables 5-1 presents emission factors for PM2.5 mass for baseline and DPF conditions. The column labeled "Count" in the table represents the number of data points in the set. Note that the emission factors exclude the sample nozzle, probe and venturi rinse results since the uncertainty of those measurements could not be determined. Therefore, the average results based on the TMF alone are lower than the true value by 26 to 49 percent for baseline conditions and 7 to 9 percent for DPF test conditions because the probe rinses are not included (see Section 4 for further discussion of probe rinse results). These results should be used with caution until they can be corroborated against the ISO sampler results to be presented in a separate report by UCR.

Table 5-1. Emissions Factors for PM2.5 Mass (Site Foxtrot).

Condition	Parameter	Emission Factor *(1)* (lb/MMBtu)	Total Uncertainty at 95% Confidence Level *(2)* (%)	95% Confidence Upper Bound *(3)* (lb/MMBtu)	5th Percentile	95th Percentile	Count
Baseline *(4)*	PM2.5 mass *(5)*	2.7E-2	35	3.5E-2	2.1E-2	3.5E-2	6
DPF, 50% load *(6)*	PM2.5 mass (5)	4.6E-3	16	5.4E-3	4.1E-3	5.3E-3	6
DPF, 75% load *(6)*	PM2.5 mass (5)	3.5E-3	15	4.0E-3	3.3E-3	3.8E-3	6

(1) Multiply lb/MMBtu by approximately 0.007 to convert to lb/hp-hr (power output)

(2) Uncertainty is calculated at the 95% confidence level using the two-tailed Student t distribution. The 95 percent confidence interval of the emission factor is two times the uncertainty (i.e., mean +/- uncertainty).

(3) 95% upper confidence bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% upper confidence bound provides a plausible upper bound (i.e. it is likely emissions are lower) for emissions.

(4) Alpha sampler only, 50 and 75 percent load results combined.

(5) Filter results only; sample nozzle, probe and venturi rinse not included. Results may be biased low. See text.

(6) Alpha and Beta samplers combined.

Particulate Carbon Emissions Factors

EC is the dominant particulate carbon species, with an emission factor ranging from 0.022 lb/MMBtu for baseline conditions to 0.0031 lb/MMBtu with the DPF installed (Table 5-2). The uncertainty of the EC emission factors is moderate to good, with total relative uncertainty ranging from 19 to 39 percent. It should be noted that, as with PM2.5 mass, the particulate carbon emission factors may be biased low because deposits in the sample nozzle, probe and venturi were apparently significant, but insufficient data were collected to determine reliable emission factors including these results. These emission factors therefore should be viewed with caution until they are corroborated by the ISO sampler results to be presented in a separate report by UCR.

Backup OC represents the potential magnitude of positive bias in the OC emission factor due to VOC adsorption on the QFFs. Since the OC and Backup Filter OC results are comparable in magnitude, the result suggests most of the OC emission factor may be due to the VOC artifact.

Ions Emissions Factors

$SO_4^=$ and NO_3^- were detected consistently only in the DPF runs at concentrations within a factor of four of the MDL. The close proximity to the MDL probably explains the relatively high variability of some of the emission factors (Table 5-3). No emission factors are reported for baseline conditions, however the in-stack MDLs for baseline tests are higher than the highest result measured with the DPF tests due to shorter sampling times, so it is not possible to determine if the emission factors with the DPF are higher or lower than baseline. NO_3^- emission factors are slightly greater than $SO_4^=$ emission factors.

Table 5-2. Particulate Carbon Emissions Factors (Site Foxtrot).

Condition	Parameter	Emission Factor *(1)* (lb/MMBtu)	Total Uncertainty at 95% Confidence Level *(2)* (%)	95% Confidence Upper Bound *(3)* (lb/MMBtu)	5th Percentile	95th Percentile	Count
Alpha Baseline *(4)*	OC *(5,7)*	5.5E-3	34	7.1E-3	4.7E-3	6.6E-3	6
	EC	2.2E-2	39	2.9E-2	1.8E-2	3.1E-2	6
	TC *(8)*	2.7E-2	37	3.6E-2	2.3E-2	3.7E-2	6
	Backup Filter OC *(9)*	2.7E-3	43	3.6E-3	2.0E-3	3.6E-3	6
50% DPF *(6)*	OC *(5,7)*	6.4E-4	20	7.6E-4	5.5E-4	7.2E-4	6
	EC	4.4E-3	19	5.2E-3	3.6E-3	4.9E-3	6
	TC *(8)*	5.1E-3	18	5.9E-3	4.3E-3	5.6E-3	6
	Backup Filter OC *(9)*	2.5E-4	24	3.1E-4	2.3E-4	2.9E-4	6
75% DPF *(6)*	OC *(5,7)*	6.2E-4	27	7.6E-4	4.6E-4	7.9E-4	6
	EC	3.1E-3	19	3.6E-3	2.6E-3	3.5E-3	6
	TC *(8)*	3.7E-3	17	4.3E-3	3.4E-3	4.2E-3	6
	Backup Filter OC *(9)*	2.5E-4	37	3.3E-4	2.1E-4	3.8E-4	6

OC - Organic Carbon
EC - Elemental Carbon
TC - Total Carbon

(1) Multiply lb/MMBtu by approximately 0.007 to convert to lb/hp-hr (power output)

(2) Uncertainty is calculated at the 95% confidence level using the two-tailed Student t distribution. The 95 percent confidence interval of the emission factor is two times the uncertainty (i.e., mean +/- uncertainty).

(3) 95% upper confidence bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% upper confidence bound provides a plausible upper bound (i.e. it is likely emissions are lower) for emissions.

(4) Alpha sampler only, 50 and 75 percent load results combined.

(5) Filter results only; sample nozzle, probe and venturi rinse not included. Results may be biased low. See text.

(6) Alpha and Beta samplers combined.

(7) OC subject to positive bias due to measurement artifacts. See footnote *(9)* and discussion in Section 4 of report.

(8) TC is the average of TC for each test run, not sum of average OC plus EC.

(9) Backup filter OC is an indicator of potential magnitude of OC measurement artifacts.

Table 5-3. Emissions Factors for Particulate Ions (Site Foxtrot).

Condition	Parameter	Emission Factor *(1)* (lb/MMBtu)*	Total Uncertainty at 95% Confidence Level *(2)* (%)	95% Confidence Upper Bound *(3)* (lb/MMBtu)	5th Percentile	95th Percentile	Count
50% DPF *(4)*	$SO_4^=$	< 2.4E-5	37	3.2E-5	2.2E-5	2.5E-5	3
	NO_3^-	8.6E-5	56	1.2E-4	3.8E-5	1.3E-4	6
75% DPF *(4)*	$SO_4^=$	< 3.3E-5	160	6.9E-5	1.4E-5	5.1E-5	3
	NO_3^-	5.4E-5	41	7.2E-5	3.3E-5	8.4E-5	6

< - detected in fewer than all test runs

(1) Multiply lb/MMBtu by approximately 0.007 to convert to lb/hp-hr (power output)

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

(3) 95% upper confidence bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% upper confidence bound provides a plausible upper bound (i.e. it is likely emissions are lower) for emissions.

(4) Alpha and Beta samplers combined.

PM2.5 SPECIATION PROFILE

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. 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.

The PM2.5 speciation profile is normalized using the reconstructed PM2.5 mass. The reconstructed PM2.5 mass is determined from the individual species measurements with adjustments to OC for hydrocarbon speciation. The OC mass was multiplied by a factor of 1.08 to account for hydrocarbon speciation (based on the total carbon fraction of all the SVOCs detected in previous tests). Undetected target substances are included as zeros in the reconstructed mass and for uncertainty calculations. The reconstructed PM2.5 mass is in very good agreement (104 to 113 percent) with the measured PM2.5 mass.

The speciation profiles for each test condition are dominated by EC (Table 5-4). Seventy-eight to eighty-five percent of the reconstructed mass is accounted for by EC, with OC accounting for 13 to 22 percent. $SO_4^=$ and NO_3^- together account for less than 2 percent of the PM2.5 mass measured with the DPF installed. Backup OC, which represents a mass fraction of 5 to 10 percent, indicates the potential magnitude of positive bias in the OC result due to the VOC adsorption artifact (discussed elsewhere in this report). This potential bias is similar in magnitude to the error in the reconstructed mass, and therefore lends support to a potential bias in the OC measurement.

Table 5-4. PM2.5 Speciation Profiles (Site Foxtrot).

Condition	Parameter	Average Mass Fraction *(1,2)* (%)	Total Uncertainty *(3)* (%)	95% Confidence Upper Bound *(4)* (%)	Number of Detected Runs *(5)*
Alpha Baseline *(6)*	OC *(7)*	22	12	24	6
	EC	78	4	81	6
	Backup Filter OC *(8)*	10	22	12	6
50% DPF *(9)*	OC *(7)*	13	20	15	6
	EC	85	19	87	6
	NO3-	1.7	56	2.4	6
	SO4=	0.21	120	0.42	3
	Backup Filter OC *(8)*	5	18	6.1	6
75% DPF *(9)*	OC *(7)*	18	27	21	6
	EC	81	7	85	6
	NO3-	1.4	44	1.9	6
	SO4=	0.45	141	0.95	3
	Backup Filter OC *(8)*	7	41	10	6

OC - Organic Carbon
EC - Elemental Carbon

(1) Mass fraction is emission factor (EMF) of species divided by EMF of sum of species - calculated from highest stable oxide form of elements and OC corrected for C, H in SVOC. NDs assumed to be zero for speciation calculations.

(2) 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, 5-2, and 5-3.

(3) 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.

(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 emissions are lower) for emissions.

(5) Non-detect runs set equal to zero for speciation calculations. Number of Detected Runs is number of runs with complete data set.

(6) Alpha sampler only, 50 and 75 percent load results combined.

(7) OC subject to positive bias due to measurement artifacts. See footnote *(9)* and discussion in Section 4 of report.

(8) Backup filter OC is an indicator of potential magnitude of OC measurement artifacts.

(9) Alpha and Beta samplers combined.

6. QUALITY ASSURANCE

SAMPLE STORAGE AND SHIPPING

All samples requiring refrigeration were stored on-site in a refrigerator prior to shipment to the lab for analysis. All of the samples except for the in-stack and impinger filters were shipped via overnight shipment to the lab in an ice chest packed with blue ice.

Upon receipt of samples at the lab, those requiring refrigeration were stored at 4°C (nominal). Samples were stored, packed and shipped in a manner to prevent sample container breakage.

DSB

DSBs and FBs were collected and analyzed:

- One DSB was collected for each dilution sampler at the beginning of each test series (i.e., once for baseline and once for DPF tests) for the same amount of time as the actual test sampling time, i.e., 20 minutes for baseline tests and 120 minutes for DPF tests. The DSBs were conducted by drawing filtered air through each of the dilution samplers and collecting samples per the normal procedures. DSB results are an indication of the background levels in the dilution sampler, likely from deposition of species on dilution sampler surfaces during sampling, or HEPA and/or carbon filter breakthrough.

- One FB was collected for each dilution sampler during the second (DPF) test series. FBs were collected by setting up and breaking down the dilution sampler sampling equipment without drawing gas through the sampling media. FB results are an indication of the species collected on the sampling media during the handling and transport of the materials.

GRAVIMETRIC ANALYSIS

Dilution Sampler Filters

Prior to testing, unused TMFs were stored for at least one month in a controlled environment, followed by one week of equilibration in the weighing environment to achieve stable filter tare weights. New and used filters were equilibrated at 20 ± 5°C and a relative humidity of 30 ± 5 percent for a minimum of 24 hours prior to weighting. Weighing was performed on a Cahn 31 electro-microbalance with ±1 microgram sensitivity. The electrical charge on each TMF 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 milligrams (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 micrograms (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.

DSB and FB results are presented as in-stack equivalents using the average dilution factor for the sampling runs. Each blank is compared to the 95 percent confidence lower bound of the average sample result presented in Section 4 of the report. The procedures used for calculating the confidence bounds were described in Section 5. If the blank is greater than the 95 percent lower bound, the data is flagged. Flags suggest the field data may not be significantly different from the background levels in the samples.

PM2.5 Mass Blank Results

Table 6-1 lists the PM2.5 mass concentrations in the DSBs and FBs calculated at equivalent in-stack concentrations for each test condition. The DSB PM2.5 represents 2 to 4 percent of the average stack PM2.5. For the Baseline tests, the average concentrations are significantly greater than the dilution sampler blank concentrations, approximately 35 times for the Alpha sampler and 25 times for the Beta sampler. For the DPF tests, the average concentrations are also significantly greater than the dilution sampler blank concentrations, approximately 35 times for the Alpha sampler and 40 times for the Beta sampler. The PM2.5 mass in the field blanks was not detectable.

Table 6-1. PM2.5 Mass Blank Results (Site Foxtrot).

	mg/dscm	
	DSB	FB
Alpha, Base, 50% Load	5.7E-1	ND
Alpha, Base, 75% Load	6.2E-1	ND
Alpha, DPF, 50% Load	1.0E-1	ND
Alpha, DPF, 75% Load	1.0E-1	ND
Beta, Base, 50% Load	3.5E-1	ND
Beta, Base, 75% Load	4.0E-1	ND
Beta, DPF, 50% Load	7.7E-2	ND
Beta, DPF, 75% Load	7.6E-2	ND

DSB - Dilution Sampler Blank
FB - Field Blank
ND - Not Detected

OC/EC Concentration Blank Results

Table 6-2 presents the OC/EC blank concentration for all of the engine tests. For the baseline tests, the average OC concentrations were noticeably higher than the dilution sampler blank concentrations, approximately five or six times greater for the Alpha sampler and 15 to 20 times greater for the Beta Sampler. The DSB concentrations of EC were all non-detectable. For the DPF tests, the 95 percent confidence lower bounds of the average concentrations were less than the DSB concentrations for both Alpha and Beta samplers. The OC field blank concentrations were detected for DPF tests. The OC FB concentrations were approximately two to three times smaller than the corresponding OC DSB concentrations.

Ion Blank Concentration Results

$SO_4^=$ and NO_3^- were detected at low levels in the DSBs for the DPF test condition and in the second field blank (Table 6-3). In some cases, the levels were significant relative to the stack samples.

Table 6-2. Organic and Elemental Carbon Blank Results (Site Foxtrot).

Condition	Parameter	mg/dscm	
		DSB	FB
Alpha, Base, 50% Load	OC*	7.6E-01	1.3E+00
Alpha, Base, 50% Load	EC	ND	ND
Alpha, Base, 50% Load	Backup Filter OC**	4.8E-01	1.1E+00
Alpha, Base, 75% Load	OC*	8.3E-01	1.4E+00
Alpha, Base, 75% Load	EC	ND	ND
Alpha, Base, 75% Load	Backup Filter OC**	5.2E-01	1.2E+00 b
Alpha, DPF, 50% Load	OC*	4.9E-01 a	2.2E-01
Alpha, DPF, 50% Load	EC	ND	ND
Alpha, DPF, 50% Load	Backup Filter OC**	6.2E-01 a	1.8E-01 b
Alpha, DPF, 75% Load	OC*	4.7E-01 a	2.2E-01
Alpha, DPF, 75% Load	EC	ND	ND
Alpha, DPF, 75% Load	Backup Filter OC**	5.9E-01 a	1.7E-01 b
Beta, Base, 50% Load	OC*	4.0E-01	1.1E+00
Beta, Base, 50% Load	EC	ND	ND
Beta, Base, 50% Load	Backup Filter OC**	3.1E-01	1.2E+00 b
Beta, Base, 75% Load	OC*	4.5E-01	1.2E+00
Beta, Base, 75% Load	EC	ND	ND
Beta, Base, 75% Load	Backup Filter OC**	3.5E-01	1.3E+00 b
Beta, DPF, 50% Load	OC*	3.8E-01	1.7E-01
Beta, DPF, 50% Load	EC	ND	ND
Beta, DPF, 50% Load	Backup Filter OC**	5.1E-01 a	1.9E-01 b
Beta, DPF, 75% Load	OC*	3.8E-01 a	1.7E-01
Beta, DPF, 75% Load	EC	ND	ND
Beta, DPF, 75% Load	Backup Filter OC**	5.0E-01 a	1.9E-01 b

DSB - Dilution Sampler Blank
FB - Field Blank
n/a- not applicable
ND - Not Detected
a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.
b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.
** OC measured on a "backup" quartz fiber filter placed downstream of Teflon membrane filter. Refer to Sections 6 & 7 for further discussion.

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

Table 6-3. Blank Results – Ions (Site Foxtrot).

		mg/dscm			
		DSB		FB	
Alpha, Base, 50% Load	NO3-	ND	d	ND	d
Alpha, Base, 50% Load	SO4=	ND	d	ND	d
Alpha, Base, 75% Load	NO3-	ND	d	ND	d
Alpha, Base, 75% Load	SO4=	ND	d	ND	d
Alpha, DPF, 50% Load	NO3-	2.5E-02	a	ND	
Alpha, DPF, 50% Load	SO4=	2.9E-02	a	ND	
Alpha, DPF, 75% Load	NO3-	2.4E-02	a	ND	
Alpha, DPF, 75% Load	SO4=	2.7E-02	d	ND	d
Beta, Base, 50% Load	NO3-	ND	d	1.1E-01	d
Beta, Base, 50% Load	SO4=	ND	d	ND	d
Beta, Base, 75% Load	NO3-	ND	d	1.2E-01	d
Beta, Base, 75% Load	SO4=	ND	d	ND	d
Beta, DPF, 50% Load	NO3-	1.3E-02		1.8E-02	
Beta, DPF, 50% Load	SO4=	ND	d	ND	d
Beta, DPF, 75% Load	NO3-	1.3E-02		1.8E-02	
Beta, DPF, 75% Load	SO4=	ND		ND	

DSB - Dilution Sampler Blank

FB - Field Blank

ND - Not Detected

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

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

7. DISCUSSION AND FINDINGS

One of the primary test objectives was to compare PM2.5 mass results measured with the newly designed dilution sampler and the Desert Research Institute sampler, referred to as the Alpha sampler in this report. The Alpha sampler is based on the benchmark California Institute of Technology design developed by Hildemann et al. (1989), which has been used extensively by researchers for more than a decade. The unique feature of this design is an aging chamber designed to provide substantial residence time after dilution for condensation and growth of low concentration organic aerosols. Hildemann's original work thoroughly characterized the performance of this design, including the effects of dilution ratio and particle losses throughout the system as a function of particle size. Therefore, this design is considered the benchmark for dilution sampler performance.

While the Hildemann design is well known and has been successfully applied to a wide range of source types, it is not considered widely applicable for routine source tests due to its large size and weight. In a separate task of this program, experiments were conducted to assess the effects of two important design parameters affecting size and weight that were not previously well characterized: particle concentration and residence time after dilution (Chang et al., 2004). The experiments also revisited the effects of dilution ratio as a function of particle concentration. The experiments indicated that results approximately comparable to the Hildemann design should be achievable with shorter residence times (10 seconds) and lower dilution ratio (20:1). Also, a recent study showed that the mixing rate between dilution air and the sample was not a first order effect so faster mixing rates than used in the original Hildemann design should be acceptable (Lyyränen et al, 2004). Based on these results, a new, more compact and lightweight dilution sampler design was constructed (the Beta sampler). Preliminary PM2.5 mass measurements made using both Alpha and Beta samplers in a pilot-scale furnace with different fuels showed generally good agreement between the systems at moderate to high particle concentrations.

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

- Shorter aging section residence time (10 seconds versus 80-90 seconds);

- More rapid mixing between the sample and dilution air (within one diameter versus 15 diameters);

- Lower diluted sample volumetric flow rate (113 L/min versus 336 L/min);

- Sample path (linear path versus convoluted path).

This test represents the first field comparison between the Alpha and Beta samplers on a Diesel fuelled compression ignition reciprocating engine. Tests were conducted simultaneously with both samplers, at nearly the same sampling locations in the exhaust duct but after establishing the absence of significant stratification of gas concentrations in the stack. PM2.5 mass, OC, EC ions and elements were measured for each sampler.

DILUTION SAMPLER PERFORMANCE

Accuracy

The absolute accuracy of the dilution sampling method was generally established based on the work of Hildemann et al. (1989). Hildemann spiked the sampler with monosize ammonium fluoroscein particles and then recovered each section of the sampler separately to quantify particle losses as a function of particle size. 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. The experiments showed that particle losses in the sample line and venturi sections declined sharply, from 21 percent down to 7 percent, with particle size from 2.4 µm down to 1.3 µm. Based on these experiments, the PM2.5 mass accuracy (bias) using only the TMF results (ignoring sampling losses upstream of the TMF) can be expected to be in the range of approximately ±7 to ±24 percent. Since the losses decrease with decreasing particle size, the average loss for a distribution of particle sizes below 2.5 µm could reasonably be in the ±10 percent range (assuming 80 percent of the particles are smaller than 1.3 µm). The cumulative 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.). Summing the particle losses and sampling bias, the overall accuracy of the benchmark Alpha dilution sampler is estimated to be in the range of ±15 percent.

The Beta sampler results appear to have a potentially significant low bias (approximately –50 percent, overall) compared to the Alpha sampler. To assess whether this apparent bias is significant, statistical tests drawn from EPA Method 301 "Field Validation of Pollutant Measurement Methods from Various Waste Media (U.S. EPA, 1992) were applied. Note, the number of valid test runs achieved in these tests (twelve altogether, with six valid paired tests) is smaller than required by Method 301 (twelve), so the statistical test results are viewed as a preliminary indication rather than conclusive validation. Method 301 specifies statistical tests at the 95 percent confidence level to determine the equivalency of an alternative method (in this case, the Beta sampler) in comparison to an existing reference method (in this case, the Alpha sampler) when the methods are run simultaneously (as they were in these tests). Method 301 first applies the statistical F-test to determine whether the variances (precision) of the two sets of results are the same, and then applies the statistical paired sample t-test to determine if the bias is significant. According to Method 301, if the bias is not significant according to the paired sample t-test at the 95 percent confidence level, no bias correction factor needs to be applied to the alternative method results. If the bias is significant, a bias correction factor of up to 20 percent must be applied to the alternative method results. If the bias is significant and exceeds 20 percent, the alternative method is rejected. Method 301 does not specifically address situations where the apparent bias is greater than 20 percent but not significant at the 95 percent confidence level, but the implication is that this is irrelevant.

Increased accuracy could potentially be achieved by recovering the particles deposited in the sample line and venturi; however, this was not performed for every test run so standard deviation could be determined for this fraction. Therefore, sample line and venturi losses are assumed similar in both the Alpha and Beta samplers[2]. Due to the flow measurement error in the Beta sampler during the baseline tests, none of the PM2.5 mass results from the TMF could be used

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[2] The Alpha sampler employs a 4-foot length of bendable heated copper tubing section connecting the probe to the venturi, whereas the probe for the Beta sampler is connected directly to the venturi. One might expect some difference in deposition as a result, and this is somewhat supported by the probe rinse results. The result of the single baseline condition Alpha sampler rinse seems unusually high. Because probe rinses were not collected for every run, statistical variation of the result cannot be determined. Therefore, any difference is neglected for the purposes of this analysis.

for this analysis, leaving only the DPF test results. This was an unfortunate loss of data that could have been avoided if a spare mass flow meter had been available (preventative maintenance and a spare are recommended for future tests). The 50 percent and 75 percent load data were combined for the paired sample t-test analysis since the mean PM2.5 mass results are similar in magnitude. The P-value is 0.55, which indicates a high probability that the mean PM2.5 masses from each sampler are the same at the 95 percent confidence level (i.e., the null hypothesis[3] H_0 falls within the 95 percent confidence interval of the mean, Figure 7-1). Performing the same test on the 50 percent load and 75 percent load DPF test results separately yields P-values of 0.84 and 0.29, respectively, indicating a high probability that the two samplers are equivalent at the 95 percent confidence level. Based on these results, the PM2.5 mass accuracies of the Alpha and Beta samplers are considered the same and no adjustment for bias is needed for the Beta sampler results.

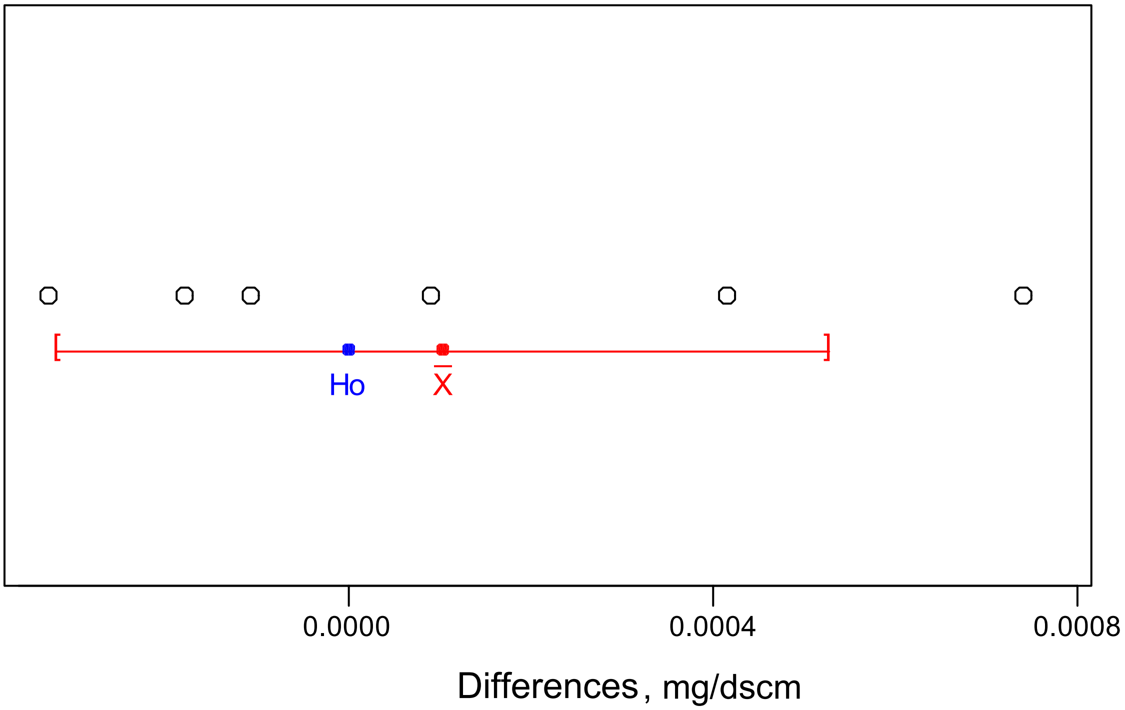

Figure 7-1. Paired Sample t-Test results for Alpha and Beta Sampler PM2.5 Mass Results (with Null Hypothesis, H_0, and 95 percent t-Confidence Interval for the Mean).

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[3] Refer to a statistical analysis textbook or other guideline (e.g., U.S. EPA, 2000) for further information on statistical tests and terms.

Tests were performed by UCR on separate test days but at identical engine operating conditions to determine total particulate mass using a constant volume dilution sampling system meeting ISO 8178 requirements for particulate emission measurements. This is considered the international standard reference method for determining particulate mass emissions from mobile reciprocating internal combustion engines. Analysis similar to that above indicates that the ISO 8178 baseline results for 50 and 75 percent load are the same, so all the baseline test are pooled for the purpose of comparing methods. Based on a 2-sample t-test, the Alpha sampler and ISO 8178 sampler baseline results are the same at the 95 percent confidence level (Figure 7-2). However, the Alpha and Beta sampler results for DPF tests are biased low by approximately 25 percent compared to the ISO 8178 results, and the difference is significant (Figures 7-3 and 7-4). These differences warrant further investigation in future tests.

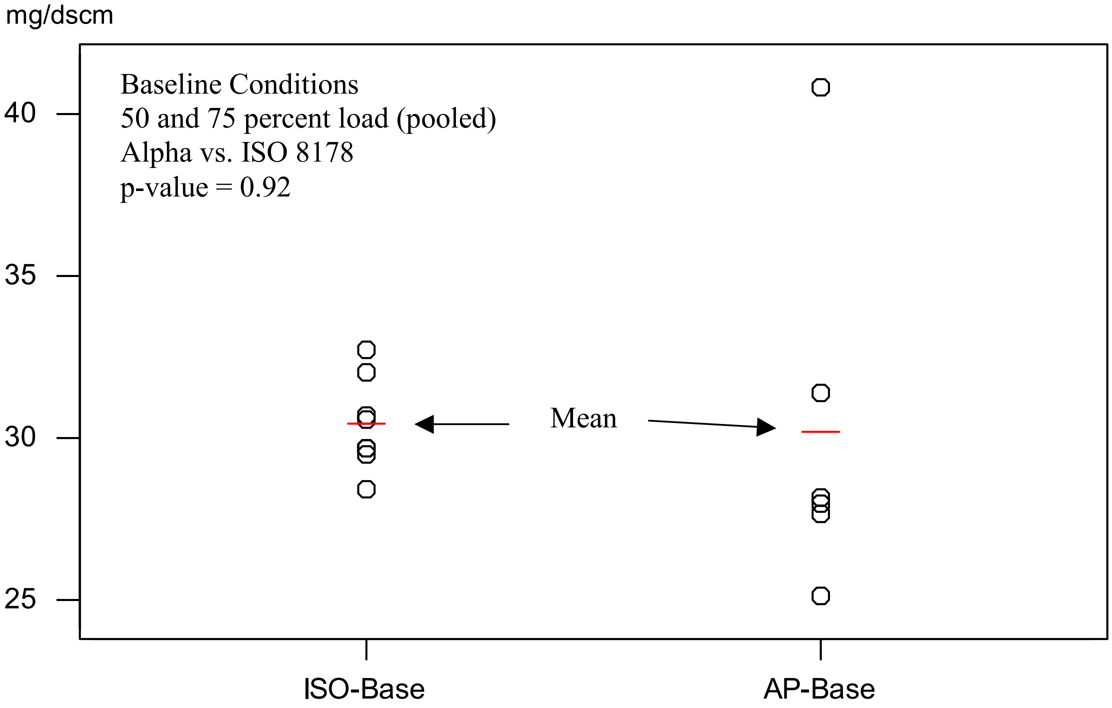

Figure 7-2. Comparison of Alpha Sampler results to ISO 8178 Results for Baseline Conditions (Site Foxtrot).

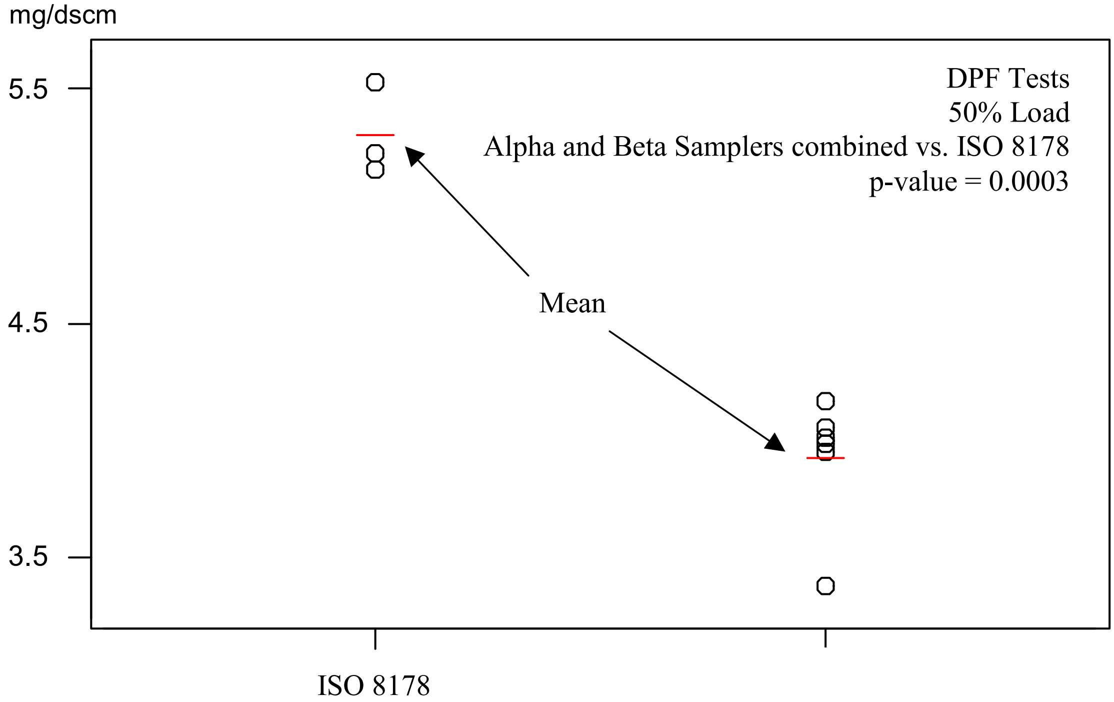

Figure 7-3. Comparison of Alpha/Beta Sampler Results to ISO 8178 Results for 50 percent Load DPF tests (Site Foxtrot).

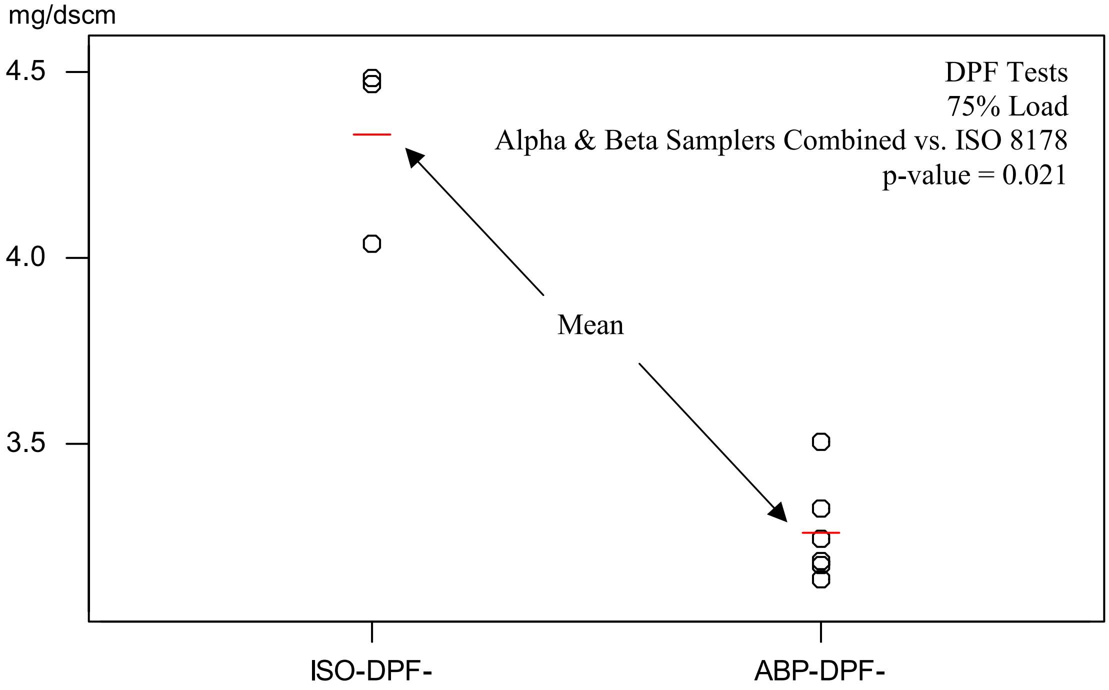

Figure 7-4. Comparison of Alpha/Beta Sampler Results to ISO 8178 Results for 75 percent Load DPF Tests (Site Foxtrot).

Precision

Precision can be assessed by calculating RSD for the Alpha and Beta sampler results, and by comparing the homogeneity of variances using the statistical F-test. Since the comparison between the two samplers is not valid for baseline test conditions (due to Beta sampler flow measurement error), the comparison is limited to the DPF test results. From Tables 4-4 and 4-5, the very low RSD of both the Alpha and Beta sampler PM2.5 mass results during the DPF tests indicates very good measurement precision. As a guide, EPA Method 301 specifies that the precision of an alternative method must be either equivalent to an accepted reference method (as established by homogeneity of variances using the statistical F-test at the 95 percent confidence level), and if they are not equivalent then the RSD must be less than 20 percent. F-test results performed for 50 percent load indicate the variances are significantly different (P-value less than 0.05); for 75 percent load, they are not (P-value greater than 0.05, Figure 7-5). The factor levels in the figure refer to the two data sets (Alpha and Beta). The highest RSD of the DPF tests for the Beta sampler is 12 percent, so the 20 percent criterion is easily met. A more rigorous series of tests to establish measurement precision relative to the Alpha sampler should involve at least 12 test runs, however these tests provide a preliminary indication that good measurement precision can be achieved in this application.

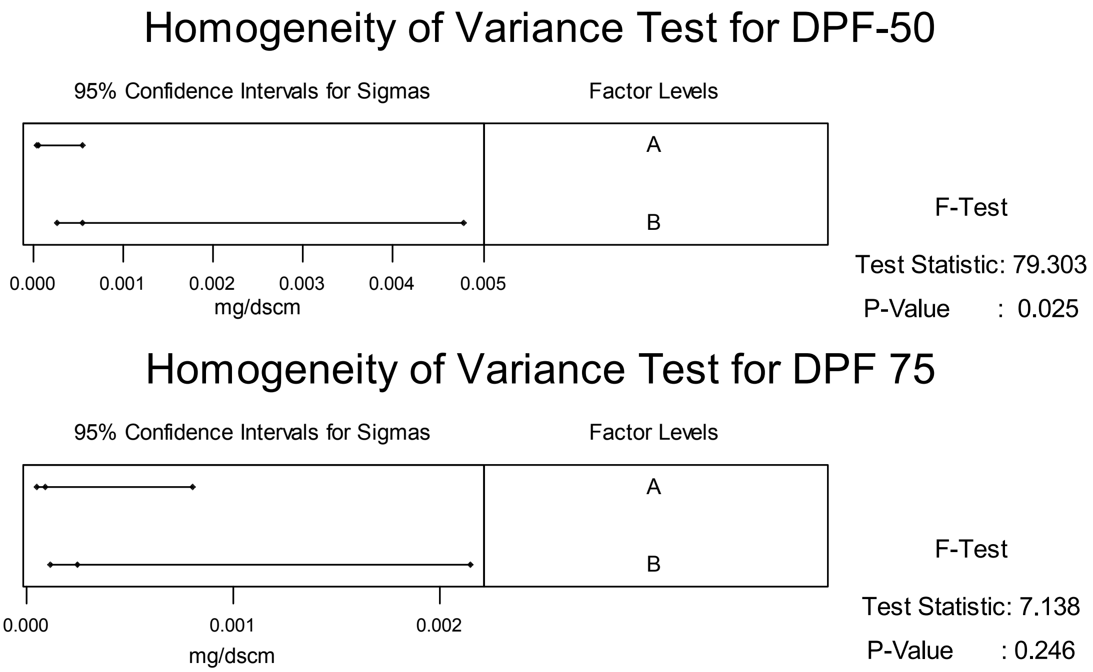

Figure 7-5. Comparison of Precision for Alpha and Beta Samplers (Site Foxtrot).

Particulate Carbon Measurements

EC is the largest component and OC is a minor component of PM2.5 measured by the dilution sampler. QFFs were used to collect PM that was then analyzed for OC and EC by TOR using the IMPROVE protocol. Previous studies have shown that OC measurements on QFFs are susceptible to an artifact: adsorption of VOCs onto the filter media and collected PM, and devolatilization of organic PM, with the adsorptive artifact dominating and causing a positive bias (Mazurek et al., 1993). In this test, a QFF was placed downstream of a TMF during sample collection and subsequently analyzed for OC and EC to determine the extent of the VOC artifact (Turpin, 1994). The OC collected on this filter may be used to evaluate the potential significance of the VOC artifact relative to the OC collected on the front-loaded (primary) QFF. This is commonly referred to as "backup OC". In some cases, this approach may overestimate the extent of the VOC artifact because the adsorptive capacity of the filter media itself and the collected particles can affect the amount of VOC adsorbed on the filter (Kirchstetter, 2001). 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.

In the tests at Site Foxtrot, the Backup Filter OC results show that there is a significant likelihood that part or all of the measured OC results from VOC adsorption artifacts. While OC comprises only a very small part of the particulate carbon emission from this engine, the results indicate the need for improved procedures for determining the organic carbon component of emissions.

Dilution Sampler Equipment and Method Improvements

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

- Direct measurement of Dilution Air Flow Rate. Dilution ratio accuracy is of first order importance in determining in-stack pollutant concentrations. In the current equipment arrangement for both the Alpha and Beta samplers, dilution air flow, and hence dilution ratio, is measured indirectly by difference, measuring the diluted sample bypass flow and the sample media flow rates, then subtracting the undiluted sample flow rate from the sum. The HiVol fan enclosure includes an orifice that is used to determine the diluted sample bypass flow rate. Since the orifice exit is open to the ambient surroundings, the readings can be affected by changes in local conditions. A direct measurement of dilution air flow rate using a calibrated venturi or flow orifice is recommended provide improved accuracy of dilution ratio under adverse conditions.

- Blanks/Contamination. Although the PM2.5 mass measurements in this test were generally not significantly affected by contamination, more blank results are needed to assess HEPA/activated carbon filter performance and life, and to assess lower quantification limits (LQLs) of the measurements. It is recommended that future tests include at least one, and preferably two, DSBs for all measured substances to assess the performance of the dilution air purification system. Procedural precautions to ensure adequate cleaning of the sampler and prevention of contamination should continue to receive special attention for gas-fired combustion sources.

- Precision and Accuracy. The results of this test are very encouraging with regard to method precision and accuracy. Results showed that particle deposits in the sample nozzle, probe and venturi were significant (7 to 49 percent of the value measured on the filters). In future tests, these deposits should be recovered after each test run to gain more complete information on uncertainty including these deposits. Although the Alpha and Beta samplers agreed well, they appeared to be biased low compared to ISO8178 results during DPF tests (but all gave similar results under baseline conditions). The cause of this difference is unresolved. After addressing probe deposit recovery, further evaluation of the overall method accuracy and precision is recommended for a more rigorous assessment of precision and accuracy. The statistical tests (paired sample t-test and F-test) used in analyzing these test results are conventionally used evaluating method performance, however a larger number of valid samples is recommended. Typically, 12 simultaneous paired samples under a single operating condition are considered statistically significant for establishing method performance. This was not feasible in the present test program due to time and budget constraints. Future test programs should consider a larger number of shorter runs for PM2.5 mass only. Paired sampling train tests should include two Beta-type samplers with analyte spiking for evaluating bias, or one Beta sampler and one Alpha sampler using the Alpha sampler as the validated test method reference. Future tests on Diesel engines comparing either the Alpha or Beta sampler design to ISO 8178 results also would be useful for investigating apparent differences under certain test conditions.

PROCESS OPERATION – PARAMETRIC EFFECTS

Tests were conducted at 50 and 75 percent load for both baseline and DPF test conditions. For baseline conditions, only the Alpha sampler results are valid. Comparing results using the 2-sample t-test, baseline PM2.5 mass concentrations are not significantly different for the two load conditions (p-value greater than 0.05, Figure 7-6).

Tests conducted with the DPF installed showed that the Alpha and Beta sampler results are the same. Comparing the combined Alpha and Beta results for 50 and 75 percent load, PM2.5 mass concentration at 75 percent load is clearly significantly lower than at 50 percent load (Figure 7-7). This is probably related to higher engine exhaust temperatures at the higher load, resulting in higher particulate reduction efficiency in the DPF.

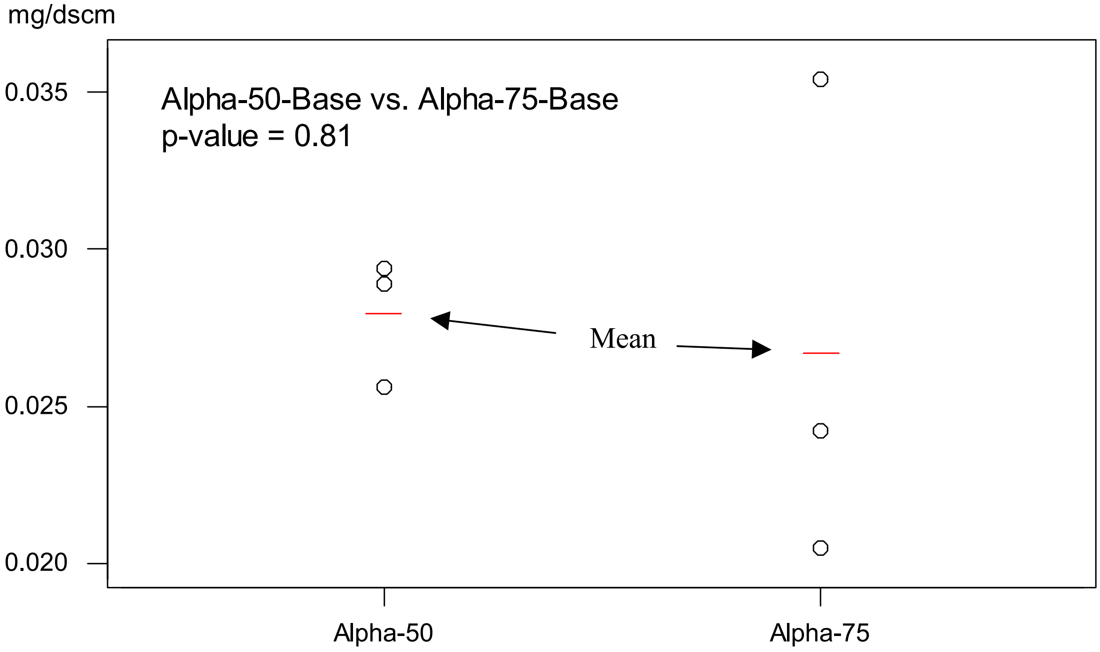

Figure 7-6. Comparison of High and Low Load Baseline PM2.5 Mass Results (Site Foxtrot).

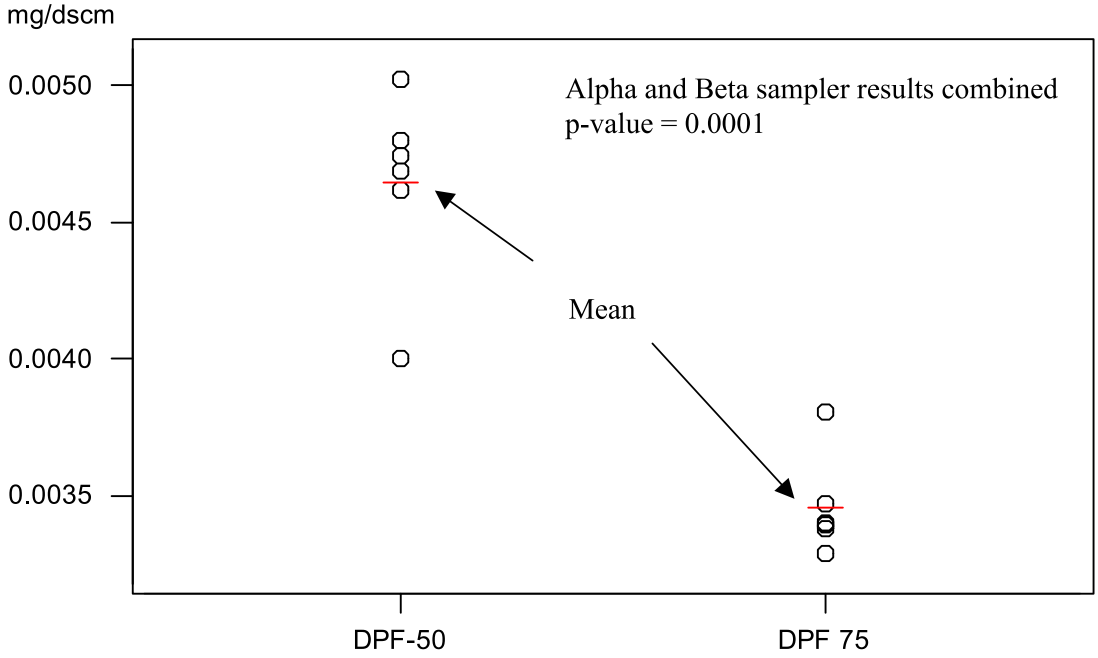

Figure 7-7. Comparison of High and Low Load PM2.5 Mass Results with DPF (Site Foxtrot).

FINDINGS

The main findings of this test are:

- PM2.5 mass emissions measured using a new, more compact dilution sampler are in good agreement (within 7 percent, on average) with the benchmark sampler design originally developed by Hildemann et al. in terms of accuracy and precision. The bias is not significant at the 95 percent confidence level, and precision of both samplers is similar. This provides preliminary validation of the design criteria used to modify the original Hildemann concept into a smaller, lighter sampler that is more practical for routine stationary source emission testing. More rigorous validation tests using paired sampling trains and a larger number of test runs are recommended.

- Particle deposits in the sample nozzle, probe and venturi were found to be significant and should be recovered separately in every run of future tests. When probe deposits are taken into account, the results from two research dilution samplers agree well with results from an ISO 8178 constant volume dilution sampler under high particulate loading conditions but appear to be biased low by approximately 25 percent under low particulate loading conditions. Further evaluation of the research sampler designs is recommended to address these differences.

- Elemental carbon accounts for approximately 66 to 78 percent of particulate carbon under baseline conditions (without DPF) and 81 to 85 percent of particulate carbon with the DPF.

- Increasing load from 50 to 75 percent did not affect PM2.5 mass concentration under baseline conditions, but decreased PM2.5 mass with the DPF. The DPF PM2.5 mass reduction efficiency was approximately 83 percent at 50 percent load and 87 percent at 75 percent load. The influence of load on PM2.5 mass with the DPF is probably attributable to the influence of exhaust temperature on DPF performance.

- Sulfate and nitrate were detected at concentrations near the detection limits under some conditions. They contributed less than 2 percent to total PM2.5 mass. Chloride, ammonium and other ions were not detected in the samples.

- Based on backup filter OC measurements, OC results are probably biased high due to VOC adsorption artifacts associated with the quartz fiber filters. The results suggest bias may account for most or all of the measured OC. Further development of OC measurement procedures is needed for reliable OC results.

- Number concentration of ultrafine particles peaked at about 65 to 75 nm. The size mode was the same with and without the DPF installed.

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APPENDIX A: LIST OF ABBREVIATIONS

<	less than the detection limit
°	degree
°C	degrees Celsius
°F	degrees Fahrenheit
µg	micrograms
µg/cm^2	micrograms per square centimeter
µm	micrometers
API	American Petroleum Institute
ARB	(California) Air Resources Board
Btu	British thermal unit
CEC	California Energy Commission
CE-CERT	UCR Bourns College of Engineering Center for Environmental Research and Technology
CEMS	continuous emissions monitoring system
CIT	California Institute of Technology
Cl^-	chloride ion
CO	carbon monoxide
CO_2	carbon dioxide
CPC	condensation particle counter
CPM	condensable particulate matter
DI	distilled deionized
DMA	differential mobility analyzer
DOE	United States Department of Energy
Dp	particle diameter
DPF	Diesel particulate filter
DRI	Desert Research Institute
DSB	dilution sampler blank
EC	elemental carbon
EPA	Environmental Protection Agency
FB	field blank
GE	General Electric
GE EER	GE Energy and Environmental Research Corporation
GE MPA	GE Mostardi Platt Associates
GRI	Gas Research Institute
H_0	null hypothesis
HEPA	high efficiency particulate arrest
HP	horse power
hp-hr	horse power-hour
ISO	International Organization for Standardization
kW	kilowatt
lb/hr	pounds per hour
lb/MMBtu	pounds of pollutant per million British thermal units of gas fired
L/min	liters per minute

LQL	lower quantification limits
MDL	method detection limit
mg	milligram
mg/dscm	milligrams per dry standard cubic meter
mL	milliliter
mL/min	milliliter s per minute
mm	millimeter
MMBtu/hr	million British thermal units per hour
MW	megawatt
Na^+	sodium ion
NAAQS	National Ambient Air Quality Standards
NCR	National Research Council
NETL	National Energy Technology Laboratory
NH_4^+	ammonium ion
nm	nanometer
NO	nitric oxide
NO_2	nitrogen dioxide
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
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 μm
PM2.5	particulate with aerodynamic diameter less than 2.5 μm
ppm	parts per million
QFF	quartz fiber filter
RH	relative humidity
RSD	relative standard deviation
S	sulfur
sLpm	standard liters per minutes
SMPS	scanning mobility particle sizer
$SO_4^=$	sulfate ion
SVOC	semivolatile organic compound
TC	total carbon
TMF	Teflon-membrane filter
TOR	thermal/optical reflectance
TSI	Thermo Scientific Incorporated
UCR	University of California at Riverside
VOC	volatile organic compound

APPENDIX B: SI CONVERSION FACTORS

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