

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

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## FOREWORD

In 1997, the United States Environmental Protection Agency (EPA) promulgated new ambient air standards for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM<sub>2.5</sub>). 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from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and/or incomplete.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. The current program was jointly funded by the U.S. Department of Energy National Petroleum Technology Office (DOE/NPTO), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) to provide improved measurement methods and reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM<sub>2.5</sub> concentrations.

The goals of this program were to:

- Develop stationary combustion source emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for sources in the oil, gas, and power generation sectors;
- Identify and characterize PM<sub>2.5</sub> precursor compound emissions from stationary combustion sources; and
- Develop improved dilution sampling technology and methods for PM<sub>2.5</sub> mass and speciation measurements.

## ABSTRACT

This report provides results from the second year of this three-year project to develop dilution measurement technology for characterizing PM<sub>2.5</sub> (particles with aerodynamic diameter smaller than 2.5 micrometers) and precursor emissions from stationary combustion sources used in oil, gas and power generation operation. Detailed emission rate and chemical speciation tests results for a gas turbine, a process heater, and a commercial oil/gas fired boiler are presented. Tests were performed using a research dilution sampling apparatus and traditional EPA methods. A series of pilot tests were conducted to identify the constraints to reduce the size of current research dilution sampler for future stack emission tests. Based on the test results, a bench prototype compact dilution sampler developed and characterized in GE EER in August 2002.

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## SI UNIT CONVERSION FACTORS

	<u>English (US) units</u>	X	<u>Factor</u>	=	<u>SI units</u>
Area:	1 ft <sup>2</sup>	x	9.29 x 10 <sup>-2</sup>	=	m <sup>2</sup>
	1 in <sup>2</sup>	x	6.45	=	cm <sup>2</sup>
Flow Rate:	1 gal/min	x	6.31 x 10 <sup>-5</sup>	=	m <sup>3</sup> /s
	1 gal/min	x	6.31 x 10 <sup>-2</sup>	=	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 <sup>2</sup>	=	g
	1 lb	x	0.454	=	kg
	1 gr	x	0.0648	=	g
Volume:	1 ft <sup>3</sup>	x	28.3	=	L
	1 ft <sup>3</sup>	x	0.0283	=	m <sup>3</sup>
	1 gal	x	3.785	=	L
	1 gal	x	3.785 x 10 <sup>-3</sup>	=	m <sup>3</sup>
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

Section 1  
EXECUTIVE SUMMARY

This annual report describes the work undertaken in the second year of the project.

Accomplishments during this period include:

- The second Ad-Hoc committee meeting was held in February, 2002, Irvine, California.
- Execution of PM<sub>2.5</sub> emissions characterization tests to (a) develop emissions profiles and (b) compare traditional and EPA test methods on a gas turbine
- Planning and execution of PM<sub>2.5</sub> emissions characterization tests on to (a) develop emissions profiles and (b) compare traditional and EPA test methods on
  - a process heater.
  - a commercial oil/gas fired boiler
- Conducting pilot tests to define the design criteria for next generation dilution tunnel.
- Development and evaluation of the next generation dilution tunnel.
- Technology transfer activities including presentation at several conferences.

Findings

Tests on a refinery gas-fired process heater at a coastal refinery were performed. The main findings from these tests are:

- Particulate mass emissions from the natural gas combustors were extremely low, consistent with levels expected for gaseous fuel combustion.
- Two methods for determining the average emissions factors for primary PM<sub>2.5</sub> mass gave results, which differ an order of magnitude lower from using dilution method than conventional in stack methods for filterable and condensable particulate.
- Sampling and analytical artifacts principally caused by gaseous SO<sub>2</sub> in the stack gas were shown to produce a relatively large positive bias in condensable particulate as measured by conventional in-stack methods. These measurement artifacts can explain most of the difference between the dilution tunnel and conventional method results. The results using conventional EPA methods are nominally consistent with published EPA emission factors for external combustion of natural gas (U.S. EPA, 1998). Therefore, the published EPA emission factors derived from tests using similar measurement methods also may be positively biased.

- Chemical species account for 2~3 times of the measured PM<sub>2.5</sub> mass were quantified.
- Organic and elemental carbon comprise approximate 80-90 % of the primary PM<sub>2.5</sub> mass measured by the dilution tunnel.
- Most elements are not present at levels significantly above the background levels in the ambient air or the minimum detection limits of the test methods.
- Most organic species are not detected at levels significantly above background levels in the ambient air or field blanks. All detected organics are present at extremely low levels consistent with gaseous fuel combustion.
- Emissions of secondary particle precursors are low and consistent with levels expected for gaseous fuel combustion.
- PM<sub>2.5</sub> emissions from the boiler were more than an order of magnitude higher when firing No. 6 oil than natural gas.
- For oil firing, the predominant component of the PM<sub>2.5</sub> is sulfate and higher percentages of Ni and V in oil combustion, reflecting the fuel content differences of No. 6 oil compared to natural gas.
- The Phase I and II pilot tests, which characterized the design criteria for smaller and more compact dilution sampler showed that very similar ultrafine particle size distributions measured at residence time of 10 and 80 seconds. The lifetime of ultrafine particle is very short, in the order of a few seconds.
- A minimum dilution air ratio of 20 was found to be sufficient to dilute the sample air and maintain the same distribution of particle number concentrations.
- The minimum dilution air ratio and residence time needed for condensable particulate formation does not depend on fuel type.

## Conclusions

- Primary PM<sub>2.5</sub> emissions from gas-fired external combustion sources are extremely low, at or below the practical quantification limits of traditional test methods.
- Dilution sampling provides more reliable PM<sub>2.5</sub> mass and chemical speciation results for gas-fired external combustion sources.
- Primary PM<sub>2.5</sub> emissions from external combustion sources are dominated by organic carbon.
- Condensable PM<sub>2.5</sub> mass concentration measured using traditional test methods based on hot filters and impinger trains (e.g., US EPA Methods 201A/202) is probably biased high due to artifacts from conversion of gaseous species, especially SO<sub>2</sub>, and oversaturation of condensable vapor species compared to the stack plume. Chemical speciation using traditional methods overstates the

significance of sulfates due to these artifacts. Therefore, PM<sub>2.5</sub> source apportionment, visibility impacts, and health risk assessments should be based on data obtained from dilution sampling.

- Because of sampling artifacts, chemical speciation results obtained using dilution sampling methods should never be applied to emission factors obtained using traditional stack test methods.
- Based on the Phase I & II pilot test results, it is feasible to design a more compact dilution sampler for stationary emission sampling.

## Section 2

### INTRODUCTION

This project is developing and implementing test technology and methods for characterizing fine particulate emissions from stationary combustion sources used in oil and gas (upstream and downstream) and power generation operations. Emission factors and chemical speciation profiles for several source types are being generated for PM<sub>2.5</sub> (particles with aerodynamic diameter smaller than 2.5 micrometers) and its precursors including VOC, SVOC, OC/EC, NO<sub>x</sub>, SO<sub>2</sub>, ammonia, sulfates, nitrates, ammonium, and 40 elements. Previous tests demonstrated that current regulatory methods for fine particulate matter were inadequate, especially when applied to gas-fired sources, and that a dilution sampling technique could provide better source characterization data. Therefore, the project is developing improved dilution sampling technology and methods. The U.S. Department of Energy National Petroleum Technology Office (NPTO), Gas Technology Institute (GTI), American Petroleum Institute (API), California Energy Commission (CEC), the New York State Energy Research and Development Authority (NYSERDA), and GE EER have agreed to cofund the project.

#### MOTIVATION FOR THE PROJECT

EPA promulgated new national ambient air quality standards (NAAQS) for PM<sub>2.5</sub> in 1997. Implementation of the PM<sub>2.5</sub> NAAQS was delayed for five years to allow collection of ambient air PM<sub>2.5</sub> data through a national monitoring network and further research into human health risk associated with PM<sub>2.5</sub>. In 1998, Congress directed EPA to arrange an independent study by The National Research Council (NRC) to identify the most important research priorities & develop a conceptual research plan relevant to setting particulate matter standards. The NRC Committee on Research Priorities for Airborne Particulate Matter identified 1 of the 10 top research priorities for fine particulate studies as "...the characterization of emissions sources...acquisition of emissions data that will be needed to formulate emissions management strategies...measurement method comparisons." Beginning in early 2003 states will be required to develop State Implementation Plans (SIPs) for achieving the PM<sub>2.5</sub> NAAQS. The existing source emissions data needed to do this are far from complete or accurate. The methodology and data generated in the proposed program will improve the reliability of PM<sub>2.5</sub> emission

inventories used in source apportionment modeling, and thereby enable industry & regulatory decision makers to develop better PM<sub>2.5</sub> attainment strategies.

## PROJECT APPROACH

The focus of the project includes two main tracks:

- Method Development. The development of dilution tunnel measurement protocols to characterize the size distribution, chemical composition, & emission rates of primary particles & reactive gases that lead to particle formation by atmospheric chemical reactions.
- Source Characterization Tests. Once developed & tested, these measurement methods will have to be applied to a large number of sources to collect the data needed to design successful management strategies. A total of 9 to 12 source tests are planned.

The overall schedule for the project is:

Year 1: Source Characterization (existing dilution system);

Year 2: Method development and source characterization (existing and new dilution systems);

Year 3: Source characterization (new dilution system) and database.

The project approach consists of six tasks (Figure 2-1):

- Task 1 – Method Definition. In this task, GE EER will conduct a series of tests on a pilot-scale combustor to investigate the effect of dilution tunnel design parameters on results under a wide range of simulated source conditions. These results will be used to develop and build a more portable, less costly dilution tunnel design – the next generation of the CalTech design developed in the late 1980's by Hildemann et al. and later improved by Desert Research Institute (DRI). The draft API generic test protocol developed in Phase 1 of the API fine PM project will be revised and updated based on recent test results and developments in sampling technology. The dilution tunnel design and sampling test protocol also will be drafted and proposed to a consensus based standards organization such as ASTM or ASME.
- Task 2 – Source Characterization. This task will provide for field tests on at least six oil & gas industry emission sources. In addition to characterization of source emissions contributing to ambient PM<sub>2.5</sub>, the tests will be designed to include comparisons of method performance against existing regulatory reference methods. This will provide both new, original data on source emissions characteristics for different source types and increased acceptance of the test

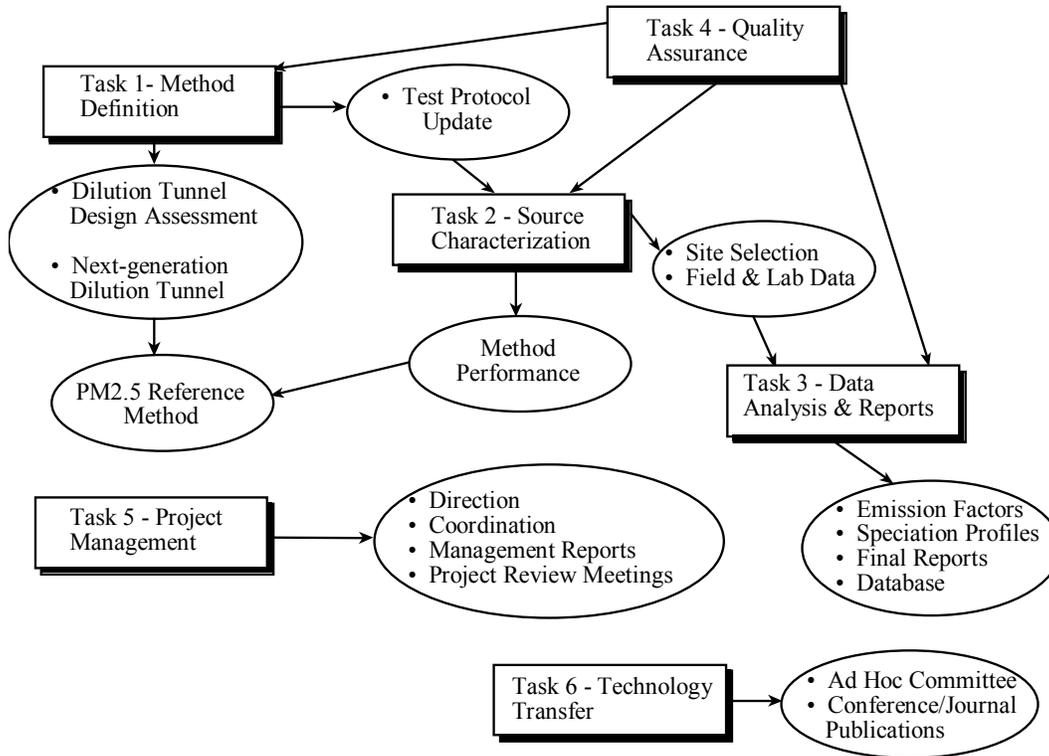


Figure 2-1. Project approach.

method among the regulatory community. A preliminary “strawman” of sites being considered for testing is provided in Table 2-1. A total of 9 to 11 sources are currently planned, depending on the final test plan for each unit. For selected sites (e.g. gas turbines), tests will include characterization of low load and startup conditions in addition to base load.

- Task 3 – Data Analysis & Reports. This task will provide for reduction of field and laboratory test results and preparation of project reports. A database of test results from this project and selected external projects also will be developed as the beginning of an industry-specific tool for estimating emissions from industry sources. The database format will be based on the API-WSPA petroleum industry air toxics emission factor database previously developed by GE EER.

Table 2-1. "Strawman" Site Selection.

Combined Cycle plant without Post Combustion NO <sub>x</sub> Controls
Combined Cycle plant with Post Combustion NO <sub>x</sub> Controls
Simple Cycle Gas Turbine
Combined Cycle plant with supplementary firing
Lean Burn Reciprocating Engine
Refinery Process Heater with NO <sub>x</sub> Controls
Refinery Process Vents (FCCU, SRU, CRU)
Refinery Process Heater without NO <sub>x</sub> Controls
Refinery Boiler with NO <sub>x</sub> Controls
Refinery Combined Cycle Cogen
Gas Fired Utility Boiler
Residual Oil Fired Utility Boiler
Dual-Fuel Fired Commercial Boiler – Albany, New York

- Task 4 – Quality Assurance. It is critical that the quality of the data produced in this project is both known and commensurate with its intended use. This task will provide for quality assurance/quality control activities necessary to accomplish this objective.
- Task 5 – Project Management. This task will provide for DOE project management reports, topical progress reports, and a comprehensive final report on project findings.
- Task 6 – Technology Transfer. For these data to be of greatest benefit for the oil and gas industry, it is important that the results be available in the open literature and that opportunities for peer review of the results are provided. This task will provide for: conference and journal publications; and Ad Hoc Committee meetings of academic, industry, and regulatory agency peers to help guide project direction.

## Section 3 FIELD TEST PROTOCOL

The emissions testing included simultaneous collection and analysis of both in-stack and diluted stack gas samples. An overview of the sampling and analysis procedures is given in Table 3-1. Dilution tunnel testing and in-stack testing were performed concurrently. All samples were collected at points of average flow through their respective ports. Process data and fuel gas samples were collected during the tests to document operating conditions.

### STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

An S-type Pitot tube (EPA Method 2) was used to determine the average stack gas velocity and volumetric flow rate. Stack gas molecular weight was calculated in accordance with EPA Method 3. Moisture content of the sample was determined based on weight gain of the impingers used in the Method 201A/202 train according to EPA Method 4. A full velocity traverse of the stack was performed before and after each test to determine total stack gas flow rate.

### O<sub>2</sub>, CO<sub>2</sub>, CO, AND NO<sub>x</sub>

Major gases and pollutant concentrations in the stack sample were monitored using the plant's continuous emission monitoring system (CEMS), which is operated and maintained in accordance with EPA 40 CFR 60 Appendix B.

### IN-STACK METHOD TESTS

Total particulate, PM<sub>10</sub> and PM<sub>2.5</sub> filterable at stack temperature were determined using in-stack methods. CPM, defined as the material collected in chilled impingers, also was measured for the in-stack samples.

Table 3-1. Summary of Test Procedures.

Sampling Location	Measurements	Sampling Approach	Sample Analyses	Reference
S1 (Stack)	Total PM, PM10, PM2.5 and composition	In-stack series cyclones and filter	Mass; organic species	U.S. EPA Method PRE-4 (preliminary method)
	Condensable PM and composition	Impingers	Mass (organic and inorganic), sulfate, chloride, nitrate, ammonium, elements	U.S. EPA Method 202
S1 (Stack)	PM2.5 mass and chemical composition	Dilution tunnel and filters	Mass, organic carbon (OC), elemental carbon (EC), elements, sulfate, nitrate, chloride, ammonium	U.S. EPA, 1999a; Hildemann et al., 1989
	Gaseous PM2.5 precursors	Dilution tunnel and K <sub>2</sub> CO <sub>3</sub> -impregnated cellulose-fiber filter	Ammonia	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution tunnel and citric acid-impregnated cellulose-fiber filter	Sulfur dioxide	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution tunnel and Tenax	Speciated VOC (C7 and greater)	Zielinska et al., 1996; Hildemann et al., 1989
	Gaseous PM2.5 precursors	Dilution tunnel and stainless steel canisters	Speciated VOC (C2 and greater)	US EPA Method TO-15
	Gaseous PM2.5 precursors	Dilution tunnel and DNPH-coated silica gel cartridges	Carbonyls	UP EPA Method TO-11A
	SVOC	Dilution tunnel and filter/PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO-13; Hildemann et al., 1989
S2 (Ground level – ambient air)	PM2.5 and chemical composition	Filters	Mass, OC, EC, elements, chloride, sulfate, nitrate, ammonium	U.S. EPA, 1999a
	Gaseous PM2.5 precursors	Dilution tunnel and potassium carbonate-impregnated cellulose-fiber filter	Ammonia	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution tunnel and citric acid-impregnated cellulose-fiber filter	Sulfur dioxide	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution tunnel and Tenax	Speciated VOC (C7 and greater)	Zielinska et al., 1996; Hildemann et al., 1989
	Gaseous PM2.5 precursors	Dilution tunnel and stainless steel canisters	Speciated VOC (C2 and greater)	US EPA Method TO-15
	Gaseous PM2.5 precursors	Dilution tunnel and DNPH-coated silica gel cartridges	Carbonyls	UP EPA Method TO-11A
	SVOC	Dilution tunnel and filter/PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO-13; Hildemann et al., 1989
S3 (Fuel gas feed to heater)	Fuel gas composition	Integrated grab sample (Tedlar bag)	Hydrocarbon speciation, CHON, sulfur content and heating value	ASTM D3588-91

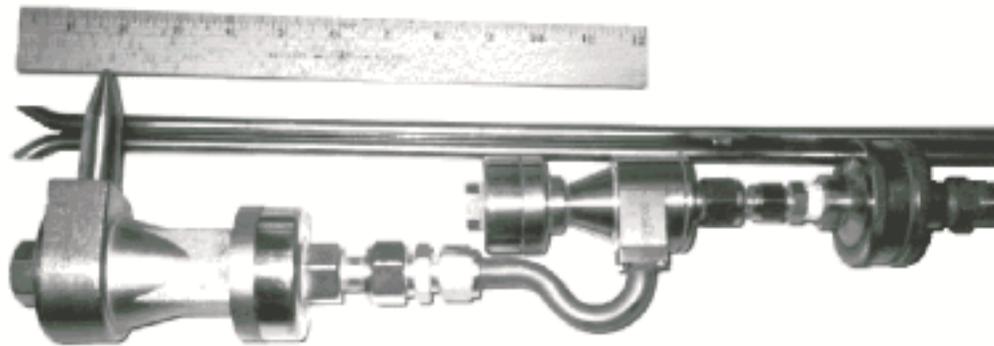
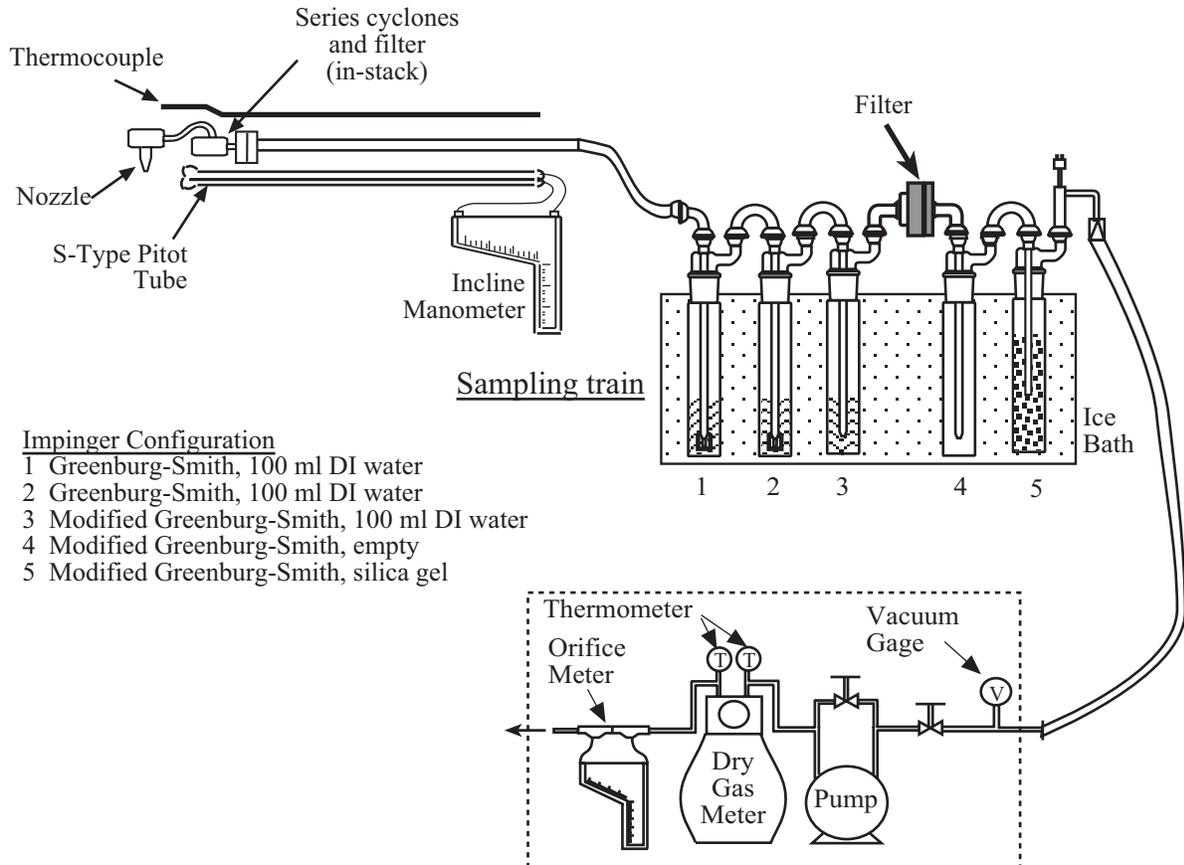
### In-Stack Total Filterable PM, PM10 and PM2.5

EPA Preliminary Method PRE-4 was used to measure total PM, PM10 and PM2.5. The method uses two in-stack cyclones (Andersen Model Case-PM10 and Case-PM2.5), the first with a cut point of 10 microns and the second with a cut point of 2.5 microns, followed by an in-stack filter in series (Figure 3-1). The sampling time was six hours for each of the four runs. Sampling was performed according to the methods as published except for the following modifications and clarifications:

- The sample was collected from a single traverse point near a point of average velocity to preserve the integrity of the dilution tunnel method comparison. It is assumed that any particulate present is small enough to mix aerodynamically in the same manner as a gas; therefore, the magnitude of the particle concentration profile was assumed to be no greater than the gas concentration profile;
- A modified filter assembly was employed in an effort to improve the precision of the gravimetric analysis for low particulate concentration. An o-ring, a filter and a filter support are all placed together in an aluminum foil pouch and weighed as a unit. All three components are recovered together into the same foil pouch after sampling to minimize negative bias due to filter breakage.

A second particulate train was run in order to compare the effect of post-test purging on the CPM catch. The front half of the second train was performed in accordance with EPA Method 17, which uses an in-stack filter to determine total particulate emissions. The back half of this train was identical to the back-half of the EPA Method PRE-4 train.

The particulate mass collected in the two cyclones and on the filter was determined gravimetrically. The filters (Pallflex No. 51575) were weighed before and after testing on an analytical balance with a sensitivity of 10 micrograms. In an effort to improve the accuracy and precision of the gravimetric results, the filters, filter support and stainless steel O-ring seals were weighed together to minimize post-test loss of filter matter during sample recovery. Pre- and post-test weighing was performed after drying the filters in a dessicator for a minimum of 72 hours, and then repeat weighings were performed at a minimum of six-hour intervals until constant weight to within 0.5 milligrams was achieved. Probe and cyclone acetone rinses were recovered in glass sample jars for



Series cyclone and filter assembly

Figure 3-1. PM10/PM2.5 Train Configuration for Method PRE-4/202.

storage and shipment, and then transferred to tared beakers for evaporation and weighing. Acetone and filter blanks also were collected and analyzed. See Section 4 for discussion of data treatment.

#### Condensable Particulate Matter Mass and Chemical Analysis

CPM was determined using EPA Method 202; total sampling time was six hours for all runs. After the in-stack filter for the Method PRE-4 train, the sample passed through a heated Teflon<sup>®</sup> line to a series of four impingers placed in the ice bath. Impingers 1 and 2 were standard Greenburg-Smith impingers containing DI water; the third was a modified Greenburg-Smith impinger containing DI water; the fourth was an empty modified Greenburg-Smith impinger; and the fifth contained silica gel. A quartz filter was placed between the third and fourth impingers to improve capture efficiency for any aerosols that may have passed the first three impingers. In order to examine the effect of a post-test nitrogen purge on CPM collected by Method 202, the impinger train of the EPA Method PRE-4 assembly was purged with nitrogen for one hour at the conclusion of each test run to eliminate dissolved SO<sub>2</sub>. The impinger train of the EPA Method 17 assembly was not purged. The contents of both impinger trains were recovered separately with distilled deionized (DI) water followed by dichloromethane.

Previous tests (England et al., 2000) found that a majority of the particulate matter emissions from gas-fired sources consists of CPM. To obtain an understanding of the composition of the material collected in the impingers, additional analysis of the inorganic CPM residue was performed to speciate its constituents. The inorganic residue was resuspended in DI water and analyzed for anions and cations (bromide, chloride, fluoride, nitrate, phosphate and sulfate) by ion chromatography, for ammonium by colorimetry, and for metals by digesting the sample in acid and analyzing by inductively coupled plasma – mass spectrometry (ICP/MS). Figure 3-2 illustrates the Method 202 analytical procedure and additional analyses performed.

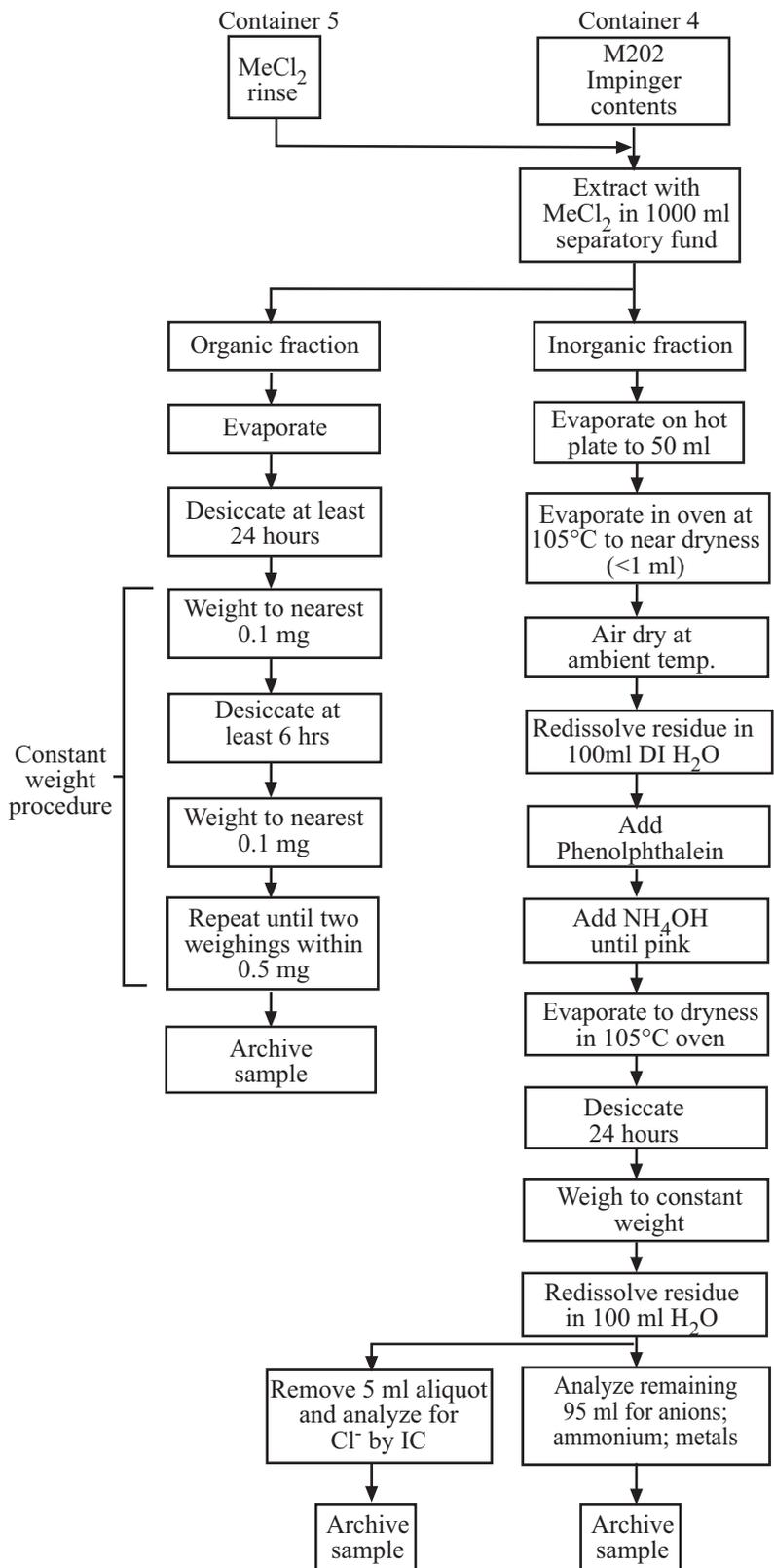


Figure 3-2. Modified Method 202 Sample Analysis Procedure.

## DILUTION TUNNEL TESTS

PM2.5 mass and chemical speciation in the stack gas was determined using a dilution tunnel (Figure 3-3). A stainless steel probe with a buttonhook nozzle was used to withdraw the stack gas sample at a rate of approximately 25 liters per minute. The sample was transported from the probe through a heated copper line into the dilution tunnel. Ambient air is drawn through a HEPA filter and a carbon filter, then through a Venturi where it is mixed with the stack gas. The mixture is then drawn through a Hi-Vol Pump and a Flow Sensor (orifice) into a Residence Time Chamber containing PM2.5 Cyclones. The sample is then directed to various Sample Collection Trains for analysis.

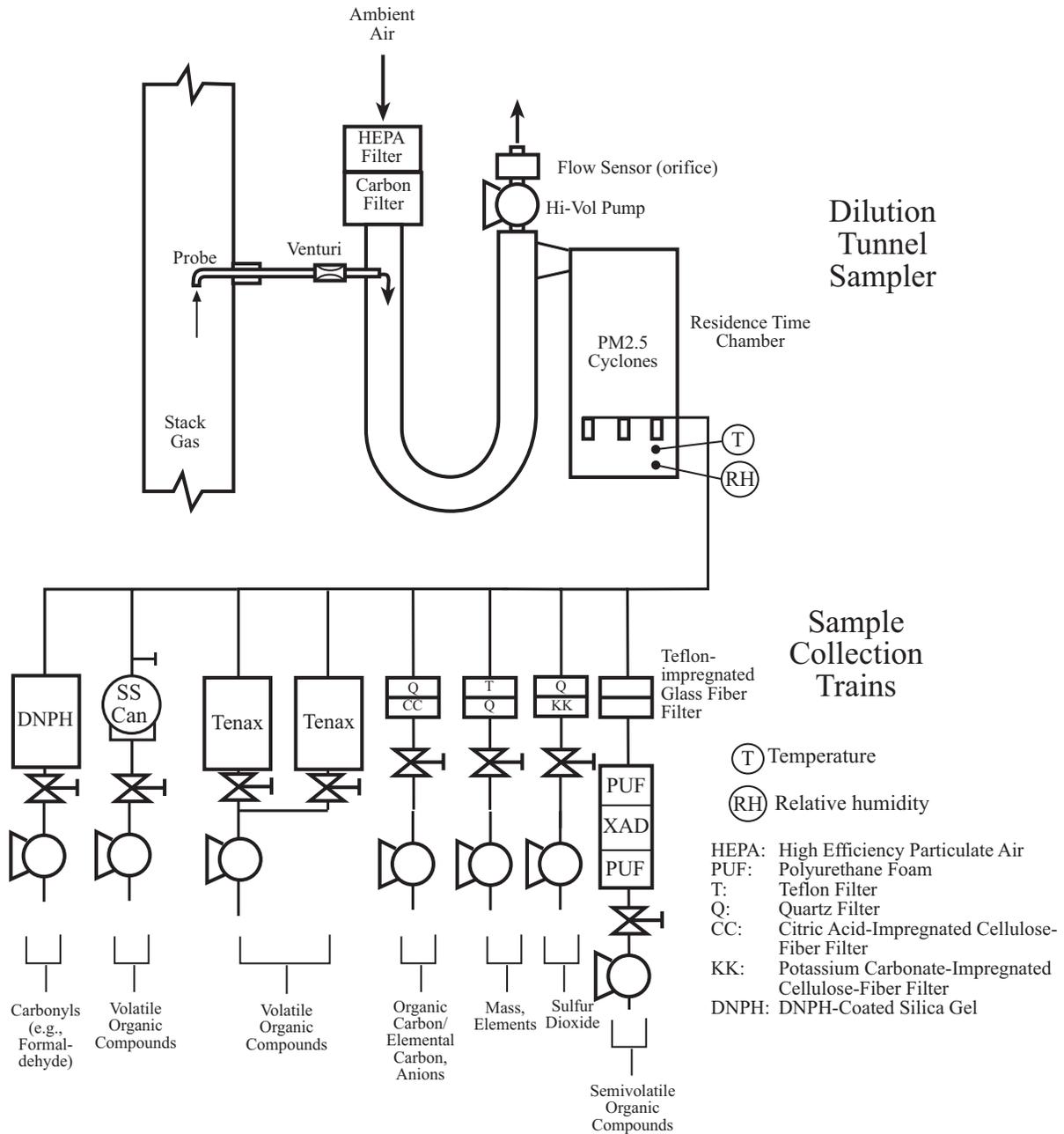


Figure 3-3. Dilution Tunnel Sampling System.

The sample was mixed in the tunnel 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 air (HEPA) filter to remove particulate matter and an activated carbon bed to remove gaseous organic compounds. After passing through a tunnel length equal to 10 tunnel diameters, approximately 50 percent of the diluted sample was withdrawn into a large chamber, where the sample aged for approximately 70 seconds to allow low-concentration aerosols (especially organic aerosols) to fully form. The aged sample was withdrawn through a sampling manifold of three cyclone separators to remove particles larger than 2.5  $\mu\text{m}$  into a sampling module to provide a uniform gas stream for the sample collection media (TMF, quartz filter,  $\text{K}_2\text{CO}_3$ -impregnated cellulose-fiber filter, citric acid-impregnated cellulose-fiber filter, Tenax tubes, DNPH-coated silica gel cartridges, stainless steel canisters and TIGF/PUF/XAD-4/PUF cartridge). The sample flow rate through the probe was monitored using a venturi flow meter and thermocouple. The venturi velocity head was measured continuously during the test using a pressure transducer and a Magnehelic<sup>®</sup> gauge. An S-type Pitot tube with electronic pressure transducer and thermocouple were used to monitor the velocity in the stack. The thermocouples and pressure transducers were connected to a laptop computer data acquisition system. The dilution airflow and backpressure were adjusted to maintain the target dilution ratio and sample flow rates. Total sampling time for each test run was six hours.

For these tests, flow rates were set in the field to achieve a target dilution ratio of approximately 20:1 (air:exhaust) to improve minimum detection limits since very low concentrations of the target substances were anticipated. The prior work of Hildemann et al. (1989) suggests that mixing between the sample and the dilution air begins to degrade below a dilution ratio of approximately 10:1.

A single ambient air sample was collected using the dilution tunnel. The dilution tunnel setup was modified by attaching a three-cyclone manifold (similar to the one inside the residence time chamber) directly to the sampling module. The ambient air sample was drawn into the module without dilution for a sampling period of six hours. The same sampling media were used as described below and in Figure 3-3.

### PM2.5 Mass

Samples for PM2.5 mass measurements were collected on a 47-mm diameter polymethylpentane ringed, 2.0 µm pore size, TMF (Gelman No. RPJ047) placed in a two-stage Savillex filter holder. The filter packs were plugged directly into the bottom of the sampling module to ensure that no handling of the filters was required in the field. The flow rate through the filter was set prior to sample collection and checked after sample collection by placing a calibrated rotameter on the inlet side of the filter pack and setting the position of the needle valve to achieve the desired flow rate. Weighing was performed on a Cahn 31 electro-microbalance with  $\pm 1$  microgram sensitivity.

### Elements

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

A KeveX Corporation Model 700/8000 ED-XRF analyzer with a side-window, liquid-cooled, 60 kilo electron volts (keV), 3.3 milliamp rhodium anode x-ray tube and secondary fluorescers was used. The silicon detector had an active area of 30 square millimeters, with a system resolution better than 165 electron volts (eV). The analysis was controlled, spectra were acquired, and elemental concentrations were calculated by software on a microcomputer, which was interfaced to the analyzer. Five separate XRF analyses were conducted on each sample to optimize the detection limits for the specified elements. The filters were removed from their petri slides and placed with their deposit sides downward into polycarbonate filter cassettes. A polycarbonate retainer ring kept the filter flat against the bottom of the cassette. The cassettes were loaded into

a carousel in the x-ray chamber. The sample chamber was evacuated to  $10^{-3}$  Torr. A computer program controlled the positioning of the samples and the excitation conditions.

#### Sulfate, Nitrate, Chloride and Ammonium

Samples for determining water-soluble  $\text{Cl}^-$ , nitrate ( $\text{NO}_3^-$ ), and  $\text{SO}_4^{=}$  were collected on quartz fiber filters. The flow rate through the filter was set prior to sample collection and checked after sample collection by placing a calibrated rotameter on the inlet side of the filter pack and setting the position of the needle valve to achieve the desired flow rate.

Each quartz-fiber filter was cut in half, and one filter half was placed in a polystyrene extraction vial with 15 ml of DI water. The remaining half was used for determination of OC and EC as described below. The extraction vials were capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material. After extraction, these solutions were stored under refrigeration prior to analysis. The unanalyzed filter half was archived in the original petri slide.  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{=}$  were measured with a Dionex 2020i ion chromatograph (IC). Approximately 2 ml of the filter extract was injected into the ion chromatograph.

A Technicon TRAACS 800 Automated Colorimetric System (AC) was used to measure  $\text{NH}_4^+$  concentrations by the indolphenol method. Each sample was mixed with reagents and subjected to appropriate reaction periods before submission to the colorimeter. Beer's Law relates the liquid's absorbency to the amount of the ion in the sample. A photomultiplier tube measured this absorbency through an interference filter specific to  $\text{NH}_4^+$ . Two ml of extract in a sample vial were placed in a computer-controlled autosampler. Technicon software operating on a microcomputer controlled the sample throughput, calculated concentrations, and recorded data.

#### Organic and Elemental Carbon

Quartz fiber filters were used to collect samples for determination of OC and EC mass (see above). The filters were heated in air for at least three hours at approximately  $900^\circ\text{C}$  prior to use. Pre-acceptance testing was performed on each lot of filters. Filters with levels exceeding 1.5 micrograms per square centimeter ( $\mu\text{g}/\text{cm}^2$ ) of OC and  $0.5 \mu\text{g}/\text{cm}^2$  of EC were refired or

rejected. Pre-fired filters were sealed and stored in a freezer prior to preparation for field sampling.

The thermal/optical reflectance (TOR) method was used to determine OC and EC on the quartz filters. The TOR method is based on the principle that different types of carbon-containing particles are converted to gases under different temperature and oxidation conditions. The TOR carbon analyzer consists of a thermal system and an optical system. Reflected light is continuously monitored throughout the analysis cycle. The negative change in reflectance is proportional to the degree of pyrolytic conversion of carbon that takes place during OC analysis. After oxygen is introduced, the reflectance increases rapidly as the light-absorbing carbon burns off the filter. The carbon measured after the reflectance attains the value it had at the beginning of the analysis cycle is defined as EC.

#### Volatile Organic Compounds

Tenax. Glass tubes filled with Tenax-TA (a polymer of 2,6-diphenyl-p-phenylene oxide) solid adsorbent were used to collect VOC samples. Two Tenax cartridges in parallel were used simultaneously for each test run due to the low concentrations expected in the sample. Each cartridge contained approximately 0.2 grams of Tenax resin. A sample rate of approximately 0.1 liters per minute (lpm) through each Tenax tube was used. The flow rate through the Tenax cartridges was set prior to sample collection and checked after sample collection by placing a mass flow meter on the outlet of each Tenax tube and setting the position of the needle valve to achieve the desired flow rate.

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

Canisters. An integrated sample was collected in a canister using a pump and flow control device to maintain a constant sample flow rate into the canister over the entire sampling period. Canisters

were used in order to quantify VOCs with a carbon number of 2 or more that are not found in the Tenax samples. The flow rate used is a function of the final desired sample pressure and the specified sampling period, for our purposes, 17 mL/min. Because the gas had already been diluted and cooled before sampling into the canister, liquid formation in the cans was not a concern.

For analysis, a known volume of gaseous sample is passed through a cryogenically cooled trap, cooled with liquid argon, cryogenically trapping out C<sub>2</sub> and heavier VOC without trapping methane. The trap containing the condensed VOC is warmed with hot water and its contents injected into a gas chromatograph (GC) capillary column where separation of the VOC takes place. Detection of the hydrocarbons and oxygenated hydrocarbons is by FID while detection of the halogenated compounds is by ECD, and the resultant peaks are quantified and recorded by an electronic integrator and by the chromatographic data system

#### Semivolatile Organic Compounds

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

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

The sample was transferred from the sampling manifold through a 3/8-inch copper manifold leading to a momentum diffuser chamber followed by the filter and cartridge holder. The flow through the sampler was monitored continuously by a calibrated rotameter and kept at a target flow rate of 113 lpm.

SVOCs were analyzed following procedures outlined in EPA Method TO-13. The samples were isotopically spiked, extracted in dichloromethane, and concentrated prior to analysis. Sample extracts were analyzed by the electron impact (EI) gas chromatography/mass spectrometric (GC/MS) technique, using a Hewlett-Packard 5890 GC equipped with a model 7673A Automatic Sampler and interfaced to a model 5970B Mass Selective Detector (MSD). To assist in the unique identification of individual compounds, selected samples were analyzed by combined gas

chromatography/Fourier transform infrared/mass spectrometry (GC/IRD/MSD) technique, i.e., using the Fourier transform infrared detector to aid mass spectrometric identification. Quantification of polycyclic aromatic hydrocarbons (PAH), and other compounds of interest, was obtained by multiple ion detection (MID).

#### Carbonyls (Aldehydes and Ketones)

Carbonyls in air were collected by drawing sample through a cartridge impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH), following procedures outlined in EPA Method TO-11A. The resulting products (hydrazones) in the cartridge are measured in the laboratory using high performance liquid chromatography (HPLC) to determine the levels of the carbonyl compounds originally present in sample gas. Typically C<sub>1</sub>-C<sub>6</sub> carbonyl compounds, including benzaldehyde, are measured effectively by this technique. The target flow rate used for this sample was 0.4 lpm.

#### Sulfur dioxide

Filter packs containing a quartz filter followed by a potassium carbonate impregnated cellulose-fiber filters were used to collect SO<sub>2</sub> gas downstream of the dilution tunnel. These filters were extracted with hydrogen peroxide and then analyzed using IC.

#### Ammonia

Filter packs containing a quartz filter followed by a citric acid impregnated cellulose-fiber filter were used to collect ammonia gas downstream of the dilution tunnel. These filters were extracted with DI water and then analyzed using automated colorimetry.

#### Background Ambient Air Sample

An ambient air sample was collected to establish background concentrations of measured substances. The same sampling and analysis procedures used for the dilution tunnel were applied for collecting ambient air samples with the exception that the MOUDI sampling and analysis were not performed.

### Process Samples

A sample of the fuel oil burned in the testing combustor 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. A sample of the natural gas burned in the testing combustor was collected on each day of source testing and analyzed for sulfur content, heating value, and carbon, hydrogen, oxygen, and nitrogen.

## Section 4

### GAS TURBINE RESULTS (SITE BRAVO)

#### EXPERIMENTAL APPROACH (TEST MATRIX)

The dilution sampling protocol was used to collect particulate emissions data from a natural gas-fired combined cycle turbine at Site Bravo on September 6-11, 2001 along with emissions data obtained from conventional sampling methods. The scope of testing is summarized in Table 4-1 and the collected samples were analyzed for the compounds listed in Table 4-2. The dilution sampler extracted a sample stream from the stack into a mixing chamber, where it was diluted approximately 21:1 with ambient air purified by passing through a HEPA filter and activated carbon.

The specific objectives of this test were to:

- Provide extensive dataset of speciated fine particulate emissions for gas turbines;
- Compare PM<sub>2.5</sub> mass measured using an in-stack filter and iced impinger train (EPA Method PRE-4/202) and mass measured using a dilution tunnel;
- Develop emission factors and speciation profiles for organic aerosols and PM<sub>2.5</sub> mass;
- Characterize sulfate, nitrate, ammonium, inorganic elements, elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media in the dilution sampler;
- Characterize key secondary particle precursors in stack gas samples: volatile organic compounds (VOC) with carbon number of 7 and above carbonyls, benzene, toluene and xylenes; sulfur dioxide (SO<sub>2</sub>); oxides of nitrogen (NO<sub>x</sub>), and ammonia (NH<sub>3</sub>);
- Compare condensable particulate matter (CPM) results obtained using two different methods: EPA Method 202 and a modified version of EPA Method 8 (the back-half isopropyl alcohol catch is dried and weighed);
- Characterize SVOC speciation (or PM<sub>2.5</sub> source apportionment);
- Compare emission factors obtained from test with similar emission factors currently available; and
- Identify issues associated with particulate measurement from sources with relatively dilute exhaust streams.

Table 4-1. Overview of Sampling Scope.

Sampling Location	Number of Samples	
	Stack	Ambient Air
EPA Method PRE-4/202 train	4	--
EPA Method 17/8 train	4	--
Dilution tunnel Teflon <sup>®</sup> filter (mass, elements) Quartz filter (ions, OC/EC) K <sub>2</sub> CO <sub>3</sub> -impregnated cellulose fiber filter (SO <sub>2</sub> ) Citric acid-impregnated cellulose fiber filter (NH <sub>3</sub> ) TIGF/PUF/XAD-4 (SVOCs) Tenax (VOCs) Stainless steel canisters (VOCs, C2-C10) DNPH-coated silica gel cartridges (carbonyls)	4	1
NO <sub>x</sub> , CO, O <sub>2</sub>	Continuous (Plant)	--
Process monitoring	Continuous	--

TIGF - Teflon<sup>®</sup>-impregnated glass fiber filter

PUF - polyurethane foam

XAD-4 - Amberlite<sup>®</sup> sorbent resin

DNPH - dinitrophenylhydrazine

Table 4-2. Summary of Analytical Targets for Site Bravo.

Parameters	In-Stack				Dilution Tunnel								
	Cyclones	Quartz filter	Imp.	Gases	Quartz filter	TIGF /PUF/ XAD	TMF	Tenax	SS cans	DNPH cartridges	K <sub>2</sub> CO <sub>3</sub> filter	Citric acid filter	Gases
Total PM mass	X	X											
PM10 mass	X	X											
PM2.5 mass	X	X					X						
Condensable particulate mass			X										
Sulfate			X		X								
Chloride			X		X								
Ammonium			X		X								
Nitrate			X		X								
Elements			X				X						
Organic carbon					X								
Elemental carbon					X								
Semivolatile organic compounds						X							
Volatile organic compounds*								X					
Volatile organic compounds**									X				
Carbonyls										X			
Ammonia (gaseous)												X	
NO <sub>x</sub>				X									
SO <sub>2</sub>											X		
CO				X									
O <sub>2</sub>				X									
Moisture or relative humidity			X										X
Velocity				X									
Temperature				X									X

TMF - Teflon® membrane filter

TIGF - Teflon®-impregnated glass fiber filter

DNPH – dinitrophenylhydrazine

SS cans – stainless steel canisters

Imp. – iced impinger train

\*Carbon number of 7 or greater

\*\*Carbon number of 2 to 10



## POLLUTION CONTROL EQUIPMENT DESCRIPTION

The unit was retrofitted with GE's dry low NO<sub>x</sub> (DLN) version 2.6 combustion system for NO<sub>x</sub> emissions control to 9 ppmv (dry, corrected to 15% O<sub>2</sub>) or less over the normal operating load range. The DLN combustion system achieves low NO<sub>x</sub> emissions by staging the fuel addition to achieve initial combustion under premixed, fuel-lean conditions. The remaining fuel is added downstream of the premix zone. Design CO concentration is less than 9 ppmv during normal operation. Combustion in the full premixed mode is maintained from 50 to 100 percent of base load.

In addition to DLN, the unit has post-combustion air pollution control equipment. The HRSG is equipped with an oxidation catalyst for control of CO emissions followed by ammonia injection and a selective catalytic reduction (SCR) system for control of NO<sub>x</sub> emissions.

## SAMPLING LOCATIONS

The turbine and HRSG exhaust through a vertical, cylindrical stack that is 233 feet tall. Emissions sampling was conducted at this stack, which has an inside diameter of 16.5 feet (198.0 inches) and has numerous ports, some of which are used for the plant CEMS. There are four six-inch diameter flanged ports positioned at 90 degrees to each other and located approximately 6 feet above the sampling platform. There are also 4 four-inch ports offset from the six-inch ports and located at 90 degrees to each other; the ports are flanged and located 4 feet above the platform. The ports are at least 60 feet (3.6 diameters) downstream from the last disturbance and 100 feet (6.1 diameters) upstream from the top of the stack. All ports are accessed from a single platform that is approximately 61 inches wide and approximately 128 feet above the ground. The stack gas O<sub>2</sub> concentration was uniform across the stack and there was no cyclonic flow present.

## RESULTS SUMMARY (EXECUTIVE SUMMARY)

This is the first dilution tunnel based dataset for gas turbines. Detail results are reported in a separate topical report. Subsequent pilot scale evaluation of the test methods and additional testing of gas turbines and other combustion units will advance our understanding of the differences noted between the dilution tunnel and other measurement methods.

Emission factors for all species measured were low, which is expected for gas-fired sources. Emission factors for primary particulate including: total particulate, PM10 (particles smaller than nominally 10 micrometers), and PM2.5; elements; ionic species; and organic and elemental carbon are presented in Table 4-3. Emission factors are expressed in pounds of pollutant per million British thermal units of gas fired (lb/MMBtu). Four six-hour runs were performed on separate, consecutive days. As a measure of the bias, precision, and variability of the results, the uncertainty and upper 95 percent confidence bound also are presented.

Emission factors for semivolatile organic species are presented in Table 4-4. The sum of semivolatile organic species is approximately five percent of the organic carbon. Emission factors for secondary particulate precursors (NO<sub>x</sub>, SO<sub>2</sub>, and volatile organic species with carbon number of 7 or greater) are presented in Table 4-5.

The preceding tables include only those substances that were detected in at least one of the four test runs. Substances of interest not present above the minimum detection limit for these tests are listed in Table 4-6.

The primary particulate results presented in Table 4-3 also may be expressed as a PM2.5 speciation profile, which is the mass fraction of each species contributing to the total PM2.5 mass. The speciation profile is presented in Figure 4-2.

The main findings of these tests are:

- Particulate mass emissions from the turbine were extremely low, consistent with levels expected for gaseous fuel combustion.
- Two methods for determining the average emission factor for primary PM2.5 mass gave results which differed by more than an order of magnitude: 0.00017 lb/MMBtu using the dilution tunnel; and 0.0031 lb/MMBtu using conventional in-stack methods for filterable and condensable particulate

Table 4-3. Summary of Primary Particulate Emission Factors for a Gas Turbine.

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Particulate Mass	Organic CPM (Method 202)	5.5E-4	n/a	n/a
	Inorganic CPM (Method 202)	2.7E-3	60	4.0E-3
	Total CPM (Method 202)	3.0E-3	48	4.1E-3
	Total CPM (Method 8)	2.3E-3	45	3.1E-3
	Total Filterable PM (Method 17/8 train)	6.1E-4	383	1.8E-3
	Total Filterable PM (Method PRE-4/202 train)	6.0E-4	201	1.5E-3
	Filterable PM10 (Method PRE-4/202 train)	2.9E-4	291	8.6E-4
	Filterable PM2.5 (Method PRE-4/202 train)	9.6E-5	n/a	n/a
	PM2.5 (dilution tunnel)	1.7E-4	259	4.6E-4
Elements (dilution tunnel)	Ag	7.6E-7	n/a	n/a
	Al	2.0E-6	872	1.0E-5
	Br	4.7E-8	805	2.3E-7
	Ca	2.7E-6	885	1.5E-5
	Cl	9.5E-6	257	2.6E-5
	Co	3.2E-8	448	1.0E-7
	Cr	6.1E-7	n/a	n/a
	Cu	4.4E-7	339	1.5E-6
	Fe	5.7E-6	298	1.7E-5
	K	1.2E-6	918	6.6E-6
	Mg	1.1E-6	244	3.0E-6
	Mn	1.6E-7	484	5.5E-7
	Mo	6.7E-8	n/a	n/a
	Ni	1.7E-7	269	4.7E-7
	P	3.2E-7	n/a	n/a
	Pb	1.0E-7	491	3.5E-7
	S	4.1E-6	284	1.2E-5
	Si	5.0E-6	349	1.7E-5
	Sr	6.0E-8	n/a	n/a
	Ti	3.7E-7	637	1.5E-6
V	1.5E-7	694	6.8E-7	
Zn	5.3E-7	318	1.7E-6	
Zr	3.9E-8	n/a	n/a	
Ions (dilution tunnel)	Chloride	9.8E-6	249	2.7E-5
	Nitrate	1.5E-5	322	4.7E-5
	Sulfate	1.2E-5	303	3.7E-5
	Ammonium	7.3E-6	n/a	n/a
	Soluble Na	7.1E-7	229	1.8E-6
Carbon (dilution tunnel)	Organic Carbon	1.4E-4	98	2.3E-4
	Elemental Carbon	1.2E-5	351	3.4E-5
	Total Carbon	1.5E-4	103	2.5E-4

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

Table 4-4. Summary of Semivolatile Organic Species Emission Factors for a Gas Turbine.

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
2-methylnaphthalene	7.0E-7	774	3.4E-6
1-methylnaphthalene	3.8E-7	731	1.8E-6
Biphenyl	2.2E-7	n/a	n/a
1+2-ethylnaphthalene	4.8E-7	35	6.3E-7
2,6+2,7-dimethylnaphthalene	2.9E-7	n/a	n/a
1,3+1,6+1,7-dimethylnaphthalene	5.2E-7	n/a	n/a
1,4+1,5+2,3-dimethylnaphthalene	1.6E-6	817	8.3E-6
Dibenzofuran	3.9E-7	n/a	n/a
A-trimethylnaphthalene	8.9E-8	180	1.7E-7
B-trimethylnaphthalene	5.0E-8	60	6.9E-8
C-trimethylnaphthalene	8.0E-8	73	1.1E-7
E-trimethylnaphthalene	3.2E-8	255	7.3E-8
F-trimethylnaphthalene	3.0E-8	85	4.4E-8
2,3,5-I-trimethylnaphthalene	2.0E-7	n/a	n/a
Acenaphthene	6.1E-7	726	2.8E-6
Fluorene	2.4E-7	n/a	n/a
Phenanthrene	4.3E-7	158	9.3E-7
Xanthone	1.6E-7	1113	1.1E-6
2-methylphenanthrene	7.0E-8	239	1.9E-7
C-methylphenanthrene	1.6E-7	n/a	n/a
1-methylphenanthrene	7.6E-8	n/a	n/a
Anthrone	2.7E-8	85	4.4E-8
C-dimethylphenanthrene	1.4E-7	n/a	n/a
E-dimethylphenanthrene	2.7E-7	n/a	n/a
Anthracene	8.0E-10	n/a	n/a
Fluoranthene	9.6E-8	158	1.7E-7
Pyrene	1.2E-7	797	5.9E-7
C-MePy/MeFl	3.2E-9	n/a	n/a
D-MePy/MeFl	3.0E-8	188	7.1E-8
4-methylpyrene	4.2E-8	n/a	n/a
7-methylbenz(a)anthracene	5.0E-8	753	2.4E-7
7-methylbenzo(a)pyrene	1.2E-7	55	1.7E-7
Sum of All SVOCs	7.7E-6		

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

Table 4-5. Summary of Secondary Particulate Precursor Emission Factors for a Gas Turbine.

Substance		Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Gases	NH <sub>3</sub> (dilution tunnel)	1.1E-3	26	1.3E-3
	NH <sub>3</sub> (BAAQMD ST-1B)	1.6E-3	25	2.0E-3
	SO <sub>2</sub>	5.1E-4	107	9.1E-4
Volatile Organic Compounds	Ethylbenzene	3.3E-6	227	8.4E-6
	m&p-xylene	8.4E-6	251	2.3E-5
	Cyclohexanone	1.1E-5	n/a	n/a
	2-methyloctane	7.0E-7	575	2.7E-6
	2-heptanone	2.2E-6	n/a	n/a
	3-methyloctane	2.2E-6	546	8.4E-6
	Styrene	2.3E-5	228	5.9E-5
	o-xylene	3.0E-6	264	8.3E-6
	1-nonene	4.6E-6	n/a	n/a
	Nonane	5.4E-6	247	1.4E-5
	Isopropylbenzene	1.6E-7	n/a	n/a
	Propylcyclohexane	6.2E-7	n/a	n/a
	Benzaldehyde	7.2E-5	208	1.7E-4
	Dimethyloctane	2.0E-6	n/a	n/a
	Propylbenzene	1.1E-6	859	5.7E-6
	m-ethyltoluene	1.9E-6	220	4.7E-6
	p-ethyltoluene	6.1E-7	140	1.2E-6
	1,3,5-trimethylbenzene	8.4E-7	669	3.7E-6
	Phenol	1.4E-5	171	3.0E-5
	o-ethyltoluene	7.0E-7	1079	4.5E-6
	2,3-benzofuran	1.8E-6	n/a	n/a
	Octanal	7.0E-6	109	1.2E-5
	1,2,4-trimethylbenzene	2.4E-6	248	6.5E-6
	1,3-dichlorobenzene	1.8E-6	n/a	n/a
	1-decene	4.6E-6	n/a	n/a
	Decane	1.1E-5	229	2.9E-5
	m-isopropyltoluene	2.0E-7	1027	1.2E-6
	p-isopropyltoluene	7.2E-6	261	2.0E-5
	Indan	3.8E-7	n/a	n/a
	(+/-)-limonene	1.1E-6	n/a	n/a
	1,3-diethylbenzene	3.2E-7	n/a	n/a
	Acetophenone	2.5E-5	157	5.1E-5
	Butylbenzene	3.3E-7	1024	2.0E-6
	5-ethyl-m-xylene	4.0E-7	n/a	n/a
	1,2-diethylbenzene	2.4E-7	n/a	n/a
	2-n-propyltoluene	4.2E-7	n/a	n/a
	2-ethyl-p-xylene	2.4E-7	n/a	n/a
	4-ethyl-o-xylene	9.1E-7	234	2.0E-6
	4-tert-butyltoluene	4.9E-7	n/a	n/a
	Nonanal	3.1E-5	102	4.7E-5
	1-undecene	6.2E-6	216	1.3E-5
Undecane	5.4E-6	280	1.6E-5	
1,2,4,5-tetramethylbenzene	2.2E-7	n/a	n/a	
1,2,3,5-tetramethylbenzene	4.0E-7	n/a	n/a	
1,2,3,4-tetramethylbenzene	2.9E-7	n/a	n/a	

Table 4-5. Summary of Secondary Particulate Precursor Emission Factors for a Gas Turbine (Continued).

Substance		Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Volatile Organic Compounds	Naphthalene	2.0E-6	209	4.7E-6
	Decanal	2.4E-5	314	6.2E-5
	Dodecene	3.5E-6	419	1.1E-5
	Dodecane	1.5E-5	239	4.0E-5
	2-methylnaphthalene	9.9E-7	853	5.2E-6
	1-methylnaphthalene	3.8E-7	n/a	n/a
	Tridecane	3.5E-6	257	9.5E-6
	Biphenyl	4.2E-6	188	9.5E-6
	1+2-ethylnaphthalene	1.6E-7	n/a	n/a
	2,6+2,7-dimethylnaphthalene	4.7E-7	n/a	n/a
	Tetradecane	1.4E-5	204	3.3E-5
	Pentadecane	2.0E-5	194	4.7E-5
	Hexadecane	1.1E-5	291	3.4E-5
	Heptadecane	1.4E-5	369	5.0E-5
	Octadecane	7.3E-6	364	2.5E-5
	Nonadecane	3.0E-6	n/a	n/a
	Eicosane	2.6E-6	498	9.1E-6
	butyl acetate	7.5E-6	n/a	n/a
	Hexadecanoic acid	1.6E-4	235	4.2E-4

n/a- Not applicable. Only one run within detectable limits.

Table 4-6. Substances of Interest Not Detected in Stack Emissions from a Gas Turbine.

Inorganic	VOC (>C7)	SVOC
Antimony	Heptanal	Naphthalene
Arsenic	t-2-heptenal	1,2-dimethylnaphthalene
Barium	alpha-Pinene	2-Methylbiphenyl
Cadmium	beta-pinene	3-Methylbiphenyl
Gallium	2-pentylfuran	4-Methylbiphenyl
Gold	t-butylbenzene	Bibenzyl
Indium	4-methylstyrene	2,4,5-trimethylnaphthalene
Lanthanum	Isobutylbenzene	J-trimethylnaphthalene
Mercury	Sec-butylbenzene	1,4,5-trimethylnaphthalene
Palladium	1,2,3-trimethylbenzene	Acenaphthylene
Rubidium	1,2-dichlorobenzene	A-methylfluorene
Selenium	Indene	1-methylfluorene
Thallium	o-isopropyltoluene	B-methylfluorene
Tin	o-methylphenol	9-fluorenone
Uranium	m-tolualdehyde	Acenaphthenequinone
Yttrium	4-n-propyltoluene + 1,4-diethylbenzene	Perinaphthenone
	m & p-methylphenol	A-methylphenanthrene
Carbonyl	2-methylbenzofuran	B-methylphenanthrene
Acrolein	5-isopropyl-m-xylene	Anthraquinone
Propionaldehyde	Isoamylbenzene	2,3-Benzofluorene
Butyraldehyde	2-methylindan	3,6-dimethylphenanthrene
M-Tolualdehyde	1-methylindan	A-dimethylphenanthrene
	1,3-diisopropylbenzene	B-dimethylphenanthrene
VOC (>C2)	Pentylbenzene	1,7-dimethylphenanthrene
1 & 2-butyne	1,2,3,4-tetrahydronaphthalene	D-dimethylphenanthrene
3-methyl-1-butene	1,2-dihydronaphthalene	9-methylanthracene
1-pentene	1,4-diisopropylbenzene	9-Anthraldehyde
4-methyl-1-pentene	A-dimethylindane	Retene
3-methyl-1-pentene	B-dimethylindane	Benzonaphthothiophene
2,2-dimethylpentane	C-dimethylindane	1-Methylfluorene+C-methylpyrene/fluorene
t-3-hexene + chloroform	D-dimethylindan	B-MePy/MeFl
cis-3-methyl-2-pentene	2-decanone	1-methylpyrene
3-methyl-2-pentene	Pentamethylbenzene	Benzo(c)phenanthrene
1-methylcyclopentene	1,6+1,3+1,7-dimethylnaphthalene	Benz(a)anthracene
Heptene-1	2,3+1,5+1,4-dimethylnaphthalene	Chrysene
2,4-dimethylheptane	Acenaphthylene	Benzanthrone
2,5-dimethylheptane	1,2-dimethylnaphthalene	Benz(a)anthracene-7,12-dionene
2-methyloctane	Acenaphthene	5+6-methylchrysene
3-methyloctane	Fluorene	chryq14
n-butylbenzene	Phenanthrene	Benzo(b+j+k)fluoranthene
1,3-dimethyl-4-ethylbenzene	propylene glycol	Benzo(e)pyrene
Undecene-1	hexyl acetate	Perylene
	2-butoxyethyl acetate	Benzo(a)pyrene
	benzoic acid	Indeno[123-cd]pyrene
	2-(2-butoxyethoxy) ethanol	Benzo(ghi)perylene
		Dibenzo(ah+ac)anthracene
		Coronene

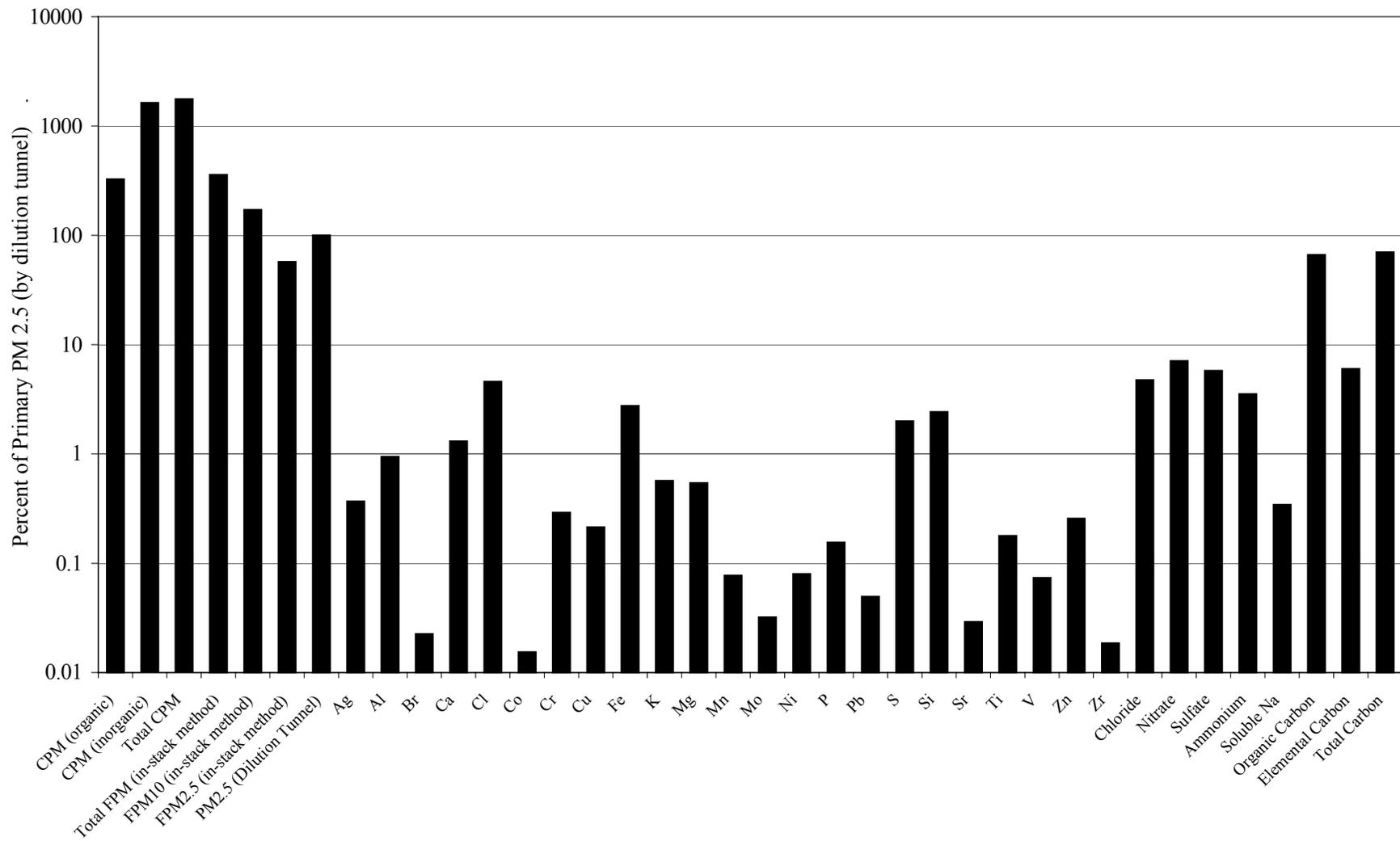


Figure 4-2. Speciation profile for primary particulate emissions from a gas turbine.

- Sampling and analytical artifacts principally caused by gaseous SO<sub>2</sub> in the stack gas were shown to produce a relatively large positive bias in condensable particulate as measured by conventional in-stack methods. These measurement artifacts can explain most of the difference between the dilution tunnel and conventional method results. The results using conventional EPA methods are nominally consistent with published EPA emission factors for external combustion of natural gas (U. S. EPA, 1998). Therefore, the published EPA emission factors derived from tests using similar measurement methods also may be positively biased.
- Chemical species accounting for 182 percent of the measured PM<sub>2.5</sub> mass were quantified.
- Organic and elemental carbon comprise approximately 90 percent of the primary PM<sub>2.5</sub> mass measured by the dilution tunnel.
- Sulfate, ammonium, nitrate and soluble sodium together account for approximately 20 percent of the measured PM<sub>2.5</sub> mass; sulfate alone accounts for approximately 7 percent.
- Chlorine, iron, silicon, calcium, aluminum, and potassium account for approximately 16 percent of the measured PM<sub>2.5</sub> mass. Smaller amounts of ten other detected elements comprise another 2 percent.
- Most elements are not present at levels significantly above the background levels in the ambient air or the minimum detection limits of the test methods.
- Most organic species are not detected at levels significantly above background levels in the ambient air or field blanks. All detected organics are present at extremely low levels consistent with gaseous fuel combustion.
- Emissions of secondary particle precursors are low and consistent with levels expected for gaseous fuel combustion.

## Section 5

### PROCESS HEATER (SITE CHARLIE) RESULTS

#### EXPERIMENTAL APPROACH (TEST MATRIX)

The dilution sampling protocol was used to collect particulate emissions data from a natural gas-fired process heater (Site Charlie) equipped with SCR for NO<sub>x</sub> reductions on December 6-12, 2001 along with emissions data obtained from conventional sampling methods. The scope of testing is summarized in Table 5-1 and the samples were analyzed for the compounds listed in Table 5-2. Process data and fuel gas samples were collected during the tests to document operating conditions. The dilution sampler extracted a sample stream from the stack into a mixing chamber, where it was diluted approximately 24:1 with ambient air purified by passing through a HEPA filter and activated carbon.

The specific objectives of this test were to:

#### Primary Objectives

- Compare PM<sub>2.5</sub> mass measured using an in-stack filter and iced impinger train (EPA Method PRE-4/202) and mass measured using a dilution tunnel;
- Develop emission factors and speciation profiles for organic aerosols and PM<sub>2.5</sub> mass;
- Characterize sulfate, nitrate, ammonium, inorganic elements, elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media in the dilution sampler;
- Characterize key secondary particle precursors in stack gas samples: volatile organic compounds (VOC) with carbon number of 7 and above; sulfur dioxide (SO<sub>2</sub>); and oxides of nitrogen (NO<sub>x</sub>);
- Document the relevant process design characteristics and operating conditions during the test;
- Identify issues associated with particulate measurement from sources with relatively dilute exhaust streams; and
- Compare emission factors with similar emission factors currently available.

#### Secondary Objectives

- Measure ammonia slip from the SCR; and
- Speciate the inorganic condensable PM residue collected using EPA Method 202.

Table 5-1. Overview of Sampling Scope.

Sampling Location	Number of Samples	
	Stack	Ambient Air
EPA Method PRE-4/202 train	4	--
SCAQMD Method 207.1	4	--
Dilution tunnel Teflon <sup>®</sup> filter (mass, elements) Quartz filter (ions, OC/EC) K <sub>2</sub> CO <sub>3</sub> -impregnated cellulose fiber filter (SO <sub>2</sub> ) Citric acid-impregnated cellulose fiber filter (NH <sub>3</sub> ) TIGF/PUF/XAD-4 (SVOCs) Tenax (VOCs, C7 and greater) Stainless steel canisters (VOCs, C2-C10) DNPH-coated silica gel cartridges (carbonyls)	4	1
O <sub>2</sub> , CO <sub>2</sub>	Every two hours	--
NO <sub>x</sub> , SO <sub>2</sub> , O <sub>2</sub>	Continuous (Plant)	--
Process monitoring	Continuous	--

TIGF - Teflon<sup>®</sup>-impregnated glass fiber filter

PUF - polyurethane foam

XAD-4 - Amberlite<sup>®</sup> sorbent resin

DNPH - dinitrophenylhydrazine

Table 5-2. Summary of Analytical Targets.

Parameters	In-Stack				Dilution Tunnel								
	Cyclones	Quartz filter	Imp.	Gases	Quartz filter	TIGF/ PUF/ XAD	TMF	Tenax	SS cans	DNPH cartridges	K <sub>2</sub> CO <sub>3</sub> filter	Citric acid filter	Gases
Total PM mass	X	X											
PM10 mass	X	X											
PM2.5 mass	X	X					X						
Condensable particulate mass			X										
Sulfate			X		X								
Chloride			X		X								
Ammonium			X		X								
Nitrate			X		X								
Elements			X				X						
Organic carbon					X								
Elemental carbon					X								
SVOCs						X							
VOCs*								X					
VOCs**									X				
Aldehydes										X			
Ammonia (gaseous)			X									X	
NO <sub>x</sub>				X									
SO <sub>2</sub>				X							X		
O <sub>2</sub>				X									
CO <sub>2</sub>				X									
Moisture or relative humidity			X										X
Velocity				X									
Temperature				X									X

DNPH – dinitrophenylhydrazine

Imp. – iced impinger train

SS cans – stainless steel canisters

SVOCs – semivolatile organic compounds

TIGF – Teflon®-impregnated glass fiber filter

TMF – Teflon® membrane filter

VOCs – volatile organic compounds

\*Carbon number of 7 or greater

\*\*Carbon number of 2 to 10

## SITE DESCRIPTION

Tests were performed on a process heater that is a preheater for the vacuum unit. The unit is a natural gas-fired, bottom-fired double box with 32 burners per box. Hot exhaust gases from the two boxes vent to the atmosphere via a common stack (Figure 5-1). The stack is equipped with a bypass duct that leads to the selective catalytic reduction (SCR) system. The heater's capacity is 300 MMBtu/hr. The facility is equipped with continuous emissions monitors (CEMS) for O<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub>.

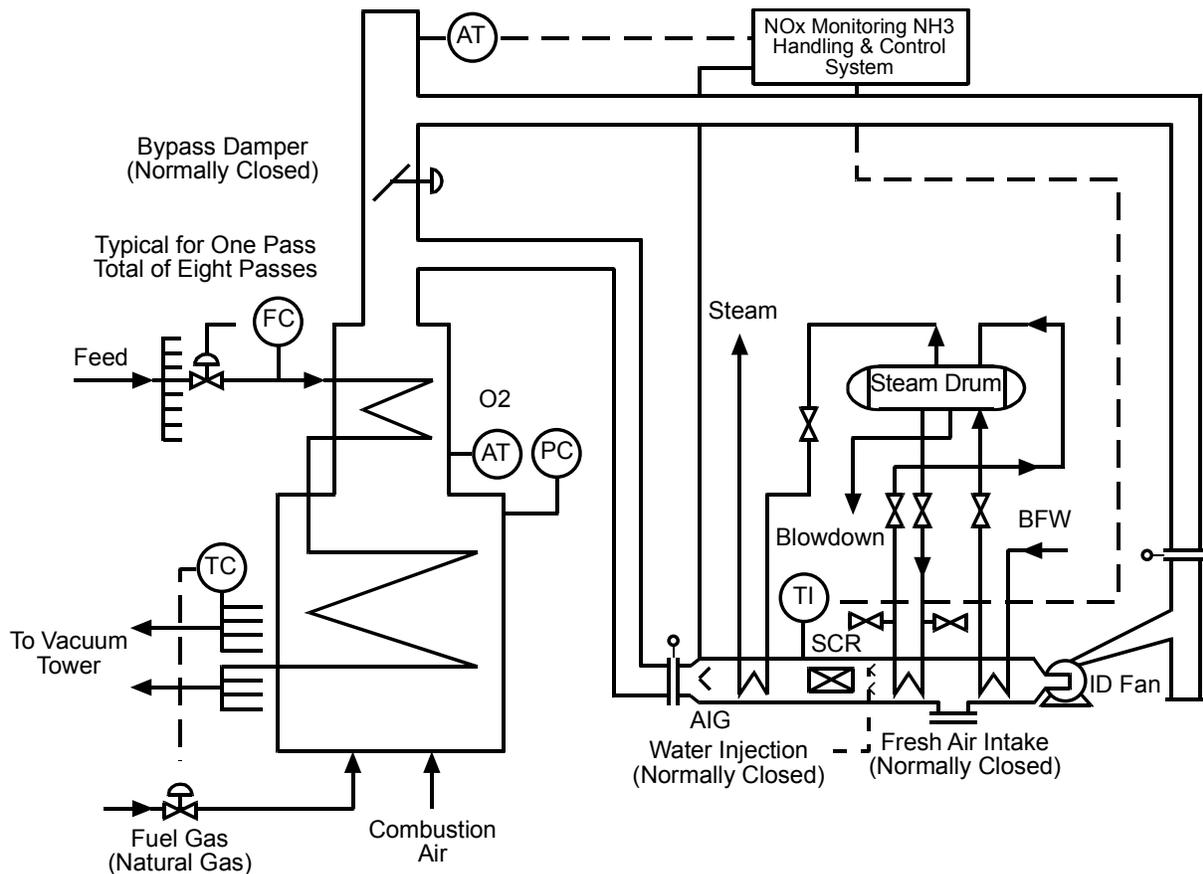


Figure 5-1. Gas-Fired Heater Process Overview.

## POLLUTION CONTROL EQUIPMENT DESCRIPTION

The unit has post-combustion air pollution control equipment in the form of an SCR with ammonia injection. The rate of injection is controlled by NO<sub>x</sub> readings in the stack and the temperature of the SCR; the permitted limit of ammonia slip is 20 ppm.

## SAMPLING LOCATIONS

The heater exhausts through a vertical, cylindrical stack that is approximately 150 feet tall and has an inside diameter of 118 inches. There are four 4-inch diameter flanged ports positioned at 90 degrees to each other, with an additional two 4-inch diameter ports offset from the other ports and located at 180 degrees to each other. The ports are 36 feet, 3 inches downstream from the last disturbance and 20 feet, 3 inches upstream from the top of the stack. The platform is approximately 130 feet above the ground. The sampling locations exceeded the minimum EPA Method 1 requirements for upstream and downstream disturbances.

## RESULTS SUMMARY (EXECUTIVE SUMMARY)

This report presents emissions data from testing performed on a natural gas-fired process heater equipped with selective catalytic reduction (SCR) with ammonia injection for NO<sub>x</sub> control. The flue gas temperature at the stack was approximately 340°F during the tests.

Emission factors for all species measured were low, which is expected for gas-fired sources. Emission factors for primary particulate including: total particulate, PM<sub>10</sub> (particles smaller than nominally 10 micrometers), and PM<sub>2.5</sub>; elements; ionic species; and organic and elemental carbon are presented in Table 5-3. Emission factors are expressed in pounds of pollutant per million British thermal units of gas fired (lb/MMBtu). Four six-hour runs were performed on separate, consecutive days. As a measure of the bias, precision, and variability of the results, the uncertainty and upper 95 percent confidence bound also are presented.

Emission factors for semivolatile organic species are presented in Table 5-4. The sum of semivolatile organic species is approximately 10 percent of the organic carbon. Emission factors for secondary particulate precursors (NO<sub>x</sub>, SO<sub>2</sub>, and volatile organic species with carbon number of 7 or greater) are presented in Table 5-5. Carbonyl emission factors are presented in Table 5-6.

Table 5-3. Summary of Primary Particulate Emission Factors for a Heater (Site Charlie).

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Particulate Mass	Organic CPM (Method 202)	2.8E-4	n/a	n/a
	Inorganic CPM (Method 202)	9.2E-4	48	1.3E-3
	Total CPM (Method 202)	1.0E-3	50	1.4E-3
	Total Filterable PM (Method PRE-4/202 train)	2.3E-4	82	3.8E-4
	Filterable PM10 (Method PRE-4/202 train)	1.0E-4	110	1.9E-4
	Filterable PM2.5 (Method PRE-4/202 train)	5.5E-5	168	1.2E-4
	PM2.5 (dilution tunnel)	1.1E-4	209	2.7E-4
	Al	3.5E-6	864	1.8E-5
Br	1.8E-8	136	3.1E-8	
Elements (dilution tunnel)	Ca	2.9E-6	221	7.8E-6
	Cl	6.4E-7	248	1.7E-6
	Co	3.8E-8	367	1.1E-7
	Cr	1.2E-7	158	2.5E-7
	Cu	1.6E-7	183	3.8E-7
	Fe	4.6E-6	199	1.1E-5
	K	1.0E-6	210	2.6E-6
	Mg	4.7E-7	273	1.3E-6
	Mn	1.1E-7	190	2.6E-7
	Mo	4.2E-8	n/a	n/a
	Na	1.1E-6	127	2.2E-6
	Ni	8.3E-8	156	1.8E-7
	P	9.1E-8	n/a	n/a
	Pb	6.4E-8	151	1.3E-7
	Rb	1.2E-8	n/a	n/a
	S	1.7E-6	110	3.1E-6
	Si	6.6E-6	208	1.7E-5
	Sr	5.0E-8	700	2.2E-7
	Ti	3.2E-7	189	7.6E-7
	V	4.0E-8	148	8.0E-8
Zn	4.1E-7	169	9.3E-7	
Zr	4.5E-8	359	1.3E-7	
Chloride	1.5E-6	n/a	n/a	
Ions (dilution tunnel)	Nitrate	4.2E-6	128	7.8E-6
	Sulfate	4.7E-6	99	8.1E-6
	Ammonium	2.2E-6	414	6.7E-6
	Soluble Na	5.0E-7	131	9.8E-7
	Organic Carbon	2.1E-4	95	3.6E-4
Carbon (dilution tunnel)	Elemental Carbon	4.0E-5	97	6.6E-5
	Total Carbon	2.4E-4	98	4.2E-4
	Total Carbon	1.5E-4	103	2.5E-4

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

Table 5-4. Summary of Semivolatile Organic Species Emission Factors for a Heater (Site Charlie).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
1-methylnaphthalene	1.0E-6	156	2.2E-6
Biphenyl	3.4E-7	146	6.0E-7
1+2-ethylnaphthalene	4.9E-7	111	8.7E-7
2,6+2,7-dimethylnaphthalene	7.1E-7	181	1.6E-6
1,3+1,6+1,7-dimethylnaphthalene	1.4E-6	177	3.1E-6
1,4+1,5+2,3-dimethylnaphthalene	6.1E-7	213	1.5E-6
1,2-dimethylnaphthalene	1.8E-7	192	3.5E-7
2-Methylbiphenyl	1.7E-6	119	3.3E-6
3-Methylbiphenyl	9.5E-7	86	1.6E-6
4-Methylbiphenyl	4.1E-7	89	6.9E-7
A-trimethylnaphthalene	2.4E-7	179	5.7E-7
B-trimethylnaphthalene	1.7E-7	170	3.9E-7
C-trimethylnaphthalene	1.5E-7	162	3.4E-7
E-trimethylnaphthalene	9.3E-8	163	2.1E-7
F-trimethylnaphthalene	8.8E-8	156	1.9E-7
2,3,5+1-trimethylnaphthalene	4.5E-7	145	9.3E-7
2,4,5-trimethylnaphthalene	4.1E-8	152	8.7E-8
J-trimethylnaphthalene	9.5E-8	453	3.1E-7
Acenaphthylene	1.7E-7	n/a	n/a
Acenaphthene	1.3E-7	302	3.3E-7
Fluorene	2.1E-7	161	4.4E-7
Phenanthrene	1.7E-7	133	3.5E-7
1-methylfluorene	3.4E-7	234	8.7E-7
B-methylfluorene	1.3E-7	n/a	n/a
Xanthone	2.4E-8	520	8.7E-8
Acenaphthenequinone	2.3E-7	66	3.5E-7
A-methylphenanthrene	6.1E-8	87	9.1E-8
2-methylphenanthrene	5.3E-8	124	1.0E-7
B-methylphenanthrene	4.6E-8	n/a	n/a
C-methylphenanthrene	5.7E-8	n/a	n/a
1-methylphenanthrene	5.2E-8	121	9.6E-8
Anthrone	2.0E-8	107	3.6E-8
3,6-dimethylphenanthrene	5.4E-8	n/a	n/a
C-dimethylphenanthrene	6.1E-8	50	8.5E-8
E-dimethylphenanthrene	4.2E-8	788	2.1E-7
Anthracene	1.8E-8	148	3.8E-8
Fluoranthene	3.6E-8	101	6.3E-8
Pyrene	3.9E-8	87	6.4E-8

Table 5-4. Summary of Semivolatile Organic Species Emission Factors for a Heater (Site Charlie) (Continued).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
9-Anthraldehyde	1.6E-7	242	4.3E-7
Benzenaphthothiophene	5.1E-9	146	1.1E-8
B-MePy/MeFl	1.7E-8	89	2.7E-8
C-MePy/MeFl	2.4E-9	50	3.3E-9
D-MePy/MeFl	1.0E-8	36	1.3E-8
4-methylpyrene	1.0E-8	110	1.9E-8
1-methylpyrene	1.2E-8	354	3.3E-8
Benzo(c)phenanthrene	2.6E-8	n/a	n/a
Benz(a)anthracene	3.7E-8	n/a	n/a
Chrysene	4.3E-9	97	7.2E-9
5+6-methylchrysene	2.2E-9	158	4.6E-9
Benzo(b+j+k)fluoranthene	9.1E-9	881	4.9E-8
7-methylbenzo(a)pyrene	1.5E-8	445	5.0E-8
Benzo(e)pyrene	1.3E-8	78	2.1E-8
Perylene	4.0E-9	152	8.3E-9
Benzo(a)pyrene	1.4E-8	64	2.1E-8
Benzo(ghi)perylene	9.4E-9	n/a	n/a
Sum of all SVOCs	1.1E-5		

n/a - not applicable; only one run was in detection limits

Table 5-5. Summary of Secondary Particulate Precursor Emission Factors for a Heater (Site Charlie).

Substance		Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Gases	NH <sub>3</sub> (dilution tunnel)	3.4E-4	102	6.0E-4
	NH <sub>3</sub> (SCAQMD 207.1)	1.2E-4	65	1.8E-4
	SO <sub>2</sub>	2.7E-4	80	4.4E-4
Volatile Organic Compounds	Ethylbenzene	7.6E-06	86	1.2E-05
	m & p-xylene	3.3E-05	96	5.7E-05
	2-methyloctane	2.2E-06	48	3.0E-06
	2-heptanone	8.1E-07	n/a	n/a
	3-methyloctane	3.8E-06	79	6.0E-06
	Styrene	3.8E-06	209	9.2E-06
	o-xylene	9.7E-06	93	1.6E-05
	Nonane	2.2E-05	76	3.5E-05
	Benzaldehyde	1.9E-04	46	2.6E-04
	Dimethyloctane	1.6E-06	73	2.4E-06
	Propylbenzene	2.6E-06	75	4.1E-06
	m-ethyltoluene	8.2E-06	87	1.4E-05
	p-ethyltoluene	4.6E-06	98	8.0E-06
	1,3,5-trimethylbenzene	3.4E-06	86	5.6E-06
Phenol	4.2E-05	48	5.7E-05	

Table 5-5. Summary of Secondary Particulate Precursor Emission Factors for a Heater (Site Charlie) (Continued).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
o-ethyltoluene	3.1E-06	74	4.8E-06
Octanal	4.4E-06	602	1.8E-05
1,2,4-trimethylbenzene	8.9E-06	101	1.6E-05
1,3-dichlorobenzene	2.0E-06	80	3.1E-06
Decane	1.4E-05	97	2.5E-05
p-isopropyltoluene	1.2E-05	146	2.5E-05
Indan	2.0E-06	537	7.4E-06
Acetophenone	1.0E-04	35	1.3E-04
5-ethyl-m-xylene	1.3E-06	410	4.0E-06
2-ethyl-p-xylene	1.0E-06	245	2.2E-06
4-ethyl-o-xylene	1.6E-06	140	3.1E-06
Nonanal	9.3E-06	n/a	n/a
Undecane	1.0E-05	104	1.8E-05
1,2,4,5-tetramethylbenzene	9.8E-07	n/a	n/a
1,2,3,5-tetramethylbenzene	8.8E-07	411	2.7E-06
2-methylindan	1.6E-06	278	3.8E-06
1-methylindan	4.2E-06	60	6.0E-06
1,2,3,4-tetramethylbenzene	1.5E-06	n/a	n/a
Naphthalene	3.5E-06	98	6.1E-06
B-dimethylindane	2.8E-06	64	3.8E-06
C-dimethylindane	1.4E-06	n/a	n/a
Dodecane	5.7E-06	99	1.0E-05
2-methylnaphthalene	2.3E-06	83	3.5E-06
1-methylnaphthalene	9.3E-07	41	1.2E-06
Tridecane	3.0E-06	74	4.6E-06
Biphenyl	6.5E-07	n/a	n/a
Tetradecane	5.2E-06	78	8.2E-06
Pentadecane	9.3E-06	33	1.2E-05
Hexadecane	3.6E-06	106	6.5E-06
Heptadecane	2.7E-06	126	5.1E-06
Octadecane	1.7E-06	494	6.0E-06
Benzoic acid	1.2E-03	199	2.9E-03
Hexadecanoic acid	6.4E-04	121	1.2E-03

n/a - not applicable

Table 5-6. Carbonyl Emission Factors for a Heater (Site Charlie).

Substance		Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Carbonyls	Formaldehyde	4.4E-5	73	6.9E-5
	Acetaldehyde	5.2E-5	80	8.4E-5
	Acetone	1.9E-4	124	3.5E-4
	Propionaldehyde	8.8E-6	69	1.4E-5
	Methyl ethyl ketone	1.8E-5	75	2.8E-5
	Butyraldehyde	1.1E-5	n/a	n/a
	Benzaldehyde	8.0E-6	78	1.3E-5
	Glyoxal	9.4E-6	91	1.6E-5
	M-Tolualdehyde	4.7E-6	n/a	n/a
	Hexanaldehyde	6.7E-6	113	1.1E-5

The preceding tables include only those substances that were detected in at least one of the four test runs. Substances of interest not present above the minimum detection limit for these tests are listed in Table 5-7.

The primary particulate results presented in Table 5-3 also may be expressed as a PM<sub>2.5</sub> speciation profile, which is the mass fraction of each species contributing to the total PM<sub>2.5</sub> mass. The speciation profile is presented in Figure 5-2.

The main findings of these tests are:

- Particulate mass emissions from the heater were low, consistent with levels expected for gaseous fuel combustion.
- Two methods for determining the average emission factor for primary PM<sub>2.5</sub> mass gave results which differed by an order of magnitude: 0.00011 lb/MMBtu using the dilution tunnel; and 0.0011 lb/MMBtu using conventional in-stack methods for filterable and condensable particulate.

Table 5-7. Substances of Interest Not Detected in Stack Emissions from Site Charlie.

Inorganic	VOC (>C7)	VOC (>C7)
Ag	Cyclohexanone	Pentamethylbenzene
As	Heptanal	1+2-ethylnaphthalene
Au	1-nonene	2,6+2,7-dimethylnaphthalene
Ba	Isopropylbenzene	1,6+1,3+1,7-dimethylnaphthalene
Cd	Propylcyclohexane	2,3+1,5+1,4-dimethylnaphthalene
Ga	t-2-heptenal	Acenaphthylene
Hg	alpha-Pinene	1,2-dimethylnaphthalene
In	beta-pinene	Acenaphthene
La	2,3-benzofuran	Fluorene
Pd	2-pentylfuran	Phenanthrene
Sb	t-butylbenzene	Nonadecane
Se	4-methylstyrene	Eicosane
Sn	1-decene	Propylene glycol
Tl	Isobutylbenzene	Butyl acetate
U	Sec-butylbenzene	Hexyl acetate
Y	1,2,3-trimethylbenzene	2-butoxyethyl acetate
	m-isopropyltoluene	2-(2-butoxyethoxy) ethanol
Carbonyl	1,2-dichlorobenzene	
Acrolein	(+/-)-limonene	SVOC
Crotonaldehyde	Indene	Naphthalene
Methacrolein	o-isopropyltoluene	2-methylnaphthalene
Valeraldehyde	o-methylphenol	Dibenzofuran
	1,3-diethylbenzene	Bibenzyl
VOC (>C2)	m-tolualdehyde	1,4,5-trimethylnaphthalene
1 & 2-butyne	4-n-propyltoluene + 1,4-diethylbenzene	A-methylfluorene
1,3-dimethyl-4-ethylbenzene	Butylbenzene	9-fluorenone
2,2-dimethylpentane	1,2-diethylbenzene	Perinaphthenone
2-methylindan	m & p-methylphenol	Anthraquinone
2-methyloctane	2-n-propyltoluene	2,3-Benzofluorene
2-methylpropanal	4-tert-butyltoluene	A-dimethylphenanthrene
2-propanol	1-undecene	B-dimethylphenanthrene
3-methyl-1-pentene	2-methylbenzofuran	1,7-dimethylphenanthrene
Acetonitrile	5-isopropyl-m-xylene	D-dimethylphenanthrene
Butanal	Isoamylbenzene	9-methylanthracene
Butanone	1,3-diisopropylbenzene	Retene
F 114	Pentylbenzene	1-MeFl+C-MePy/Fl
Methacrolein	1,2,3,4-tetrahydronaphthalene	7-methylbenz(a)anthracene
n-butylbenzene	1,2-dihydronaphthalene	Benzanthrone
tert-butanol	1,4-diisopropylbenzene	Benz(a)anthracene-7,12-dione
	A-dimethylindane	chryq14
	D-dimethylindan	Indeno[123-cd]pyrene
	2-decanone	Dibenzo(ah+ac)anthracene
	Decanal	Coronene
	Dodecene	

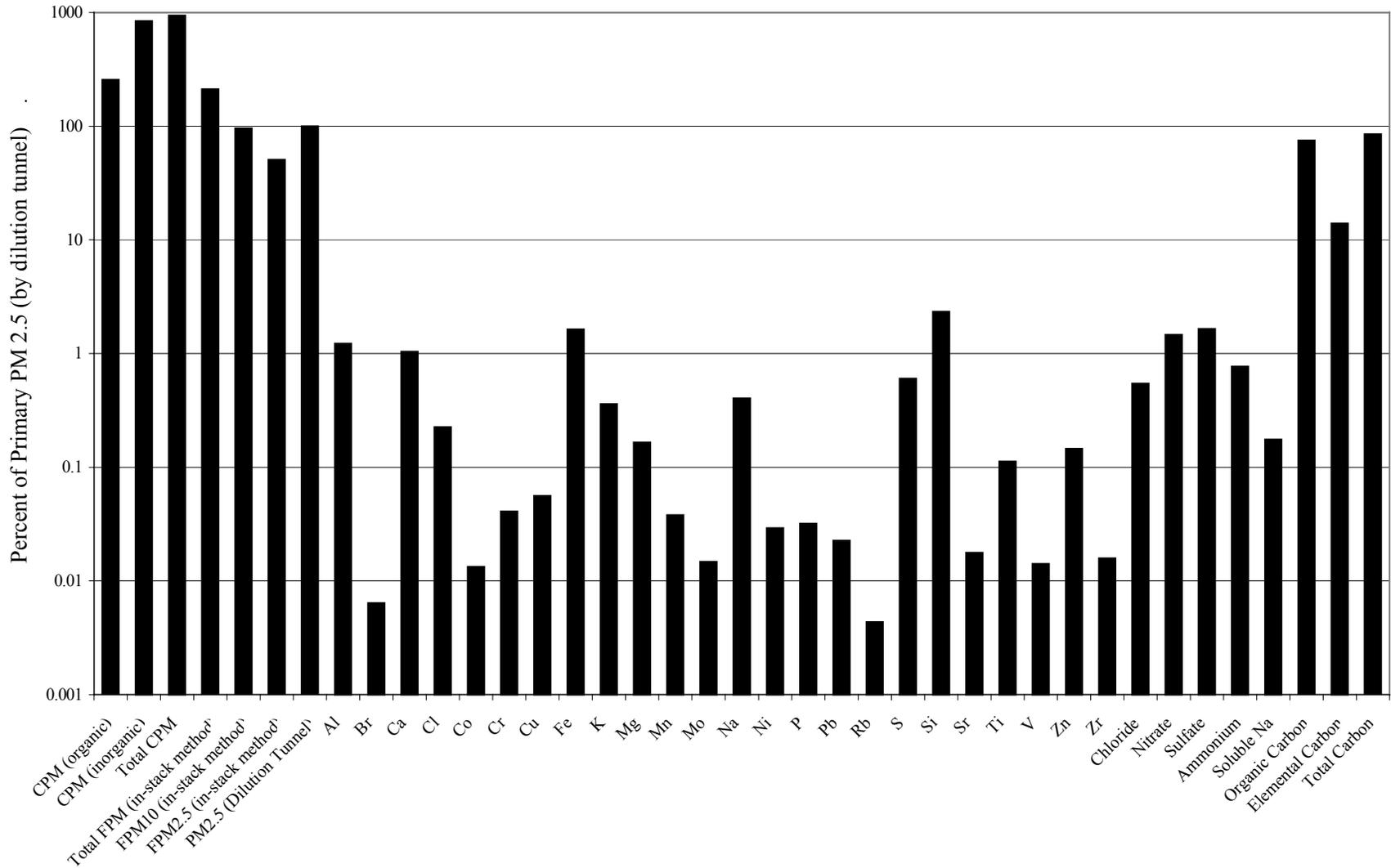


Figure 5-2. Speciation Profile for Primary Particulate Emissions from a Heater.

- Sampling and analytical artifacts principally caused by gaseous SO<sub>2</sub> in the stack gas were shown to produce a relatively large positive bias in condensable particulate as measured by conventional in-stack methods. These measurement artifacts can explain most of the difference between the dilution tunnel and conventional method results. The results using conventional EPA methods are nominally consistent with published EPA emission factors for external combustion of natural gas. Therefore, the published EPA emission factors derived from tests using similar measurement methods also may be positively biased.
- Chemical species accounting for 290 percent of the measured PM<sub>2.5</sub> mass were quantified.
- Organic and elemental carbon comprise approximately 85 percent of the primary PM<sub>2.5</sub> mass measured by the dilution tunnel.
- Silicon, sulfate, iron, nitrate, and aluminum together account for approximately 20 percent of the measured PM<sub>2.5</sub> mass; sulfate alone accounts for approximately 4 percent.
- Calcium, ammonium, chloride, sodium, potassium, magnesium, zinc, titanium and copper account for approximately 9 percent of the measured PM<sub>2.5</sub> mass. Smaller amounts of 12 other detected elements comprise another 0.6 percent.
- Most elements are not present at levels significantly above the background levels in the ambient air or the minimum detection limits of the test methods.
- Most organic species are not detected at levels significantly above background levels in the ambient air or field blanks. All detected organics are present at extremely low levels consistent with gaseous fuel combustion.
- Emissions of secondary particle precursors are low and consistent with levels expected for gaseous fuel combustion.

## Section 6

### COMMERCIAL OIL/GAS FIRED BOILER (SITE DELTA) RESULTS

#### EXPERIMENTAL APPROACH (TEST MATRIX)

This test was performed on two dual fuel (natural gas and number 6 fuel oil) -fired industrial package boilers at Site Delta on March 22 – 28, 2002 (number 6 fuel oil operation) and April 2 – 8, 2002 (natural gas operation). The scope of testing is summarized in Table 6-1 and the samples were analyzed for the compounds listed in Table 6-2. Dilution sampling was used to characterize PM<sub>2.5</sub> including aerosols formed in the near-field plume. The dilution sampler extracted a sample stream from the stack into a mixing chamber, where it was diluted with purified ambient air approximately 24:1 during natural gas operation and 35:1 during number 6 oil firing.

The specific objectives of this test were to:

#### Primary Objectives

- Develop emission factors and chemical speciation profiles for organic aerosols and PM<sub>2.5</sub> mass;
- Characterize sulfate, nitrate, ammonium, inorganic elements, elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filter media in the dilution sampler;
- Determine sulfur trioxide emissions using the controlled condensation method and compare to sulfate emissions measured using the dilution tunnel;
- Characterize key secondary particle precursors in stack gas samples: volatile and semivolatile organic compounds (VOC and SVOC, respectively) with carbon number of 2 and above; sulfur dioxide (SO<sub>2</sub>); ammonia (NH<sub>3</sub>) and oxides of nitrogen (NO<sub>x</sub>);
- Determine the fraction and size distribution of PM<sub>2.5</sub> mass comprised by ultrafine (<0.3 microns) particles;
- Document the relevant process design characteristics and operating conditions during the test;
- Identify issues associated with particulate measurement from sources with relatively dilute exhaust streams; and
- Compare emission factors with similar emission factors currently available.

#### Secondary Objectives

- Speciate nickel compounds in the emissions;
- Qualitatively determine total filterable particulate emissions; and
- Determine the morphology of total filterable particulate matter.

Table 6-1. Overview of Sampling and Monitoring Scope.

Sampling Procedure (Analytes)	Sampling Location		
	Number of Samples		
	Fuel Header	Exhaust Duct	Ambient Air (Combustion Inlet)
Controlled condensation train (SO <sub>3</sub> , SO <sub>2</sub> )	--	8	--
Dilution tunnel	--	8	1
Teflon <sup>®</sup> filter (mass, elements) Quartz filter (ions, OC/EC) K <sub>2</sub> CO <sub>3</sub> -impregnated cellulose fiber filter (SO <sub>2</sub> ) Citric acid-impregnated cellulose fiber filter (NH <sub>3</sub> ) TIGF/PUF/XAD-4 (SVOCs) Tenax (VOCs: C7 +) Stainless steel canisters (VOCs: C2-C10) DNPH-coated silica gel cartridges (carbonyls)  MOUDI (ultrafine PM mass size distribution, elements)			(b)
CEMS (SO <sub>2</sub> , NO <sub>x</sub> , CO, CO <sub>2</sub> , O <sub>2</sub> )	--	8 (a)	--
Grab Sample - Fuel Oil	4	--	--
Grab Sample - Natural Gas	4	--	--

TIGF - Teflon<sup>®</sup>-impregnated glass fiber filter

PUF - polyurethane foam

XAD-4 - Amberlite<sup>®</sup> sorbent resin

DNPH – dinitrophenylhydrazine

MOUDI – micro-orifice uniform deposit impactor

CEMS – continuous emissions monitoring system

a. Concentrations monitored for duration of all 8 test runs

b. MOUDI sample not collected during ambient air sampling.

Table 6-2. Summary of Exhaust Gas Analytical Targets.

Analytes	Undiluted Exhaust Gas Samples				Dilution Tunnel Samples									
	Coil	Quartz filter	Imp.	Gases	Quartz filter	TIGF/PU F/ XAD	TMF	Tenax	SS cans	DNPH cartridges	K <sub>2</sub> CO <sub>3</sub> filter	Citric acid filter	MOU DI	
PM2.5 mass							X							
Ultrafine PM PSD													X	
SO3/Sulfate		X			X									
Chloride					X									
Ammonium					X									
Nitrate					X									
Elements							X						X	
Organic carbon					X									
Elemental carbon					X									
Semivolatile organic compounds						X								
Volatile organic compounds*							X							
Volatile organic compounds**								X						
Aldehydes									X					
Ammonia (gaseous)												X		
NO <sub>x</sub>				X										
SO <sub>2</sub>			X	X						X				
CO				X										
O <sub>2</sub>				X										
CO <sub>2</sub>				X										
Moisture or relative humidity			X											
Velocity				X										
Temperature				X										

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

## SITE DESCRIPTION

Tests were performed on a common duct from two industrial package boilers. Each unit is a dual fuel-fired unit that can fire either No. 6 fuel oil or natural gas (Figure 6-1). Each boiler's fuel heat input capacity is 65 MMBtu/hr. Tests were performed on the units firing fuel oil first, followed by the natural gas tests. Hot exhaust gases from the two operating boilers vent to a common vertical stack for the building via a common horizontal rectangular duct with a cross-section of approximately 6 feet by 9 feet. The facility is equipped with continuous emissions monitors for CO<sub>2</sub>, O<sub>2</sub>, CO, SO<sub>2</sub>, and NO<sub>x</sub>.

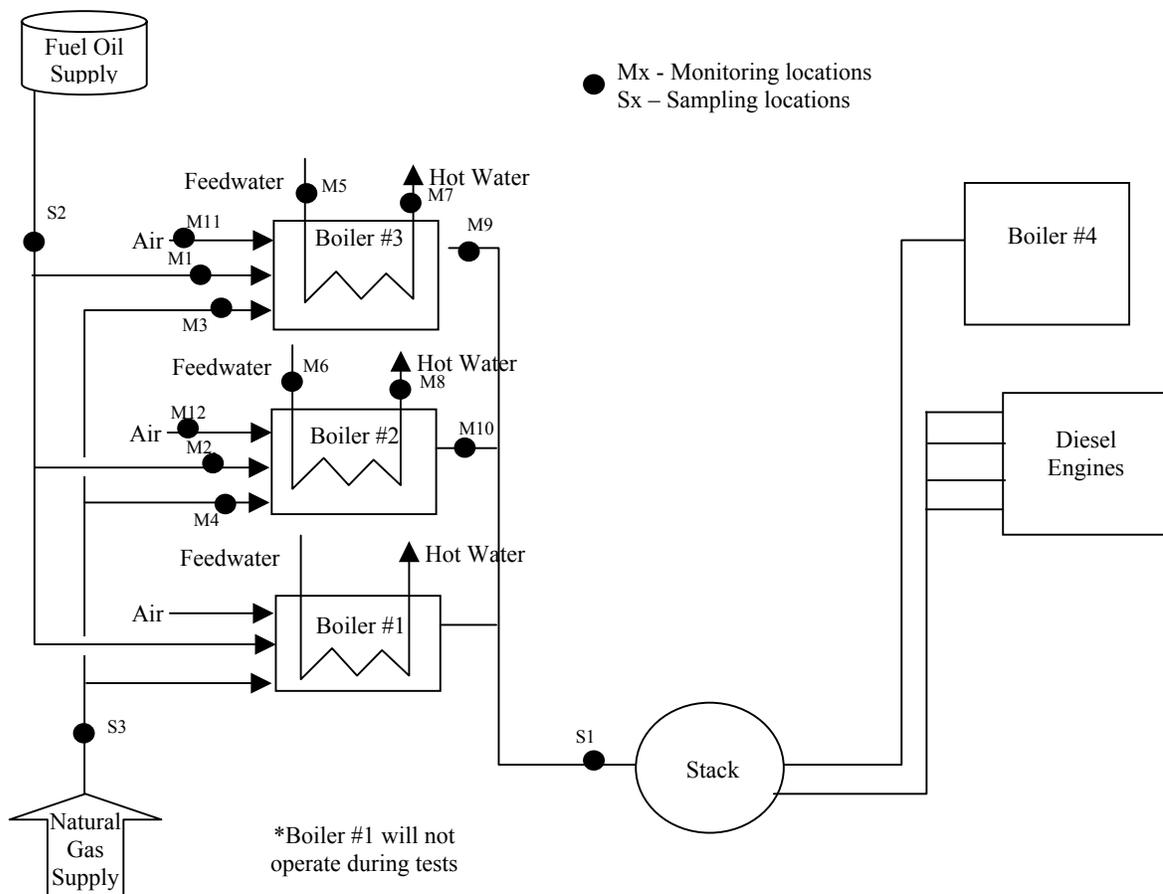


Figure 6-1. Site Delta Process Overview.

## POLLUTION CONTROL EQUIPMENT DESCRIPTION

The boilers do not have post-combustion air pollution control equipment.

## SAMPLING LOCATIONS

### Flue Gas Sampling Locations

Emissions samples were collected the boilers common horizontal, rectangular exhaust duct. The duct has inside dimensions of 103 inches by 67 inches for an inside equivalent diameter of 80.2 inches at the sampling location. There are three 2.5-inch diameter capped ports positioned in a vertical alignment approximately 33.5, 57.25 and 81.5 inches above the sampling platform. The ports are 144 inches downstream (1.80 diameters) from a 90° bend in the duct and 114 inches upstream from a convergence of the duct. The sampling locations did not meet the minimum EPA Method 1 requirements for upstream (2 diameters) disturbances, but the criterion for downstream disturbances (0.5 diameters) was meet. All ports were accessed from a single platform that is approximately 54 inches wide. The platform is approximately 14 feet above the ground and was accessed by a set of stairs. A preliminary velocity check was performed to determine the point of average flow and sampling was performed at points with velocities close to average flow. A test for cyclonic flow determined cyclonic flow was not present.

## RESULTS SUMMARY

The emissions data from testing performed on a dual fuel-fired commercial boiler with no pollution controls is reported. Testing was performed first firing No. 6 oil, then firing natural gas. The flue gas temperature at the sampling location was approximately 415°F for oil and 314°F for natural gas firing during the tests.

Emission factors for primary particulate including: total particulate and PM2.5; elements; ionic species; and organic and elemental carbon are presented in Tables 6-3a and 6-3b. Emission factors are expressed in pounds of pollutant per million British thermal units of fuel fired (lb/MMBtu). Four six-hour runs were performed for each fuel on separate, consecutive days. As a measure of the bias, precision, and variability of the results, the uncertainty and upper 95 percent confidence bound also are presented. Emission factors for semivolatile organic species (SVOCs) are presented in Tables 6-4a and 6-4b. The sum of SVOCs (polycyclic aromatic

Table 6-3a. Summary of Primary Particulate Emission Factors (Site Delta – NG).

Substance		Average Emmision Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Particulate Mass	PM2.5 (dilution tunnel)	3.7E-4	60	5.5E-4
	SO <sub>3</sub> (CCT)	1.1E-3	107	2.0E-3
Elements	Al	1.7E-6	140	3.6E-6
	As	9.0E-8	n/a	n/a
	Br	5.1E-8	80	8.1E-8
	Ca	4.2E-6	58	6.0E-6
	Cl	2.7E-7	n/a	n/a
	Co	7.6E-8	94	1.3E-7
	Cr	5.8E-8	289	1.4E-7
	Cu	4.0E-7	106	7.2E-7
	Fe	3.6E-6	82	5.8E-6
	K	1.3E-6	64	1.9E-6
	Mg	5.3E-7	86	8.8E-7
	Mn	6.7E-8	69	1.0E-7
	Na	2.2E-6	96	3.8E-6
	Ni	8.5E-7	131	1.7E-6
	Pb	6.7E-8	n/a	n/a
	S	3.5E-5	74	5.4E-5
	Si	4.9E-6	57	7.1E-6
	Sr	2.8E-8	n/a	n/a
Ti	1.9E-7	126	3.6E-7	
V	2.0E-7	212	4.8E-7	
Zn	1.4E-6	58	2.0E-6	
Ions	Cl <sup>-</sup>	3.5E-6	81	5.5E-6
	NO <sub>3</sub> <sup>-</sup>	5.7E-6	153	1.2E-5
	SO <sub>4</sub> <sup>=</sup>	8.3E-5	106	1.4E-4
	NH <sub>4</sub> <sup>+</sup>	2.2E-5	107	3.7E-5
	Soluble Na	1.2E-06	80	1.9E-06
Carbon	Organic Carbon	2.5E-4	80	3.8E-4
	Elemental Carbon	4.6E-5	147	9.3E-5
	Total Carbon	2.9E-4	83	4.6E-4

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

Table 6-3b. Summary of Primary Particulate Emission Factors (Site Delta – Oil).

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
Particulate Mass	PM2.5 (dilution tunnel)	1.2E-2	40	1.6E-2
	PM (CCT)	5.6E-3	97	9.7E-3
	SO <sub>3</sub> (CCT)	1.7E-2	74	2.6E-2
Elements (dilution tunnel)	Al	5.9E-5	21	7.0E-5
	As	6.4E-7	34	8.2E-7
	Ba	3.5E-6	44	4.8E-6
	Ca	1.2E-4	30	1.4E-4
	Co	1.6E-5	22	1.9E-5
	Cr	1.9E-6	19	2.3E-6
	Cu	8.5E-6	39	1.1E-5
	Fe	1.2E-4	24	1.5E-4
	Ga	6.1E-7	43	8.2E-7
	K	1.3E-5	34	1.7E-5
	La	1.2E-5	23	1.4E-5
	Mg	6.5E-7	319	2.0E-6
	Mn	1.4E-6	23	1.7E-6
	Mo	4.0E-6	49	5.6E-6
	Ni	2.5E-4	21	3.0E-4
	P	1.2E-5	94	2.1E-5
	Pb	7.3E-6	44	9.8E-6
	S	8.9E-4	31	1.1E-3
	Sb	1.1E-5	26	1.3E-5
	Se	7.3E-8	n/a	n/a
	Si	1.6E-4	19	1.9E-4
	Sn	2.0E-6	53	2.8E-6
	Sr	8.1E-7	22	9.7E-7
	Ti	5.2E-6	20	6.2E-6
Tl	1.5E-7	38	2.0E-7	
V	4.2E-5	26	5.1E-5	
Y	1.0E-7	44	1.3E-7	
Zn	1.4E-4	44	1.8E-4	
Zr	1.9E-7	24	2.3E-7	
Ions	Cl <sup>-</sup>	1.2E-5	34	1.6E-5
	SO <sub>4</sub> <sup>=</sup>	4.7E-3	47	6.4E-3
	NH <sub>4</sub> <sup>+</sup>	2.5E-4	39	3.3E-4
	Soluble Na	1.3E-5	45	1.8E-5
Carbon	Organic Carbon	5.4E-4	42	7.2E-4
	Elemental Carbon	5.0E-4	64	7.5E-4
	Total Carbon	1.0E-3	34	1.3E-3

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

Table 6-4a. Summary of Semivolatile Organic Species Emission Factors (Site Delta – NG).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence
			Upper Bound (lb/MMBtu)
Naphthalene	1.1E-5	166	2.4E-5
2-methylnaphthalene	5.4E-6	75	8.5E-6
1-methylnaphthalene	3.1E-6	74	4.9E-6
Biphenyl	2.8E-7	70	4.4E-7
1+2-ethylnaphthalene	2.2E-6	99	3.8E-6
2,6+2,7-dimethylnaphthalene	3.0E-6	80	4.9E-6
1,3+1,6+1,7-dimethylnaphthalene	1.7E-5	80	2.8E-5
1,4+1,5+2,3-dimethylnaphthalene	1.4E-6	85	2.3E-6
1,2-dimethylnaphthalene	7.7E-7	79	1.2E-6
2-Methylbiphenyl	2.4E-6	189	5.6E-6
3-Methylbiphenyl	2.1E-6	172	4.6E-6
4-Methylbiphenyl	3.7E-7	982	2.2E-6
Dibenzofuran	2.8E-7	76	4.5E-7
A-trimethylnaphthalene	1.4E-6	93	2.5E-6
B-trimethylnaphthalene	1.2E-6	98	2.1E-6
C-trimethylnaphthalene	1.3E-6	104	2.3E-6
E-trimethylnaphthalene	6.7E-7	111	1.2E-6
F-trimethylnaphthalene	6.2E-7	99	1.1E-6
2,3,5+1-trimethylnaphthalene	7.3E-7	92	1.2E-6
2,4,5-trimethylnaphthalene	2.0E-7	106	3.5E-7
J-trimethylnaphthalene	2.5E-7	121	4.9E-7
Acenaphthylene	2.4E-7	296	6.0E-7
Acenaphthene	6.1E-7	743	2.8E-6
Fluorene	4.2E-7	146	8.4E-7
Phenanthrene	8.5E-7	83	1.4E-6
A-methylfluorene	3.5E-7	67	5.4E-7
1-methylfluorene	2.2E-7	484	7.5E-7
9-fluorenone	1.4E-6	127	2.7E-6
Xanthone	4.6E-8	75	7.3E-8
A-methylphenanthrene	2.1E-7	138	4.1E-7
2-methylphenanthrene	2.7E-7	93	4.7E-7
C-methylphenanthrene	2.9E-7	60	4.3E-7
1-methylphenanthrene	8.4E-8	379	2.4E-7
Anthrone	2.8E-7	121	5.3E-7
Anthraquinone	1.3E-7	258	2.9E-7
3,6-dimethylphenanthrene	6.1E-8	123	1.2E-7
A-dimethylphenanthrene	9.5E-8	n/a	n/a
C-dimethylphenanthrene	2.0E-7	111	3.6E-7

Table 6-4a. Summary of Semivolatile Organic Species Emission Factors (Site Delta – NG)  
(Continued).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence
			Upper Bound (lb/MMBtu)
D-dimethylphenanthrene	1.2E-7	304	3.1E-7
E-dimethylphenanthrene	7.4E-8	250	1.7E-7
Anthracene	7.9E-8	142	1.6E-7
9-methylanthracene	2.3E-7	251	5.3E-7
Fluoranthene	1.8E-7	96	3.1E-7
Pyrene	3.5E-7	111	6.4E-7
9-Anthraldehyde	2.1E-7	n/a	n/a
Benzonaphthothiophene	1.2E-8	252	2.7E-8
B-MePy/MeFl	1.5E-7	124	2.9E-7
C-MePy/MeFl	3.8E-8	127	7.3E-8
D-MePy/MeFl	1.4E-7	113	2.5E-7
4-methylpyrene	2.5E-7	122	4.8E-7
1-methylpyrene	1.3E-7	114	2.4E-7
Benz(a)anthracene	1.5E-7	177	3.5E-7
7-methylbenz(a)anthracene	1.4E-8	245	3.1E-8
Chrysene	2.9E-7	163	6.4E-7
Benzanthrone	1.9E-7	165	4.3E-07
5+6-methylchrysene	8.6E-8	168	1.9E-07
Benzo(b+j+k)fluoranthene	1.7E-8	76	2.6E-08
7-methylbenzo(a)pyrene	2.1E-8	n/a	n/a
Benzo(a)pyrene	3.4E-8	542	1.3E-07
Sum of all SVOCs	6.4E-5		

n/a - not applicable; only one run was in detection limits

Table 6-4b. Summary of Semivolatile Organic Species Emission Factors (Site Delta – Oil).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence
			Upper Bound (lb/MMBtu)
Naphthalene	1.2E-5	103	2.0E-5
2-methylnaphthalene	6.9E-6	62	1.0E-5
1-methylnaphthalene	3.8E-6	64	5.7E-6
Biphenyl	3.2E-7	167	6.8E-7
1+2-ethylnaphthalene	2.2E-6	57	3.2E-6
2,6+2,7-dimethylnaphthalene	3.4E-6	53	4.8E-6
1,3+1,6+1,7-dimethylnaphthalene	1.9E-5	57	2.7E-5
1,4+1,5+2,3-dimethylnaphthalene	1.5E-6	41	2.0E-6
1,2-dimethylnaphthalene	8.7E-7	49	1.2E-6
2-Methylbiphenyl	6.8E-6	n/a	n/a
3-Methylbiphenyl	2.5E-6	632	1.0E-5
4-Methylbiphenyl	2.3E-6	n/a	n/a
Dibenzofuran	3.6E-7	56	5.3E-7
A-trimethylnaphthalene	1.7E-6	87	2.8E-6
B-trimethylnaphthalene	1.3E-6	96	2.2E-6
C-trimethylnaphthalene	1.3E-6	99	2.3E-6
E-trimethylnaphthalene	6.9E-7	98	1.2E-6

Table 6-4b. Summary of Semivolatile Organic Species Emission Factors (Site Delta – Oil)  
(Continued).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)
F-trimethylnaphthalene	6.7E-7	75	1.1E-6
2,3,5+1-trimethylnaphthalene	8.5E-7	80	1.4E-6
2,4,5-trimethylnaphthalene	2.4E-7	90	4.0E-7
J-trimethylnaphthalene	2.4E-7	164	5.4E-7
1,4,5-trimethylnaphthalene	2.5E-7	59	3.4E-7
Acenaphthylene	3.8E-7	519	1.4E-6
Acenaphthene	7.5E-7	89	1.3E-6
Fluorene	3.9E-7	50	5.5E-7
Phenanthrene	1.4E-6	72	2.2E-6
A-methylfluorene	3.7E-7	306	9.4E-7
1-methylfluorene	2.7E-7	94	4.5E-7
9-fluorenone	6.8E-7	46	9.4E-7
Xanthone	7.6E-8	112	1.4E-7
Acenaphthenequinone	4.5E-8	521	1.6E-7
A-methylphenanthrene	6.1E-7	115	1.1E-6
2-methylphenanthrene	7.7E-7	106	1.4E-6
B-methylphenanthrene	1.3E-7	n/a	n/a
C-methylphenanthrene	1.0E-6	144	2.1E-6
1-methylphenanthrene	6.0E-7	242	1.6E-6
Anthrone	3.4E-7	87	5.6E-7
Anthraquinone	3.1E-7	87	5.2E-7
3,6-dimethylphenanthrene	2.8E-7	119	5.4E-7
A-dimethylphenanthrene	3.2E-7	174	7.0E-7
B-dimethylphenanthrene	1.2E-7	124	2.3E-7
C-dimethylphenanthrene	9.6E-7	129	1.9E-6
1,7-dimethylphenanthrene	1.9E-7	140	3.8E-7
D-dimethylphenanthrene	4.5E-7	146	9.5E-7
E-dimethylphenanthrene	1.2E-7	156	2.4E-7
Anthracene	1.1E-7	139	2.2E-7
Fluoranthene	5.3E-7	86	8.8E-7
Pyrene	1.7E-6	125	3.3E-6
9-Anthraldehyde	1.0E-7	n/a	n/a
Benzonaphthothiophene	1.0E-7	341	3.4E-7
B-MePy/MeFl	7.3E-7	78	1.2E-6
C-MePy/MeFl	2.7E-7	93	4.5E-7
D-MePy/MeFl	6.3E-7	110	1.1E-6
4-methylpyrene	9.9E-7	109	1.8E-6
1-methylpyrene	4.1E-7	137	8.2E-7
Benzo(c)phenanthrene	7.4E-8	n/a	n/a
Benz(a)anthracene	4.2E-7	150	8.9E-7
7-methylbenz(a)anthracene	1.7E-8	n/a	n/a
Chrysene	2.5E-7	105	4.5E-7
Benzanthrone	9.7E-8	119	1.8E-7
5+6-methylchrysene	2.3E-8	82	3.7E-8
chryq14	1.4E-8	387	5.2E-8
7-methylbenzo(a)pyrene	7.3E-8	174	1.4E-7
Benzo(a)pyrene	7.0E-8	87	1.2E-7

n/a - not applicable; only one run was in detection limits

hydrocarbons (PAHs)) is approximately 26 percent of the organic carbon for oil firing and 16 percent for natural gas firing.

The preceding tables include only those substances that were detected in at least one of the four test runs. Substances of interest not present above the minimum detection limit for these tests are listed in Tables 6-5a and 6-5b.

The primary particulate results presented in Tables 6-3a and 6-3b also may be expressed as a PM<sub>2.5</sub> speciation profile, which is the mass fraction of each species contributing to the total PM<sub>2.5</sub> mass. The speciation profile is presented in Figure 6-2.

The main findings of these tests are:

- Particulate mass emissions from the boiler firing gas were low, consistent with levels expected for gaseous fuel combustion, but still higher than any previously tested gas-fired source. PM<sub>2.5</sub> emissions from the boiler were more than an order of magnitude higher when firing No. 6 oil.
- Two methods for determining the average emission factor for primary PM mass from oil firing gave results, which corresponded relatively well: 0.012 lb/MMBtu using the dilution tunnel; and 0.023 lb/MMBtu using a controlled condensation train (this result includes filterable and condensable particulate).
- Chemical species accounting for 190 percent of the measured PM<sub>2.5</sub> mass from gas firing and 65 percent from oil firing were quantified.
- Organic and elemental carbon comprise approximately 85 percent of the primary PM<sub>2.5</sub> mass from gas firing, but only 8 percent of the primary PM<sub>2.5</sub> mass from oil firing.
- For oil firing, the predominant component of the PM<sub>2.5</sub> is sulfate (38 percent), reflecting the higher sulfur content of No. 6 oil compared to natural gas. There are also higher percentages of Ni and V in the oil combustion emissions, again reflecting the fuel differences.
- Most organic species are not detected at levels significantly above background levels in the ambient air or field blanks. All detected organics are present at extremely low levels consistent with gaseous fuel combustion.

Table 6-5a. Substances of Interest Not Detected in Stack Emissions from Site Delta (NG).

Inorganic	VOC (>C2)	VOC (>C7)
Ag	Butanal	Biphenyl
Au	Butanone	1+2-ethylnaphthalene
Ba	2,2-dimethylpentane	Acenaphthylene
Cd	Mechloroform	1,2-dimethylnaphthalene
Ga	3,3-dimethylheptane	Acenaphthene
Hg	n-butylbenzene	Fluorene
In	1,3-dimethyl-4-ethylbenzene	Propylene glycol
La	2-methylindan	hexyl acetate
Mo		2-butoxyethyl acetate
P	VOC (>C7)	Benzoic acid
Pd	2-heptanone	2-(2-butoxyethoxy) ethanol
Rb	alpha-Pinene	Hexadecanoic acid
Sb	beta-pinene	Pentamethylbenzene
Se	2-pentylfuran	
Sn	t-butylbenzene	
Tl	4-methylstyrene	
U	Isobutylbenzene	
Y	Sec-butylbenzene	SVOC
Zr	1,2,3-trimethylbenzene	1,4,5-trimethylnaphthalene
	Indene	B-methylfluorene
Carbonyl	o-isopropyltoluene	Acenaphthenequinone
Acrolein	o-methylphenol	Perinaphthenone
Propionaldehyde	m-tolualdehyde	B-methylphenanthrene
Crotonaldehyde	Butylbenzene	2,3-Benzofluorene
Butyraldehyde	1,2-diethylbenzene	1,7-dimethylphenanthrene
Hexanaldehyde	2-n-propyltoluene	Retene
	4-tert-butyltoluene	1-MeFl+C-MePy/Fl
VOC (>C2)	2-methylbenzofuran	Benzo(c)phenanthrene
F 114	5-isopropyl-m-xylene	Benz(a)anthracene-7,12-dionene
1-butene&i-butene	1,3-diisopropylbenzene	1,4-chrysenequinone
1 & 2-butyne	Pentylbenzene	Benzo(e)pyrene
Acetonitrile	1,2,3,4-tetrahydronaphthalene	Perylene
tert-butanol	1,2-dihydronaphthalene	Indeno[123-cd]pyrene
2-methylpropanal	1,4-diisopropylbenzene	Benzo(ghi)perylene
Methacrolein	C-dimethylindane	Dibenzo(ah+ac)anthracene
3-methyl-1-pentene	2-decanone	Coronene



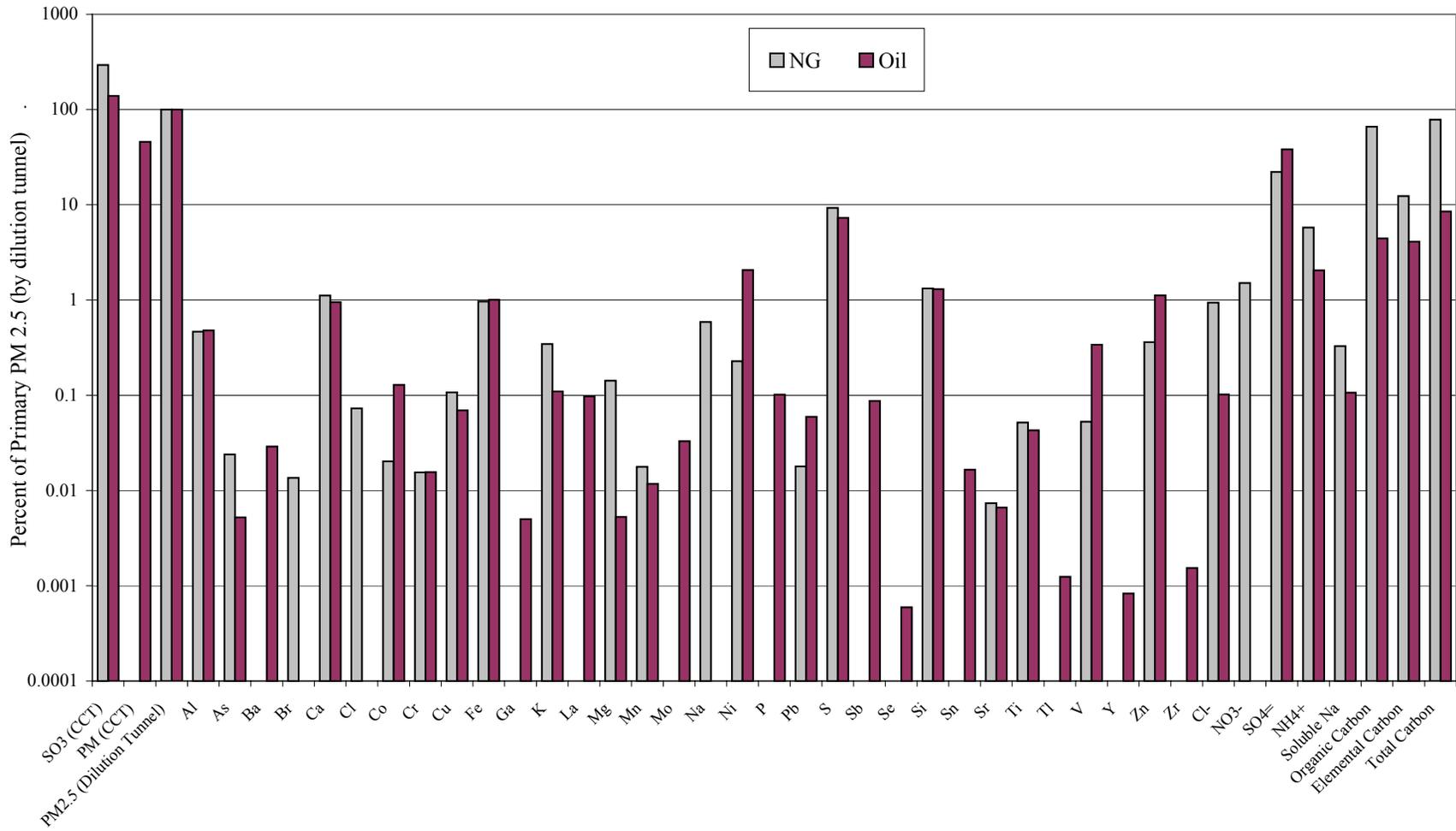


Figure 6-2. Speciation Profile for Primary Particulate Emissions from Site Delta.

## Section 7

### DILUTION SAMPLER DEVELOPMENT

#### PILOT TEST RESULTS

##### Introduction

Particles in combustion exhaust derive from mineral matter in the fuel, carbonaceous particles formed during combustion, and deterioration of fire bricks and metal parts in the combustion system. Hot exhaust is rapidly cooled and mixed with ambient air resulting in gases nucleating homogeneously and heterogeneously or condensing on pre-existing particles. Condensational growth of particles in a diluted plume depends on temperature, relative humidity, aging time, mixing rate, and partitioning of species between the gaseous and solid phases. Stationary source air emission sampling methods used for compliance testing (U.S. EPA Method 201/202A) tend to underestimate or overestimate the emitted  $PM_{2.5}$  because the hot front filter does not collect condensable species and the cold aqueous impingers collect gaseous as well as condensable components<sup>8-12</sup>. The condensable components dominate  $PM_{2.5}$  and thus the artifacts are first order effects in the measurements and should not be ignored. A more realistic representation of actual  $PM_{2.5}$  mass emissions and chemical compositions could be achieved by diluting, cooling, and aging the hot exhaust prior to sampling, similar to actual conditions in the atmosphere<sup>11-12</sup>. Hinds,

Dilution sampling methods simulate the cooling and dilution processes that occur as combustion exhaust mixes with the atmosphere. Exhaust dilution sampling has been used as the reference method (e.g., ISO 8178)<sup>13,14</sup> for mobile source sampling<sup>15-21</sup>, but it has been used only in research applications for stationary sources<sup>12, 23,32</sup>. Combustion exhaust is drawn through an isokinetic probe and a heated sampling line, then mixed with clean filtered ambient air. The clean air is supplied using High Efficiency Particulate Arresting (HEPA) filter that removes particles followed by a bed of activated carbon granules that removes gases and volatilized particles not collected by the HEPA filter. The mixed air stream is aged to permit the particle to cool, coagulate, and condensate prior to collection on filters for mass and chemical analysis. Hildemann *et al*<sup>12</sup> conservatively estimated an aging time of 80-90 seconds for organic species to condense on particles with dilution air ratios greater than 27. However, large dilution air ratios

and long aging times required a large aging chamber that is impractical for the limited space available in many stack-testing situations. In addition, prolonged aging times may result in excessive diffusive wall losses for small particles.

Lipsky *et al*<sup>32</sup> investigated how particle size distributions and mass emissions from a pilot scale pulverized coal combustor changed by several dilution air ratios (15, 70 and 150 times) and aging times (0, 1.5, and 12 minutes). The results suggested that dilution air ratio and aging time did not change the mass emission rate. Particle number decreased and particle size increased with longer aging times, consistent with coagulation theory<sup>33</sup>. Higher number counts and smaller particle sizes were found for higher dilution air ratios over a given aging time, consistent with lower probabilities of particle collisions. The high ash content in coal provides large a surface area on which smaller particle could collide and gases could condense. The results may differ for other fuels and combustion exhaust that do not produce a large abundant of primary particles as is typically for coal.

This study reports experimental results to determine (1) the minimum aging time and dilution air ratio required to achieve stable number distributions of ultrafine particles, (2) minimum aging times and dilution air ratios to achieve stable mass emission rates, and (3) the dependence of ultrafine particle size distributions on combustion fuels (coal, oil and natural gas) and temperatures. Ultrafine particles in this study are defined as those with electric mobility diameter in the range of 10-420 nm that include both particle nucleation and condensational modes in ambient air, rather than conventional ambient particle size  $< 0.1\mu\text{m}$  in aerodynamic diameter. The study was undertaken to define optimal operating conditions for a new generation of practical dilution samplers.

#### EXPERIMENTAL METHODS:

Experiments were conducted by sampling combustion exhaust of coal, oil, and gas from the Fuel Evaluation Facility (FEF, GE EER, Irvine, CA), shown in Figure 7-1, which operated at a nominal fuel heat input rate of 160kW and 3% excess oxygen. The dilution sampler shown in Figure 7-2 drew  $20\text{-}25\text{ L}\cdot\text{min}^{-1}$  of the combustion exhaust from the center of the 15.5 cm diameter duct through a PM10/2.5 cyclone (Case PM<sub>10</sub>, Case PM<sub>2.5</sub>, ThermoAnderson, Smyrna,

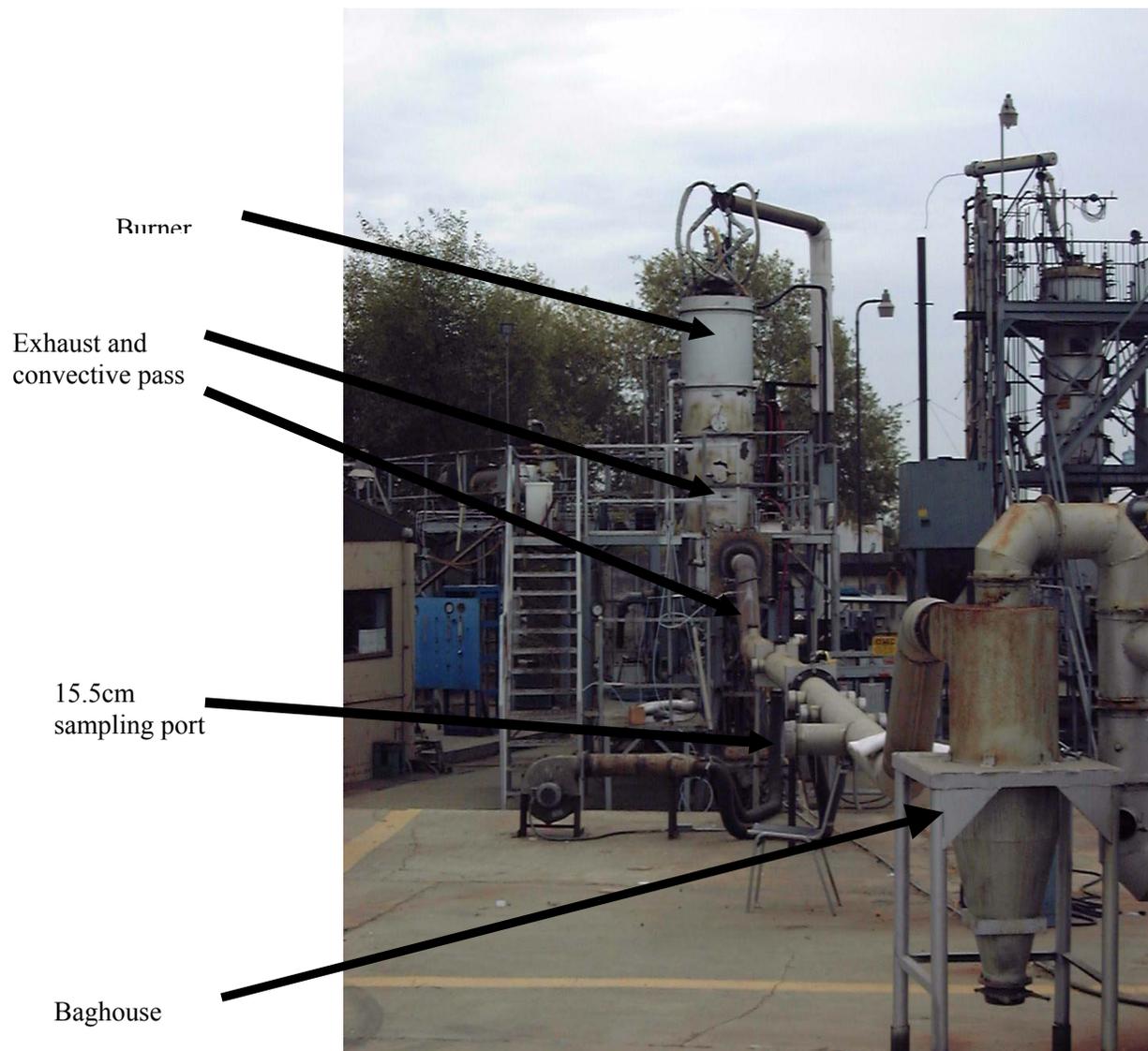


Figure 7-1 Diagram of the pilot-scale test combustor (Fuel Evaluation Facility) at GE EER, Irvine, CA. The nominal rate fuel heat input rate is 160kW with 3% excess oxygen.

GA) to remove particles larger than 2.5  $\mu\text{m}$  in aerodynamic diameter. Combustion exhaust passed through a 6 feet long flexible sampling line heated at 445K to reduce particle thermophoresis losses and gases condensation on the wall, before mixing and dilution with clean ambient air in the U-shape mixing chamber (15 cm in diameter and 207cm long). At the end of mixing chamber, 226  $\text{L}\cdot\text{min}^{-1}$  of diluted sample was drawn to an aging chamber of 45 cm in diameter and 183 cm in height (shown in Figure 7-2) to provide a total aging time of 80-90 seconds prior to sample collection, and the excess flow was removed by a high-vol pump (Hi-Vol., model 1E5070, Tisch, Cleveland, OH). It is assumed that plug flow exists throughout dilution sampler and an aging time of 80-90 seconds is sufficient to complete short-term evaluation of the emissions for particle size distributions. Emitted particles will continue to interact with substances in the ambient air over longer period, but these should be treated in air quality models once the primary emission characteristics are known.

Table 7-1 shows the test matrix as a function of dilution air ratios, aging times, combustion exhaust temperatures and fuel types. Three fuel types, Kittanning coal (high ash level), No. 6 residual oil (medium ash level), and natural gas (low to zero ash fraction), were tested. Fuel analyses are listed in Tables 7-2 and 7-3. Effects of combustion exhaust temperature on PM formation were evaluated at  $450\text{K} \pm 10\text{K}$  and  $645\text{K} \pm 10\text{K}$ .

Particles were extracted from the dilution sampler with aging time of 2, 10 and 80 seconds corresponding to locations L1, L2, and L4 for 10 times dilution air ratio, and L2, L3, L4 for the 50 times dilution air ratio (Figure 7-2). A Scanning Mobility Particle Sizer (SMPS, DMA model 3071 and CPC model 3025, TSI, Shoreview, MN) measured the particle number concentrations from 10 to 420 nm in five minutes scanning time and several measurements were made for each dilution air ratio and aging time combinations. These real time measurements are used to quantify the changes of particle mass and size distribution throughout the tests.

In addition, at these three aging time sampling port, 30  $\text{L}\cdot\text{min}^{-1}$  was drawn and split to two parallel channels (15  $\text{L}\cdot\text{min}^{-1}$  each) containing a pre-weighed Teflon membrane filter and a pre-fired quartz fiber filter. A DustTrak (model 8520, TSI, Shoreview, MN), a forward light

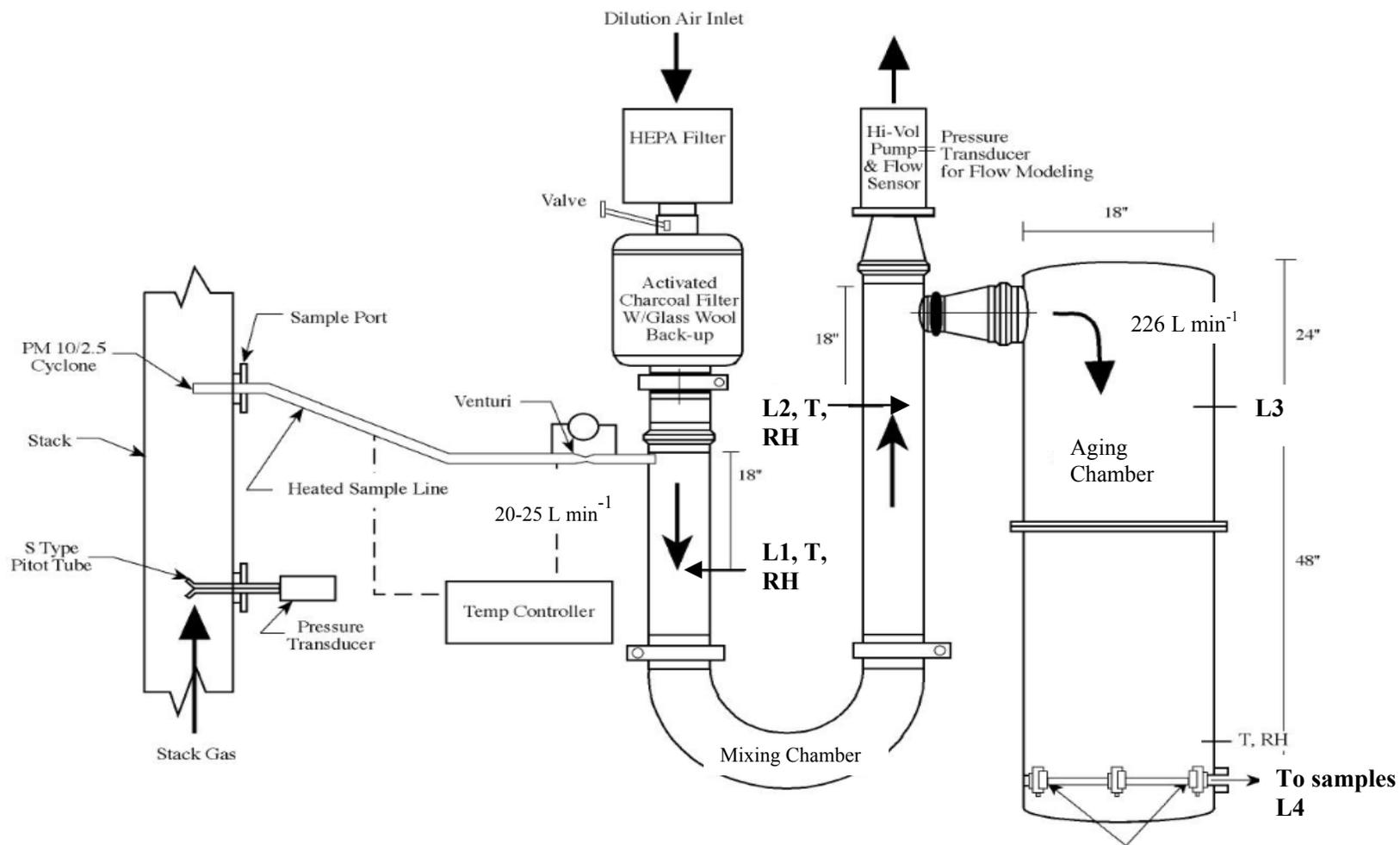


Figure 7-2. Schematic of dilution sampler setup. Locations of L1, L2 and L4 correspond to particle aging time of 2, 10 and 80 seconds for dilution air ratio of 10; and L2, L3 and L4 for 50, respectively.

Table 7-1. Variables Evaluated in Separate Experiments.

Testing Parameters	Operating conditions and fuels		
Particle aging Time	2 second,	10 second,	and 80 second
Dilution Ratios <sup>(a)</sup>	10 X	and	50 X
Fuel Types	Natural gas,	No. 6 residual oil,	and Kittanning coal
Flue gas temperatures	450K	and	645K

a.  $DilutionRatio = \frac{Q_{filteredAir} + Q_{FlueGas}}{Q_{FlueGas}}$

Table 7-2. Ultimate analysis of Kittanning coal and No. 6 residual oil

Fuel Analysis (wt%)		
Fuel Name	Kittanning Coal	No. 6 residual Oil
C	72.4	86.56
H	4.20	10.76
N	1.21	0.48
S	1.22	1.47
O	7.02	0.54
Ash	10.85 <sup>a</sup>	0.19
H <sub>2</sub> O	3.10	0.3

a. Ash analysis of Kittanning coal

Ash Mineral	wt%
SiO <sub>2</sub>	57.81
Al <sub>2</sub> O <sub>3</sub>	26.38
TiO <sub>2</sub>	1.33
Fe <sub>2</sub> O <sub>3</sub>	7.38
CaO	1.47
MgO	0.62
K <sub>2</sub> O	2.81
Na <sub>2</sub> O	0.33
SO <sub>3</sub>	0.61
P <sub>2</sub> O <sub>5</sub>	0.40
SrO	0.20
BaO	0.00
Mn <sub>3</sub> O <sub>4</sub>	0.00
Undetermined	0.66
TOTAL	100.00

Table 7-3. Typical Gas Composition in Southern California Gas System.

Components <sup>a</sup>	Weighted Average
N <sub>2</sub> +O <sub>2</sub>	0.7
CO	1.25
CH <sub>4</sub>	95.41
C <sub>2</sub> H <sub>6</sub>	2.12
C <sub>3</sub> H <sub>8</sub>	0.39
I-C <sub>4</sub> H <sub>10</sub>	0.04
n-C <sub>4</sub> H <sub>10</sub>	0.06
I-C <sub>5</sub> H <sub>12</sub>	0.01
n-C <sub>5</sub> H <sub>12</sub>	0.01
C <sub>6</sub> +	0.01
Total	100

a. Hydrogen sulfide 0.01grains/100scf

scattering detector, samples at  $1.7 \text{ L}\cdot\text{min}^{-1}$  with a PM2.5 inlet and was connected to the L4 sampling port (80 second aging time) to estimate the real time particle mass concentration. Samplers were of 2 to 6 hour sampling duration, as determined by the cumulated DustTrak signal, long enough to obtain a detectable sampling loading. Filters were submitted to gravimetric, elemental (XRF)<sup>34</sup>, ion (IC)<sup>35</sup> and carbon analyses (TOR)<sup>36</sup>, depending on the type of tests.

Thermocouples were placed at L1, L2 and L4 in dilution sampler to monitor the relative humidity and temperature of the diluted sample. The dilution airflow and backpressure were adjusted to maintain the target dilution air ratio and sample flow rates. Flowrates were calibrated at 293 K and 1.0 atm. Pressure reductions (flowrate), temperature and relative humidity were recorded by a laptop computer data acquisition system.

## RESULTS AND DISCUSSION

Continuous size distributions of particles were estimated using an inversion routine for the SMPS and are presented as  $dN/d\log(dp)$ , where N is the number concentration and dp is the electric mobility diameter. The particles number concentrations from combustion exhaust are converted as per unit exhaust gas volume (multiplying particle number concentration measured

by the dilution air ratio). The ambient particle size distributions in March 2002, Irvine, CA, in Figure 7-3, show a wide size range (15-420nm) and relatively low number counts (1,000-3,000 particle•cm<sup>-3</sup>).

Figures 7-4 and 7-5 show how different dilution air ratios and aging times affected the number distributions for coal, oil and gas at the combustion exhaust temperature of 450K. Figures 7-4a, 7-4b and 7-4c show particle number concentration modes from Kittanning coal, No. 6 residual oil and natural gas combustions at 50-80 nm, 70-100 nm, and 15-25 nm, respectively, at an aging time of 80 seconds. The modes of particle size distribution did not change with different dilution air ratios for Kittanning coal and No. 6 residual oil, but increased slightly for natural gas as the dilution air ratio decreased from 20-50 to 10. For Kittanning coal and No. 6 residual oil, particle number concentrations increased with larger dilution air ratio as seen in Figure 7-4a and 7-4b, respectively. The coal results are consistent with those of Lipsky *et al*<sup>32</sup>. However, Figure 7-4c shows the opposite behavior for natural gas, with decreasing particle number concentration as the dilution air ratio increases. Figure 7-4c also shows that particle size distributions from natural gas exhaust were similar when the dilution air ratio exceeded 20. This implies that a dilution air ratio of 10 cannot adequately simulate plume equilibrium in the atmosphere and a minimum dilution air ratio of 20 is needed for sampling emissions from natural gas.

The very different trends of particle number concentrations affected by dilution can be explained by the difference in fuels, i.e., low particle concentrations from natural gas exhaust in contrast to high ash content from Kittanning coal and No. 6 residual oil. Particle nucleation occurs due to the supersaturation of vapor species when cooled and diluted. A low dilution air ratio for natural gas results in a higher vapor pressure and a higher nucleation rate for the condensable species. Therefore, the particle concentrations increase and shift the particle size distribution slightly to the larger size for low dilution air ratio. The high soot/ash concentrations in Kittanning coal and No. 6 residual oil rapidly coagulate and form much larger particles (> 420nm) due to high particle number concentrations at 10 time dilution air ratios. This also explains the larger particle modes of No. 6 residual oil (Figure 7-4b) due to the condensational growth with a higher fraction of condensable material than for Kittanning coal.

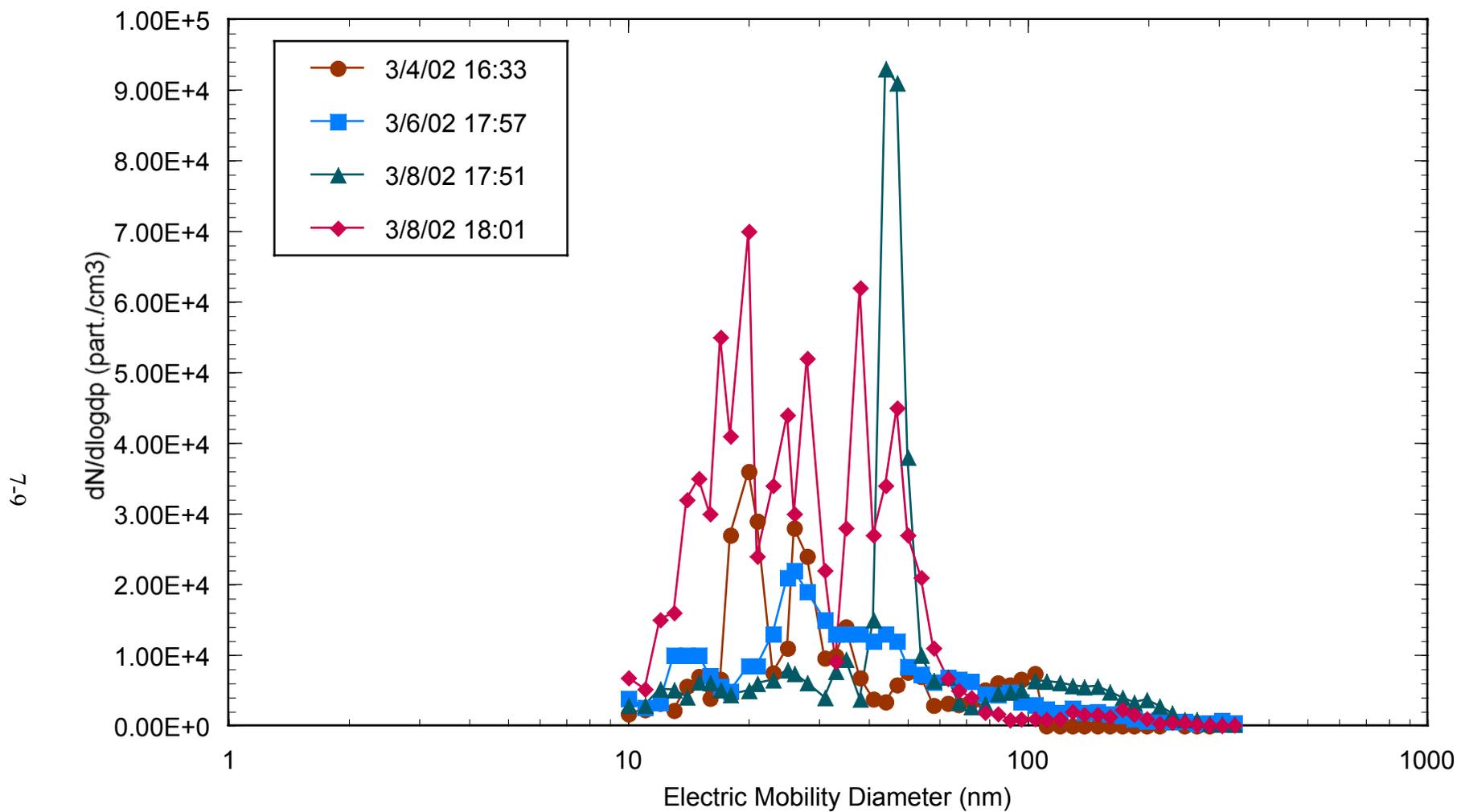


Figure 7-3. Ambient ultrafine particle size distribution measured in Irvine, CA, during March 4<sup>th</sup>–8<sup>th</sup>, 2002

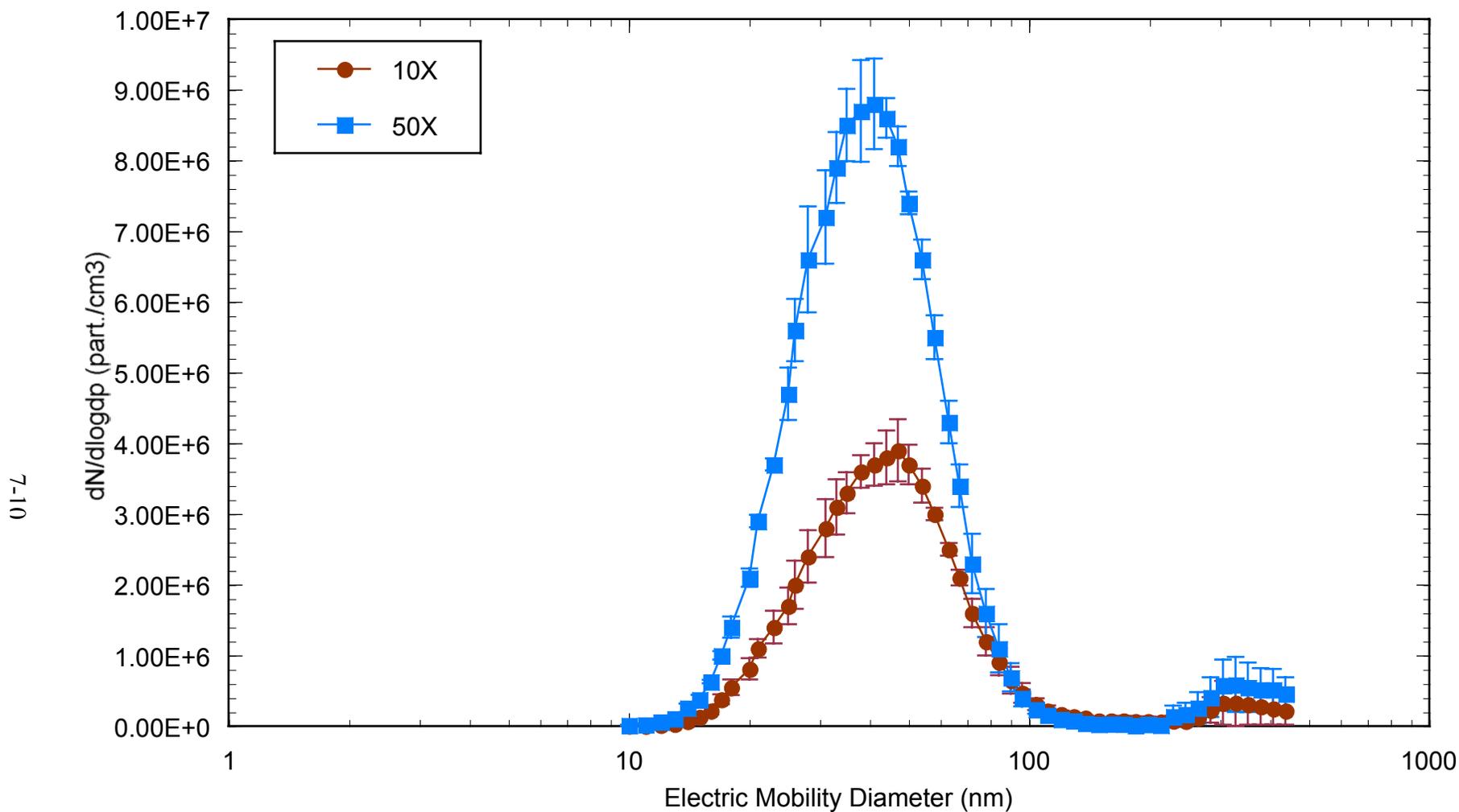


Figure 7-4a. Comparisons of ultrafine particle size distribution (per unit combustion exhaust) measured by Scanning Mobility Particle Sizer (SMPS) as a function of different dilution air ratio at combustion exhaust temperature 450K and residence time of 80 seconds, from Kittanning coal combustion

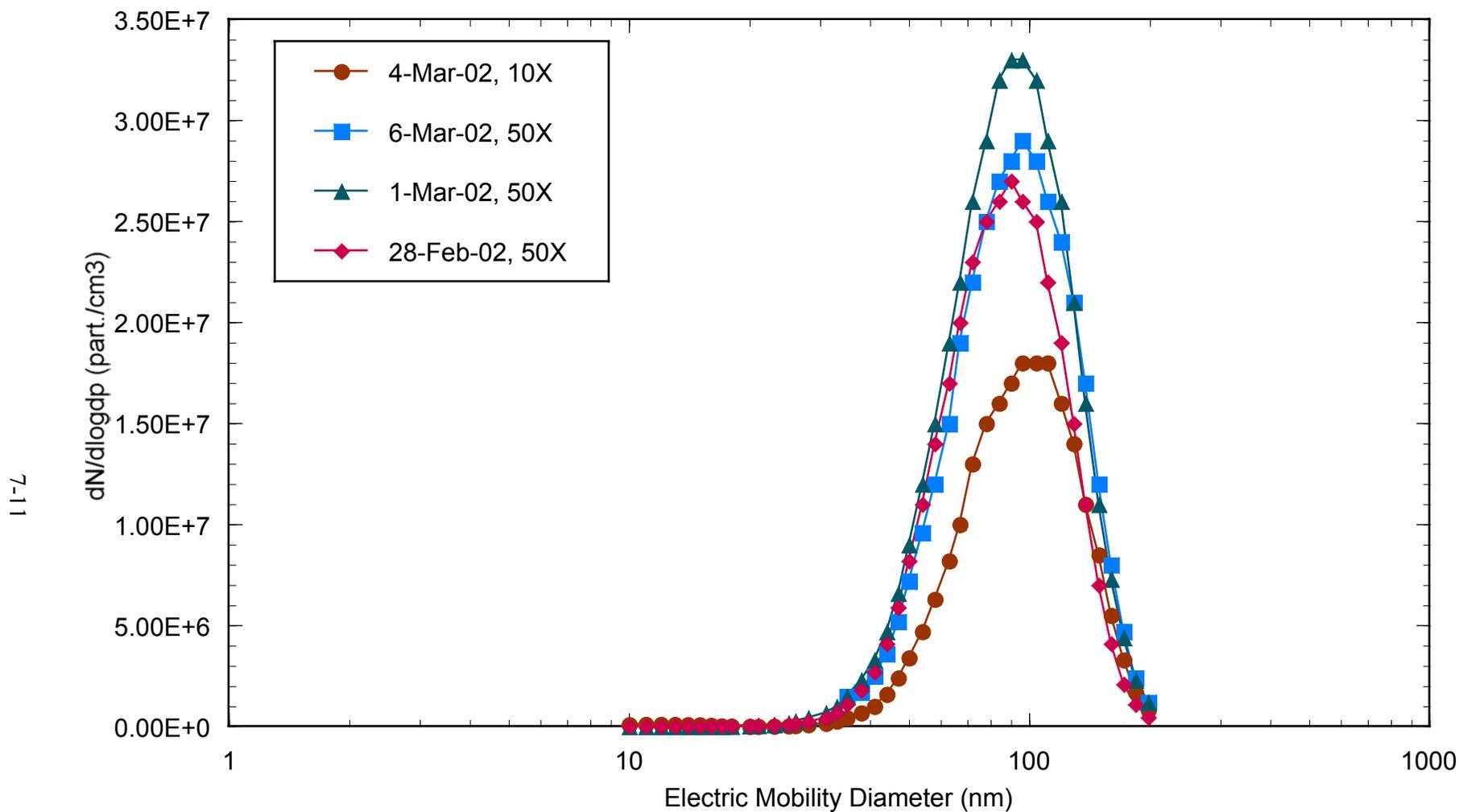


Figure 7-4b. Comparisons of ultrafine particle size distribution (per unit combustion exhaust) measured by Scanning Mobility Particle Sizer (SMPS) as a function of different dilution air ratio at combustion exhaust temperature 450K and residence time of 80 seconds, from No. 6 residual oil combustion

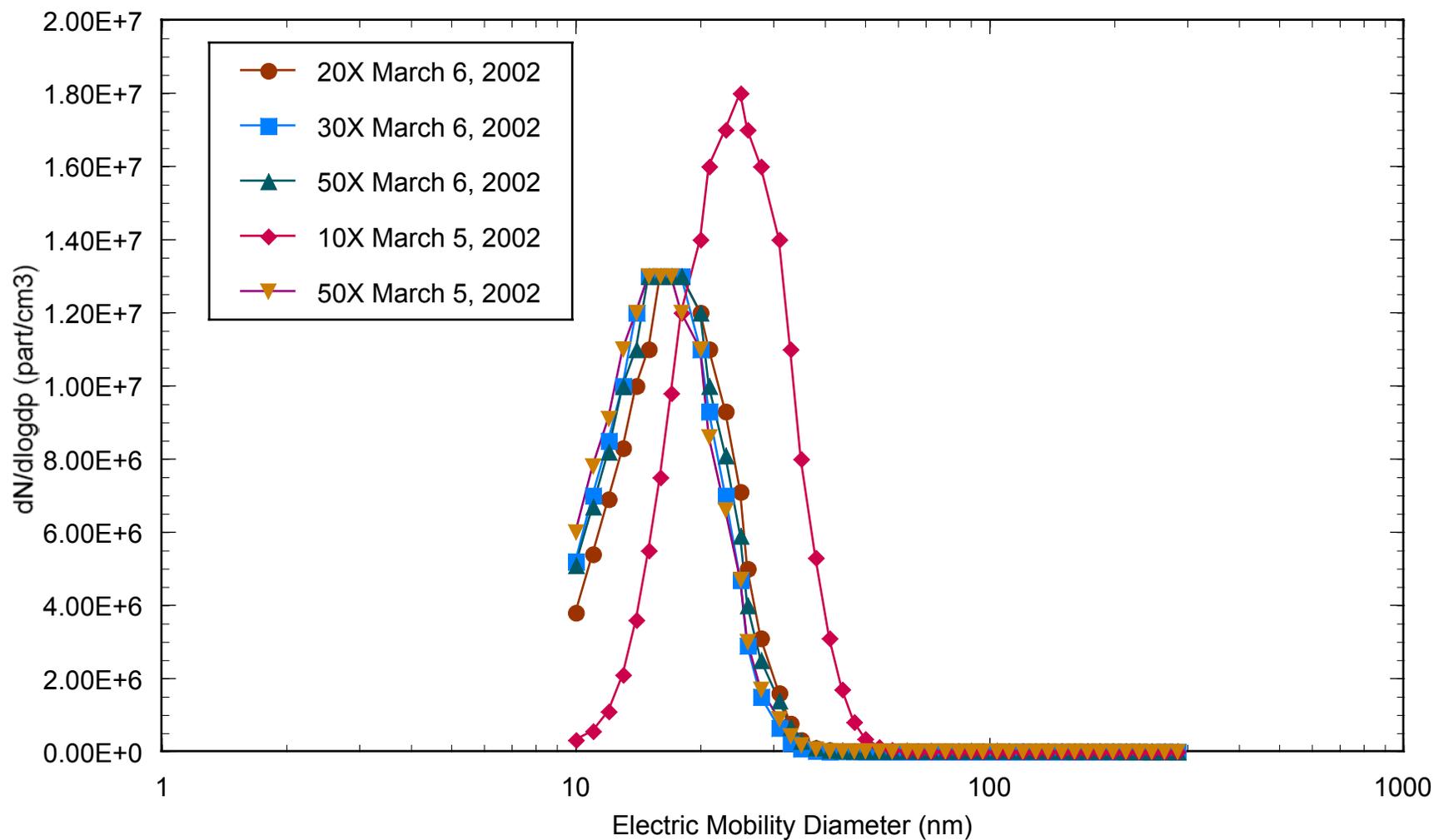


Figure 7-4c. Comparisons of ultrafine particle size distribution (per unit combustion exhaust) measured by Scanning Mobility Particle Sizer (SMPS) as a function of different dilution air ratio at combustion exhaust temperature 450K and residence time of 80 seconds, from natural gas combustion

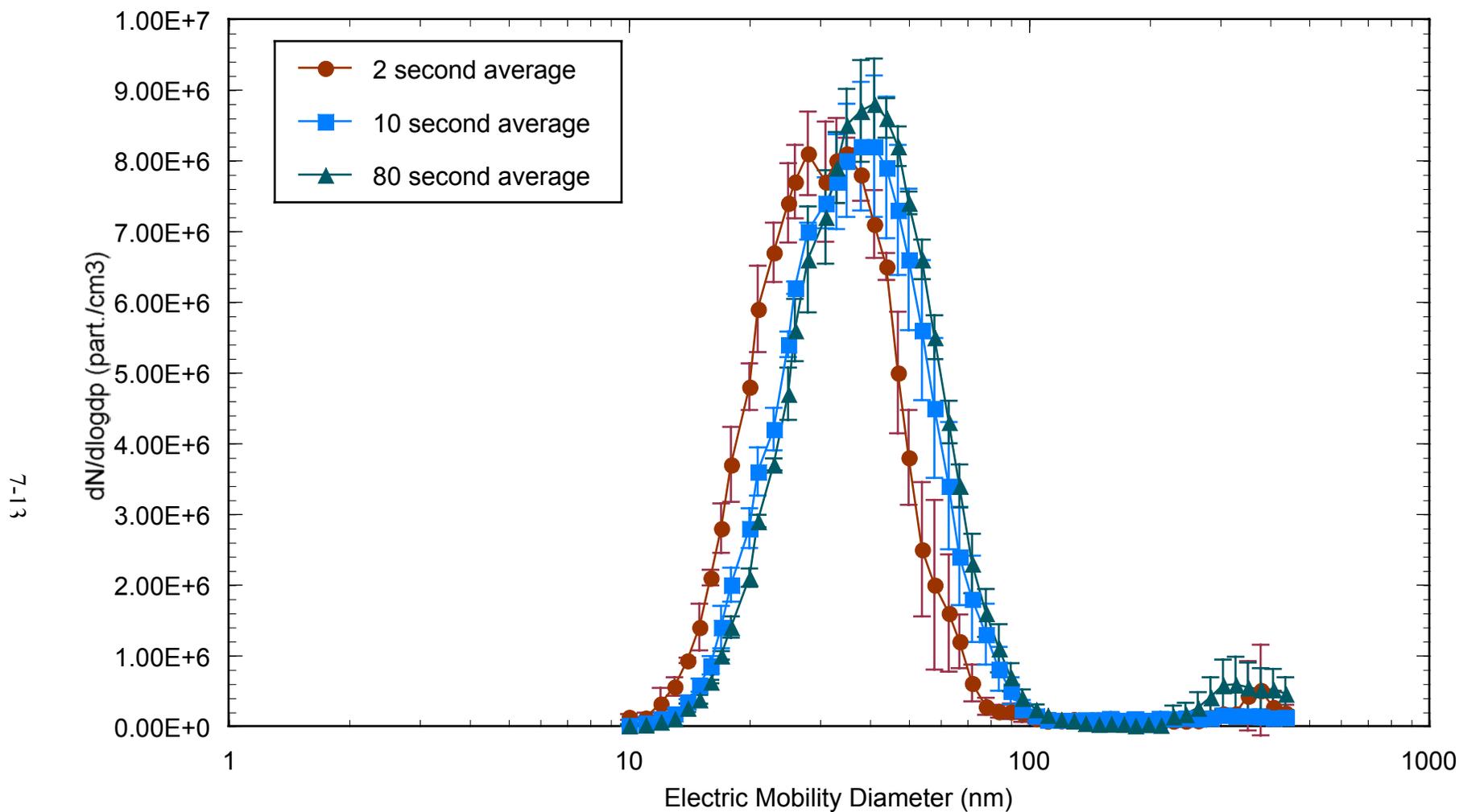


Figure 7-5a. Comparisons of ultrafine particle size distribution (per unit combustion exhaust) measured by Scanning Mobility Particle Sizer (SMPS) as a function of aging time at combustion exhaust temperature 450K and dilution air ratio of 50 times, from Kittanning coal combustion

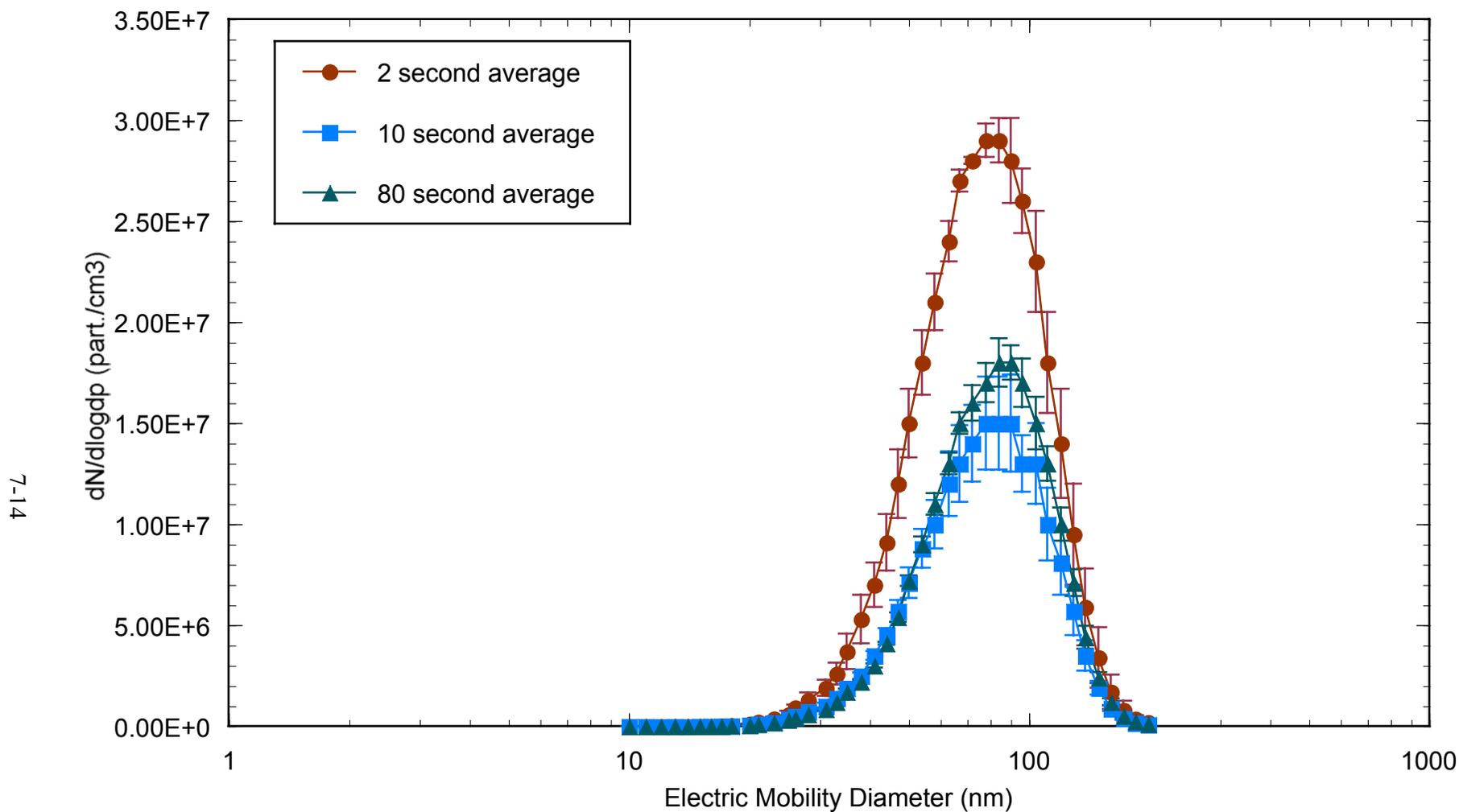


Figure 7-5b. Comparisons of ultrafine particle size distribution (per unit combustion exhaust) measured by Scanning Mobility Particle Sizer (SMPS) as a function of aging time at combustion exhaust temperature 450K and dilution air ratio of 50 times, from No. 6 residual oil combustion

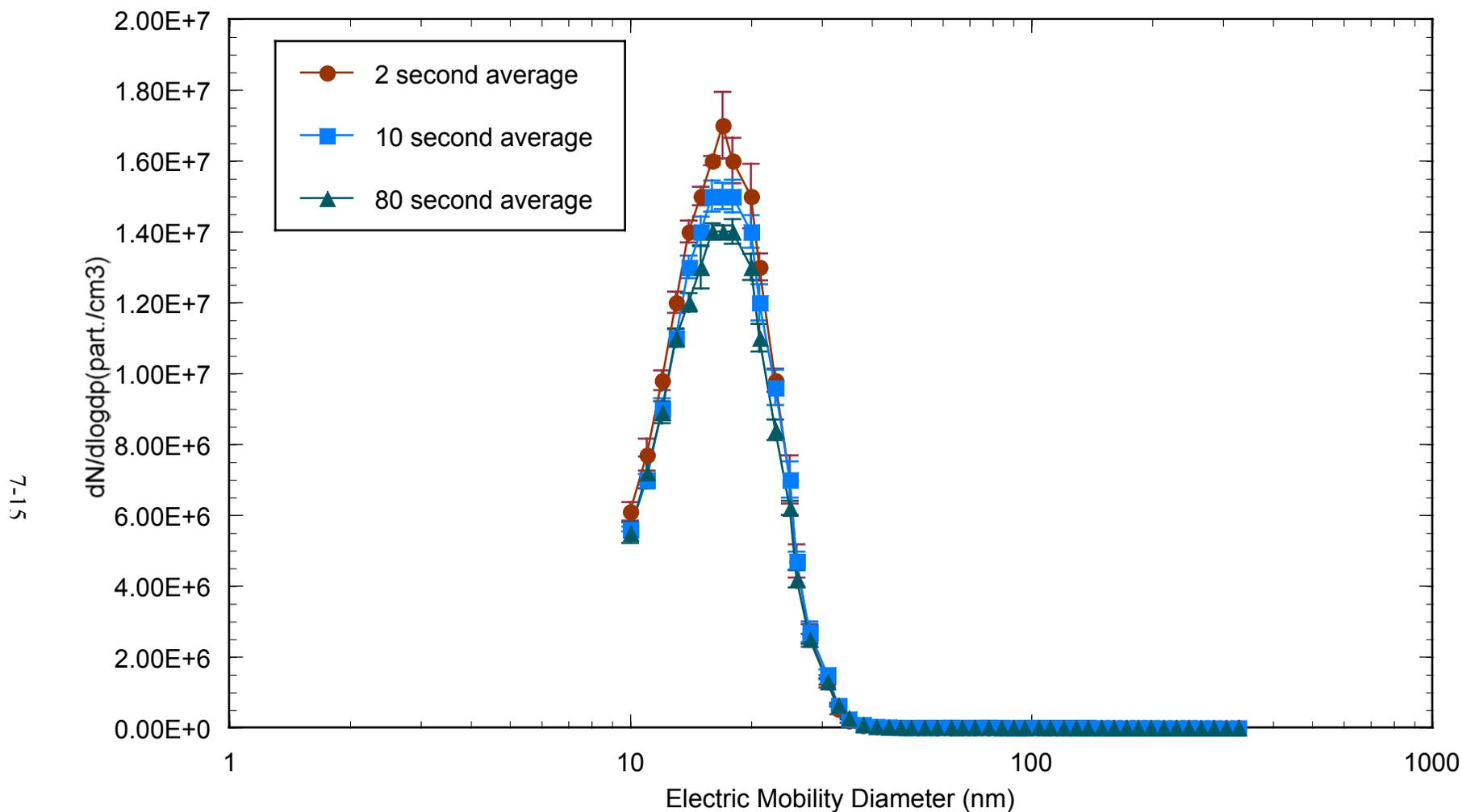


Figure 7-5c. Comparisons of ultrafine particle size distribution (per unit combustion exhaust) measured by Scanning Mobility Particle Sizer (SMPS) as a function of aging time at combustion exhaust temperature 450K and dilution air ratio of 50 times, from natural gas combustion

Particle number concentrations as a function of aging time for coal, oil and gas are shown in Figures 7-5a, 7-5b and 7-5c, respectively. Number concentrations are highest for aging time of 2 second, and are virtually the same between 10 second and 80 second. Figure 5a shows a shift to larger sizes as the aging time increases from 2 second to 10 second for Kittanning coal, but it stays the same for aging time larger than 10 second. This shift is probably due to condensational growth. For No.6 residual oil and natural gas (Figure 7-5b, 7-5c), size distribution is similar with aging, but the number concentration decreases as the aging time increases for the No. 6 residual oil. Differences in number concentration between 2 and 10 seconds for No. 6 residual oil (Figure 7-5b) results from particle transformation by condensational growth and coagulation. In a closed system such as dilution chamber, particle coagulation and condensational growth rates are highest where combustion exhaust mixes with dilution air, slowing with the decrease in number concentration (coagulation) and depletion of vapor species (condensational growth). The similarities in particle size distributions between 10 second and 80 second aging time imply that particle transformation occurs very rapidly. These results imply that a total particle aging time of slightly more than 10 second should be sufficient for a dilution sampler to provide a reasonable sample for analysis.

Formation of particles due to nucleation followed by condensational growth is illustrated in Figures 7-6a and 7-6b. In Figure 7-6a, a concentration of 30 ppm sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was atomized into the furnace where the combustion exhaust temperature at 1,145K during natural gas combustion to simulate combustion sources with high condensable sulfur but low ash content. The dilution sampler was operated with a dilution air ratio of 50. The dominant particle size increased from 20 nm in natural gas to 60-70 nm when  $\text{H}_2\text{SO}_4$  was injected. As particle aging time increases, the dominant particle size mode slightly increases from 40 nm to 50 nm. Particle number concentrations rapidly decrease from  $7.0\text{E}+7$  particles $\bullet\text{cm}^{-3}$  to  $4.0\text{E}+7$  particles $\bullet\text{cm}^{-3}$  as the aging time increased from 2 to 10 seconds but slowly from 10 to 80 seconds. Comparing particle size distributions at dilution air ratios of 10 and 50 during the  $\text{H}_2\text{SO}_4$  tests in Figures 7-6, higher dilution air ratios produced higher number concentrations and large particle size as the dilution air ratio decreased. The impact of pre-existing particles and condensable species on particle formation is shown in Figure 7-6b, conducted with a combination of solid ZnO (geometric mean diameter of 2  $\mu\text{m}$ ) and  $\text{H}_2\text{SO}_4$  doping with a dilution

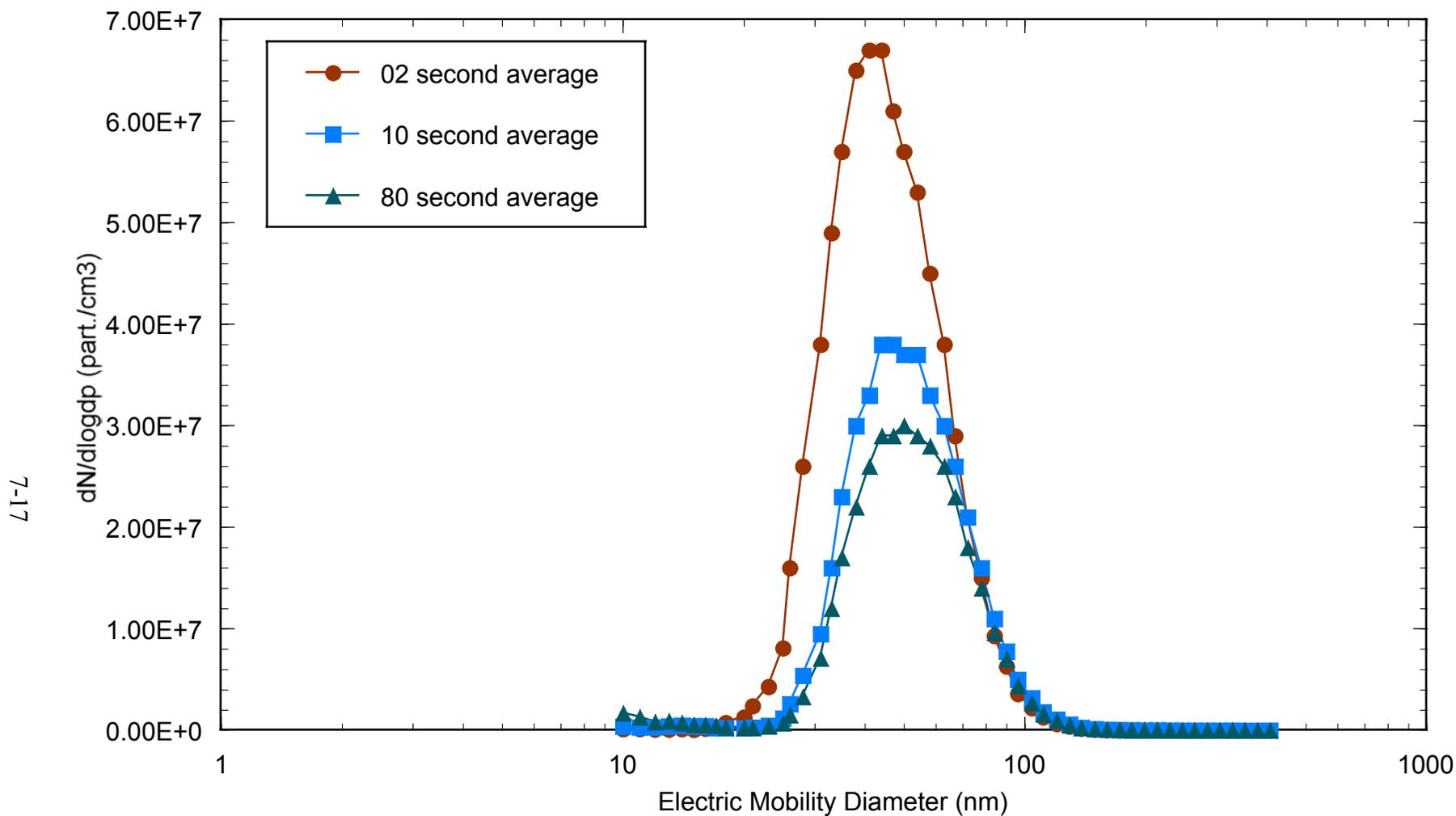


Figure 7-6a. Comparisons of ultrafine particle size distribution (per unit combustion exhaust) at different aging time with sulfuric acid doping at a rate of 30ppm in natural gas combustion, dilution air ratio of 50 and combustion exhaust temperature of 450K.

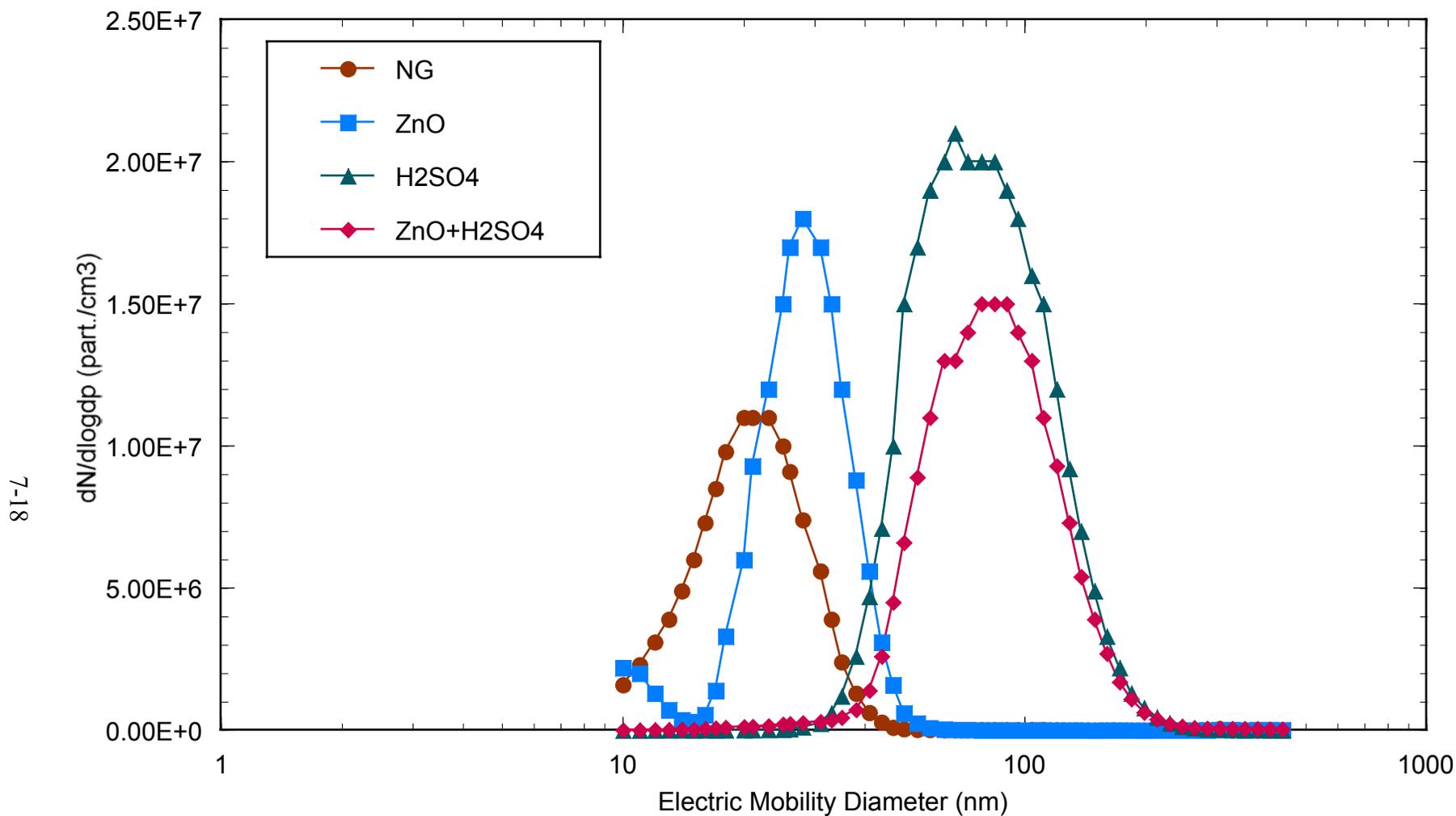


Figure 7-6b. Comparisons of ultrafine particle size distribution (per unit combustion exhaust) at H<sub>2</sub>SO<sub>4</sub> and ZnO injection in natural gas combustion with a dilution air ratio of 10X and combustion exhaust temperature of 450K.

air ratio of 10. Comparison of particle size distributions between natural gas with and without H<sub>2</sub>SO<sub>4</sub> doping shows the shift to larger sizes. The median diameter for ZnO doping increases from the mode of 30-40 nm to 90-100 nm with H<sub>2</sub>SO<sub>4</sub> in combustion exhaust, whereas, the particle number concentration for H<sub>2</sub>SO<sub>4</sub> decreases with ZnO. The results from H<sub>2</sub>SO<sub>4</sub> doping agree with and validate the explanation for the results from No.6 oil and Kittanning coal tests. The formation with both the high condensable species (H<sub>2</sub>SO<sub>4</sub>) and solid particles (lower tail of ZnO particles) seems to be a complex combination of particle coagulation and condensational growth.

Figures 7-7 to 7-8 show how the combustion exhaust temperature affects ultrafine particle concentrations and sizes as well the applicability of the dilution air ratios and aging times. Figures 7-7a and 7-7b show that the minimum aging time of 10 second is still validate at high combustion exhaust temperature. The more pronounced decrease of particle number concentrations between 2 and 10 second aging time was observed in Kittanning coal than No. 6 residual oil at combustion exhaust temperature 645K, comparing to those in 450K. Number concentrations and particle sizes increase as the combustion exhaust temperature increases (Figures 7-8a, 7-8b). At a 50 times dilution air ratio, the particle number concentration at 645K is 2 to 3 times that at 450K and size of particle distribution maximum change from 80 nm and 45 nm to 130 nm and 85 nm for both No. 6 residual oil and Kittanning coal, respectively. This is probably due to higher concentrations of condensable species at the higher combustion exhaust temperature and higher temperature gradient with dilution air. On the other hand, particle number concentrations increase as the dilution air ratio increases for oil and Kittanning coal in agreement with the lower combustion exhaust temperature.

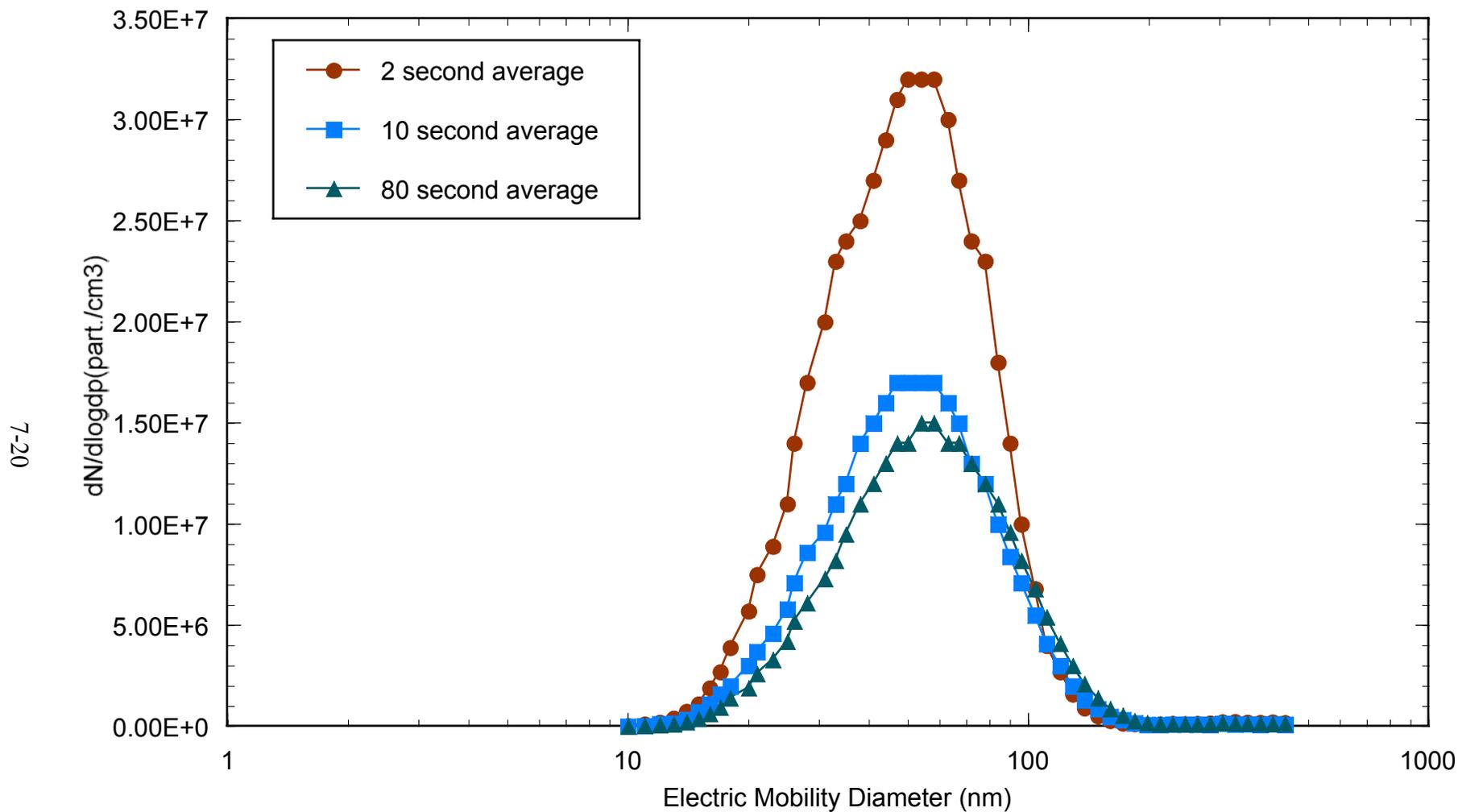


Figure 7-7a. Comparison of ultrafine particle size distributions at different aging time measured by Scanning Mobility Particle Sizer (SMPS) at combustion exhaust temperature of 645K at the dilution air ratio of 50 from Kittanning coal.

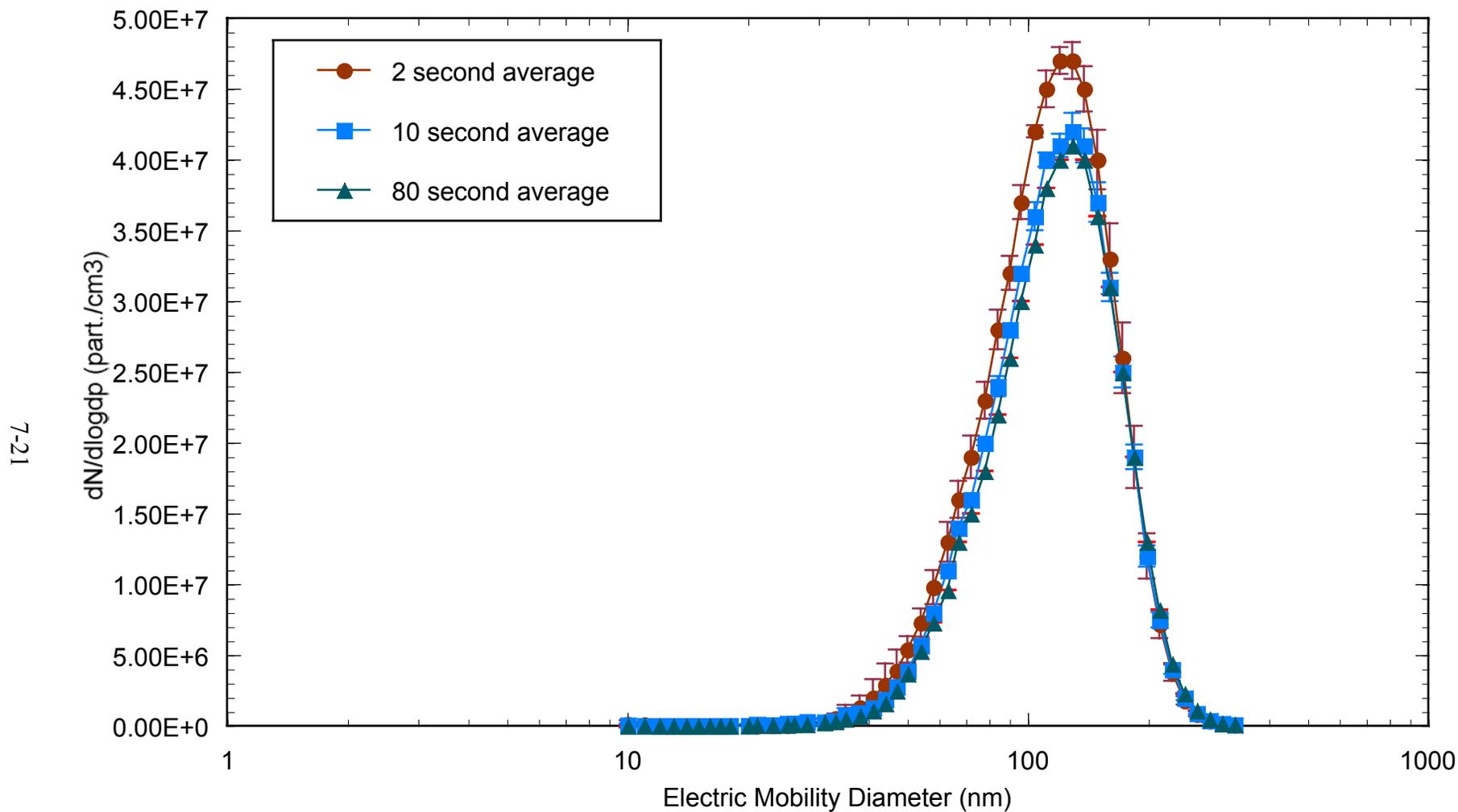


Figure 7-7b. Comparison of ultrafine particle size distributions at different aging time measured by Scanning Mobility Particle Sizer (SMPS) at combustion exhaust temperature of 645K at the dilution air ratio of 50 from No. 6 residual oil.

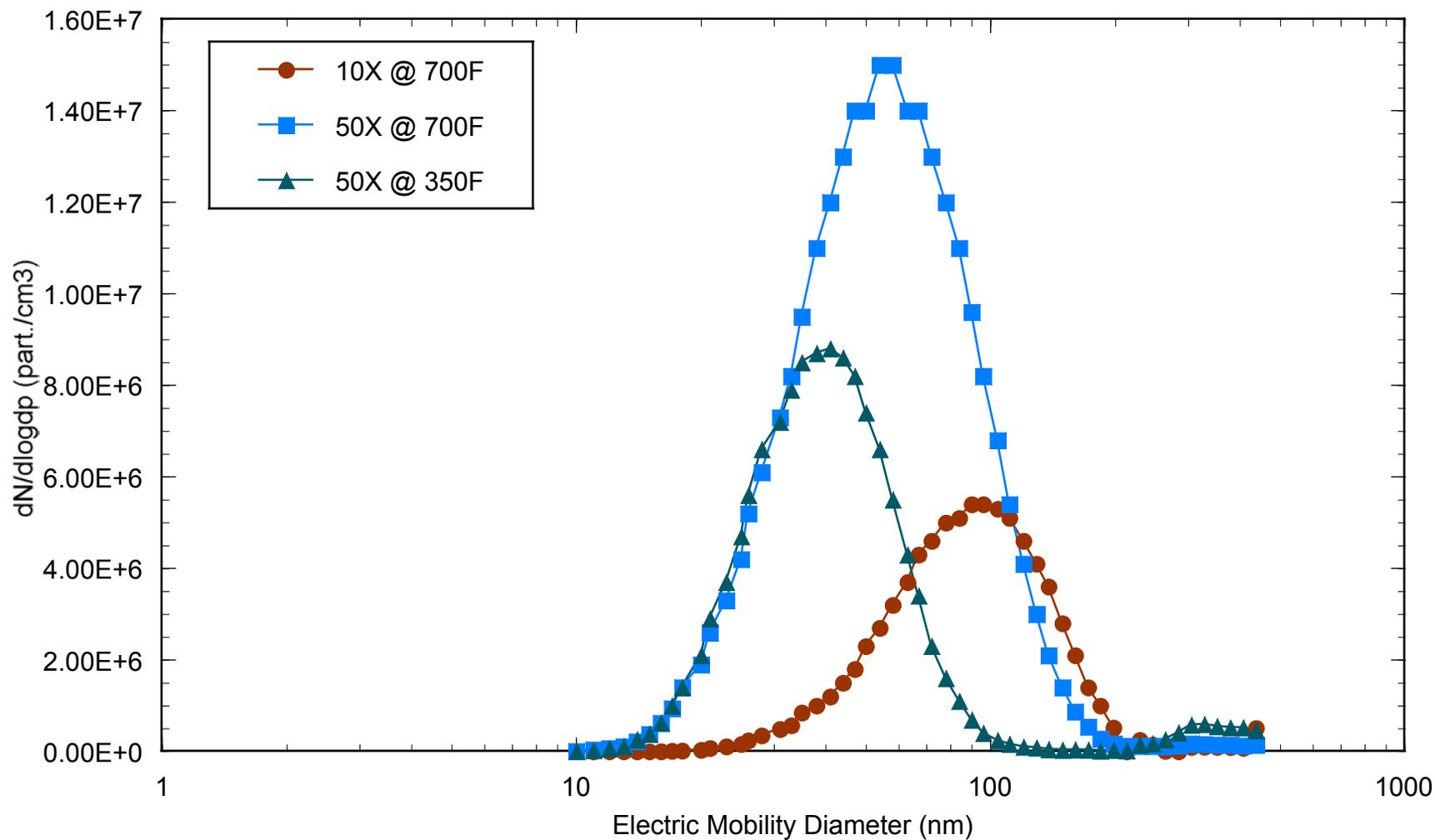


Figure 7-8a. Comparisons of ultrafine particle size distributions measured by Scanning Mobility Particle Sizer (SMPS) as a function of combustion exhaust temperature at dilution air ratios of 10 and 50 from Kittanning coal.

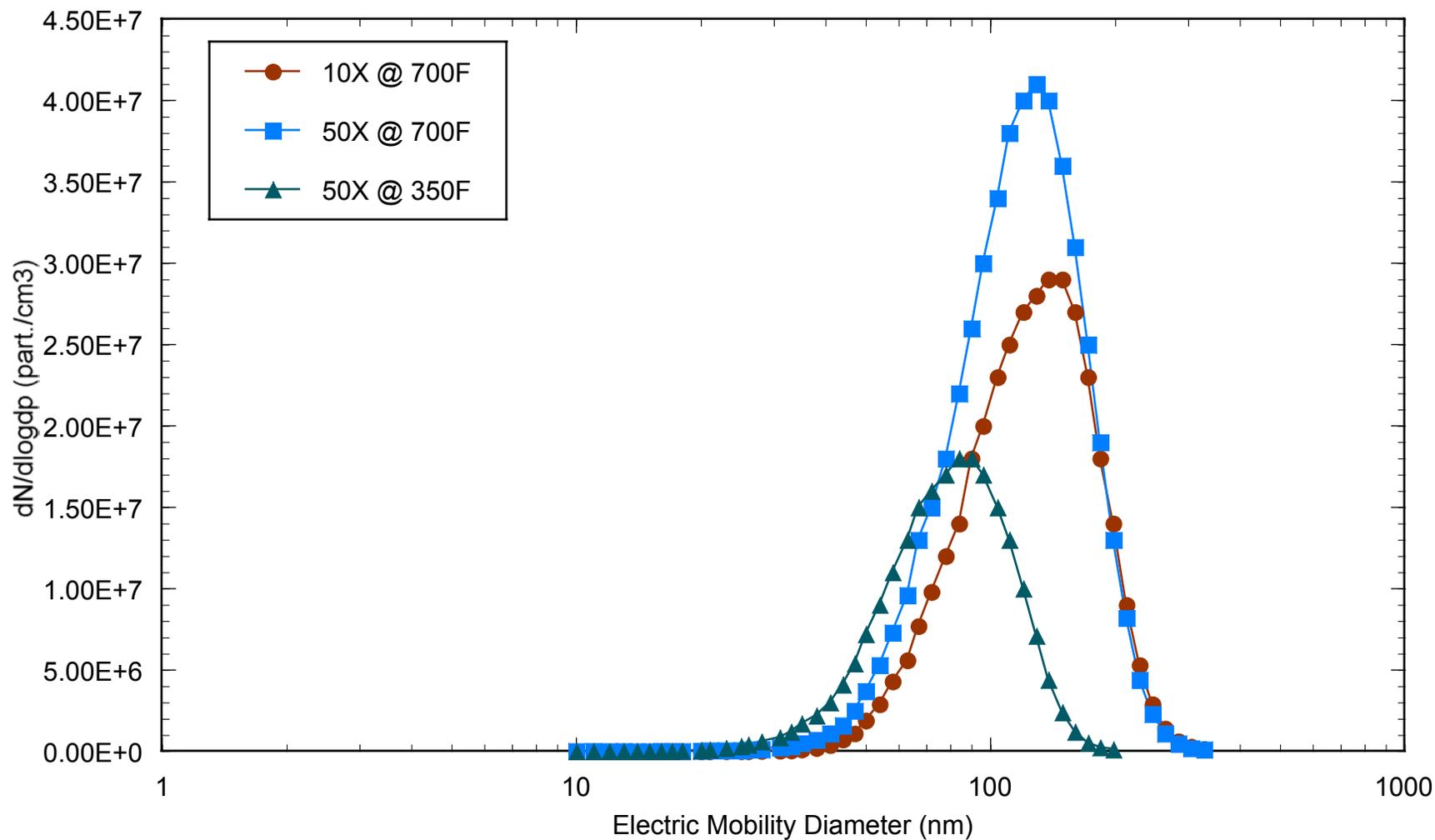


Figure 7-8b. Comparisons of ultrafine particle size distributions measured by Scanning Mobility Particle Sizer (SMPS) as a function of combustion exhaust temperature at dilution air ratios of 10 and 50 from No. 6 residual oil.

## ADVANCE DILUTION SAMPLER DESIGN

### Introduction

The purpose of these tests is to characterize the new generation of dilution sampler based on the results of design criteria assessment, i.e., dilution air ratio, residence, fuel type for PM<sub>2.5</sub> measurement conducted in Phase I and II. Test results of dilution sampler evaluation based on Hildemann *et al* (1989) suggest a dilution ratio of 20 and residence time of 10-15 seconds are the optimal operating conditions of dilution sampler at various fuel types. The knowledge of optimal dilution sampler operating conditions developed in Phase I and II will allow designing a new generation of dilution sampler, which is smaller and more compact or stationary source emission sampling, and still maintain the PM<sub>2.5</sub> physicochemical properties prior than sample collection. The new dilution sampler will be fully characterized in terms of solid particle losses as a function of particle size.

In the Phase III pilot tests, a series of tests aimed to (1) design of a new compact dilution sampler for stack application, (2) characterization of the new dilution tunnel, (3) investigate the effects of mixing patterns on particle formation mechanism, (4) investigate the formation of controlled condensable H<sub>2</sub>SO<sub>4</sub> in dilution sample and (5) comparison of performances between new dilution sampler and other designs.

### Methods and Test Matrix

The GE EER dilution sampler was manufactured at GE EER machine shop and shown in Figure. 7-9. The GE EER dilution sampler draws flue gas sample at the flowrate of 20-25 LPM through a PM<sub>10/2.5</sub> cyclone, which is used to eliminate the penetration of coarse particles into dilution sampler. The flue gas is heated at 150°C and the flowrate is monitored by a maghelic gauge

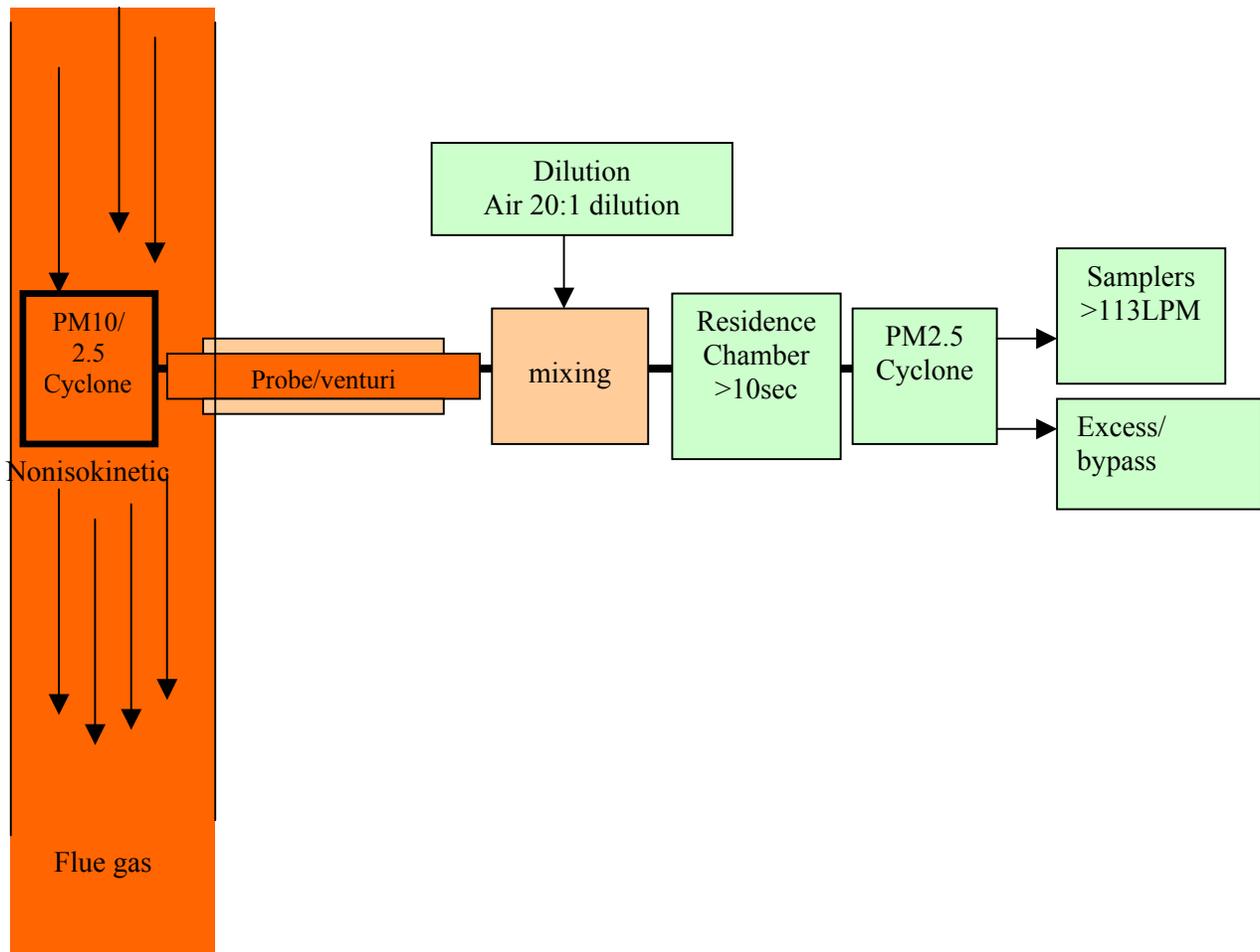


Figure 7-9. One-step dilution.

reading off an inline venturi flow meter. The flue gas then entered a dilution sampler mixing with clean ambient air, which first filtered by a HEPA filter than passing through active carbon granite to remove gaseous species. The sample flow was heat-insolated from dilution air, which passed through a perforated plate with nozzles arrayed symmetrically (Figure 7-10a and Figure 7-10b). The dilution air ratio, defined as between flowrate of diluted samples to flue gas sample is approximate 20-25 (calibrated at 20°C, 1 atm) with a mixing length of 15” in a 8” pipe, thereafter, diluted sample further splits to a flowrate of 113LPM continuing to a chamber of additional length of 24” for a residence time of 10 seconds of particle condensational growth before sample collection and the excess flow is bypassed to a high-vol pump. The sample flow then passes through a PM2.5 cyclone to a conical module which connects to sampling media as required. Thermocouples were placed where the flow splits to bypass and in the end of residence chamber to monitor the relative humidity and temperature of sample. The measurement of flowrate, temperature and relative humidity were recorded by a computer-based data acquisition system.

Detail comparison of old and new dilution sampler design was illustrated in Table 7-4. The intention of the new dilution sampler is based on a dilution air ratio of 20 and residence time of 10-15 seconds. The conceptual design of new dilution sampler is shown in Figure 7-11, a one-step dilution. By operating at the optimal dilution air ratio (i.e., 20X), PM concentration in dilution sampler will be maximized so that more representative sample can be collected for bulk chemical analysis.

The new generation of dilution sampler was characterized by light scattering SPECTRO .3 (CLIMET Instruments, Redland, CA). The model Spectro .3 samples at  $3\text{L min}^{-1}$  and can measure number concentrations of particle from 0.3-20 $\mu\text{m}$  in 16 channels (ranges). Spectro .3 measures particle number concentration at different locations: before the bypass flow, right after bypass flow and before the internal PM2.5 cyclone, in the dilution sampler to evaluate particle losses in these 16 size ranges. Detail test plan for investigating H<sub>2</sub>SO<sub>4</sub> collection in dilution sampler and impaction on PM formation due to mixing pattern can be shown in Table 7-5. The newly developed GE EER dilution sampler will be characterized at the GE EER Fuel Evaluation Facility (FEF) in Irvine, CA from August 15<sup>th</sup> – 30<sup>th</sup>.

Table 7-4. Comparison of Old and New Dilution Sampler Design

<b>Operating Parameters</b>	<b>Old Design</b>	<b>New Design</b>	<b>Basis</b>
Residence time	60 seconds for 339LPM 80 seconds for 226LPM	10-15 seconds in chamber	Pilot Test
Dilution ratio	1:20 to 1:40	1:20 to 1:40	Pilot Test
Sample flow from Flue Gas (Qf)	20-30 LPM	20-30	D50 for instack cyclone
Sampler Flowrate in chamber (Qc)	339 LPM	<ul style="list-style-type: none"> <li>• 113 LPM (1ft<sup>3</sup>)</li> <li>• 226 LPM (2ft<sup>3</sup>)</li> </ul>	Filter pack and Puff samplers
Mixing	1 step	1 step: Rapid	Objectives in Phase III
Fraction to chamber (bypassing)	60%	30-100%	Flexibility of varying dilution ratio for different emission level

Table 7-5. Pilot Phase III Test Matrix

Test Objectives		Particle losses	Mixing		Condensable H2SO4			Comparison with other sampler			
	Type of test	Tunnel Characterization	Natural Gas	#6 heating oil	Tunnel Blank	Gas Fired + H2SO4	Tunnel Blank	Natural Gas	#6 heating oil	Kittanning coal	Operator
<b>Numbers of tests</b>			2	3	1	5	1	3	3	3	
<b>Days needed</b>		2	2	1	1	3	1	3	2	2	
<b>Flue Gas / FEF condition</b>	<b>Flue Gas Temp (F)</b>	Ambient	350	350	350	350	350	350	350	350	FEF
	<b>Excess O2 (%)</b>	Ambient	3	3	3	3	3	3	3	3	FEF
	<b>Dilution Ratio of X H2SO4 Feeding concentration</b>		20-25	20-25	20-25	20-25	20-25	20-25	20-25	20-25	Oliver
	<b>Other factors</b>					30 ppm		30ppm	30 ppm		FEF
	<b>Manual Method</b>		M201	M201		CCS		M201	M201	M201	Bob Z.
<b>Time Integrated</b>	<b>47 mm PTFE at 10 sec</b>	No	No	No							Oliver
	<b>47 mm Quartz, 10 sec</b>	No	No	No							Oliver
<b>Physicochemical analysis</b>	<b>Gravimetric on 47 mm PTFE filters</b>	No	No	No							DRI
	<b>XRF on 47 mm PTFE filters</b>	No	No	No							DRI
	<b>IC, EC/OC on 47 mm Quartz filters</b>	No	No	No							DRI
<b>Continuous Monitor</b>	<b>Dust Tracker at ambient</b>										Oliver
	<b>Dust Tracker at 10 sec</b>										Oliver
	<b>CLIMET at Ambient</b>										Oliver
	<b>CLIMET at 2 sec</b>										Oliver
	<b>CLIMET at 10 sec</b>										Oliver
	<b>URG/EPA dilution sampler</b>							Yes	Yes	Yes	TBD
	<b>Sample collection interval</b>	N.A.	6	2	6	2~3	6	6	2	2	Oliver
	<b>FEF Operator</b>	No									TBD
	<b>CEMs:SO2, CO, O2, Nox</b>										FEF
	<b>Tunnel Cleaning/ FEF shakedown time (day)</b>	No	No	Yes	No	Yes	No	2	No	2	

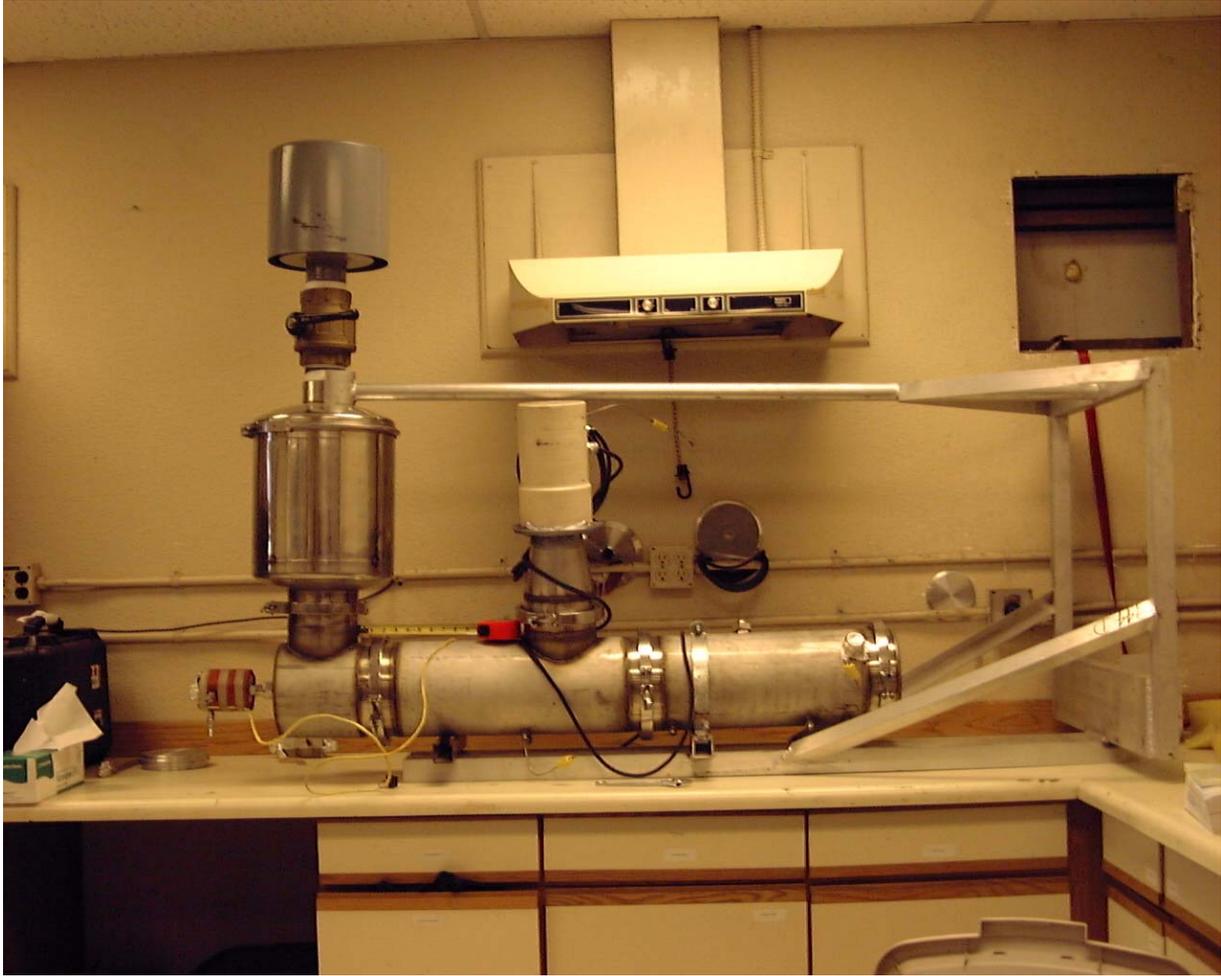


Figure 7-10. GE EER dilution sampler.

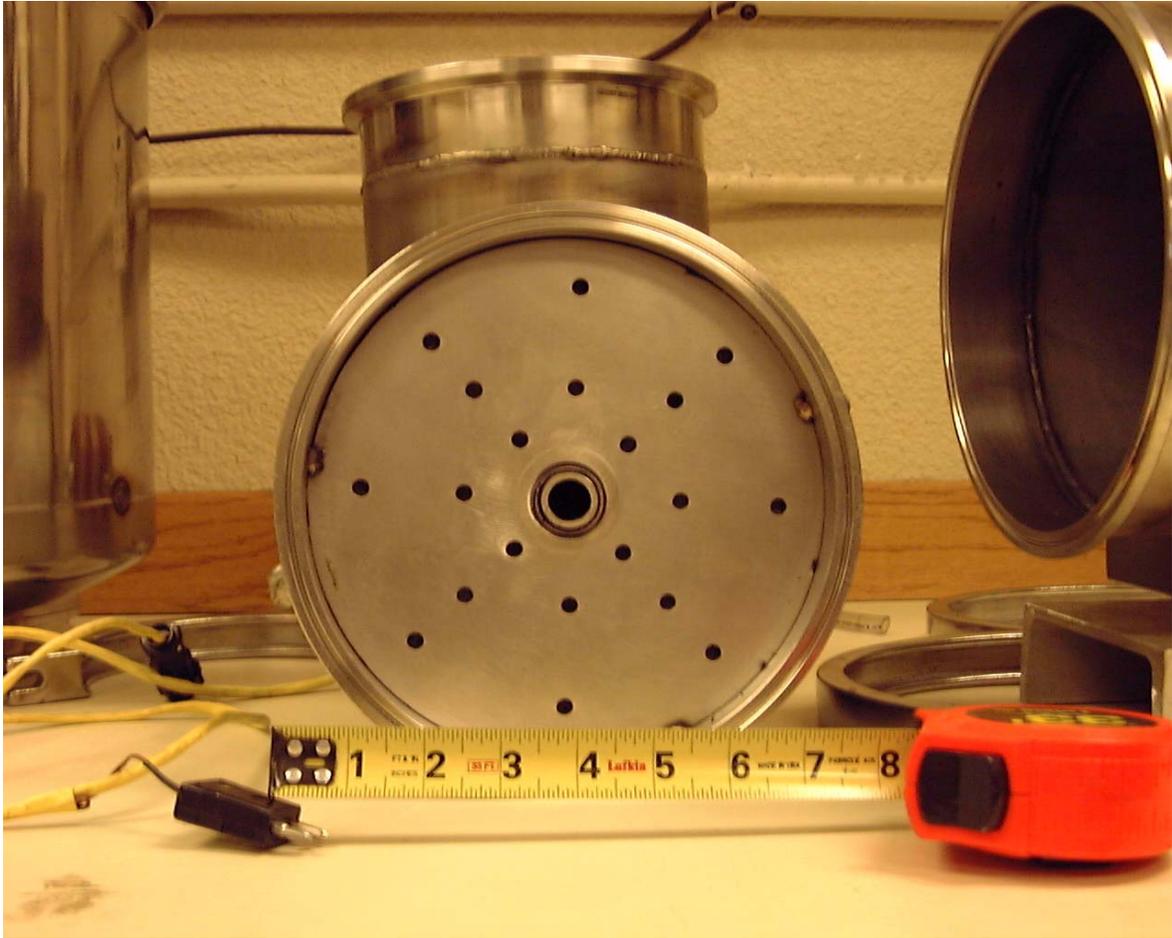


Figure 7-11a. The mixing plate

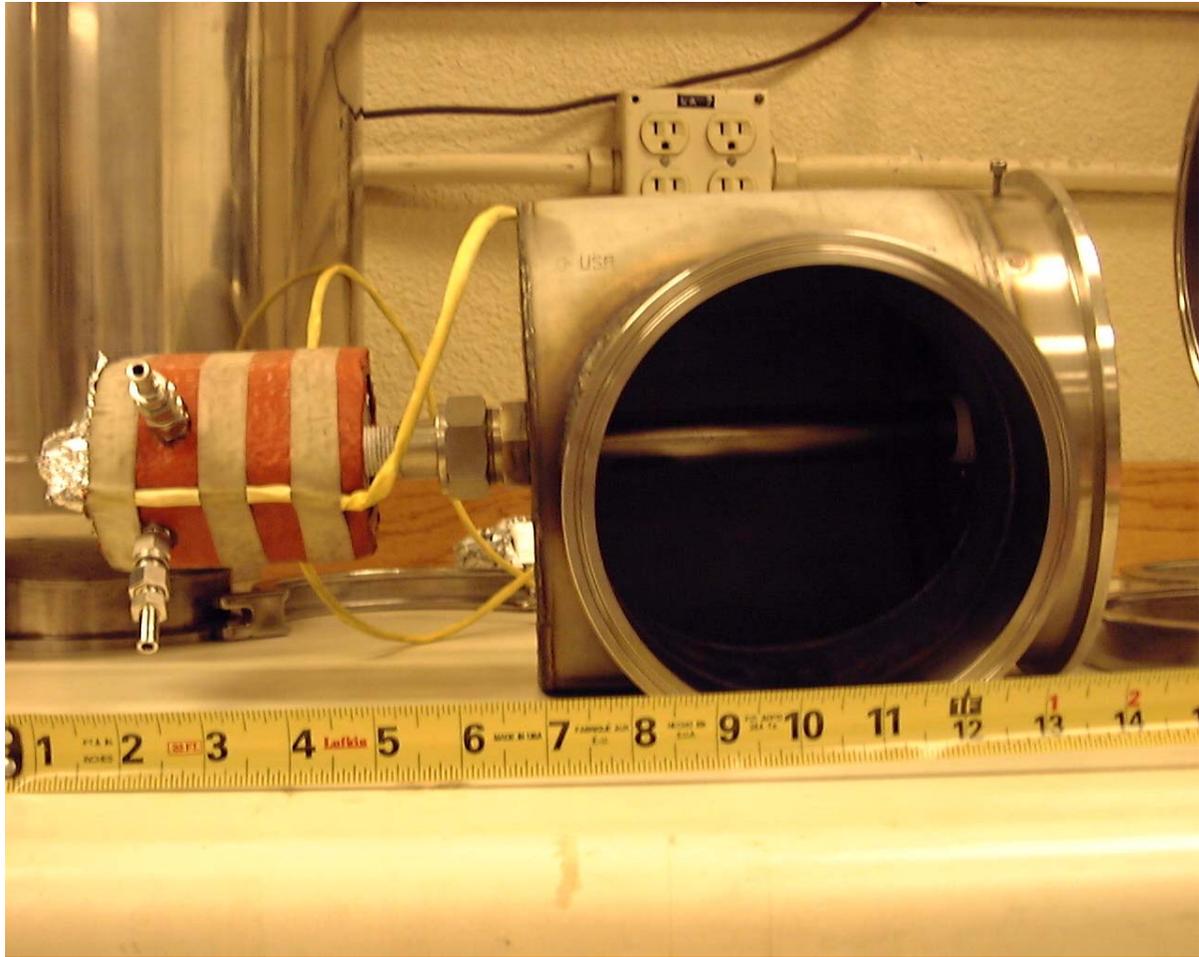


Figure 7-11b. The mixing inlet

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## Section 8 CONCLUSION

### GAS TURBINE

Filterable PM 2.5 measured by the in-stack method (9.6 E-5 lb/MMBtu) is less than the dilution tunnel value of 1.7 E-4 lb/MMBtu. 99 percent of the mass found by Method PRE-4/202 was contained in the condensable fraction collected in the impingers. Most of the inorganic CPM mass is composed of sulfate, chloride and ammonium, with small contributions from Na, Ca, Zn, Ba, Mn, and Sr (Figure 8-1). When all species are summed, the total mass is less than the inorganic CPM mass, with approximately 24 percent of the mass unaccounted for by the sum of species. The instrumental analysis (presented in Section 4) of the impinger solutions does not show any significant levels of other elements.

Table 8-1 presents a comparison of the sulfate measurements, expressed as sulfate ion in mg/dscm. The sulfate levels in the impinger aliquot from the Method 202 train and those from the Method 8 train are approximately equal, and are consistent with previous tests of gas-fired units. The sulfate measured in the Method 202 aliquot is approximately two times higher than the SO<sub>2</sub> (as SO<sub>4</sub><sup>2-</sup>) measured on the potassium carbonate-impregnated cellulose-fiber filter in the dilution tunnel. Run 4 of the dilution tunnel SO<sub>2</sub> measurement is an order of magnitude lower than the others, caused by an unknown factor. Historical data of the expected sulfur in the natural gas typical range from 0.22 to 0.26 mg/dscm (as in-stack equivalent), which equals approximately 0.65 mg/dscm of sulfate in the stack. This estimated fuel sulfur level compares relatively well with that measured by the dilution tunnel potassium carbonate-impregnated cellulose-fiber filter. Compared to the measured SO<sub>2</sub> value, the sulfate levels measured by the dilution tunnel account for approximately one percent of the SO<sub>2</sub> in the flue gas and are within an order of magnitude of sulfate measured in the ambient sample.

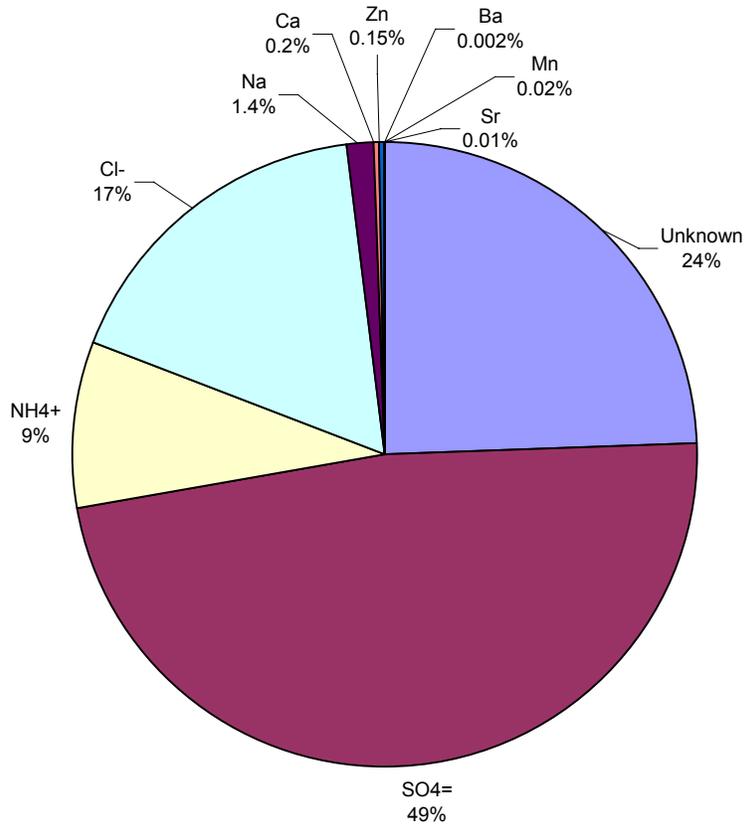


Figure 8-1. Inorganic CPM Residue Speciation Results (as Measured by PRE4/202).

Table 8-1. Comparison of Sulfate Measurements (mg/dscm).

	Run 1	Run 2	Run 3	Run 4	Average
Fuel sulfur (as SO <sub>4</sub> <sup>=</sup> , in-stack equiv.)	0.65	--	--	--	0.65
Impinger aliquot (M202)	1.1	1.1	0.76	0.99	0.99
Impinger aliquot (M8)	1.2	1.2	0.79	1.1	1.1
Dilution tunnel	0.0032	0.020	0.0019	NV	0.0084
Ambient (1)	0.0021	--	--	--	0.0021
Dilution tunnel SO <sub>2</sub> measurement (as SO <sub>4</sub> <sup>=</sup> )	0.69	0.86	0.48	0.06	0.52

(1) One ambient sample taken on separate day.

Figure 8-2 presents the mass emissions for all PM fractions without adjustments for negative net weights from gravimetric analysis. All results, including the filter net weights, are corrected for blanks. Placing the filter in the filter holder and performing all test preparation steps, including a leak check, produced the filter blanks. The acetone rinse blanks range from approximately 6 to 140 percent of the front-half rinse, averaging 48 percent. The proximity of the samples to the levels in the blanks – in one case, the blank was greater than the sample – implies low

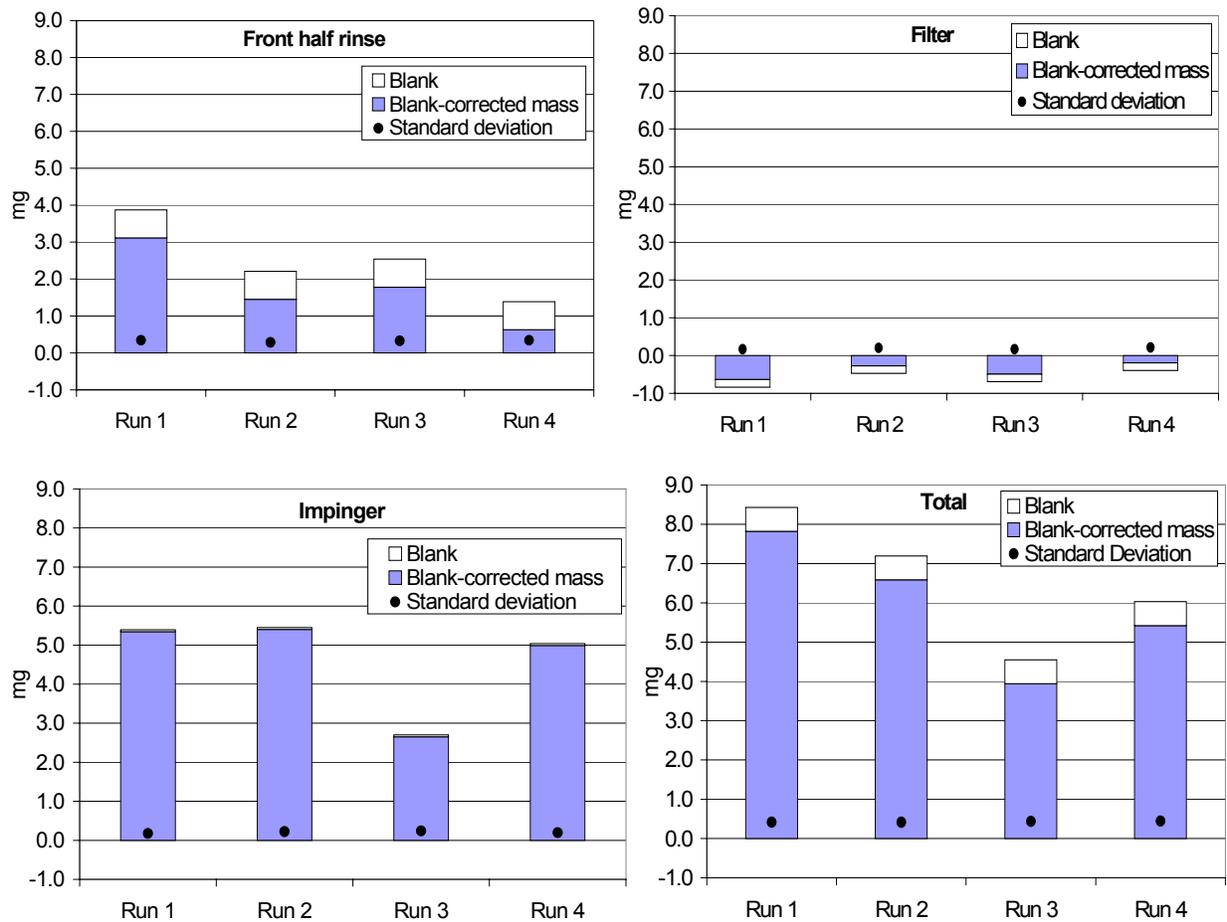


Figure 8-2. Results of Measurements using EPA Method PRE-4/202 (Site Bravo).

confidence in the absolute magnitude of the results. All of the net filter weights were negative. This is common when using quartz fiber filters where small fibers may be lost during filter handling; for example the filter may stick to the filter holder or filter support. Since a negative filter weight has no physical significance, these results conventionally are reported as zero rather than as a negative emission or in summing different fractions of the sampling train. However, this convention lends false credibility to the accuracy of the measurement method. The filter blank can be significant; in this case the filter blank was also negative but ranged from 24 to 51 percent of the filter net weights.

## FORMALDEHYDE

Formaldehyde emissions from the turbine were measured using DNPH cartridges downstream of the dilution tunnel. A number of field blanks were taken during the test in addition to a tunnel blank, which sampled only ambient air through the tunnel. Although the field blanks did not contain any detectable amounts of formaldehyde, the tunnel blank did. Figure 8-3 shows the stack sample results corrected for the concentration in the tunnel blank and the tunnel blank and ambient concentrations, uncorrected. In some cases, the concentration in the tunnel blank was greater than the sample concentration, causing the result to be negative. All concentrations have been corrected for the dilution ratio, and are in-stack concentrations. It is apparent from the figure that the formaldehyde concentrations are significantly different when the duct burners are on compared to when they are off and the gas turbine is the only emission source. In addition, the emissions from the gas turbine only are below the detection limit, indicating that the gas turbine is not a significant source of formaldehyde emissions.

Concentrations of all detected species have a higher in-stack average concentration than their concentrations in the ambient air sample (Figure 8-4), indicating that the species originate from the combustion process. The average concentrations of Br, Cl, K, Mg, Na, Pb, S, chloride, nitrate, and sulfate are within a factor of ten of their respective ambient air concentrations. OC, EC and ammonium are the species with the higher concentrations that are more than an order of magnitude greater than the ambient concentrations, and might be potential marker species.

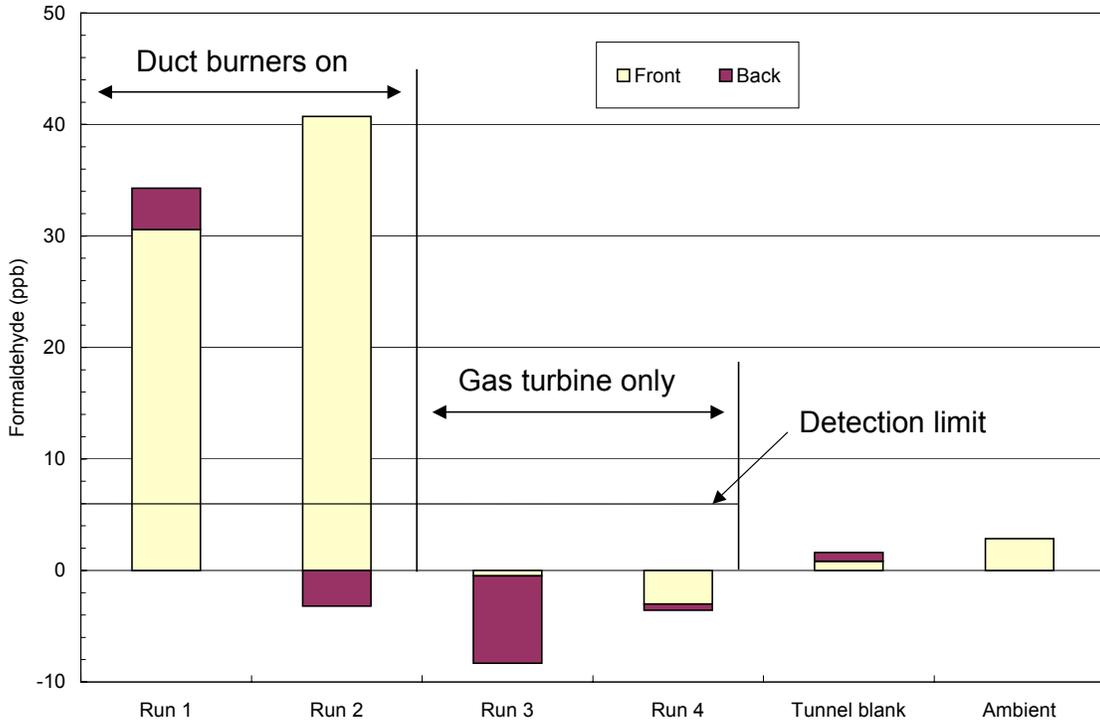


Figure 8-3. Tunnel Blank-Corrected Formaldehyde Concentrations, as Measured by the Dilution Tunnel (Site Bravo).

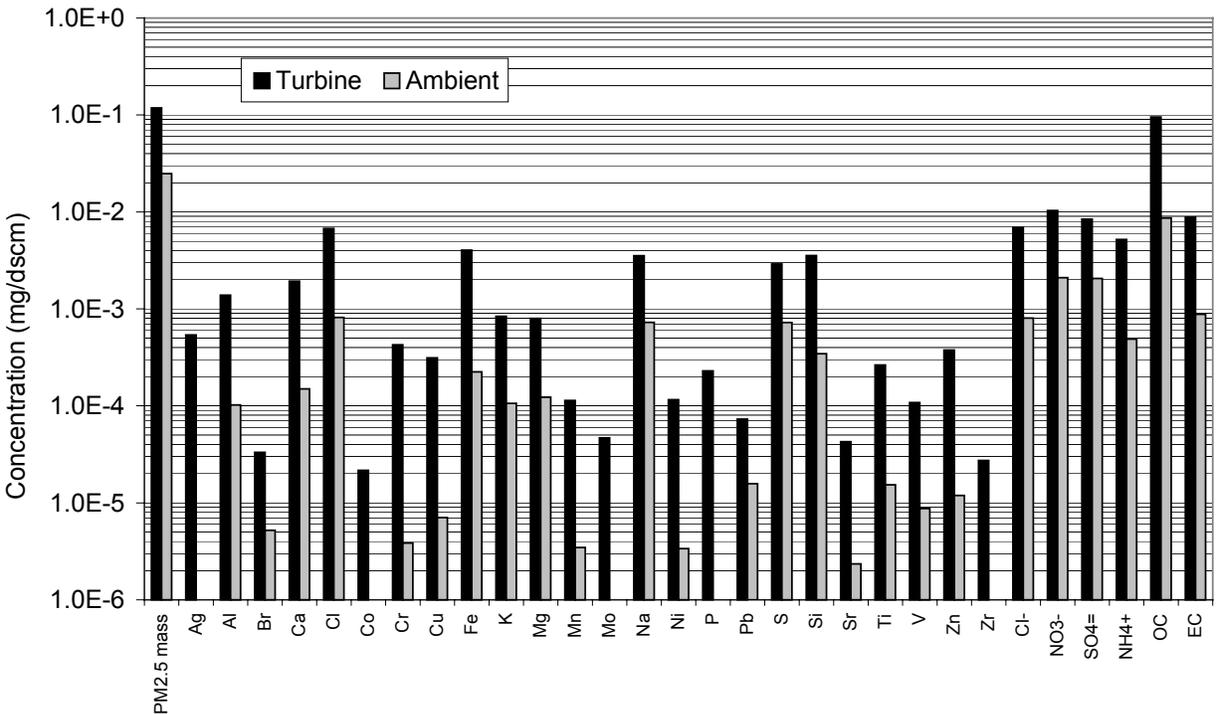


Figure 8-4. Mass Speciation for Dilution Tunnel Ambient and Stack Samples (Site Bravo).

PROCESS HEATER

Dilution tunnel PM2.5 ( $1.1 \times 10^{-4}$  lb/MMBtu) is approximately 2 times higher than the filterable PM 2.5 measured by the in-stack method ( $5.5 \times 10^{-5}$  lb/MMBtu. 94 percent of the mass found by Method PRE-4/202 was contained in the condensable fraction collected in the impingers. Most of the inorganic CPM mass is composed of sulfate ( $\text{SO}_4^{--}$ ), chloride ( $\text{Cl}^-$ ) and sodium (Na), with small contributions from Ca,  $\text{NO}_3^-$ , Zn, Mg, and others (Figure 8-5). When all species are summed, the total mass slightly exceeds the inorganic CPM mass. The sum of the species represents 110 percent of the inorganic CPM mass. This result illustrates that both methods (speciated mass and gravimetric number) are in general agreement. The instrumental analysis of the impinger solutions does not show any significant levels of other elements.

Table 8-2 presents a comparison of the sulfate measurements, expressed as sulfate ion in mg/dscm. The sulfate measured in the Method 202 aliquot is approximately two times higher than the  $\text{SO}_2$  (as  $\text{SO}_4^{--}$ ) measured by the potassium carbonate-impregnated cellulose-fiber filter downstream of the dilution tunnel, on average. Compared to the measured  $\text{SO}_2$  value, the sulfate levels measured by the dilution tunnel account for approximately 1 percent of the  $\text{SO}_2$  in the flue gas and are within an order of magnitude of sulfate measured in the ambient sample.

Table 8-2. Comparison of Sulfate Measurements (mg/dscm).

	Run 1	Run 2	Run 3	Run 4	Average
Impinger aliquot (M202)	0.62	0.53	0.92	0.84	0.73
Dilution tunnel	0.010	0.007	0.003	0.003	0.006
Ambient (1)	0.0013	--	--	--	0.0013
Dilution tunnel $\text{SO}_2$ measurement (as $\text{SO}_4^{--}$ )	0.78	0.60	0.30	0.28	0.49

(1) One ambient sample taken on separate day than stack sample runs.

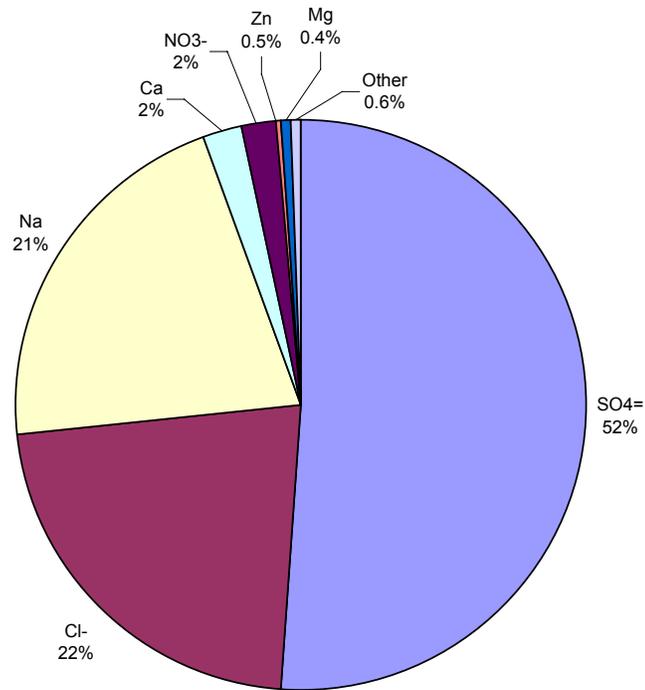


Figure 8-5. Inorganic CPM Residue Speciation Results.

The average in-stack concentrations of Cl and NO<sub>3</sub><sup>-</sup> are approximately equal to their ambient sample concentrations (Figure 8-6), indicating that these two species do not originate from the combustion process, but are present in the ambient air used for combustion. Ba was detected in the ambient air but not for the in stack sample (n.b., the detection levels for in-stack samples are approximately 25 times higher than those for ambient air samples). All the other detected species have a higher in-stack average concentration than their concentrations in the ambient air sample, indicating that the species originate from the combustion process. The average concentrations of PM<sub>2.5</sub> mass, Br, Ca, Fe, K, Mg, Mn, Na, Pb, S, Si, Sr, Ti, V, Zn, chloride, sulfate, ammonium and EC are within a factor of ten of their respective ambient air concentrations. OC, Al, Co, Cr, Cu, Mo, Ni, Rb, and Zr have average sample concentrations that are more than an order of magnitude greater than their ambient concentrations, and might be potential marker species.

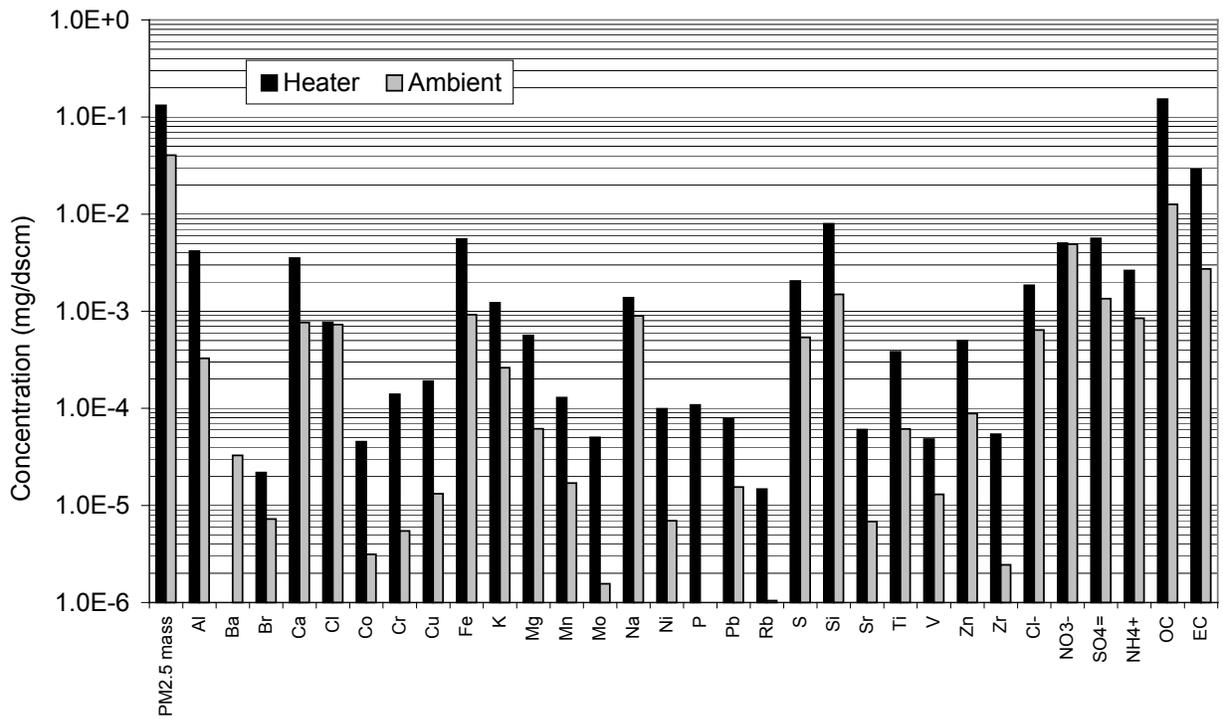


Figure 8-6. Mass Speciation for Dilution Tunnel Ambient and Stack Samples (Site Charlie).

## FORMALDEHYDE

Formaldehyde emissions from the process heater were measured using DNPH cartridges downstream of the dilution tunnel. A number of field blanks were taken during the test in addition to a tunnel blank, which sampled only ambient air through the tunnel. Formaldehyde was detected in only one field blank at 87 mg/m<sup>3</sup>; this concentration was used to blank correct the sample run results. There was also a detectable level of formaldehyde in the tunnel blank. Figure 8-7 shows the stack sample results with the concentration in the tunnel blank subtracted out, and the tunnel blank and ambient concentrations; the tunnel blank concentration is an in-stack equivalent concentration using an average dilution ratio. In Run 4, the concentration in the tunnel blank was greater than the sample concentration, causing the result to be negative. All concentrations have been corrected for the dilution ratio, and are in-stack concentrations. In general, the emissions from the gas process heater are above the detection limit, indicating that the natural gas fired process heater is a source of formaldehyde emissions.

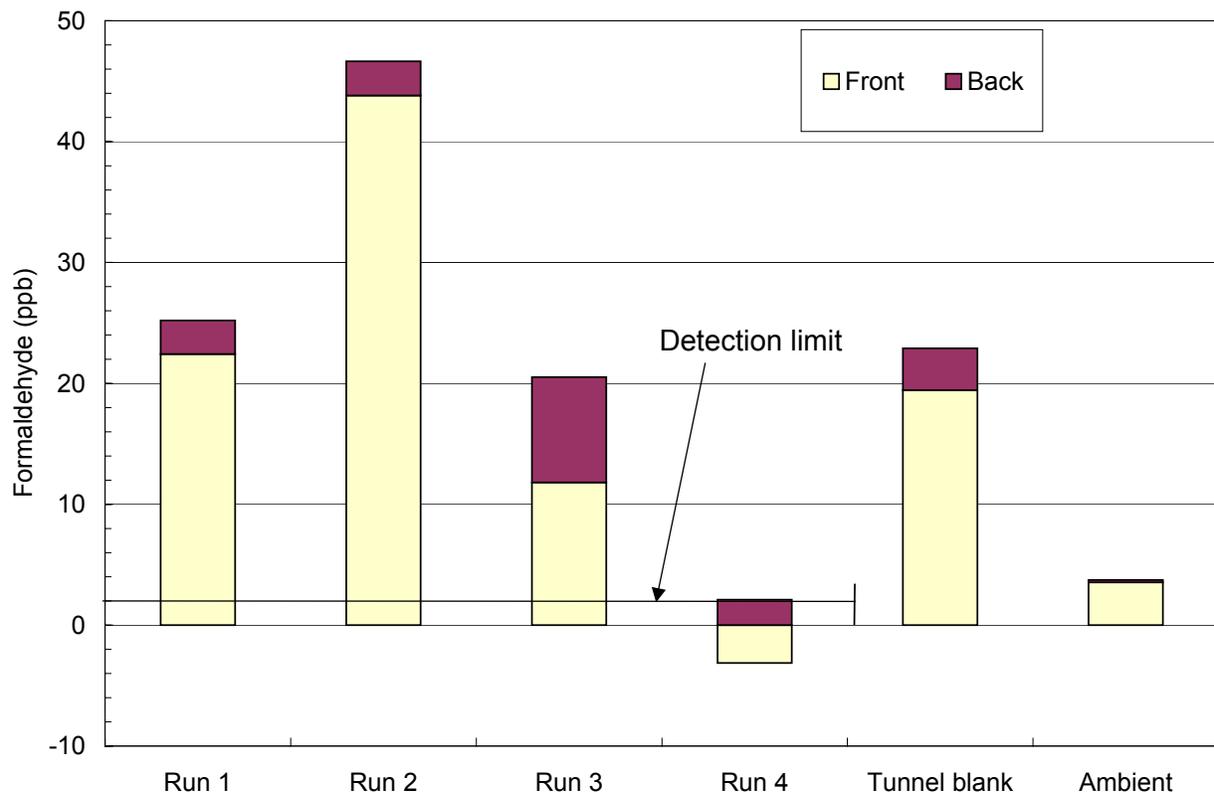


Figure 8-7. Tunnel Blank-Corrected Formaldehyde Concentrations, as Measured by the Dilution Tunnel (Site Charlie).

#### COMMERCIAL GAS/OIL BOILER

Filterable PM emissions from oil combustion measured by the controlled condensation train ( $5.6 \text{ E-3 lb/MMBtu}$ ) are less than the dilution tunnel value of  $1.2 \text{ E-2 lb/MMBtu}$ . This difference is most likely attributable to the difference in filter temperatures; the controlled condensation train (CCT) has a filter temperature of approximately  $650 \text{ }^\circ\text{F}$ , thus some constituents may still be in the vapor phase. A more useful comparison would be to look at the filterable PM combined with the condensable fraction captured in the CCT. Adding the two fractions yields an emission factor of  $2.3\text{E-2 lb/MMBtu}$ , which is almost two times the emission factor for oil firing, obtained from the dilution tunnel; some of this discrepancy is likely because the CCT measures total PM, while the dilution tunnel only measures PM<sub>2.5</sub>.

Emissions of PM<sub>2.5</sub> from oil firing are over thirty times higher than those from combustion of natural gas in the boiler. The higher sulfur content of the oil results in higher sulfur emissions from oil combustion than from gas.

Tables 8-3a and 8-3b present comparisons of the various sulfur measurements, expressed as sulfate ion in units of lb/MMBtu. The sulfur, as measured by XRF, and sulfate, as measured by IC, from the DT samples for natural gas combustion as close to the 3:1 (sulfate:sulfur) ratio expected based on relative molecular weights (Table 8-3a). The ratio for oil combustion is elevated, indicating a possible adsorption artifact for sulfate in the oil samples. For natural gas combustion, the total sulfur measured by the dilution tunnel (sum of sulfur dioxide and sulfate = 3.6E-3 lb/MMBtu) is comparable to the total sulfur measured by the CCT (3.75E-3 lb/MMBtu), and both are approximately 3.5 times higher than the sulfur measured in the fuel (1.05E-3 lb/MMBtu). However, the sulfur levels in the natural gas were near detection limits, so this result is within acceptable parameters.

For oil combustion, SO<sub>2</sub> concentrations were obtained using the portable CEMS, which was below detection limits for the natural gas combustion tests. The portable CEMS reading, expressed as sulfate (4.33E-1 lb/MMBtu), is comparable to expected levels from the fuel analysis (3.97E-1 lb/MMBtu). The CCT total sulfur, expressed as sulfate (2.54E-1 lb/MMBtu), is slightly lower, but still within 2 times of the expected levels from the fuel. However, the total sulfur measured by the dilution tunnel is lower than expected, possibly due to the capacity of the sulfur dioxide filter. Further investigation is needed to determine the upper collection limits of the potassium carbonate-impregnated cellulose-fiber filters used to collect SO<sub>2</sub> in cases of higher sulfur levels, such as oil combustion.

The formation of artifact sulfate caused by SO<sub>2</sub> absorption and conversion in the aqueous solutions appears likely. Both SO<sub>2</sub> and oxygen are soluble in water and the dissolved H<sub>2</sub>SO<sub>3</sub> can slowly oxidize to sulfate. This is implicitly recognized by Method 202, which recommends purging the impingers with nitrogen (air is also acceptable) to minimize this bias. Method 202

Table 8-3a. Comparison of Sulfate Measurements – Natural Gas Combustion (lb/MMBtu).

	NG-Run 1	NG-Run 2	NG-Run 3	NG-Run 4	Average
Fuel SO <sub>4</sub> <sup>=</sup>	8.95E-4	7.73E-4	1.21E-3	1.34E-3	1.05E-3
DT S as SO <sub>4</sub> <sup>=</sup>	1.31E-4	6.60E-5	1.13E-4	1.07E-4	1.04E-4
DT SO <sub>2</sub> as SO <sub>4</sub> <sup>=</sup>	5.33E-3	2.21E-3	3.02E-3	NV	3.52E-3
DT SO <sub>4</sub> <sup>=</sup>	9.32E-5	5.69E-5	9.76E-5	NV	8.26E-5
CCT SO <sub>2</sub> as SO <sub>4</sub> <sup>=</sup>	4.10E-3	1.28E-3	1.69E-3	2.68E-3	2.44E-3
CCT SO <sub>3</sub> as SO <sub>4</sub> <sup>=</sup>	2.21E-3	9.40E-4	9.03E-4	1.19E-3	1.31E-3

DT - dilution tunnel

CCT - controlled condensation train

NV - not valid

Table 8-3b. Comparison of Sulfate Measurements – Oil Combustion (lb/MMBtu).

	Oil-Run 1	Oil-Run 2	Oil-Run 3	Oil-Run 4	Average
Fuel SO <sub>4</sub> <sup>=</sup>	3.87E-1	3.80E-1	4.06E-1	4.16E-1	3.97E-1
DT S as SO <sub>4</sub> <sup>=</sup>	3.06E-3	1.96E-3	2.91E-3	2.81E-3	2.68E-3
DT SO <sub>2</sub> as SO <sub>4</sub> <sup>=</sup>	6.96E-2	6.63E-2	6.26E-2	6.68E-2	6.63E-2
DT SO <sub>4</sub> <sup>=</sup>	4.90E-3	2.61E-3	5.65E-3	5.48E-3	4.66E-3
CCT SO <sub>2</sub> as SO <sub>4</sub> <sup>=</sup>	3.25E-1	1.14E-1	2.37E-1	2.60E-1	2.34E-1
CCT SO <sub>3</sub> as SO <sub>4</sub> <sup>=</sup>	2.86E-2	6.81E-3	2.12E-2	2.47E-2	2.03E-2
Plant CEMS SO <sub>2</sub> as SO <sub>4</sub> <sup>=</sup>	4.38E-1	3.91E-1	4.59E-1	4.45E-1	4.33E-1

DT - dilution tunnel

CCT - controlled condensation train

also provides the option of omitting the post-test purge if the pH of the impingers is above 4.5; while the pH of the impingers met this criterion in our test, we performed the nitrogen purge anyway. However, earlier studies of systems having SO<sub>2</sub> levels of approximately 2000 ppm show that that these artifacts occur in spite of post-test purging (Filadelfia and McDaniel, 1996).

In the absence of any documented reports to evaluate artifact formation at low SO<sub>2</sub> concentrations, a laboratory scale study was conducted in a prior program evaluating potential bias at these concentrations (GE EER, 1999). The experiments passed simulated combustion gas containing representative amounts of O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, NO<sub>x</sub>, and SO<sub>2</sub> through Method 202 impinger

trains. No condensable substances were added. Tests were performed both with and without post-test nitrogen purges for 1-hour and 6-hour sampling runs for mixtures containing 0, 1, and 10 ppm SO<sub>2</sub>.

Significant amounts of sulfate, proportional to the SO<sub>2</sub> concentration in the gas, were found to be present in impingers that had not been purged. However, while the post-test purge definitely reduced the sulfate concentrations it did not eliminate artifact formation. Purging was less efficient for the 6-hour runs relative to the 1-hour runs, indicating that most of the SO<sub>2</sub> oxidation occurs within this period. This result shows that the sulfate, and hence most of the condensable particulate collected by Method 202 in our field test results can come from this mechanism of artifact sulfate formation from dissolved SO<sub>2</sub>. However, unlike previous tests, in these tests the amount of SO<sub>2</sub> present is insufficient to account for the entire measured sulfate in the Method 202 train. Corio and Sherwell (2000) reviewed emissions data collected from fossil fuel fired units by Methods 201/201A and 202, and noted the potential significance of artifact formation.

Table 8-4 presents a comparison of data collected during the current program (for DOE/CEC/NYSERDA/GTI/API) for gas-fired sources (Sites Alpha, Bravo, Charlie and Delta), its predecessor conducted for API/DOE/GTI (Sites A, B and C), and published emission factors from EPA's AP-42 database for commercial/industrial external combustion boilers. These data compare results from the filterable and condensable particulate fractions; it should be noted that the data from the previous sites was collected using EPA Methods PRE-4 and 202 for filterable and condensable PM, respectively.

As can be seen in Table 8-4, the DT PM<sub>2.5</sub> result for Site Delta firing natural gas are comparable to the previous gas-fired boiler test at Site A, but are still the highest level seen of any gas-fired source to date. This high emission factor result may be due to contamination; oil-fired testing was performed prior to the natural gas fired testing and PM emissions were much higher during the oil-fired operation than during normal natural firing. The tunnel was cleaned between the two sets of tests; however, there is some suspicion that residue remained in the tunnel prior to the natural gas tests. This residue may have caused the high tunnel blank values (as noted in Section 6) and also biased the natural gas-fired emissions data.

Table 8-4. Comparison of Previous and Current Test Data to EPA Emission Factor Data.

Source	Unit Type	Total PM10 (1) lb/MMBtu	Filterable PM		Condensable PM		PM2.5 by DT (2) lb/MMBtu
			lb/MMBtu	% of Total PM10	lb/MMBtu	% of Total PM10	
AP-42	Natural Gas Combustion	0.0077	0.0019	25	0.0058	75	--
AP-42	Commercial Boiler (No. 6 Oil)	0.032	0.023	69	0.0099	31	--
Site A	Refinery Gas-fired Boiler	0.0092	0.000026	0.07	0.0092	99.9	0.00036
Site B	Refinery Gas-fired Process Heater	0.0052	0.00064	12	0.0046	88	0.000054
Site C	Natural Gas-fired Steam Generator	0.0013	0.00008	6	0.0012	94	0.000056
Site Alpha	Refinery Gas-fired Process Heater	0.0083	0.00054	6	0.0078	94	0.000037
Site Bravo	Natural Gas-fired Turbine	0.0032	0.00029	9	0.0029	91	0.00017
Site Charlie	Natural Gas-fired Process Heater with SCR	0.0010	0.000096	9	0.00095	91	0.00011
Site Delta	Dual Fuel-fired Commercial Boiler (Nat. Gas)	0.0011 (3)	--	--	0.0011 (3)	--	0.00037
Site Delta	Dual Fuel-fired Commercial Boiler (No. 6 Oil)	0.023 (3)	0.0056 (3)	25	0.017 (3)	75	0.0056

(1) Data collected using EPA Method PRE-4/202 train.

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

(3) Data collected using controlled condensation train; filterable PM is total PM, not PM10.

The total PM10 emission factor for oil firing at Site Delta, obtained using the CCT method, are in general agreement with those found in the EPA's AP-42 emission factor database (0.023 lb/MMBtu from tests versus 0.032 lb/MMbtu in AP-42) for a commercial boiler firing No. 6 oil (Table 8-4), but the test results show the majority of the particulate to be in the condensable fraction rather than the filterable fraction, as indicated in the AP-42 factor (EPA, 2000). The EPA results were obtained using a different method, which may account for some of the difference in the results. Nevertheless, the semi-quantitative agreement of our results with those presented in the EPA database provides additional confidence in the validity of the results found here.

The low filterable PM results indicate that the actual mass collected on the filters was at, or below, the practical limits of the method as practiced in these tests. Because dilution tunnels provide conditions that more closely simulate true atmospheric condensation conditions, as compared to impinger condensation, results obtained by this technique are more representative of the actual particulate emissions from gas- and oil-fired combustion sources such as this boiler.

## FORMALDEHYDE

Formaldehyde emissions from the boiler were measured using DNPH cartridges downstream of the dilution tunnel. A field blank was taken during each test day in addition to a tunnel blank, which sampled only ambient air through the tunnel. Although the field blanks did not contain any detectable amounts of formaldehyde, the tunnel blank did. As discussed previously, the tunnel blank levels were more than an order of magnitude lower than the average stack sample, however, if expressed as “in-stack equivalent” by multiplying by an average dilution ratio, the levels of formaldehyde in the tunnel blank become almost equal to the average stack levels. This result indicates that the levels in the samples may be due to artifacts from the sampling system. However, the formaldehyde emission factor for the No. 6 oil tests ( $1.8\text{E-}4$  lb/MMBtu) is comparable to the AP-42 emission factor ( $1.59\text{E-}4$  lb/MMBtu). The emission factor from the natural gas tests ( $2.5\text{E-}4$  lb/MMBtu) is higher than the AP-42 emission factor ( $7.65\text{E-}5$  lb/MMBtu), but may have been affected by contamination from the preceding oil tests.

## POTENTIAL EMISSIONS MARKER SPECIES

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

Concentrations of all detected species have a higher in-stack average concentration than their concentrations in the ambient air sample (Figures 8-8a and 8-8b), indicating that the species originate from the combustion process. For the natural gas fired tests (Figure 8-8a), the 95% confidence lower bound of the average concentrations (as presented previously in Section 6) of Al, Mn, V, and nitrate are less than their corresponding concentrations in the ambient sample. Cl, Pb and Sr are within a factor of ten of their respective ambient air concentrations. OC, EC and sulfate are the species with the higher concentrations that are more than an order of magnitude greater than the ambient concentrations, and might be potential marker species for gas combustion.

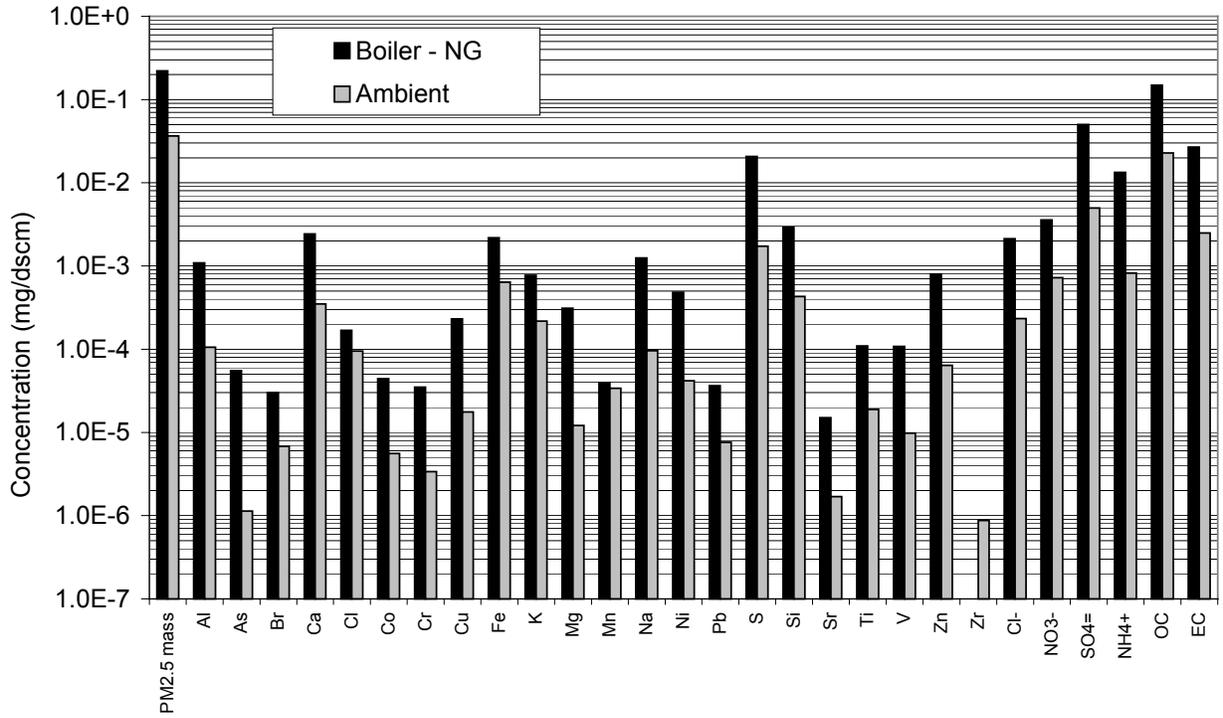


Figure 8-8a. Mass Speciation – Dilution Tunnel Ambient and Stack Samples (Site Delta – NG).

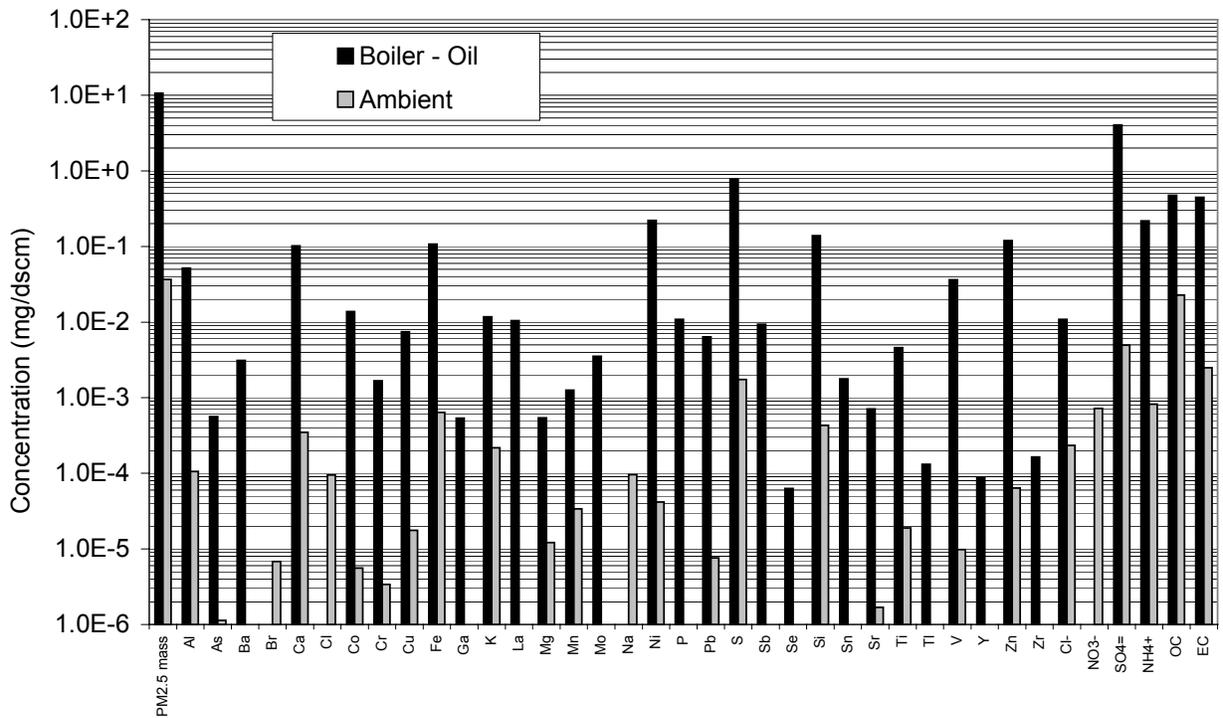


Figure 8-8b. Mass Speciation - Dilution Tunnel Ambient and Stack Samples (Site Delta – Oil).

For oil combustion (Figure 8-8b) only Mg has a 95% confidence lower bound of the average concentration less than its corresponding ambient concentration, leaving a larger number of potential marker species. OC, EC, sulfate, Ni, V and Zn are potential marker species for No. 6 oil combustion.

However, some species cannot reliably be distinguished because their in-stack concentrations are within a factor of ten from the minimum method detection limits. These include, for natural gas combustion (Figure 8-9a): Al, As, Br, Cl, Co, K, Mn, Pb, Sr, Ti, V, chloride, nitrate, ammonium, and EC; and for No. 6 oil combustion (Figure 8-2b): As, Ba, Ga, La, Se, Sn, Tl, Y, Zr, and chloride. The above two criteria leave OC and sulfate as potential marker species for natural gas combustion and OC, EC, sulfate, Ni, V and Zn as potential marker species for No. 6 oil combustion in commercial boilers.

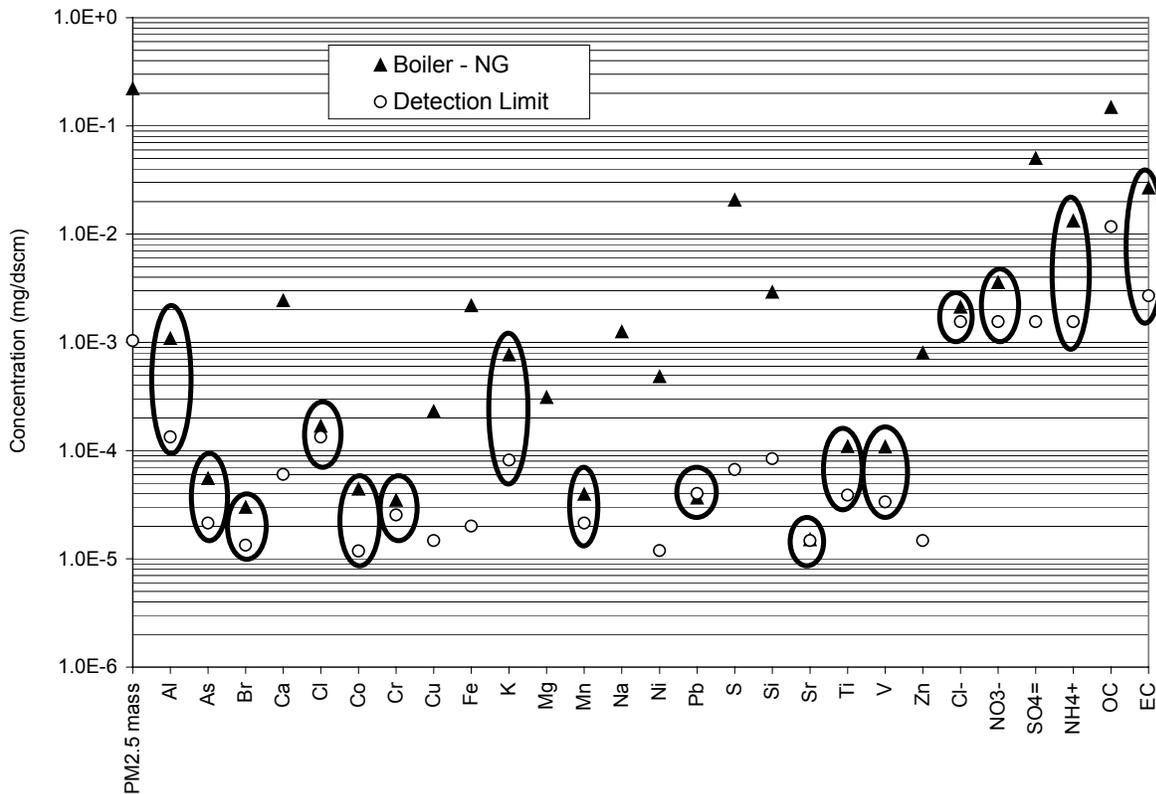


Figure 8-9a. Average Sample Concentration and Detection Limits (Site Delta – NG).

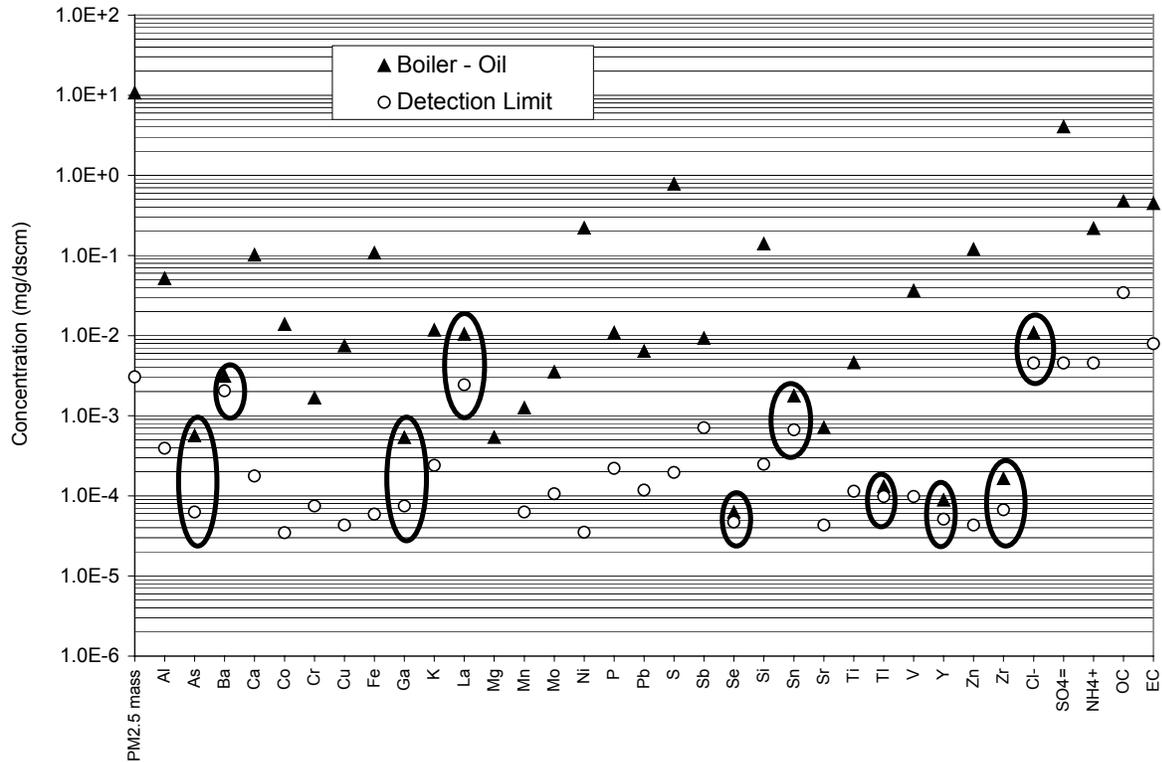


Figure 8-9b. Average Sample Concentration and Detection Limits (Site Delta – Oil).

Subtraction of the ambient from in-stack concentrations provides an indication of which species can be considered to be emissions markers. Ignoring species found near detection limits, the resulting emissions profiles (Figure 8-10a and 8-10b) suggest that the marker species for natural gas combustion remain the same as stated above, with the possible addition of Si and as a marker species for oil combustion.

The uncertainty of several of these values is large, as reflected in the high standard deviations, casting doubt on those species being definitively used as emissions markers.

Another potentially useful marker for source emissions is the organic emissions profile. All of the PAHs (SVOCs) detected at site Delta were present at low concentrations. Approximately 30 percent of the SVOC compounds from the natural gas tests and 50 percent from the oil tests had a 95 percent confidence lower bound that was less than the tunnel blank concentration. Total SVOCs account for approximately 26 percent of the OC measured by the dilution tunnel for

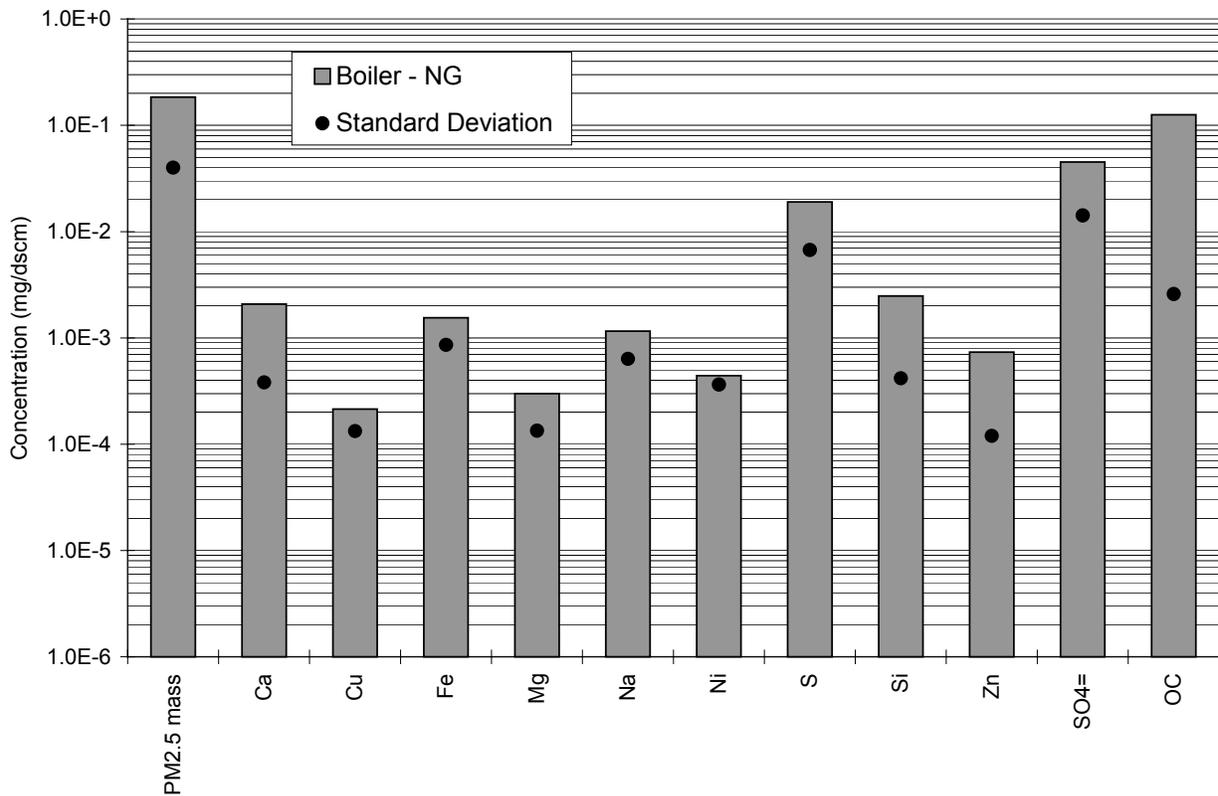


Figure 8-10a. Average Sample Concentration Minus Ambient Concentration (Site Delta – NG).

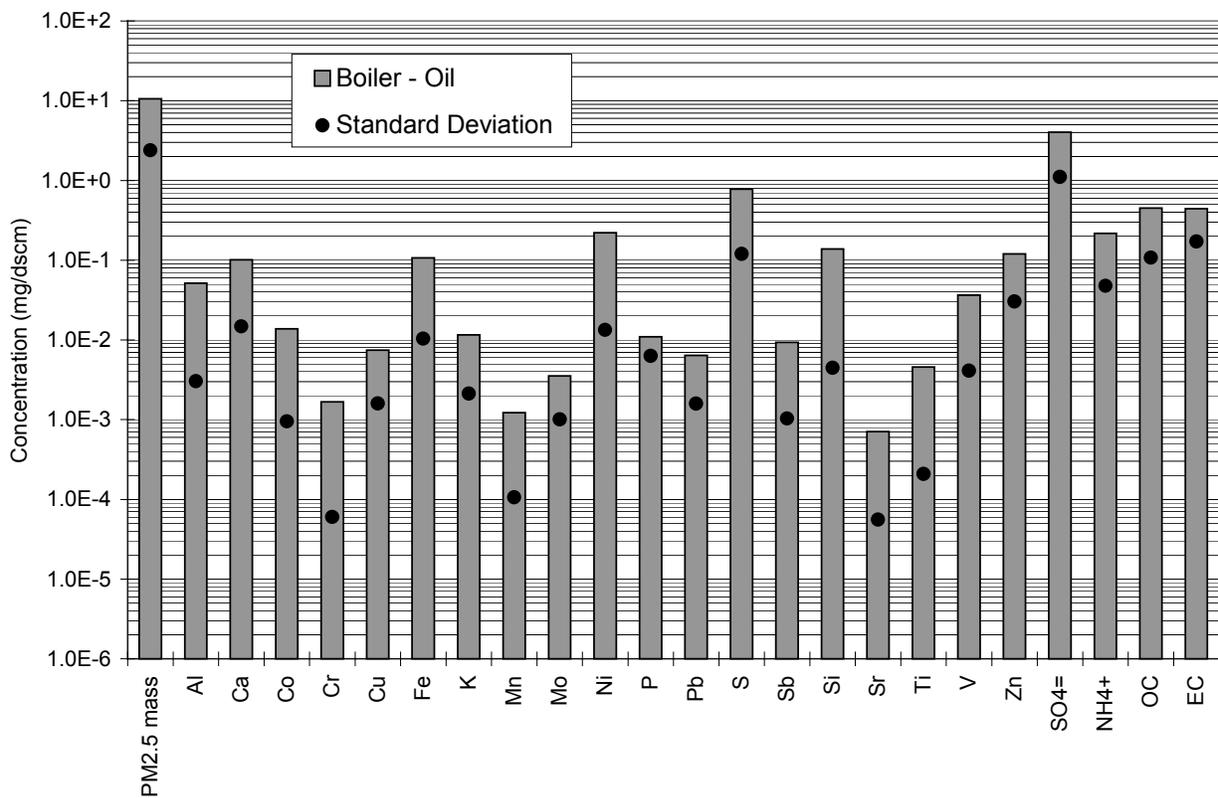


Figure 8-10b. Average Sample Concentration Minus Ambient Concentration (Site Delta – Oil).

natural gas combustion and 16 percent of the OC for oil combustion, indicating the presence of unspciated organics. This large difference is at least partly due to the difference in analytical methods since the TOR method defines OC somewhat arbitrarily, as well as by the presence of organics that are not quantified by the methods used in this study (only PAHs are identified in the SVOC analysis used).

Organic carbon emissions for the Site Delta gas-fired tests were approximately equal to those found at Site C, and similar to the emissions at the previous boiler tested at Site A (Table 8-5). The OC emissions from the oil-fired tests are the highest seen so far. Measurable SVOC emissions at Site Delta were also higher than previous tests for both gas and oil firing, resulting in a greater percentage of OC being speciated. VOC emissions from gas-fired tests at Site Delta were comparable to other sites to date, while those from the oil-fired tests were higher than all but Site Charlie.

Table 8-5. Average Organic Aerosol Emission Factor Comparison (lb/MMBtu).

Source	Unit Type	Organic Carbon	Elemental Carbon	Total Carbon	Sum of All SVOCs	Sum of All VOCs
Site A	Refinery Gas-fired Boiler	1.5E-4	9.4E-5	2.5E-4	4.1E-6	1.6E-4
Site B	Refinery Gas-fired Process Heater	2.8E-5	1.9E-5	3.4E-5	6.6E-7	4.0E-4
Site C	Natural Gas-fired Steam Generator	2.3E-4	9.2E-6	2.4E-4	1.5E-5	4.1E-5
Site Alpha	Refinery Gas-fired Process Heater	6.5E-5	7.1E-6	7.2E-5	1.6E-5	7.6E-4*
Site Bravo	Natural Gas-fired Turbine	1.4E-4	1.2E-5	1.5E-4	7.7E-6	5.6E-4*
Site Charlie	Refinery Gas-fired Heater	1.3E-4	2.4E-5	1.5E-4	1.3E-5	2.4E-3*
Site Delta	Dual-fuel Commercial Boiler - NG	2.5E-4	4.6E-5	2.9E-4	6.4E-5	8.7E-4*
Site Delta	Dual-fuel Commercial Boiler - No. 6 Oil	5.4E-4	5.0E-4	1.0E-3	8.6E-5	1.3E-3*

\* Does not include VOCs from canister samples.

Elevated levels of organic compounds in the stack samples as compared to levels detected in the blank and the ambient air indicate that potential marker species are more likely to be found within the volatile and semivolatile organic compounds. For Site Bravo, approximately half of the SVOCs present at detectable levels were at least 10 times greater than levels in the ambient air. In particular, 1,4+1,5+2,3-dimethylnaphthalene, 1+2-ethylnaphthalene, 2,3,5+I-trimethylnaphthalene and xanthone are present at elevated concentrations relative to the other SVOCs and their respective ambient concentrations, and might be potential marker species. However, motor vehicles are also predominant sources of dimethylnaphthalenes and methylnaphthalenes, and the sampling location was present within 2 miles of a major highway.

Because the ambient air was only sampled on one day, it is possible that elevated levels of these compounds were present in the ambient air during source sampling that were not present when the ambient sample was taken. In addition, the relative concentrations of these compounds may not be unique enough to clearly distinguish this source from other external combustion sources. For Site Charlie, approximately 65 percent of the SVOCs present at detectable levels were at least 10 times greater than levels in the ambient air. In particular, 2-methylbiphenyl, 3-methylbiphenyl, 2,3,5-trimethylnaphthalene and 4-methylbiphenyl are present at elevated concentrations relative to the other SVOCs and their respective ambient concentrations, and might be potential marker species. Because the ambient air was only sampled on one day, it is possible that elevated levels of these compounds were present in the ambient air during source sampling that were not present when the ambient sample was taken. For the Site Delta gas-fired tests 1,3+1,6+1,7-dimethylnaphthalene, 1-methylnaphthalene, and 2-methylnaphthalene are present at elevated concentrations relative to the other SVOCs and their respective ambient concentrations, and might be potential marker species. For the No. 6 oil tests 1,3+1,6+1,7-dimethylnaphthalene, 1-methylnaphthalene, 2-methylnaphthalene and 2,6+2,7-dimethylnaphthalene might be potential marker species. However, motor vehicles are also predominant sources of dimethylnaphthalenes and methylnaphthalenes, and the sampling location was present within 2 miles of a major highway. Because the ambient air was only sampled on one day, it is possible that elevated levels of these compounds were present in the ambient air during source sampling that were not present when the ambient sample was taken. In addition, the relative concentrations of these compounds may not be unique enough to clearly distinguish this source from other external natural gas combustion sources. Also, for the oil tests, a high tunnel blank value may be an indication of contamination, although the tunnel blank was taken after stack sampling so may overestimate contamination. In the future, it is recommended that a tunnel blank be taken before and after testing, if the schedule and budget allow, to improve the quality of the test data.

More comparison to existing speciation profiles is necessary to gauge the uniqueness of the profile produced by this test. In addition, further testing of similar sources is recommended to provide a more robust basis for the emission factors and speciation profiles described herein.

### Evaluation of Dilution Sampler Design Criteria

The size distributions of particles less than 420 nm in electrical mobility diameter emitted from three fuel types: Kittanning coal, No. 6 residual oil and natural gas; have been measured using a dilution sampler. The modes of particle number concentrations are at 50-80 nm, 70-100 nm and 15-25 nm from Kittanning coal, No. 6 residual oil and natural gas, respectively, for the combustion exhaust temperature of 445K. Particle number concentration increases as the dilution air ratio increases for No. 6 residual oil and Kittanning coal, but decreases for natural gas.

Particle size distributions are virtually the same when the dilution air ratio is higher than 20. Particle number size concentrations were similar for aging time of 10 and 80 seconds, but differ from those at 2 seconds due to decrease of particle coagulation rate and depletion of condensable species on particle growth. The aging time and dilution air ratio required in dilution sampler is not strongly affected by combustion exhaust temperature. However, the number concentrations and particle size drastically increase at higher combustion exhaust temperature.

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## LIST OF ACRONYMS AND ABBREVIATIONS

$\mu\text{g}/\text{cm}^2$	micrograms per square centimeter
AC	automated colorimetry system
acfm	actual cubic feet per minute
ACS	American Chemical Society
Ag	silver
Al	aluminum
API	American Petroleum Institute
As	arsenic
ASME	American Society of Mechanical Engineers
Ba	barium
Br	bromine
Btu/scf	British thermal units per standard cubic foot
Ca	calcium
Cd	cadmium
CEMS	continuous emissions monitoring system
C <sub>x</sub>	compound containing 'x' carbon atoms
Cl <sup>-</sup>	chloride ion
Cl	chlorine
Co	cobalt
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
CPM	condensable particulate matter
Cr	chromium
Cu	copper
DI	distilled deionized
DRI	Desert Research Institute
dscfm	dry standard cubic feet per minute
dscmm	dry standard cubic meters per minute
ED-XRF	energy dispersive x-ray fluorescence
EER	GE Energy and Environmental Research Corporation
EC	elemental carbon
EI	electron impact
EPA	Environmental Protection Agency
ERA	Environmental Research Associates
°F	degrees Fahrenheit
Fe	iron
FID	flame ionization detection
FPM	filterable particulate matter
FTIR	Fourier transform infrared detection
ft/sec	feet per second
Ga	gallium
GC	gas chromatography
GC/IRD/MSD	gas chromatography/infrared detector/mass selective detector
GC/MS	gas chromatography/mass spectrometry

GE	General Electric
GE EER	General Electric Energy and Environmental Research Corporation
gr/100dscf	grains per hundred standard cubic feet
G-S	Greenburg-Smith
Hg	mercury
H <sub>2</sub> S	hydrogen sulfide
HCl	hydrochloric acid
HEPA	high efficiency particulate air
HHV	higher heating value
IC	ion chromatography
In	indium
K	potassium
KHP	potassium hydrogen phthalate
La	lanthanum
lb/hr	pounds per hour
lb/MMBtu	pounds of pollutant per million British thermal units of gas fired
m/sec	meters per second
Mg	magnesium
mg	milligram
mg/dscm	milligrams per dry standard cubic meter
MID	multiple ion detection
Mlb/hr	thousand pounds per hour
MMBtu/hr	million British thermal units per hour
Mn	manganese
Mo	molybdenum
MSD	mass spectrometric detector
MSD/FTIR	mass selective detector/Fourier transform infrared detection
Na	sodium
Na <sub>2</sub> CO <sub>3</sub>	sodium carbonate
NaCl	sodium chloride
NaHCO <sub>3</sub>	sodium bicarbonate
NaNO <sub>3</sub>	sodium nitrate
NaOH	sodium hydroxide
(Na) <sub>2</sub> SO <sub>4</sub>	sodium sulfate
NDIR	non-dispersive infrared
NH <sub>4</sub> <sup>+</sup>	ammonium ion
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	ammonium sulfate
Ni	nickel
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO <sub>2</sub>	nitrogen dioxide
NO <sub>3</sub> <sup>-</sup>	nitrate ion
NO <sub>x</sub>	oxides of nitrogen
O <sub>2</sub>	molecular oxygen
OC	organic carbon
P	phosphorus

PAH	polycyclic aromatic hydrocarbon
Pb	lead
PCA	Portland Cement Association
Pd	palladium
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 micrometers
PM2.5	particulate with aerodynamic diameter less than 2.5 micrometers
ppmv	parts per million (volume)
psig	pounds per square inch (gauge)
PUF	polyurethane foam
QA	quality assurance
Rb	rubidium
RSD	relative standard deviation
S	sulfur
Sb	antimony
Si	silicon
Sn	tin
SO <sub>2</sub>	sulfur dioxide
SO <sub>4</sub> <sup>=</sup>	sulfate ion
Sr	strontium
SRM	standard reference material
SVOC	semivolatile organic compound
TFE	tetrafluoroethylene
Ti	titanium
TIGF	Teflon-impregnated glass fiber
Tl	thallium
TMF	Teflon-membrane filter
TOR	thermal/optical reflectance
U	uranium
V	vanadium
VOC	volatile organic compound
XRF	x-ray fluorescence
XAD-4	Amberlite® sorbent resin (trademark)
Y	yttrium
Zn	zinc
Zr	zirconium