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

TOPICAL REPORT: IMPACT OF OPERATING PARAMETERS ON FINE PARTICULATE EMISSIONS FROM NATURAL GAS-FIRED COMBINED CYCLE AND COGENERATION POWER PLANTS



When citing this document, please use the following citation: England, G.C., "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Impact of Operating Parameters On Fine Particulate Emissions From Natural Gas-Fired Combined Cycle And Cogeneration Power Plants," 2004.

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TOPICAL REPORT: IMPACT OF OPERATING PARAMETERS ON FINE PARTICULATE EMISSIONS FROM NATURAL GAS-FIRED COMBINED CYCLE AND COGENERATION POWER PLANTS

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Prepared for: National Petroleum Technology Office National Energy Technology Laboratory United States Department of Energy (DOE Contract No. DE-FC26-00BC15327)

Gas Research Institute California Energy Commission – Public Interest Energy Research (PIER) New York State Energy Research and Development Authority (GRI contract No. 8362)

> American Petroleum Institute (API Contract No. 00-0000-4303)

Draft (Revision 0.2): July 8, 2004 Final (Revision 1.2): November 5, 2004

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

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

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

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

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

SITE BRAVO OPERATING CONDITIONS (a)

SITE BILLY & OFERITING CONDITIONS										
	Run 1	Run 2	Run 3	Run 4						
GT (Load) (%)	100	100	93	85						
Duct Burner	ON	ON	PARTIAL ^(b)	OFF						
SCR	ON	ON	ON	ON						
Oxidation Catalyst	ON	ON	ON	ON						
Power Augmentation	Yes	Yes	Yes	Yes						

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

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

SITE ECHO OPERATING CONDITIONS ^(a)

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

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

	SILL GOLL O		ing .
	Run 1	Run 2	Run 3
GT (Load) (%)	99	99	99
Duct Burner	ON	ON	ON
SCR	ON	ON	ON
Oxidation Catalyst	ON	ON	ON

SITE GOLF OPERATING CONDITIONS (a)

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

ACKNOWLEDGEMENTS

The following people are recognized for their contributions of time and expertise during this study and in the preparation of this report:

GE ENERGY AND ENVIRONMENTAL RESEARCH CORPORATION PROJECT TEAM MEMBERS Glenn England, Project Manager Stephanie Wien, Project Engineer Dr. Oliver M.C. Chang, Project Engineer Prof. Judith Chow, Desert Research Institute Prof. John Watson, Desert Research Institute Prof. Barbara Zielinska, Desert Research Institute Prof. Lynn Hildemann, Stanford University Prof. Philip Hopke, Clarkson University Prof. Glen Cass, Georgia Institute of Technology

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PROJECT SPONSORS Kathy Stirling, U.S. Department of Energy Marla Mueller, California Energy Commission Dr. Paul Drayton, Gas Research Institute Karin Ritter, American Petroleum Institute Barry Liebowitz, New York State Energy Research and Development Authority Janet Joseph, New York State Energy Research and Development Authority

FOREWORD

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

The goals of this program were to:

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

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

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1. INTRODUCTION

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM), including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (µm) referred to as PM2.5. PM2.5 in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and incomplete. Primary aerosol includes both filterable particles that are solid or liquid aerosols at stack temperature plus those that form as the stack gases cool through mixing and dilution processes in the plume downwind of the source. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. These deficiencies in the current methods can have significant impacts on regulatory decision-making. PM2.5 measurement issues were extensively reviewed by the American Petroleum Institute (API) (England et al., 1998), and it was concluded that dilution sampling techniques are more appropriate for obtaining a representative particulate matter sample from combustion systems for determining PM2.5 emission rate and chemical speciation. These techniques have been widely used in recent research studies. For example, Hildemann et al. (1994) and McDonald et al. (1998) used filtered ambient air to dilute the stack gas sample followed by 80-90 seconds residence time to allow aerosol formation and growth to stabilize prior to sample collection and analysis. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source-receptor and source apportionment analysis for PM2.5 NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities. The U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the API jointly funded this project.

Historical test results for PM emissions from power and cogeneration plants employing gas turbines exhibit a broad distribution, even for similar types of systems and fuels. This creates a challenging situation for power generation plant owners, equipment manufacturers and regulators who seek to accurately estimate emissions from such power plants. Part of the difficulty lies in applying particulate test methods that were originally designed for particulate loadings typical of coal-fired boilers to measure emissions from gas-fired systems that have particulate loadings that are orders of magnitude smaller. A previous report identified potential sources of variability in measured PM emission results in three key areas: emission measurement methods and their application; plant design and operating conditions; and external factors (Lanier and England, 2004). Data from field tests of three different power/cogeneration plants employing gas-fired gas turbines that were tested in this program are reviewed in this report to determine if they shed further light on sources of variation. Two of these plants, Site Bravo (Wien et al., 2004a) and Site Echo (England et al., 2004b), are natural gas-fired combined cycle power plants employing heavy duty frame gas turbines, heat recovery steam generators and air emission control systems nearly identical in size and gas path configuration (although they were operated differently during the tests). Site Golf (England and McGrath, 2004a) is a refinery fuel gas-fired cogeneration plant employing an aeroderivative gas turbine, a much smaller unit but with a similar gas path configuration. Limited tests enable comparison of results between the different sites, and for different operating conditions at the same sites. Multiple replicate test runs were made for two different loads at Site Echo, and both duct burner operation and load were varied for each of four runs at Site Bravo. This report attempts to address the following questions:

- Did this research answer why there is variation in the historical PM emission data for gas turbines?
- What does the data tell us might be a big factor in determining PM emissions?
- Did the research fill in any critical data gaps?
- How did the research help regulators, equipment makers and testing companies identify how to measure PM emissions correctly?

This report provides a brief discussion of the measurement results from the three sites and the key findings from the tests. The report is organized in the following sections:

- Section 1 Introduction
- Section 2 Site Descriptions
- Section 3 Test Results
- Section 4 Discussion and Findings

2. SITE DESCRIPTIONS

SITE BRAVO

Tests were performed on an natural gas-fired combined cycle power plant (NGCC-SF) employing a heavy-duty gas turbine with supplementary firing, steam augmentation and postcombustion emission control equipment. The unit is a single shaft design, with the single generator driven by a shaft common to both the gas and the steam turbine. Hot exhaust gases from the gas turbine pass through a heat recovery steam generator (HRSG) before venting to the atmosphere via the stack (Figure 2-1). The HRSG contains supplementary duct burners for additional steam production. The steam from the HRSG is used both for power generation using the steam turbine and to provide process steam for a neighboring manufacturing facility. The total nominal electrical generation capacity of the cogeneration facility is 240 megawatts (MW). The unit fired natural gas for these tests. The facility is equipped with a continuous emissions monitoring system (CEMS) for carbon monoxide (CO), molecular oxygen (O₂) and oxides of nitrogen (NO_X).

Pollution Control Equipment

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

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

Flue Gas Sampling Locations

The exhaust gases vent to atmosphere through a vertical, cylindrical stack that is 233 feet tall. Emissions sampling was conducted in the stack, downstream of the duct burners and all the air pollution control equipment. The stack has an inside diameter of 16.5 feet (198.0 inches). During these tests, the average stack gas temperature was 230 degrees Fahrenheit (°F) and the average stack gas flow rate was 19,450 dry standard cubic meters per minute (dscm/min).



Figure 2-1. Site Bravo Process Overview.

SITE ECHO

The host facility for this test cogenerates both process steam for a nearby manufacturing facility and electricity for sale to the grid. The combined peak load power output of the two gas turbine generators and one steam turbine generator is 554 MW (at ambient temperature of 90 °F). The plant employs two heavy-duty gas turbines and one common steam turbine in a combined cycle arrangement. The hot exhaust gases from each gas turbine pass through a separate HRSG before

venting to the atmosphere via the stack (Figure 2-2). The HRSG is equipped with supplementary firing for additional steam production and post-combustion emission control equipment. The unit fired pipeline natural gas during these tests (natural gas samples were not collected for analysis). The stack is equipped with continuous emissions monitors for CO, O_2 and NO_x .

Pollution Control Equipment

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

In addition to the lean premix combustion system, the unit has post-combustion air pollution control equipment. The HRSG is fitted with an oxidation catalyst for reduction of CO emissions followed by a SCR system for reduction of NO_X emissions. The SCR reagent, NH_3 , is injected through a grid just upstream of the SCR catalyst.

Flue Gas Sampling Locations

The exhaust gases vent to atmosphere through a vertical, cylindrical stack that is 139 feet tall. Emissions sampling was conducted at the stack, downstream of the duct burners and all the air pollution control equipment. The stack has an inside diameter of 19.5 feet (234 inches). During these tests, the average stack gas temperature was 219 °F and 206 °F and the average stack gas flow rate was 22,046 dscm/min and 16,732 dscm/min, at high load and low load, respectively.

Fuels

Analyses of four samples of the natural gas (one sample for each of the test days) indicate total sulfur levels ranging from 0.254 to 0.403 grains per 100 standard (0 degrees Celsius (°C) cubic feet (gr/100 scf) (sum of all sulfur species expressed as elemental S) (Table 2-1). Most of the sulfur is present in the fuel as methyl mercaptan (added as an odorant) and thiophane. Applying the gross Btu content measured in the four samples to the measured fuel flow rates reported by

the plant process data, the calculated gross heat inputs compare very well (within 2 percent) with the value reported by the process data system.



Figure 2-2. Site Echo Process Overview.

	Unite		uturur Gub I	Results	buitb.		
Test Condition	Units	Dup 2 High	Dun 4 Uigh	Pup 2 Louy	Dup 2 Lou	Avorago	DSD (0/)
Non Hydrogerbon Cases		Kuli 5 High	Kull 4 High	Kull 2 LOW	Kull 5 LOw	Average	KSD (70)
Nitrogen	0/2 1/1	1.05	1.2	3 03	3 76	2 40	63
Carbon Diovido	/0 V/V 0/. 1/1	0.84	0.80	3.93 0.78	0.83	0.84	5
Hydrogerbong	/0 V/V	0.04	0.89	0.78	0.85	0.04	5
Mathana	0//	01.4	00.2	00.1	00 2	90.5	2
Education	%0 V/V	91.4 5.22	90.3 5.70	88.1 5.21	88.5	89.5 5.42	2
Ethane	%0 V/V	5.55	5.79	5.51	5.24	5.42) 11
Propane	%0 V/V	1.07	1.34	1.37	1.35	1.28	11
1-Butane	%0 V/V	0.114	0.148	0.158	0.151	0.143	14
n-Butane	% V/V	0.146	0.189	0.208	0.202	0.186	15
1-Pentane	% V/V	0.031	0.042	0.049	0.046	0.042	19
n-Pentane	% V/V	0.023	0.031	0.037	0.036	0.032	20
Hexane +	% V/V	0.0318	0.0431	0.0514	0.0452	0.0429	19
Hydrogen Sulfide	% V/V	ND	0.00002	ND	ND	< 0.00002	n/a
Calculated Elemental Compositio	on						
Carbon	% W/W	/3.37	73.26	70.23	70.33	71.80	2
Hydrogen	% w/w	23.44	23.26	22.31	22.36	22.84	3
Nitrogen	% w/w	1.67	1.89	6.08	5.84	3.87	62
Oxygen	% w/w	1.52	1.59	1.38	1.47	1.49	6
Heat of Combustion % Physical I	Properties*						
Lower Heating Value (dry)	Btu/scf	955.3	963.2	937.5	937.1	948.3	1
Higher Heating Value (dry)	Btu/scf	1058.6	1067	1038.5	1038.1	1,050.6	1
Specfic Gravity		0.6093	0.6171	0.6262	0.6249	0.6194	1
Wobbe Index		1356.2	1358.3	1312.4	1313.2	1335.03	2
Extended Hydrocarbon Analysis	by GC-FID						
Cycloalkanes							
Cyclopentane	% v/v	0.002	0.0028	0.0033	0.0029	0.0028	20
Methylcyclopentane	% v/v	0.0027	0.0037	0.0056	0.0047	0.0042	30
Cyclohexane	% v/v	0.0036	0.0048	0.0061	0.0052	0.0049	21
Methylcyclohexane	% v/v	0.0024	0.0029	0.0044	0.0036	0.0033	26
Aromatics							
Benzene	% v/v	0.0011	0.0015	0.0015	0.0015	0.0014	14
Toluene	% v/v	0.0011	0.0013	0.0015	0.0015	0.00135	14
Ethylbenzene	% v/v	0.0001	0.0001	0.0001	0.0001	0.0001	0
m,p-Xylene	% v/v	0.0002	0.0002	0.0002	0.0002	0.0002	0
o-Xylene	% v/v	0.0001	0.0001	0.0001	0.0001	0.0001	0
c3 Benzenes	% v/v	ND	ND	ND	0.0001	< 0.0001	n/a
Parraffins							
Hexanes	% v/v	0.0133	0.0191	0.0199	0.018	0.01758	17
Heptanes	% v/v	0.0035	0.0046	0.0057	0.0049	0.00468	19
2,2,4-Trimethylpentane	% v/v	0.0002	0.0002	0.0003	0.0002	0.00023	22
Octanes	% v/v	0.0011	0.0013	0.0019	0.0015	0.00145	24
Nonanes	% v/v	0.0004	0.0005	ND	0.0007	< 0.00053	29

Table 2-1. Site Echo Natural Gas Analysis Results.

ND - Not Detected; RSD = relative standard deviation

* At 60 $^{\rm o}{\rm F}$ and 14.696 psia; ** At 0 $^{\rm o}{\rm C}$ and 14.696 psia

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

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

	Units			Results	5		
Test Condition		Run 3 High	Run 4 High	Run 2 Low	Run 3 Low	Average	RSD (%)
Trace Sulfur Species (ASTM D6	228-98)***						
Hydrogen Sulfide	ppmv	ND	0.19	~ 0.06	~ 0.06	< 0.10	73
Methyl Mercaptan	ppmv	ND	1.57	1.45	1.72	< 1.58	9
Ethyl Mercaptan	ppmv	ND	0.28	0.22	0.2	< 0.23	18
i-Propyl Mercaptan	ppmv	ND	0.08	0.07	0.06	< 0.07	14
t-Butyl Mercaptan	ppmv	0.05	1.27	1.08	1.12	0.88	64
Dimethyl Disulfide	ppmv	0.12	ND	ND	~ 0.02	< 0.07	101
Methyl Ethyl Disulfide	ppmv	0.06	ND	ND	ND	< 0.06	n/a
Methyl i-Propyl Disulfide	ppmv	~ 0.02	ND	ND	ND	< 0.02	n/a
Methyl t-Butyl Disulfide	ppmv	0.83	ND	ND	ND	< 0.83	n/a
Di-i-Propyl Disulfide	ppmv	0.22	ND	ND	ND	< 0.22	n/a
i-Propyl t-Butyl Disulfide	ppmv	0.03	ND	ND	ND	< 0.03	n/a
Dimethyl Trisulfide	ppmv	~ 0.01	ND	ND	0.04	< 0.03	85
Diethyl Trisulfide	ppmv	0.19	0.02	ND	ND	< 0.11	114
Di-t-Butyl Trisulfide	ppmv	0.35	ND	ND	ND	< 0.35	n/a
Benzothiophene	ppmv	0.11	ND	ND	ND	< 0.11	n/a
Thiophane	ppmv	2.02	1.48	1.18	1.54	1.56	22
Unidentified Sulfur (as	ppmv	0.05	ND	ND	0.13	< 0.09	63
monosulfides)	**	6.4.4	4.02	1.0.6	4.00	5.1.1	10
Total Sulfur	ppmv	6.44	4.93	4.06	4.99	5.11	19
Total Sulfur (as S)**	gr/100 scf	0.403	0.308	0.254	0.312	0.319	19
Total Sulfur (calculated, as SO ₄)	lb/MMBtu	1.5E-03	1.2E-03	9.9E-04	1.2E-03	1.2E-03	19

Table 2-1 (continued). Site Echo Natural Gas Analysis Results.

ND - Not Detected; RSD = relative standard deviation

* At 60 $^{\rm o}\!F$ and 14.696 psia; ** At 0 $^{\rm o}\!C$ and 14.696 psia

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

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

SITE GOLF

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



Figure 2-3. Site Golf Process Overview.

Pollution Control Equipment

The combustion turbine employs water spray injection into the annular combustor to suppress peak combustion temperatures and thereby reduce NOx formation. The heat recovery steam generator is equipped with an oxidation catalyst for control of CO emissions followed by a SCR system for control of NO_x emissions. The SCR reagent (NH₃) is injected immediately upstream of the SCR catalyst. The stack is equipped with continuous emissions monitors for CO, O_2 and NO_x.

Flue Gas Sampling Locations

The cogeneration unit exhausts through a vertical, cylindrical stack. Emissions sampling was conducted at the stack, downstream of the duct burners and all air pollution control equipment.

The stack has an inside diameter of 10 feet (120 inches) and is at least 80 feet tall. During these tests, the average stack gas temperature was 408 °F and the average stack gas flow rate was 7,067 dscm/min.

Fuels

Fuel gas analyses for Site Golf indicate an average total sulfur level of 25 to 29 parts per million by volume (ppmv), as elemental sulfur (Table 2-2). These sulfur level correspond to approximately 1.5 to 1.8 gr/dscf expressed as elemental sulfur, or 0.0039 to 0.0045 pounds per million British thermal units (lb/MMBtu) expressed as sulfur dioxide (SO₂).

	Units	Units Golf-Run1 Golf-Run2 Golf-Run3 Average				RSD (%)
Non-Hydrocarbon Ga	ses					
Nitrogen	% v/v	6.24	6.06	5.68	5.99	5
Oxygen/Argon	% v/v	0.09	0.07	0.07	0.08	15
Carbon Dioxide	% v/v	1.21	1.16	1.11	1.16	4
Carbon Monoxide	% v/v	1.11	1.13	1.07	1.10	3
Hydrogen	% v/v	29.5	29.2	29.8	29.5	1
Helium	% v/v	< 0.01	< 0.01	< 0.01	< 0.01	n/a
Hydrocarbons						
Methane	% v/v	32.30	32.10	31.60	32.0	1
Ethane	% v/v	11.4	11.6	11.4	11.5	1
Ethene	% v/v	6.63	6.56	6.32	6.50	2
Ethyne	% v/v	ND	ND	ND	ND	n/a
Propane	% v/v	2.47	2.64	2.95	2.69	9
Propene	% v/v	5.42	5.93	6.09	5.81	6
Propadiene	% v/v	ND	ND	ND	ND	n/a
Propyne	% v/v	0.025	0.030	0.029	0.028	9
i-Butane	% v/v	0.651	0.653	0.694	0.666	4
n-Butane	% v/v	0.685	0.729	0.728	0.714	4
1-Butene	% v/v	0.158	0.180	0.204	0.181	13
i-Butene	% v/v	0.151	0.170	0.199	0.173	14
trans-2-Butene	% v/v	0.108	0.118	0.149	0.125	17
cis-2-Butene	% v/v	0.070	0.075	0.095	0.080	17
1,3-Butadiene	% v/v	ND	ND	ND	ND	n/a
i-Pentane	% v/v	0.843	0.762	0.810	0.805	5
n-Pentane	% v/v	0.306	0.288	0.320	0.305	5
neo-Pentane	% v/v	ND	ND	ND	ND	n/a
Pentenes	% v/v	0.224	0.119	0.289	0.211	41
Hexanes +	% v/v	0.447	0.394	0.403	0.415	7
Hydrogen Sulfide	% v/v	ND	ND	ND	ND	n/a
Carbonyl Sulfide	% v/v	ND	ND	ND	ND	n/a
Calculated Elemental	Composition					
Carbon	% w/w	68.60	68.99	69.63	69.07	1
Hydrogen	% w/w	19.40	19.41	19.51	19.44	0
Oxygen	% w/w	3.04	2.93	2.78	2.92	4
Nitrogen	% w/w	8.96	8.67	8.08	8.57	5
Sulfur	ppmv	26.0	29.3	24.6	26.6	9
Sulfur	gr/100 scf**	1.6	1.8	1.5	1.7	9
Sulfur (as SO ₂)	lb/MMBtu	4.0E-03	4.5E-03	3.8E-03	4.1E-03	9
Helium	% w/w	< 0.01	< 0.01	< 0.01	< 0.01	n/a
Heat of Combustion %	6 Physical Prope	rties*				
Lower Heating Value	Btu/scf	964	974	988	975	1
Higher Heating Value	Btu/scf	1,060	1,069	1,066	1,065	0
Higher Heating Value	Btu/lb	20,642	20,719	20,523	20,628	0
Specfic Gravity	vs dry/normal air	0.674	0.677	0.682	0.678	1
n/a - not applicable	2					

Table 2-2. Site Golf Refinery Fuel Gas Analysis Results.

ND - Not Detected.

* At 60 $^{\rm o}{\rm F}$ and 14.696 psia; ** At 0 $^{\rm o}{\rm C}$ and 14.696 psia

3. TEST RESULTS

The data in this report were developed using an experimental dilution test method applied to three sources operating under one or more conditions with different sources of emissions that are not necessarily representative of the source category or the typical operation of the specific source tested. Accordingly, GE Energy does not recommend using any emissions factors contained herein for any regulatory and/or commercial applications. The data in this report may be useful for future refinement and validation of the experimental dilution method for specific applications so that it may be applied in future tests to develop more robust emission factors. Due to the small number of tests and limitations of the test results described above, any findings with respect to parametric effects are necessarily preliminary and qualitative. Also, it should be noted that whereas dilution sampling is widely accepted for demonstrating compliance with mobile source particulate emission standards and for stationary source receptor and source apportionment analysis, it is not currently accepted by regulatory agencies for demonstrating compliance with stationary source PM emission standards or permit limits. At this time, the method remains developmental for stationary sources. Recently, EPA published a conditional test method (CTM-039) for stationary source dilution sampling and conducted limited tests on coal- and oil-fired boilers (U.S. EPA, 2003a). EPA proposed the method as an alternative for testing needed to develop PM2.5 emission inventories (U.S. EPA, 2003b). While the equipment and procedures specified in CTM-039 differ from those used in this program, it indicates such methods may become more generally accepted in the future.

SITE BRAVO

Process Operating Conditions

A total of four six-hour test runs were conducted at Site Bravo. Process operating conditions varied from run to run (Table 3-1). Runs 1 and 2 were performed with duct burners on throughout the runs with the gas turbine operating at 100 percent of rated heat input. Runs 3 and 4 were performed with the duct burners off (except for 30 minutes of the total 360-minute duration of Run 3). The gas turbine (GT) load also was approximately 7 and 15 percent below rated heat input for Runs 3 and 4, respectively.

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

Table 3-1. Site Bravo Operating Conditions ^(a)

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

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

Particulate Measurement Results

PM was measured concurrently by four different methods during each six-hour test run at Site Bravo (Table 3-2):

- EPA Method PRE-004 for filterable PM2.5, particulate with aerodynamic diameter less than 10 µm (PM10) and total (traditional method with in-stack cyclones and filter);
- EPA Method 202 for condensable PM (traditional iced impinger method);
- A dilution sampler was used to measure PM2.5 (Hildemann-style sampler employing long mixing tunnel and large residence time chamber to age aerosols for 80-90 seconds);
- Modified EPA Method 8 was used to measure condensable PM (traditional iced impinger method, but with modified impinger analysis procedure).

Filterable particulate matter (FPM) results are strongly dominated by apparent measurement limitations. The Method PRE-004 results for FPM are clouded by negative net weights for all of the filters and several of the blank-corrected acetone rinses. The negative net filter weights physically represent filter weight loss between the initial pre-test and final post-test weights, probably due to loss of a few fibers from the filter during handling. The negative net acetone rinse weights occur because the acetone rinse blank net weight, which is subtracted from the raw sample result, is greater than the sample net weight. Results like these are not unusual for application of this and similar methods to gas-fired sources, and are symptomatic of in-stack PM

	<u> </u>	Ĺ				Ré	esults (mo	dscm	Results (mg/dscm)						
Mathad	Deremeter		$\mathbf{P}_{un} = 1 (\mathbf{i})$		$P_{iin} 2 (i)$		Pup 3 (iii)		$P_{\rm up} A_{(iii)}$		Avorago	SD.	PSD		
wiethou	Falalletel		Kull I (I)		$\operatorname{Kun} 2(i)$		$\operatorname{Kun} \mathcal{S}(u)$		$\operatorname{Kun} + (uu)$		Average	3D	KSD		
PRE-004	FPM >10 µm (rinse)**		0.71		0.32	ND			0.055	<	0.36	0.33	91%		
1	FPM >2.5 μm to <10 μm (rinse)**		0.47		0.069	ND		ND		<	0.27	0.28	105%		
	FPM <2.5 µm (rinse)**	ND		ND			0.062	ND		<	0.0616	n/a	n/a		
	FPM <2.5 µm (filter)**	ND		ND		ND		ND		<	n/a	n/a	n/a		
	Total FPM**	<	1.18	<	0.39	<	0.062	<	0.055	<	0.42	0.53	126%		
	FPM <10 µm**	<	0.47	<	0.069	<	0.062	ND		<	0.20	0.23	117%		
PRE-004	FPM >10 µm (rinse)		0.71		0.32	ND	-0.15		0.055	<	0.23	0.37	160%		
	FPM >2.5 μ m to <10 μ m (rinse)		0.98		0.069	ND	-0.085	ND	-0.14	<	0.20	0.52	256%		
	FPM <2.5 µm (rinse)	ND	-0.10	ND	-0.074		0.062	ND	-0.18	<	-0.0747	0.1023	-137%		
	FPM <2.5 μm (filter)	ND	-0.25	ND	-0.14	ND	-0.19	ND	-0.11	<	-0.1718	0.0621	-36%		
	Total FPM	<	1.34	<	0.18	<	-0.37	<	-0.38	<	0.19	0.81	424%		
	FPM <10 μm	<	0.63	<	-0.14	<	-0.22	ND	-0.44	<	-0.04	0.46	1086%		
202	Inorganic CPM (Method 202)		1.2		2.4		1.3		2.4		1.8	0.65	36%		
	Organic CPM (Method 202)		0.39	ND		ND		ND		<	0.39	n/a	n/a		
	Total CPM (Method 202)		1.7	<	2.4	<	1.3	<	2.4	<	2.0	0.54	28%		
8	Total CPM (Method 8)		1.7		1.7		0.87		1.7		1.5	0.41	26%		
Dilution	PM2.5 mass		0.11		0.38		0.033		NV	с	0.18	0.18	104%		

Table 3-2. Site Bravo Particulate Concentration Results.

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

 $\,<\,$ - one or more of the sample fractions are lower than the minimum detection limit.

n/a - not applicable

ND - not detected

NA - not analyzed

SD - standard deviation

RSD - relative standard deviation

CPM - condensable particulate matter

*Method 17 results are not considered reliable in this test due to problems with filter tare weights.

**All of the filter net weights and some of the blank-corrected acetone rinse net weights were negative, and are treated as zeros in summing the data. All of the reported particulate mass is from the acetone rinses. FPM<2.5 um includes 1 acetone rinse, FPM<10 um includes 2 acetone rinses, and Total FPM includes 3 acetone rinses (see Method PRE-4 for further details).

c - 95% Confidence Lower Bound of the Average concentration is lower than the Ambient concentration indicating it is likely the results are not significantly different at the 95% confidence level.

(i) Duct burners on.

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

(iii) Duct burners off.

concentrations that are near or below the lower quantification limits of the test method. When this occurs, it is convention to treat negative net weights as zero in results calculations for determining compliance with emission limits. While this convention provides conservatively high results, it dramatically under-represents the true variability (standard deviation) of the results. To illustrate, the Method PRE-004 results in Table 3-2 are presented two ways: with negative weights treated as zeros and with the actual results. Filterable PM10 (FPM < 10 μ m) concentration averages 0.20 mg/dscm with a standard deviation of 0.23 mg/dscm (117 percent) when negative net weights are ignored. When negative net weights are included, the average filterable PM10 is -0.04 mg/dscm with a standard deviation of 0.46 mg/dscm (1086 percent). The acetone rinse results dominate both the mass average and standard deviation. Obviously a

negative filterable PM10 concentration has no physical meaning, but the standard deviation provides an indication of the lower quantification limit of the method. Since the in-stack concentrations can be considered "near zero" for this method, a multiple of the standard deviation can be used to estimate in-stack minimum detection limits (MDL, 3 times standard deviation) and lower quantification limits (LQL, 10 times standard deviation). Combining the standard deviations of the actual FPM results (including the three rinses and the filter) by addition in quadrature, the in-stack MDL is approximately 0.9 mg/dscm and the in-stack LQL is approximately 3 mg/dscm. A larger population of results ideally should be used for estimating MDL and LQL, however if this analysis is considered representative then it is clear that all the FPM results are below the LQL and all but one are below the MDL.

Condensable particulate matter (CPM), defined as the mass of solid residue remaining after the impinger contents are analyzed, was measured concurrently using EPA Method 202 and an experimental modification of EPA Method 8 proposed by Rubenstein (2001). CPM is typically included in regulatory definitions of PM10 and PM2.5. The EPA Method 202 sample collection and analysis included optional procedures to minimize SO₂ interference (by purging the impingers with nitrogen for one hour immediately following sample collection) and loss of sulfuric acid (H₂SO₄, by titrating the inorganic sample fraction with ammonium hydroxide prior to final evaporation and weighing). These steps also were performed on the modified Method 8 (MM8) samples. The Method 202 and MM8 results agree remarkably well, and follow a similar trend among the different test runs. CPM results are dominated by the inorganic fraction, which chemical analysis shows to be predominantly sulfate related. Method 202 results tend to be a little higher than the MM8 results, which is largely attributed to non-sulfate residues. The net weight of the residues, determined from the difference between the initial weight and final weight of beakers in which the samples are dried, is well above the analytical resolution (5.6 to 9.9 mg sample net weights compared to analytical resolution of 0.1 mg) and above the analytical LQL for the gravimetric procedure (approximately 2 mg based on these results). Thus, most of the variability in the CPM results is due to other factors. The standard deviation of the CPM results suggests an in-stack LQL of approximately 5 mg/dscm, which is greater than all of the CPM test results. It should be noted that CPM results are probably biased high due to aqueous phase oxidation of dissolved SO_2 gas to sulfites/sulfates in the impingers during sample collection and storage (Wien et al., 2001). Further, condensation of vapors in the impingers is

excessive compared to the actual exhaust plume because the sample cools without dilution. Thus, it is likely that CPM measurement results from iced impinger methods applied to gas-fired sources depend more on the natural gas sulfur content than on process operating conditions and do not represent actual CPM that exists in the exhaust plume.

The dilution sampler collects PM2.5 mass, including both aerosols present at stack temperature and those that condense under simulated exhaust plume conditions, on a single 47-millimeter (mm) Teflon[®] membrane filter (TMF). The sample collection and analysis procedure is identical to that typically used for ambient air sampling and has an analytical uncertainty of approximately 3 micrograms (μ g) (analytical resolution 1 μ g). The net TMF weights ranged from 29 to 300 μ g, well above the analytical uncertainty. However, a procedural error (over tightening of the filter cassettes) during this test that caused slight tearing of the TMFs for Runs 3 and 4 introduced atypical variation among the net weights. Thus, the uncertainty at the 95 percent confidence level (0.46 mg/dscm) is large relative to the mean result. Despite the random uncertainty contributed by this error, the mean and 95 percent confidence upper bound of the average dilution sampler PM2.5 concentrations (approximately 0.5 mg/dscm) are significantly lower than the total PM/PM10/PM2.5 (FPM plus CPM) concentrations measured with the traditional methods. Subsequent tests at Site Echo identified that approximately 20 percent of ambient PM2.5 penetrated through the dilution air purifier, which probably contributes to background levels in the dilution air corresponding to in-stack equivalent PM2.5 on the order of 0.05 to 0.1 mg/dscm. This is approximately similar in magnitude to the stack PM2.5 measured for Runs 2 and 3. Subtracting estimated background levels in the dilution air from stack PM2.5 shows that Site Bravo stack and ambient PM2.5 are of approximately similar magnitude. Thus, the only strong conclusion with respect to the impact of different operating conditions on stack PM2.5 that can be made is that such effects are very small, less than 0.2 mg/dscm, and below the present capability of any of these methods to measure with high confidence. Because of this and other limitations of the test data discussed in detail in the site-specific test report, and because of the developmental status of the dilution sampling method, the dilution sampler results should be used with caution.

There is no clear trend in any the PM test results by any of the methods used in this test that appear to correspond to the changes in operating conditions from run to run. It is interesting to

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note that the PM2.5 concentration for Run 3 (0.033 mg/dscm), during which duct burners were on for approximately 8 percent of the test run and off for the remaining 92 percent of the run, is much lower than the PM2.5 concentrations for Runs 1 and 2 (0.11 and 0.38 mg/dscm) during which the duct burners were on throughout the runs. Due to the single measurement for each condition, the limitations of the test results described above and changes in more than one parameter from run to run, any findings with respect to parametric effects are necessarily preliminary and qualitative. A larger number of samples and accurate procedures would be needed to quantify the effect of operating parameters on PM concentration. It can be said with reasonable confidence that any effect of the process variations that occurred among these four test runs appears to be smaller than the variability of the measurements during these tests.

SITE ECHO

Process Operating Conditions

During these tests, four replicate six-hour test runs were conducted at approximately 100 percent of rated heat input (high load) and three replicate six-hour test runs were conducted at approximately 59 percent of rated heat input (low load) (Table 3-3). Although the heat recovery steam generator is fitted with duct burners, they remained off during all of the tests.

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

Table 3-3. Site Echo Operating Conditions ^(a)

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

Particulate Measurement Results

PM2.5 was measured concurrently using two different dilution samplers over each six-hour test duration (Table 3-4):

- Alpha Sampler: A Hildemann-style dilution sampler employing a long U-shaped mixing tunnel and a large residence time chamber to age aerosols for 80-90 seconds;
- Beta Sampler: A newly developed compact dilution sampler based on the Hildemann concept of mixing followed by aging, but with faster mixing, shorter residence time (approximately 10 seconds) and a linear sample path to reduce size, weight and inertial particle losses.

(a) High Load							
		Results (mg/dscm)					
Run Number	Run 1	Run 1Run 2Run 3Run 4AverageSD					RSD
Alpha Sampler	(i) 0.102	(i) 0.136	(i) 0.119	0.099	0.114	0.017	15
Beta Sampler	0.060	0.078	0.018	0.067	a 0.056	0.026	47
All (high load)				0.085	0.037	44	
All (high load, excl. Alpha Runs 1-3) 0.064 0.0				0.030	46		

Table 3-4.	Site Echo PM2.5 Concentration Results.
	(a) High Load

(b) Low Load

		(-	,				
	Results (mg/dscm)						
Run Number	Run 1	Run 2	Run 3		Average	SD	RSD
Alpha Sampler	0.087	0.069	0.048		0.068	0.020	29
Beta Sampler	0.058	0.047	0.083		0.062	0.019	30
All (low load)					0.065	0.017	27

(c) High and Low Load			
All (high and low load)	0.076	0.031	41
All (high and low load, excl. Alpha high load Runs 1-3)	0.065	0.022	35

SD - standard deviation

RSD- relative standard deviation

a - 95% confidence lower bound of the average concentration is less than the dilution sampler blank concentration.

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

At high load, there is an apparent low bias in the average Beta sampler results of 51 percent compared to the Alpha sampler, while at low load the results are only 8 percent apart. Statistical analysis shows that the bias is not significant at the 95 percent confidence level due to the variation in the results; however, it should be recognized that the number of tests is somewhat small (seven paired tests, compared to a typical validation test series of 12 paired tests) so the

statistical tests of the bias and precision provide only a preliminary indication of the comparability of the two samplers. During the first three runs at high load, flow measurement instrumentation on the Alpha sampler was affected by high winds. It is likely that results from those runs are significantly biased high (on the order of perhaps 20 percent) and therefore not considered completely reliable. There are several ways to look at these data. Comparing only the Beta sampler results, there is very little difference in the average PM2.5 concentration at high load and part load (0.056 versus 0.062 mg/dscm, respectively, or approximately 12 percent difference referenced to high load) and the difference is well within one standard deviation of the results. Comparing only the Alpha sampler results, the mean results at high and low load differ by approximately 41 percent. Pooling all the results, the difference is approximately 23 percent. Excluding the Alpha sampler runs 1 to 3 from the pool, the difference is approximately 10 percent. In all cases, these differences between PM2.5 measured at full and part load operation are not significant at the 95 percent confidence level (see, for example, Figure 3-1 which compares all the results). Based on these results, no difference between PM2.5 measured at full load and part load is discernable above the variation in the measurements. It seems likely that any actual difference is smaller than 41 percent, the maximum observed difference, and more likely on the order of 10 percent or less.

The units tested at Site Echo and Site Bravo are very similar in size and gas path configuration. Comparing the dilution method results from Sites Bravo and Echo, the average PM2.5 concentration from Site Echo (0.065 mg/dscm) is approximately one-third of the average PM2.5 concentration measured at Site Bravo (0.18 mg/dscm). The difference is not significant at the 95 percent confidence level (p-value 0.4) due to the wide range of variation observed at Site Bravo. The Site Echo PM2.5 concentration results are in much closer agreement with Site Bravo Run 3 results (0.033 mg/dscm) than with Site Bravo Runs 1 and 2 (0.11 and 0.38 mg/dscm), which is interesting because the Site Echo test runs and most of Site Bravo Run 3 were performed without duct burners operating. There is insufficient data to attribute this difference to duct burner operation with high confidence, however it indicates a potential area for future investigation. (means are indicated by lines)



Figure 3-1. Comparison of High and Low Load PM2.5 Mass Results (Site Echo).

The quality assurance results at Site Echo showed that approximately 20 percent of ambient PM2.5 penetrated through the dilution air purifiers in both samplers, which probably contributes to background levels in the dilution air corresponding to in-stack equivalent PM2.5 on the order of 0.05 to 0.1 mg/dscm. This is very similar in magnitude to the measured stack PM2.5. Subtracting estimated background levels in the dilution air from stack PM2.5 shows that Site Bravo stack and ambient PM2.5 are of approximately similar magnitude and not significantly different at the 95 percent confidence level. Thus, the only strong conclusion with respect to the impact of different operating conditions on stack PM2.5 that can be made is that such effects are very small, less than 0.2 mg/dscm, and below the present capability of any of these methods to measure with high confidence. Because of this and other limitations of the test data discussed in detail in the site-specific test report, and because of the developmental status of the dilution sampling method, the dilution sampler results should be used only with caution.

SITE GOLF

Process Operating Conditions

Process operation during the tests at Site Golf was very steady and reproducible from run to run at approximately 99 percent of rated heat input (Table 3-5). The unit fired refinery gas in both the gas turbine and through the duct burners during all three six-hour test runs. No unusual process events occurred during the tests.

		6	
	Run 1	Run 2	Run 3
GT (Load) (%)	99	99	99
Duct Burner	ON	ON	ON
SCR	ON	ON	ON
Oxidation Catalyst	ON	ON	ON

Table 3-5. Site Golf Operating Conditions ^(a)

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

Particulate Measurement Results

PM2.5 concentration was measured using the Beta dilution sampler described above for Site Echo. Three replicate six-hour test runs were performed. The stack sample TMF net weights are small (47 to 97 μ g) but much greater than the analytical uncertainty (2 μ g). PM2.5 mass averages 0.16 mg/dscm (Table 3-6) and the standard deviation is small, 0.04 mg/dscm (23 percent). A dilution sampler blank (DSB) was not collected at Site Golf, however the stack results are 4 to 6 times higher than the PM2.5 DSB collected at Site Echo, which is significant at the 95 percent confidence level.

Table 3-6. Site Golf PM2.5 Concentration Results.

	Results (mg/dscm)					
Run Number	Run 1	Run 2	Run 3	Average	SD	RSD
PM2.5	0.12	0.18	0.19	0.16	0.04	23%

RSD- Relative Standard Deviation

Comparing only dilution sampler results, the average PM2.5 concentration for Site Golf is approximately 3 times higher than the PM2.5 concentration measured at Site Echo and within 10 percent of the average PM2.5 concentration measured at Site Bravo. Including only the Beta

sampler results, the difference between Sites Golf and Echo is significant at the 95 percent confidence level (p-value 0.047). Including the Alpha sampler results from Site Echo does not change the difference appreciably, but raises the standard deviation slightly making the difference insignificant at the 95 percent confidence level (p-value 0.05). It is interesting to note the similarity of the Site Bravo and Site Golf PM2.5 concentrations (p-value 0.92), despite the large difference in plant size. Site Echo tests were conducted without duct burners operating, whereas duct burners were operating during Site Golf tests and most of the Site Bravo tests. Another potential reason for the higher stack PM2.5 measured at Site Golf is the water used for spray intercooling and NOx control in the combustion turbine. A water sample was not collected and analyzed for these tests. Typical upper limits for total dissolved solids of 5 part per million (weight) ppmw and total trace elements of 0.5 ppmw correspond to approximately 0.13 and 0.013 mg/dscm in the exhaust gas under the conditions tested at Site Golf. Thus, the water is a potentially significant source of stack PM2.5. Although the data set is much too limited to draw firm conclusions (small populations, large relative standard deviations, varying operating conditions, possible background interferences, developmental method, etc.), the results hint that the observed differences in PM2.5 concentration between Site Echo and the other two sites may be related to duct burner operation or water injection.

STACK PM2.5 COMPARED TO DILUTION AIR BACKGROUND AND AMBIENT PM2.5

Hourly ambient PM2.5 data from a nearby ambient monitoring station (AMS) were obtained for all test periods at Sites Echo and Golf. The average hourly AMS PM2.5 ranged from 0.007 to 0.020 mg/dscm during the tests. During a single six-hour ambient PM2.5 measurement run at Site Echo, the average hourly AMS PM2.5 (0.012 mg/dscm) and the measured ambient PM2.5 (0.014 mg/dscm) are in very good agreement (Figure 3-2).

Any significant PM2.5 in the dilution air background has a direct effect on the measure stack results. Mass measured on Teflon membrane filters includes both PM2.5 from the sample plus any PM2.5 in the dilution air. The PM2.5 concentration in the diluted sample is determined from the measured net mass on the filter divided by the measured volume of diluted sample drawn through the filter. The PM2.5 concentration in the diluted sample is multiplied by the dilution factor (1+ dilution ratio) to correct the result back to in-stack concentration::

 $Stack PM 2.5[mg / dscm] = (1 + Dilution Ratio) * \frac{PM 2.5 mass[mg]}{Diluted SampleVolume[dscm]}$

Thus, any mass in the sample contributed by the dilution air contributes to the calculated in-stack mass concentration. DSB results for Site Echo indicate that the PM2.5 concentration in the dilution air, although very low, was significant relative to the very low stack PM2.5 concentrations. AMS PM2.5 and the pre-test DSB results were used to calculate the ambient PM2.5 penetration through the dilution air purifiers – i.e., the measurement background level in the dilution air. The PM2.5 penetration factors (PF) for the two samplers are approximately similar: 16 percent for the Alpha sampler and 24 percent for the Beta sampler (84 and 76 percent PM2.5 removal efficiency, respectively). PF, which is equivalent to (1 – removal efficiency), was calculated as follows:

$$PF = 1 - \frac{AmbientPM2.5[mg/dscm] - DSBPM2.5[mg/dscm]}{AmbientPM2.5[mg/dscm]}$$

A typical high efficiency particulate arrest (HEPA) filter has a removal efficiency of 99.9 percent for particles 0.3 μ m and larger. The relatively low overall removal efficiencies estimated at Site Echo suggest that a significant fraction of the ambient PM2.5 mass is smaller than 0.3 μ m, for which the HEPA filter is not as efficient.

The PF was applied to the AMS PM2.5 during each stack test run to estimate dilution air background PM2.5 for each test. This is relevant because it provides an estimate of the measurement background PM2.5 for each individual test run against which the stack PM2.5 results may be compared. The PF was assumed to be the same for all test runs. This is reasonable because the dilution air HEPA and activated charcoal filters were not changed or disassembled during the field campaign and the dilution air flow rate was approximately the same for all runs; therefore, there should be no significant change in removal efficiency from run to run. With the exception of one of the seven data points for each dilution sampler, there is a fairly strong correlation between the variations in estimated dilution air background and stack PM2.5, and the levels are very similar (Figure 3-3). The variation in estimated dilution air background PM2.5 is primarily due to variation in AMS PM2.5 rather than sampling conditions. This implies that the observed variations are in fact systematic rather than random; therefore, the stack results can be corrected for the dilution air background. Subtracting estimated dilution air background PM2.5 from the measured stack PM2.5, it can be seen that the corrected stack PM2.5 is very near zero, and practically indistinguishable from the AMS PM2.5 (Figure 3-4).

Similar data analysis was extended to the Site Bravo and Site Golf results (shown also in Figures 3-2 to 3-4). The AMS was not yet in operation during the Site Bravo tests (conducted in 2001), so stack and ambient PM2.5 measurement results are compared to the average AMS PM2.5 for several similar periods in 2003. Considering this along with the wide scatter in the Site Bravo results and very small data set (3 runs), the corrected stack PM2.5 for this site is highly uncertain. At Site Golf, there is a significant (at the 95 percent confidence level) difference and no correlation between estimated dilution air background PM2.5 and stack PM2.5. The average corrected stack PM2.5 for Site Golf⁴ (0.11 mg/dscm) is approximately ten times higher than the value for Site Echo (0.01 mg/dscm).

Because the variation in the estimated dilution air background PM2.5 is more systematic than random, it is probably greater than the true measurement "noise." Nevertheless, if this variation is used as a conservative estimate of measurement noise, it implies that the in-stack MDL is approximately 0.05 mg/dscm and the in-stack LQL is approximately 0.2 mg/dscm. Since the Site Golf results lay between the MDL and the LQL, this indicates that stack PM2.5 is detectable, but not quantifiable below the LQL, with high confidence.

Thus, we can say it is likely that stack PM2.5 from Site Echo is below 0.05 mg/dscm, the estimated in-stack MDL for this test. Site Golf stack PM2.5 is significantly above both the measurement background and ambient PM2.5, and it is likely that the concentration is between 0.05 and 0.2 mg/dscm but quantification is uncertain. For comparison, PM2.5 measured at Site Bravo with traditional methods averages 2.0 mg/dscm. Dilution sampling indicates that actual stack PM2.5 is much lower than indicated by traditional method measurements. Also, for Site Echo, it is likely that stack PM2.5 is near or below ambient PM2.5 concentrations.

¹ As noted earlier in Section 3, trace solids and elements in the water used for interstage spray cooling and combustor NOx control at Site Golf are potentially a significant source of the observed stack PM2.5.



*No AMS data available for Bravo; 2003 data from 3-week period centered around the Site Bravo test periods shown for information only.

Figure 3-2. Stack PM2.5 and Ambient PM2.5 (Sites Bravo, Echo and Golf).



Figure 3-3. Stack PM2.5 and Estimated Dilution Air Background (Sites Bravo, Echo and Golf).



Figure 3-4. Corrected Stack PM2.5 and Ambient PM2.5 (Sites Bravo, Echo and Golf).

4. DISCUSSION AND FINDINGS

DID THIS RESEARCH ANSWER WHY THERE IS VARIATION IN THE HISTORICAL PM EMISSION DATA FOR GAS TURBINES?

This research identified potential sources of variability in measured PM emissions from power generation and cogeneration systems employing gas turbines. The reason for comparing results from units with different designs and operating conditions is to determine if any insights into the broad range of PM concentrations exhibited among the wide variety of units in the existing database can be gained. The intent with these limited tests is not to quantify the effect of each single parameter on PM emissions to a high degree of accuracy, but to determine whether gross differences in PM emissions are discernable among the different tests, and whether any such differences might be attributable to process operation and/or design. Regardless of several measurement issues during this program, the results (from dilution sampling) show that PM differences due to duct burners, size, load, gas fuel composition, and various other differences (design, location, weather, etc.) among the tests are very small in comparison to the wide PM range exhibited in the existing database. The results show that traditional method measurement variation is much larger than these differences and probably explains much of the variation in the existing database. Due to the limited number of tests performed, variable sources of emissions tested and variable operating conditions, definitive conclusions with respect to the effects of process design and operating variables could not be drawn. Further, many of the stack PM2.5 results could not be clearly distinguished from measurement background; in these cases, the true stack PM2.5 is difficult to quantify by any of the methods used in this study. Analysis of the data suggests that stack PM2.5 is not significantly greater than ambient PM2.5 in most cases. These factors make it difficult to draw strong conclusions with regard to the impact of operating and/or design parameters on stack PM2.5. However, the test results provided insights into the approximate orders of magnitude and relative significance of potential source of variability with respect to the observed range of PM emissions measured for these and other similar systems:

• <u>Emission measurement methods and their application</u> –Measurement variability inherent in traditional EPA test methods was identified as the largest component of variation in measured PM concentrations for gas-fired sources based on these tests. Traditional EPA hot filter/iced impinger methods were not validated for measuring the extremely low concentrations of PM present in gas-fired gas turbines. This research explored only the component of variability among tests performed by the same test crew and using the same techniques at each site. Even with this limitation, it is likely that this component of measurement variability accounts for much of the apparent range observed in the historical data. Test results using dilution sampling show both lower PM levels and smaller measurement variation on an absolute scale compared to traditional EPA methods, although the relative variation ranges from moderate to large.

- Plant design and operating conditions. The test results comparing stack PM concentration among the three sites and at different operating conditions at the same site generally revealed no effects of process operating conditions that were clearly distinguishable above the measurement variability background. Based on dilution sampling results, there is some evidence that the effect of load on stack PM2.5 concentration is probably small (10 percent or less). There is some evidence that stack PM2.5 concentrations are higher with duct burners operating than when they are off, but the observed differences are not significant at the 95 percent confidence level given the variation in the results. Another difference among the sites is fuel, with Sites Bravo and Echo firing natural gas and Site Golf firing refinery fuel gas. The sulfur content of the natural gas at Site Echo and the refinery fuel gas at Site Golf, which is expected to be the most significant fuel factor affecting stack PM2.5, was similar. Also, dissolved solids and trace elements in water used for spray intercooling and NOx control may be a significant contributing factor to stack PM2.5. Again, these findings are very preliminary and qualitative due to data limitations mentioned previously.
- <u>External factors</u> Comparing stack (corrected for dilution air background) and ambient PM2.5 at all three sites did not show a correlation between stack and ambient PM2.5. The stack and ambient air PM2.5 levels appear to be the same at Site Echo, and stack PM2.5 appears to be somewhat higher than ambient PM2.5 (significant at the 95 percent confidence level) at Site Golf. Although the range of ambient air PM2.5 concentrations (0.007 to 0.020 mg/dscm) among the different sites and the population of data are small, this suggests that any contribution of external factors to variation in PM concentration measurements is smaller than the measurement variability of either dilution or traditional test methods.

WHAT DOES THE DATA TELL US MIGHT BE A BIG FACTOR IN DETERMINING PM EMISSIONS?

The answer to this depends on the measurement technique:

• Based on the in-stack hot filter (with in-stack PM10/2.5 cyclones and filter) methods used in these and selected historical tests, filterable PM is generally below the MDL and always below the LQL of the method. Test results showed that filter weights frequently were below the MDL and always below the LQL of the normal gravimetric procedure. Moreover, net filter weights from both stack samples and field blanks were negative (less than zero) in every case. Since negative filter weights are conventionally reported as zero net weight (which is should not be overlooked when evaluating MDLs, LQLs and measurement variability), all of the reported FPM in these and selected historical tests was derived from acetone rinses of the sampling components upstream of the filter. An evaluation of acetone rinse and blank data from this and historical tests showed that the acetone blanks frequently comprised a large fraction (greater than 20 percent) of the raw sample result, and that the absolute blank values from different tests showed a wide range. Although EPA Methods limit the blank correction to 20 percent of the raw sample result (to provide a conservatively high, not an accurate, estimate of actual PM emissions), historical results were found to deviate from this limitation. All the net acetone rinse results are below the LQL and most below the MDL. Thus, the biggest factors determining filterable PM emissions as defined by these methods is believed to be the background levels in the acetone reagent (determined from the acetone recovery blanks) and the specific methods, techniques, procedures and reporting protocols used when applying the test methods to low PM concentrations.

- Based on the iced impinger methods used in these tests (EPA Method 202 and Method 8 with post-test nitrogen purge and optional procedures to minimize H₂SO₄ loss during analysis), the majority of the condensable PM mass is inorganic (sulfate/sulfuric acid) with lesser amounts of other substances. Other tests indicated that most of the sulfate/sulfuric acid in the condensable PM majority of the PM mass is likely "pseudo-particulate matter" caused by a measurement artifact (aqueous phase oxidation of dissolved gaseous SO₂ to sulfite/sulfate in the impingers during sampling and sample storage prior to analysis). Thus, the biggest factors determining measured condensable PM emissions from gas-fired sources are believed to be sulfur content of the fuel and the specific methods, procedures, techniques and reporting protocols used for determining condensable PM emission using iced impinger methods. Because these measurement artifacts dominate the results, the biggest factors governing true condensable emissions cannot be determined from results using this method.
- Based on dilution sampling methods, which yields far lower PM2.5 concentrations than • the methods discussed above, organic carbon and sulfate account for nearly all of the measured PM2.5 mass. However, the extremely low levels of organic carbon measured in the stack samples could not be distinguished from that in the ambient air, blanks, or dilution air. This indicates it is likely that there is a large positive bias in the organic carbon measurement accounting for most or potentially all of the measured results. Organic carbon measurements and the representativeness of blanks for this measurement are the subjects of considerable controversy. Based on these results, it is likely that the contribution of organic carbon to PM mass is much lower than the measurements indicate. Without organic carbon, however, a large fraction (typically more than 50 percent) of the PM mass would remain chemically unresolved so the amount of bias is indeterminate. Although unlikely, if organic carbon were the major constituent of emitted PM2.5, it is likely the biggest factor would be trace levels of organic compounds emitted from the combustion process. Although trace amounts of ammonia (due to ammonia slip through the SCR catalysts) were measured in exhaust gases, very little of the PM2.5 mass measured by this method was accounted for by particulate ammonium.

There is fairly high confidence in the particulate sulfate results, however, and the biggest factor determining particulate sulfate concentration for these types of systems is probably sulfur content of the fuel.

DID THE RESEARCH FILL IN ANY CRITICAL DATA GAPS?

The test program provided new data regarding the relative influence of normal measurement variability and load, duct burners and plant design, at least to an order of magnitude. However, much more data is needed before effects can be definitively established. Further tests would be needed to quantify more precisely the effect of design and operating variables on emission rates among a broader range of equipment types. Given the relatively small effects seen in these tests it is recommended that the initial focus be on further development and validation of dilution methods for PM measurements before undertaking further tests to characterize process effects on PM2.5 emissions.

HOW CAN THE RESEARCH HELP REGULATORS, EQUIPMENT MAKERS AND TESTING COMPANIES IDENTIFY HOW TO MEASURE PM EMISSIONS CORRECTLY?

Traditional Hot Filter/Iced Impinger Methods

It is likely that traditional hot filter/iced impinger methods will continue to be used in the foreseeable future for measuring PM emissions from gas-fired systems. During the course of this research project, several techniques were applied in attempts to minimize measurement problems. While the results did not conclusively demonstrate the value of every technique, a few new insights were gained into the limitations of traditional methods when measuring low concentrations from gas combustion. These techniques are summarized below:

Size-Selective Probe Inlet: It is widely held that all PM produced by gas-fired systems is smaller than 10 µm. Anecdotal evidence from an informal survey of testers indicates that random variation in PM concentration can occur due to spurious large particles in the samples. The most likely source of such particles is contamination from scraping the sample nozzle on the sides of the sample port during probe insertion and withdrawal. Spurious large particles in the stack gas also may originate from deterioration of materials in the unit and/or contamination (e.g., wooden pallets, rags, other foreign substances that may be left in the system following a maintenance outage). Adding a cyclone or impactor to the sample probe inlet should eliminate variability introduced due to spurious large particles.

- Contamination: Since the slightest contamination is significant relative to typical exhaust concentrations, techniques to minimize contamination during sample equipment preparation and sample handling should be followed rigorously. This includes the use of powderless laboratory gloves when handling samples and sample containers, use of recently manufactured high-grade reagents, proper cleaning procedures and appropriate facilities with a high degree environmental dust control.
- Long Run Times: 6-hour test runs were used in this program, but the results show it is still not sufficient to produce FPM results that are above the in-stack LQL. When using the same type of sampling equipment for FPM, longer test runs may reduce in-stack detection limits and the significance of background levels in the sample media. Longer runs would not be beneficial for CPM measurements using iced impingers. Laboratory results showed that bias in CPM results might increase with longer test runs due to increased aqueous-phase conversion of SO₂ to solid residues (Wien et al., 2001). The tradeoff between potentially better FPM measurements and worse CPM measurements with longer run times, in addition to the increased cost of longer tests, makes the net advantages of longer run times unclear.
- Post-test impinger purge: The impingers should be purged for one hour immediately following sample collection to reduce uncontrolled bias and variation due to aqueous phase SO₂ oxidation;
- Gravimetric analysis: Standard EPA methodology specified weighing samples to the nearest 0.1 mg and to perform repeat weighings until two consecutive weights agree within 0.5 mg. These specifications are not adequate for gas-fired sources, since the propagated errors can equate to as much as 30 percent of the measured emission rate. A five-place analytical balance (0.01 mg resolution) should be used to improve precision of weighing filters and acetone rinses. A minimum of three to five weighings within a tolerance of 0.1 mg are recommended for determining analytical uncertainty and to establishing a new tolerance level for repeat weights.
- Filter Handling: Techniques to eliminate random loss of filter material during handling should be implemented. For example, EPA Method 5I incorporates an integral sample filter/holder assembly that does not require disassembly prior to weighing. In this test program, a conventional filter holder was used but filters were weighed together with backup supports and gaskets to minimize loss of filter fragments. Techniques such as this should be evaluated to assess whether negative net filter weights can be eliminated. Other filter types to reduce fragmentation during handling also should be explored.
- Acetone blanks: The acetone rinse procedure used to recover deposits from surfaces upstream of the filter (nozzle, probe, filter housing) should be modified or replaced for low concentration measurements. Variability and background levels masked true sample levels in these parts of the sampler. It is not clear if the limitation is background levels in the reagents or some problem in the evaporation and drying of the samples. At a minimum, very high purity reagent should be used. Improvements to the acetone rinse

procedure are needed, or an alternative procedure developed, to improve quantification of recovered deposits at extremely low concentrations.

• Impinger analysis and reporting: Variability of CPM measurements appears to be a major source of variability in the historical emission database. This research showed that sulfate-related substances dominate CPM measurements. Previous studies indicated that artifact conversion of gaseous SO₂ to solid residues during sample collection and storage can dominate results at low concentrations. Since conditions affecting this artifact are rarely controlled, it remains a source of considerable random uncertainty in the measurements. If the sulfate related substances include sulfuric acid (H₂SO₄), random variation can be introduced when drying the samples since H₂SO₄ is relative volatile and can be lost during analysis unless measures are taken to stabilize it. There are a number of significant variations of the iced impinger method employed by state and local agencies, with different analytical and reporting protocols that can lead to differences in the final results. For example, the South Coast Air Quality Management District in southern California requires an analysis of the impinger solutions for sulfate and total acid, with the difference (presumably free H₂SO₄) subtracted from the final gravimetric results. Texas Commission on Environmental Quality does not allow the post-test nitrogen purge recommended above. In this research program, impingers were purged and analysis included stabilization of H₂SO₄ before final drying and analysis, plus direct analysis of the sample residue for a range of substances was performed to identify its origin. These steps are recommended for tests using EPA Method 202. Also, iced impinger method procedures among different states and regions should be harmonized to eliminate variation caused by differences. The results showed that sulfate related compounds dominate; therefore, it is likely that any controlled or uncontrolled variations in parameters affecting sulfate-related substances are potential important and should be considered when comparing data from historical tests.

Based on all the above considerations, it appears that stack PM2.5 from the units tested in this program is below the capability of traditional measurement hot filter/iced impinger methods used in these tests.

Dilution Methods

One of the goals of this research program is to advance the application of dilution sampling to stationary sources. A new compact dilution sampler was developed and preliminary validation tests against a benchmark dilution sampler system achieved comparable PM2.5 concentration results. As experience was gained and improvements to procedures made over the course of the program the precision of the measurements improved significantly (from nearly 300 percent relative standard deviation in early tests to 23 percent in the last test). The capability to measure

extremely low PM2.5 concentrations in the stack, much lower than the capability of traditional hot filter/iced impinger methods and comparable to PM2.5 concentrations in the ambient air, was demonstrated. As the capabilities of the dilution sampling system were evaluated, a number of improvements and areas for further development and validation were identified for application of dilution sampling to gas-fired systems:

- Dilution air cleanup: based on results of field blanks, trip blanks and dilution system blanks, background levels of PM2.5 in the dilution air were discovered at occasionally significant levels compared to the extremely low levels in the exhaust. This indicates the need for further development of the dilution air filtration system to reduce PM2.5 concentration for these applications, and for collection of dilution system blanks in future tests.
- Recovery of deposits in the sampler: Deposits in the sampler components that contact the undiluted sample were identified as a minor potential source of variability for this application. Deposits were recovered with acetone following EPA Method 5 procedures. The acetone rinse procedure lacks sufficient sensitivity for the very low levels of emissions in these tests, as noted above for traditional test methods. An improved acetone rinse procedure, or an alternative procedure, is needed for application to such low levels.
- Tightening of filter cassettes: Filter cassettes were pre-loaded in the laboratory prior to the field campaign. During two of the test campaigns, Sites Bravo and Charlie (Wien et al., 2004b), field procedures included "snugging" the filter cassettes to ensure they were leak tight. This is believed to be the cause of damage to the filter media, introducing atypical and significant variation in the sample gravimetric results. After this problem was identified, the field procedure was modified to avoid over tightening of the filter cassettes.
- Dilution air flow measurement: In the original benchmark dilution sampler system, dilution air was determined indirectly by measurements of other flows. Uncertainties in the other flow measurements indicated that a direct measurement is preferred, and this was implemented in the compact dilution sampler.
- Further refinement and testing of the dilution sampling equipment and procedures is needed to minimize procedural errors and improve knowledge of method precision and accuracy for PM2.5 concentration.

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APPENDIX A LIST OF ABBREVIATIONS

°C	degrees Celsius
°F	degrees Fahrenheit
μg	micrograms
μm	micrometers
AMS	ambient monitoring station
API	American Petroleum Institute
Btu	British thermal units
CEC	California Energy Commission
CEMS	continuous emissions monitoring system
CO	carbon monoxide
Cogen-SF	supplementary firing
CPM	condensible particulate matter
DOE	United States Department of Energy
DSB	dilution sampler blank
dscm	dry standard cubic meters
EPA	Environmental Protection Agency
FPM	filterable particulate matter
GE	General Electric
GE EER	General Electric Energy and Environmental Research Corporation
gr/100 scf	grains per hundred standard cubic feet
GRI	Gas Research Institute
GT	gas turbine
H ₂ SO ₄	sulfuric acid
HEPA	high efficiency particulate arrest
HRSG	heat recovery steam generator
HSO ₃ -	bisulfite ion
lb	pounds per hour
LOL	lower quantification limits
MDL	method detection limit
mg	milligram
min	minute
MM8	modified Method 8
mm	millimeter
MMBtu	million British thermal units
MW	megawatts
NAAOS	National Ambient Air Quality Standards
NETL	National Energy Technology Laboratory
NGCC-SF	natural gas-fired combined cycle power plant
NH ₃	ammonia
NO _x	oxides of nitrogen
NYSERDA	New York State Energy Research and Development Authority
O ₂	molecular oxygen
PF	penetration factor
PM	particulate matter
PM	particulate matter

PM10 PM2.5	particulate with aerodynamic diameter less than 10 micrometers particulate with aerodynamic diameter less than 2.5 micrometers
ppmv	parts per million (volume)
ppmw	parts per million (weight)
scf	standard cubic feet
SCR	selective catalytic reduction
SO ₂	sulfur dioxide
TMF	Teflon [®] -membrane filter

APPENDIX B SI CONVERSION FACTORS

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