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TOPICAL REPORT: TEST RESULTS FOR A GAS-FIRED PROCESS HEATER WITH SELECTIVE CATALYTIC REDUCTION (SITE CHARLIE)

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FOREWORD

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from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and/or incomplete.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

The goals of this program were to:

- Develop 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

- 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.

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

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EXECUTIVE SUMMARY

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

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- 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.

This report presents emissions data from testing performed on a natural gas-fired process heater equipped with selective catalytic reduction (SCR) for NO_x control. The flue gas temperature at the stack was approximately 340°F during the tests.

The PM measurements at the stack were made using both dilution sampling technology and traditional methods used for regulatory enforcement of particulate regulations. Four six-hour runs were performed on separate, consecutive days. Dilution sampling is attractive because the sample collection media and analysis methods are identical to those used for ambient air sampling, thus the results are directly comparable with ambient air data. Also, dilution sampling is believed to provide representative results for solid, liquid and condensable aerosols together on a single analytical sample. Traditional hot filter/impinger methods are attractive because they are readily accepted by regulatory agencies and have been used extensively on a wide variety of source types; however, sampling/analytical options are limited and existing regulatory methods for condensable aerosols may be subject to significant bias. The results of this test will be used with the results of a subsequent laboratory evaluation of dilution sampling technology and additional field testing of other combustion units to advance understanding of the observed differences between results obtained with dilution sampling and other measurement methods.

Emission factors for primary particulate matter including: total particulate matter, PM10 (particles smaller than nominally 10 micrometers), and PM2.5; elements; ionic species; and organic and elemental carbon; were extremely low, which is expected for natural gas-fired sources (Table ES-1). Emission factors are expressed in pounds of pollutant per million British thermal units of gas fired (lb/MMBtu). As a measure of the bias, measurement precision, process variability and other sources of uncertainty inherent in the results, the uncertainty (at the 95 percent confidence level) and upper 95 percent confidence bound were calculated. Table ES-1 includes only those elements that were detected in at least two of the four test runs at concentrations greater than blank concentrations. Species with emission factors with an uncertainty greater than 100 percent should be considered potentially unrepresentative.

Table ES-1. Primary Emissions (PM2.5 Mass, Elements, Ions, and Carbon) Results (Site Charlie).

		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	No. of Detected Sample Runs
Particulate Mass	PM2.5 mass (Dilution Sampler)	< 1.6E-4	210	3.9E-4	3
Elements (Dilution Sampler)	Si	9.8E-6	210	2.5E-5	4
	Fe	6.8E-6	200	1.7E-5	4
	Ca	4.3E-6	220	1.1E-5	4
	K	1.5E-6	210	3.8E-6	4
	Cl	< 9.5E-7	250	2.5E-6	3
	Mg	< 6.9E-7	270	2.0E-6	3
	Zn	6.1E-7	170	1.4E-6	4
	Ti	4.7E-7	190	1.1E-6	4
	Cu	2.3E-7	180	5.5E-7	4
	Mn	1.6E-7	190	3.8E-7	4
	Pb	< 9.5E-8	150	1.9E-7	3
	Al	< 5.1E-6	860	2.7E-5	2
	Co	< 5.6E-8	640	3.7E-7	2
	Sr	< 7.4E-8	700	3.3E-7	2
	Zr	< 6.6E-8	360	1.8E-7	2
Ions (Dilution Sampler)	NO3-	< 6.2E-6	130	1.2E-5	3
	Soluble Na	7.4E-7	130	1.5E-6	4
	NH4+	< 3.2E-6	420	9.9E-6	2
	SO4=	6.9E-6	97	1.2E-5	4
	Cl-	< 2.3E-6	n/a	n/a	1
Carbon (Dilution Sampler)	Organic Carbon*	1.9E-4	93	3.2E-4	4
	Elemental Carbon	< 3.6E-5	95	5.9E-5	3
	Total Carbon**	2.2E-4	96	3.7E-4	-
Particulate Mass (Manual Methods)	Organic CPM (Method 202) ***	2.8E-4	n/a	n/a	1
	Inorganic CPM (Method 202) ***	9.2E-4	48	1.3E-3	4
	Total CPM (Method 202) ***	1.0E-3	50	1.4E-3	4
	Total Filterable PM (Method PRE-4/202 train) ***	2.3E-4	82	3.8E-4	4
	Filterable PM10 (Method PRE-4/202 train) ***	1.0E-4	110	1.9E-4	4
	Filterable PM2.5 (Method PRE-4/202 train) ***	5.5E-5	170	1.2E-4	4

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

* OC measurements are subject to a potential positive bias from adsorption of VOC species. Refer to Section 7 for further discussion of OC artifact.

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

*** Emission factors not recommended for emission estimation purposes.

Emission factors for semivolatile organic species were very low (Table ES-2). The sum of quantified semivolatile organic species is approximately 12 percent of the organic carbon. Table ES-2 includes only those substances that had uncertainties less than or equal to 100% and were detected in at least two of the four test runs at concentrations greater than blank concentrations.

Table ES-2. Primary Emissions – SVOCs (Site Charlie).

Substance		Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	No. of Detected Sample Runs
3-Methylbiphenyl		1.6E-6	85	2.6E-6	4
4-Methylbiphenyl		6.9E-7	88	1.2E-6	4
Acenaphthenequinone		3.9E-7	61	5.8E-7	4
C-dimethylphenanthrene	<	1.0E-7	48	1.4E-7	3
Pyrene		6.5E-8	86	1.1E-7	4
B-MePy/MeFl	<	2.8E-8	97	4.9E-8	3
Benzo(e)pyrene		2.2E-8	89	3.9E-8	4
D-MePy/MeFl	<	1.7E-8	80	3.0E-8	3
A-methylphenanthrene	<	1.0E-7	81	1.5E-7	2

Potential secondary particle precursors include sulfur dioxide, ammonia, nitrogen oxides, and volatile organic compounds with carbon number greater than seven. Measurements of volatile organic compounds with carbon number greater than seven were below detection limits or considered unrepresentative due to high uncertainty. Emission factors for ammonia, sulfur dioxide and nitrogen oxides are presented in Table ES-3. With regard to the two different ammonia measurements shown in Table ES-3, the dilution tunnel method is believed to be the most representative because it has better resolution than the SCAQMD method at the low concentration (less than 1 part per million) measured in the stack gas. The preceding tables typically include only those substances that were detected in at least two of the four test runs. Substances of interest not present above the minimum detection limit for these tests are listed in Table ES-4.

Table ES-3. Dilution System Fine PM Precursors Results (Site Charlie).

Substance		Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	No. of Detected Sample Runs
Gases	NH_3 (DS)	5.1E-4	99	8.8E-4	4
	NH_3 (SCAQMD 207.1)	1.2E-4	65	1.8E-4	4
	SO_2 (DS)	4.0E-4	78	6.4E-4	4
	NOx as NO_2 (CEMS)	1.4E-2	18	1.7E-1	4

DS - dilution sampler

CEMS - continous emissions monitoring system.

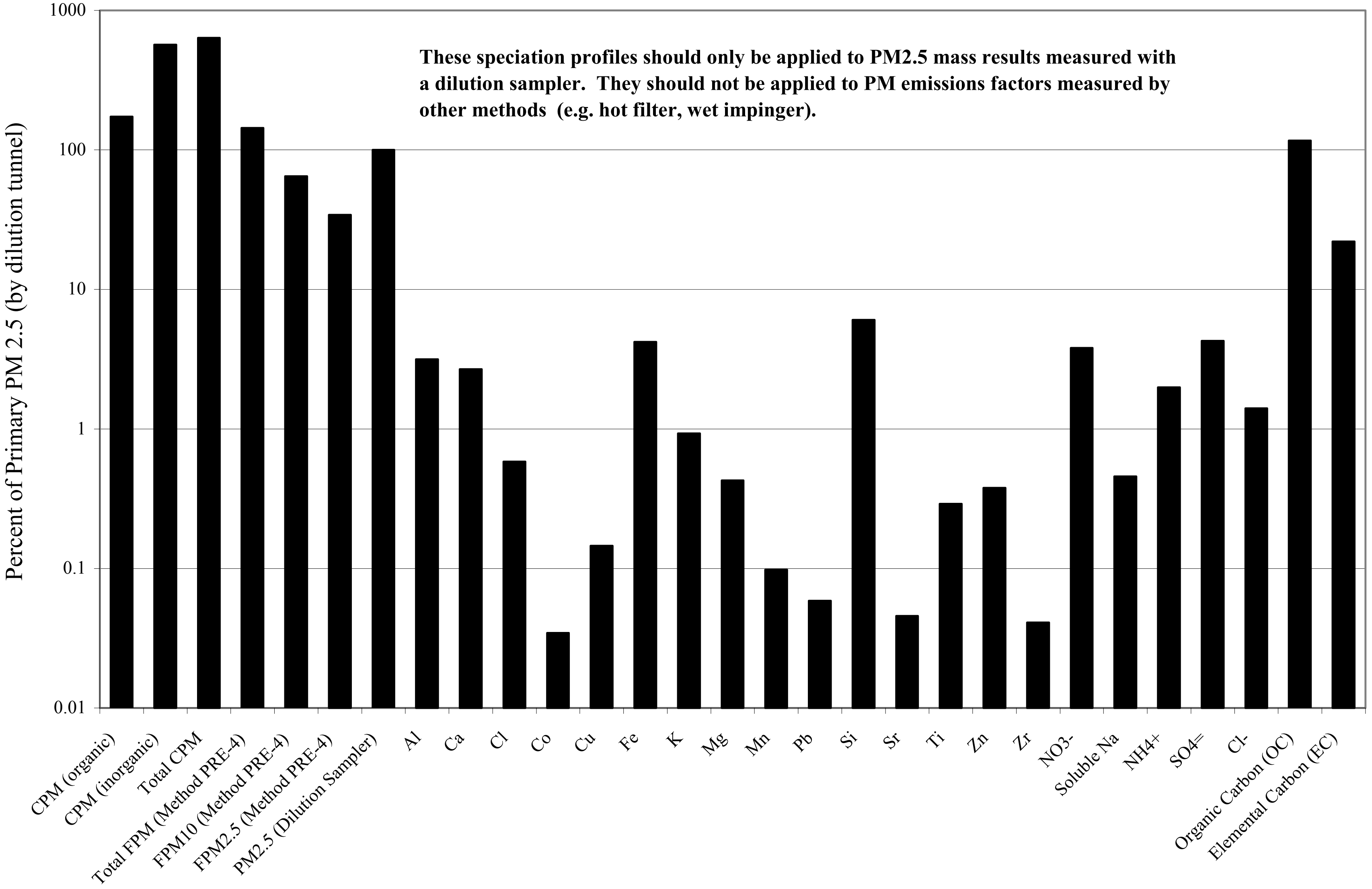
Table ES-4. Substances of Interest Not Detected in Stack Emissions from Site Charlie.

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-dionene
	A-dimethylindane	chryq14
	D-dimethylindan	Indeno[123-cd]pyrene
	2-decanone	Dibenzo(ah+ac)anthracene
	Decanal	Coronene
	Dodecene	

The primary particulate emission factor results presented in Table ES-1 also may be expressed as a PM2.5 speciation profile (Figure ES-1), which is the mass fraction of each species contributing to the total PM2.5 mass as measured by the dilution sampler. The emission factor of each species is divided by the PM2.5 emission factor from the dilution sampler PM filter. Manual method results are also presented for comparison.

The main findings of these tests are:

- Particulate mass emissions from the heater were extremely low, consistent with levels expected for gaseous fuel combustion. Ammonia injection does not appear to impact PM2.5 emissions.
- Two methods for determining the average emission factor for primary PM2.5 mass gave results that differed by an order of magnitude: 0.00016 lb/MMBtu using the dilution sampler; and 0.0011 lb/MMBtu using conventional hot filter and iced impinger methods for filterable and condensable particulate. This difference is attributed to three likely causes:
    - Solid particle emissions are extremely low, below the capability of traditional hot filter methods to measure with high confidence. Over 90 percent of the total PM2.5 emission measured by the hot filter/iced impinger method was found in the impinger fraction (condensable particulate matter);
    - Traditional impinger methods are subject to significant positive bias, especially for gas-fired sources. Sampling and analytical artifacts principally caused by gaseous SO_2 in the stack gas sample are known to produce a relatively large positive bias in condensable particulate as measured by impinger methods. The large amount of $SO_4^=$ in the impinger residue compared to much smaller amounts of $SO_4^=$ in the dilution sampler found in these tests indicates this artifact was probably a significant factor.
    - Aerosol thermo-physics dictates that condensation of vapor phase substances in the impingers of traditional methods will be greater than condensation in the dilution sampler. Vapor phase substances in the stack gas will not condense until cooled, and if this cooling occurs without dilution, as in the impingers of the Method 202 train, more material will condense than in a real-world plume, where dilution occurs at the same time as the stack gases are cooled. Thus, the results obtained with impinger methods are positively biased, and dilution sampling results are considered more representative of true emissions.



These speciation profiles should only be applied to PM2.5 mass results measured with a dilution sampler. They should not be applied to PM emissions factors measured by other methods (e.g. hot filter, wet impinger).

Figure ES-1. Speciation Profile for Primary Particulate Emissions from a Heater.

- 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.

- OC and EC comprise approximately 85 percent of the total PM2.5 chemical species measured by the dilution sampler; however, the quartz filter used for ion and carbon speciation is subject to organic absorptive bias, especially in low load sources, such as gas-fired heaters, so a likely source of this difference is the high organic carbon value. A backup quartz filter sampled behind the TMF indicated that about three-quarters of the organic carbon might be due to adsorption bias.

- Most elements and organic compounds are not present at levels significantly above the background levels in the ambient air and blanks or above the minimum detection limits of the test methods. These extremely low levels are consistent with gaseous fuel combustion, and combined with the variability in the emission rates, result in large uncertainties for many of the reported emissions. The 95% confidence upper bounds for the emission factors provide conservative estimates of the PM emission factors that are much lower and more reliable than those determined by Method 202 and its gas absorption bias.

Section 1
PROJECT DESCRIPTION

PROJECT OVERVIEW

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (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 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. Primary aerosol includes both filterable particles that are solid or liquid aerosols at stack temperature plus those that form as the stack gases cool through mixing and dilution processes in the plume downwind of the source. These deficiencies in the current methods can have significant impacts on regulatory decision-making. PM2.5 measurement issues were extensively reviewed by the American Petroleum Institute (API) (England et al., 1997), which concluded that dilution sampling techniques are more appropriate for obtaining a representative sample from combustion systems. These techniques have been widely used in research studies (e.g., Hildemann et al., 1994; McDonald et al., 1998), using clean ambient air to dilute the stack gas sample and providing 80-90 seconds residence time for aerosol formation prior to sample collection and analysis. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source-receptor and source apportionment analysis for PM2.5 NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

Dilution sampling was used to collect PM data from a natural gas-fired process heater (Site Charlie) equipped with selective catalytic reduction (SCR) for nitrogen oxides (NO_x) reduction on December 6-12, 2001, along with emissions data obtained from conventional sampling methods. The U.S. Department of Energy (DOE), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and API jointly funded the tests. This test program is designed to provide reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM2.5 concentrations.

The goals of this program were to:

- Develop 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
- 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.

It should be noted that the project team chose to complete the process heater test in advance of a pilot scale study of the dilution sampler test method to address a compelling need for detailed data on fine and ultrafine particulate emissions. The pilot-scale study is evaluating dilution ratio and residence time design criteria established by Hildemann et al. (1989) as part of the development of a more compact and field portable sampler that gives comparable results. A dilution sampler based on the original Hildemann design was used for this test.

PROJECT OBJECTIVES

Primary Objectives

- Compare PM2.5 mass measured using an in-stack filter and iced impinger train (EPA Method PRE-4/202) and mass measured using a dilution sampler;
- Develop emission factors and speciation profiles for organic aerosols and PM2.5 mass;

- 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_2); oxides of nitrogen ($NO_{x)}$; and ammonia (NH_3);
- Characterize hazardous air pollutants, such as benzene and aldehydes;
- 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 NH_3 slip from the SCR; and
- Speciate the inorganic condensable PM residue collected using EPA Method 202.

TEST OVERVIEW

The scope of testing is summarized in Table 1-1. The emissions testing included simultaneous collection and analysis of both undiluted and diluted stack gas samples. All emission samples were collected from the exhaust stack downstream of all combustion processes and emission controls. The samples were analyzed for the compounds listed in Table 1-2. Process data were collected during the tests to document operating conditions.

Source Level (Undiluted Exhaust Gas) Samples

In-stack sampling and analysis for hot-filtered PM (total PM, PM with aerodynamic diameter less than 10 micrometers (PM10) and PM2.5) and CPM was performed using traditional EPA methods. In-stack cyclones and filters were used for filterable particulate matter. CPM was measured by collection in iced impinger trains. Molecular oxygen (O_2) and carbon dioxide

Table 1-1. Overview of Sampling Scope.

	Number of Samples	
Sampling Location	Stack	Ambient Air
EPA Method PRE-4/202 train	4	--
SCAQMD Method 207.1	4	--
Dilution sampler Teflon® filter (mass, elements) Quartz filter (ions, OC/EC) K_2CO_3-impregnated cellulose fiber filter (SO_2) Citric acid-impregnated cellulose fiber filter (NH_3) 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_2, CO_2	Every two hours	--
NO_x, O_2	Continuous (Plant)	--
Process operating data monitoring	Continuous	--

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

(CO_2) were monitored periodically during the runs using a portable electrochemical analyzer. Continuous plant data were collected for O_2 and NO_X. South Coast Air Quality Management District (SCAQMD) Method 207.1 was used to measure NH_3 slip. This method absorbs ammonia in iced impingers followed by wet chemistry to determine the amount of free NH_3 emitted in the stack gas.

Diluted Exhaust Gas Samples

Dilution sampling was used to characterize PM2.5 including aerosols formed in the near-field plume. The dilution sampler extracted a sample stream from the stack into a mixing chamber, where it was diluted approximately 36:1 with ambient air purified by passing through a high

Table 1-2. Summary of Analytical Targets.

Parameters	In-Stack				Dilution Sampler								
	Cyclones	Quartz filter	Imp.	Gases	Quartz filter	TIGF/ PUF/ XAD	TMF	Tenax	SS cans	DNPH cartrid-ges	K_2CO_3 filter	Citric acid filter	Gases
Total PM mass	X	X											
PM10 mass	X	X											
PM2.5 mass	X	X					X						
CPM 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			
NH_3 (gaseous)			X									X	
NO_x				X									
SO_2											X		
O_2				X									
CO_2				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

efficiency particulate air (HEPA) filter and activated carbon. Because PM2.5 behaves aerodynamically approximately like a gas at typical stack conditions, the samples were extracted nonisokinetically. A slipstream of the mixed and diluted sample was conveyed to a residence time chamber where it resided for approximately 70 seconds to allow time for low-concentration aerosols, especially organics, to condense and grow. The diluted and aged sample then passed through cyclone separators sized to remove particles larger than 2.5 microns, after which samples were collected on various media: high-purity quartz filters for ions and carbon speciation, Teflon® membrane filters (TMF) for PM2.5 mass and elements, potassium carbonate-impregnated cellulose fiber filters for SO_2, citric acid-impregnated cellulose fiber filters for NH_3 and Teflon®-impregnated glass fiber (TIGF) filters for particle phase semivolatile organic compounds (SVOCs); a polyurethane foam (PUF)/Amberlite® sorbent resin (XAD-4)/PUF cartridge to collect gas phase SVOCs; Tenax tubes to capture VOCs with a carbon number greater than seven; a stainless steel canister to capture VOCs with a carbon number greater than two; and dinitrophenylhydrazine (DNPH)-coated silica gel cartridges to capture carbonyls (aldehydes). Four samples were collected over six hours on four separate test days.

An ambient air sample was collected to establish background concentrations of measured substances. The same sampling and analysis procedures used for the dilution sampler were applied for collecting ambient air samples.

KEY PERSONNEL

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

- Glenn England (GE EER) – Program Manager (949) 859-8851 ext. 136
- Stephanie Wien (GE EER) – Project Engineer (949) 859-8851 ext. 155
- Bob Zimperman and Neal Conroy (GE MostardiPlatt (GE MP)) – Field Team Leaders (949) 552-1803
- Judith Chow, John Watson, and Barbara Zielinska (Desert Research Institute (DRI)) – Consulting and Laboratory Analysis (775) 674-7050

- Karl Loos (Shell Global Solutions U.S.) – API Work Group Chairman (281) 544-7268
- Karin Ritter (API) – API Project Officer (202) 682-8472
- Jim McCarthy and Paul Drayton (GRI) – GRI Project Manager (847) 768-0694)
- Guido Franco and Marla Mueller (CEC) – CEC Project Manager (916) 654-4894)
- Dan Gurney and Kathy Stirling (DOE) – DOE Contracting Officer Representative (918) 699-2008)
- Barry Liebowitz (NYSERDA) – NYSERDA Project Manager (518) 862-1090 ext. 3248

Section 2

PROCESS DESCRIPTION

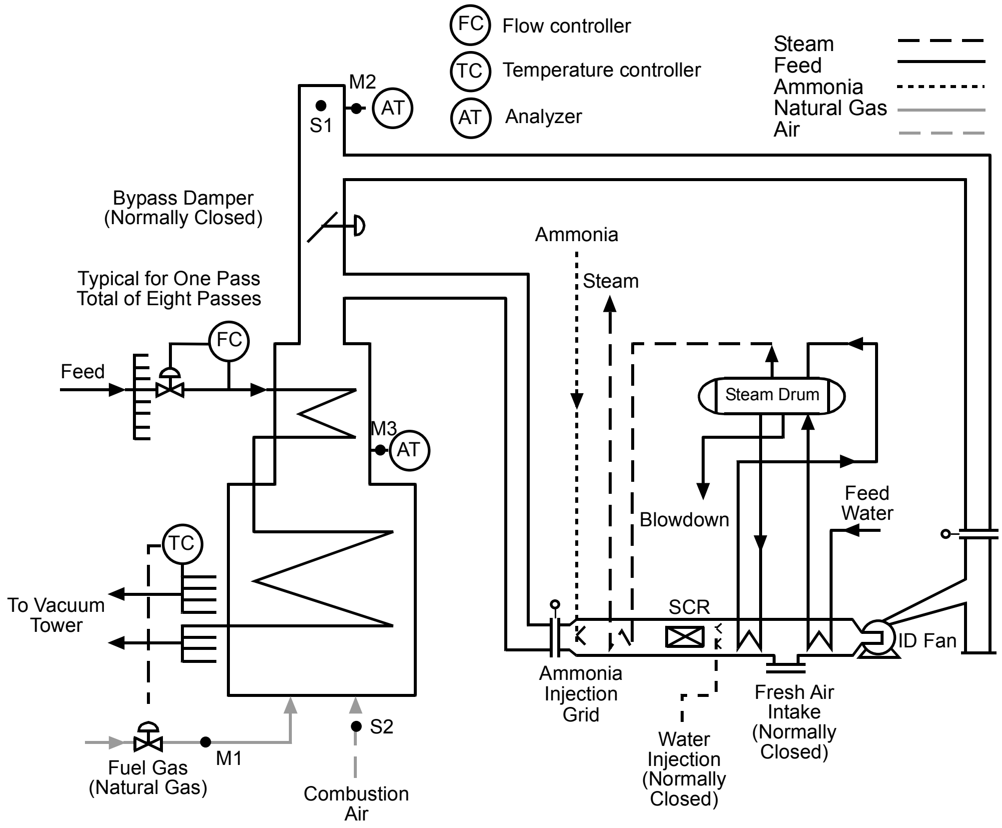
Tests were performed on a refinery process heater that is a feed preheater for the refinery vacuum unit. The unit is a natural gas-fired, bottom-fired double box heater with 32 burners per box. Typical natural gas composition data provided by the supplier shows an average sulfur content of 0.08 gr S/100scf with a range of 0.03 to 0.25 gr S/100scf. Hot exhaust gases from the two boxes vent to the atmosphere via a common stack (Figure 2-1). The stack is equipped with a duct that directs flue gas to the SCR system. An induced draft fan drives the flue gas flow through the SCR reactor and back to the stack. The heater's firing capacity is 300 million British thermal units per hour (MMBtu/hr). The facility is equipped with continuous emissions monitors (CEMS) for O_2 and NO_x.

POLLUTION CONTROL EQUIPMENT DESCRIPTION

The unit has post-combustion air pollution control equipment in the form of an SCR system. Ammonia is introduced through a grid of injectors to uniformly distribute the ammonia in the flue gas upstream of a catalyst bed. The SCR reactor includes a steam heat recovery loop that both maintains the flue gas temperature entering the SCR catalyst bed within the SCR reaction temperature window and protects the induced draft fan while extracting useful heat from the heater flue gases. The final stack gas temperature is approximately 340 degrees Fahrenheit (ºF). The rate of ammonia injection is controlled based on NO_x readings in the stack and the temperature of the SCR. The operating permit includes an emission limit for ammonia slip of 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



Location	Description	Parameters
S1	Stack	
S2	Ambient Air	See Table 3-1
M1	Fuel Gas Feed	Fuel flow rate, fuel specific gravity, fuel heat content
M2	Stack	NOx, O_2
M3	Preheater	O_2

Figure 2-1. Gas-Fired Heater Process Overview.

approximately 130 feet above the ground. The sampling locations exceeded the minimum EPA Method 1 requirements for upstream and downstream disturbances.

A preliminary velocity check was performed to determine the point of average flow. Sampling was performed at the traverse point closest to the point of average flow through each port used. Absence of cyclonic flow was established from previous test results at this unit.

A single ambient air sample was collected at ground level, near the air inlet for the heater.

Section 3

TEST PROCEDURES

An overview of the sampling and analysis procedures is given in Table 3-1. Figure 3-1 shows the testing chronology for the dilution sampling and in-stack methods. The time of day for the start and finish of each measurement run is shown on the figure. For example, Method PRE-4/202 Run 1 began at 10:15 hours and finished at 16:15 hours on Thursday, December 6. Dilution sampling and in-stack testing were performed concurrently. All samples were collected at points of average flow through their respective ports to allow for comparability of results, assuming that the fine particles will follow the gas streamlines and hence were as well-mixed as the gases. A sample run time of six hours was chosen so that sufficient material would be collected to exceed detection limits.

STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

An S-type Pitot tube (EPA Method 2) was used to determine the average stack gas velocity and volumetric flow rate. Stack gas molecular weight was calculated in accordance with EPA Method 3. Moisture content of the sample was determined based on weight gain 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_2, CO_2, AND NO_x

O_2 and NO_x concentrations in the stack were monitored using the plant's CEMS. These CEMS are operated and regularly audited consistent with the operating permit and local regulations. In addition, O_2 and CO_2 readings were taken periodically during the runs with a portable electrochemical analyzer (NOVA Analytical Systems Model 375WP) that was calibrated with EPA Protocol gases before the test program.

IN-STACK METHOD TESTS

Total PM, PM10 and PM2.5 filterable at stack temperature were determined using in-stack, hot filtration methods. CPM, defined as the material collected in chilled impingers, also was

Table 3-1. Summary of Test Procedures.

Sampling Location	Measurements	Sampling Approach	Sample Analyses	Reference
Stack	Total PM, PM10, PM2.5 and composition	In-stack series cyclones and filter	Mass; organic species	EPA Method PRE-4 (preliminary method)
	Condensable PM and composition	Impingers	Mass (organic and inorganic), ions, elements	EPA Method 202
	Ammonia	Acid impingers	Ammonia	SCAQMD 207.1
	PM2.5 mass and chemical composition	Dilution sampler and filters	Mass, organic carbon (OC), elemental carbon (EC), elements, sulfate, nitrate, chloride, ammonium	EPA, 1999a; Hildemann et al., 1989
	Gases	Electrochemical cell	O_2, CO_2	EPA CTM-030
	Gaseous PM2.5 precursors	Dilution sampler and potassium carbonate-impregnated cellulose-fiber filter	Sulfur dioxide	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution sampler and citric acid-impregnated cellulose-fiber filter	Ammonia	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution sampler and Tenax	Speciated VOC (C7 and greater	Zielinska et al., 1996; Hildemann et al., 1989
	VOC	Dilution sampler and stainless steel canisters	Speciated VOC (C2 - C10)	EPA Method TO-15
	Hazardous air pollutants	Dilution sampler and DNPH-coated silica gel cartridges	Carbonyls	EPA Method TO-11A
	SVOC	Dilution sampler and filter/PUF/XAD-4/PUF	Speciated SVOC	EPA Method TO-13; Hildemann et al., 1989
Process Heater air inlet – ambient air	PM2.5 and chemical composition	Filters	Mass, OC, EC, elements, chloride, sulfate, nitrate, ammonium	EPA, 1999a
	Gaseous PM2.5 precursors	Potassium carbonate-impregnated cellulose-fiber filter	Sulfur dioxide	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Citric acid-impregnated cellulose-fiber filter	Ammonia	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Tenax	Speciated VOC (C7 and greater	Zielinska et al., 1996; Hildemann et al., 1989
	VOC	Stainless steel canisters	Speciated VOC (C2 –C10)	EPA Method TO-15
	Hazardous air pollutants	DNPH-coated silica gel cartridges	Carbonyls	EPA Method TO-11A
	SVOC	TIGF/PUF/XAD-4/PUF	Speciated SVOC	EPA Method TO-13; Hildemann et al., 1989

	Time	Process Heater Stack				Combustion Air Inlet
		Velocity	Method PRE-4/202	SCAQMD 207.1	Dilution Sampler	Ambient Sample
05-Dec-01 Wed.	7:00					
	8:00					
	9:00				Sampler Blank	
	10:00				10:30	
	11:00				▨	
	12:00				▨	
	13:00				▨	
	14:00				▨	
	15:00				▨	
	16:00				16:30	
	17:00					
06-Dec-01 Thurs.	7:00					
	8:00					
	9:00	9:19	Run 1	Run 1	Run 1	
	10:00		10:15	10:15	10:15	
	11:00		▨	▨	▨	
	12:00		▨	▨	▨	
	13:00		▨	▨	▨	
	14:00		▨	▨	▨	
	15:00		▨	▨	▨	
	16:00		16:15	16:15	16:15	
	17:00	17:10				
07-Dec-01 Fri.	7:00	7:52				
	8:00		Run 2	Run 2	Run 2	
	9:00		9:00	9:00	9:00	
	10:00		▨	▨	▨	
	11:00		▨	▨	▨	
	12:00		▨	▨	▨	
	13:00		▨	▨	▨	
	14:00		15:00	15:00	15:00	
	15:00	15:48				
	16:00					
	17:00					

Figure 3-1. Chronology for Natural Gas-Fired Process Heater Tests (Site Charlie).

	Time	Process Heater Stack				Combustion Air Inlet
		Velocity	Method PRE-4/202	SCAQMD 207.1	Dilution Sampler	Ambient Sample
10-Dec-01	7:00					
Mon.	8:00	8:02	Run 3	Run 3	Run 3	
	9:00		9:30	9:30	9:30	
	10:00					
	11:00					
	12:00					
	13:00					
	14:00					
	15:00	16:00	15:30	15:30	15:30	
	16:00					
	17:00					
11-Dec-01	7:00					
Tues.	8:00	8:15	Run 4	Run 4	Run 4	
	9:00		9:00	9:00	9:00	
	10:00					
	11:00					
	12:00					
	13:00					
	14:00		15:00	15:00	15:00	
	15:00					
	16:00	16:22				
	17:00					
12-Dec-01	7:00					
Wed.	8:00					
	9:00					
	10:00					10:00
	11:00					
	12:00					
	13:00					
	14:00					
	15:00					16:00
	16:00					
	17:00					

Figure 3-1. Chronology for Natural Gas-Fired Process Heater Tests (Site Charlie) (Continued).

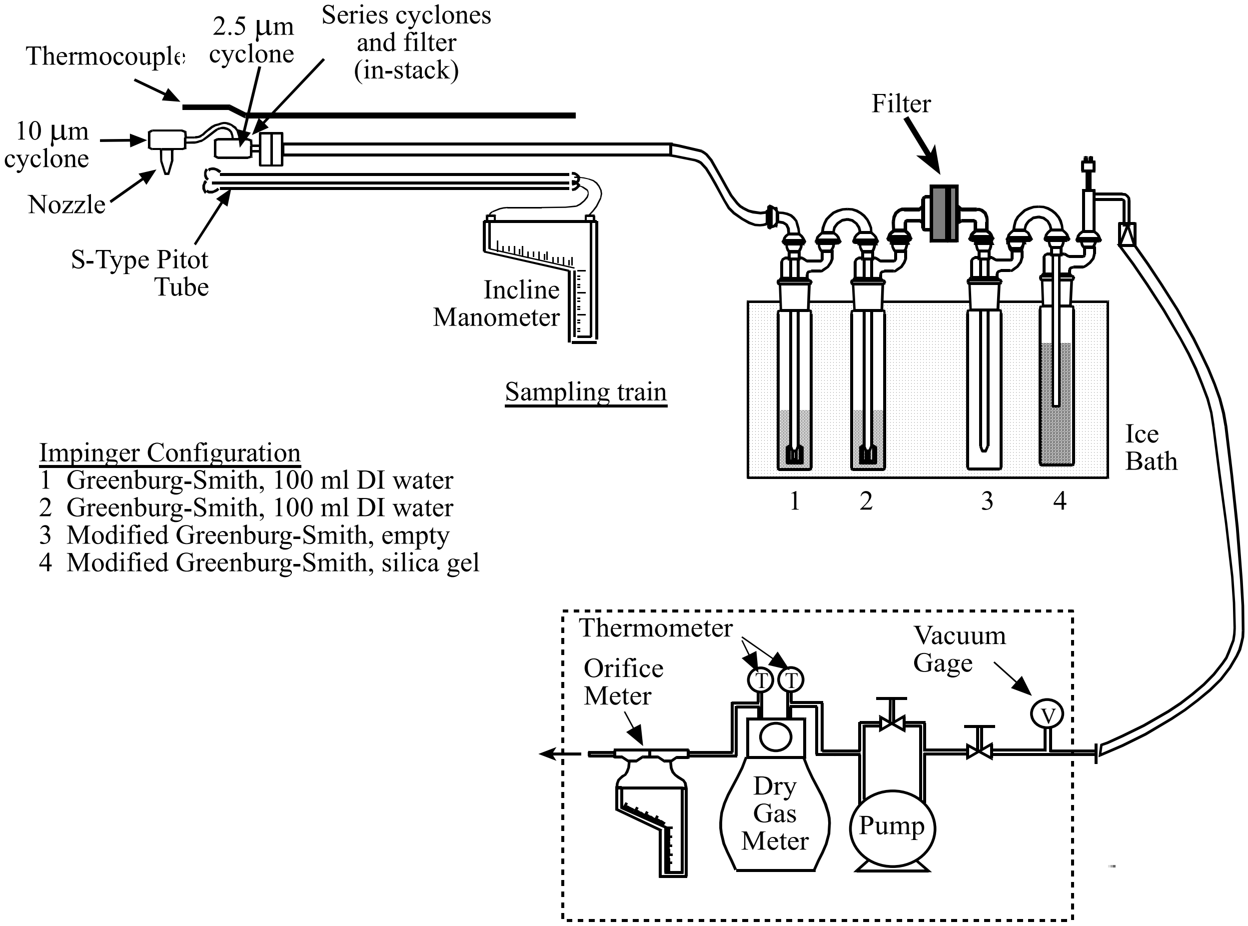
measured for the in-stack samples. Ammonia was measured using a wet impingement sampling method described below.

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

EPA Preliminary Method PRE-4 was used to measure total filterable 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 a hot, in-stack filter in series (Figure 3-2). The sampling time was six hours at a sampling rate of approximately 0.4 cubic feet per minute (cfm) for each of the four runs. Sampling was performed according to the method as published except for the following modifications and clarifications:

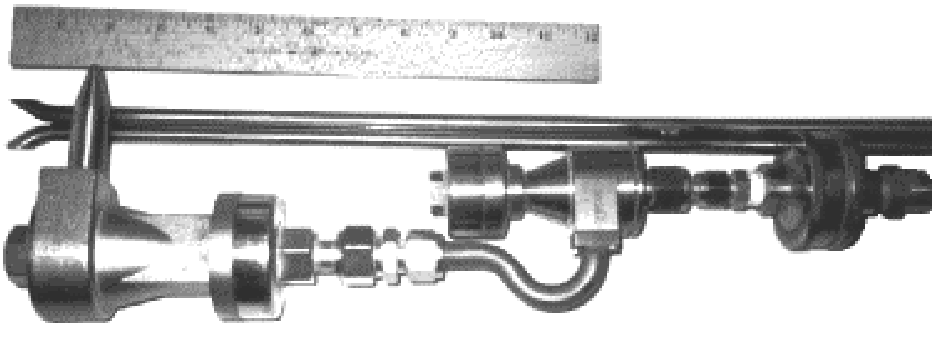
- The sample was collected from a single traverse point near a point of average velocity to preserve the integrity of the dilution sampler method comparison. It is assumed that any particulate present is small enough to mix aerodynamically in the same manner as a gas; therefore, the particle concentration and gas concentration profiles were assumed to be similar;
- 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.

The particulate mass collected in the two cyclones and on the filter was determined gravimetrically. The quartz filters (Pallflex Tissuequartz 2500QAT-UP-47 millimeter (mm)) 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 desiccator for a minimum of 72 hours. Filter weighing was repeated at a minimum of six-hour intervals until constant weight (within 0.5 milligrams (mg)) was achieved. Probe and cyclone acetone rinses were recovered in glass sample jars for storage and shipment, and then transferred to tared beakers for evaporation and weighing. Acetone and filter blanks also were collected and analyzed. See Section 4 for discussion of data treatment.



Sampling train

Impinger Configuration
1 Greenburg-Smith, 100 ml DI water
2 Greenburg-Smith, 100 ml DI water
3 Modified Greenburg-Smith, empty
4 Modified Greenburg-Smith, silica gel



Series cyclone and filter assembly

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

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

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 3-3 illustrates the Method 202 analytical procedure and additional analyses performed.

Ammonia

Concentrations of NH_3 were measured using South Coast Air Quality Management District (SCAQMD) Method 207.1. Flue gas was isokinetically withdrawn from the source through a stainless steel probe and free and combined NH_3 were collected in a Greenburg-Smith impinger train (Figure 3-4). The sampling train consists of four impingers connected in series. The first and second impingers contain 0.1 N sulfuric acid (H_2SO_4), the third impinger is empty, and the fourth impinger contains a weighed amount of silica gel. NH_3 in the sampled gas is collected in the impingers and in rinses of the sample probe and

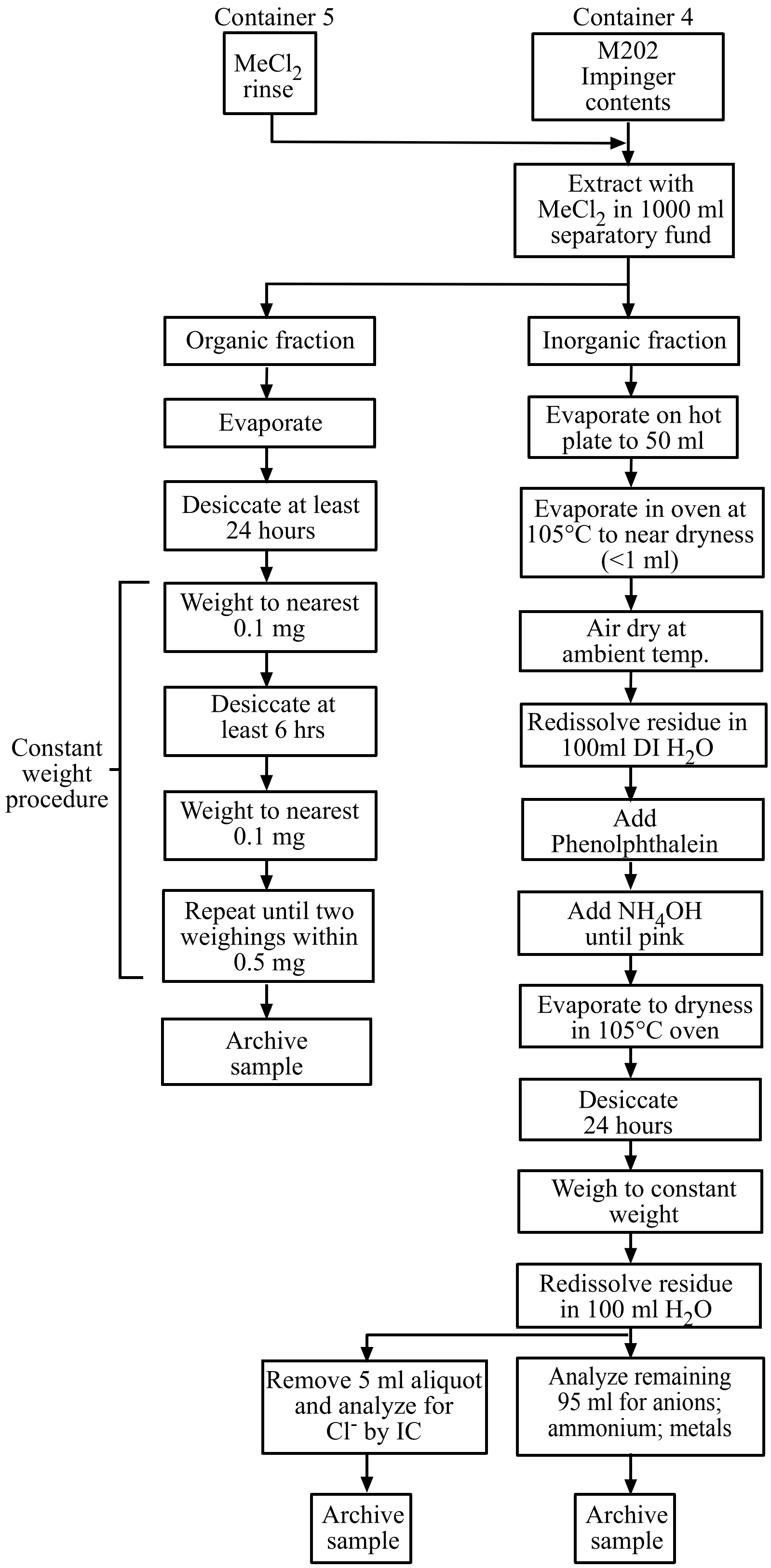


Figure 3-3. Modified Method 202 Sample Analysis Procedure.

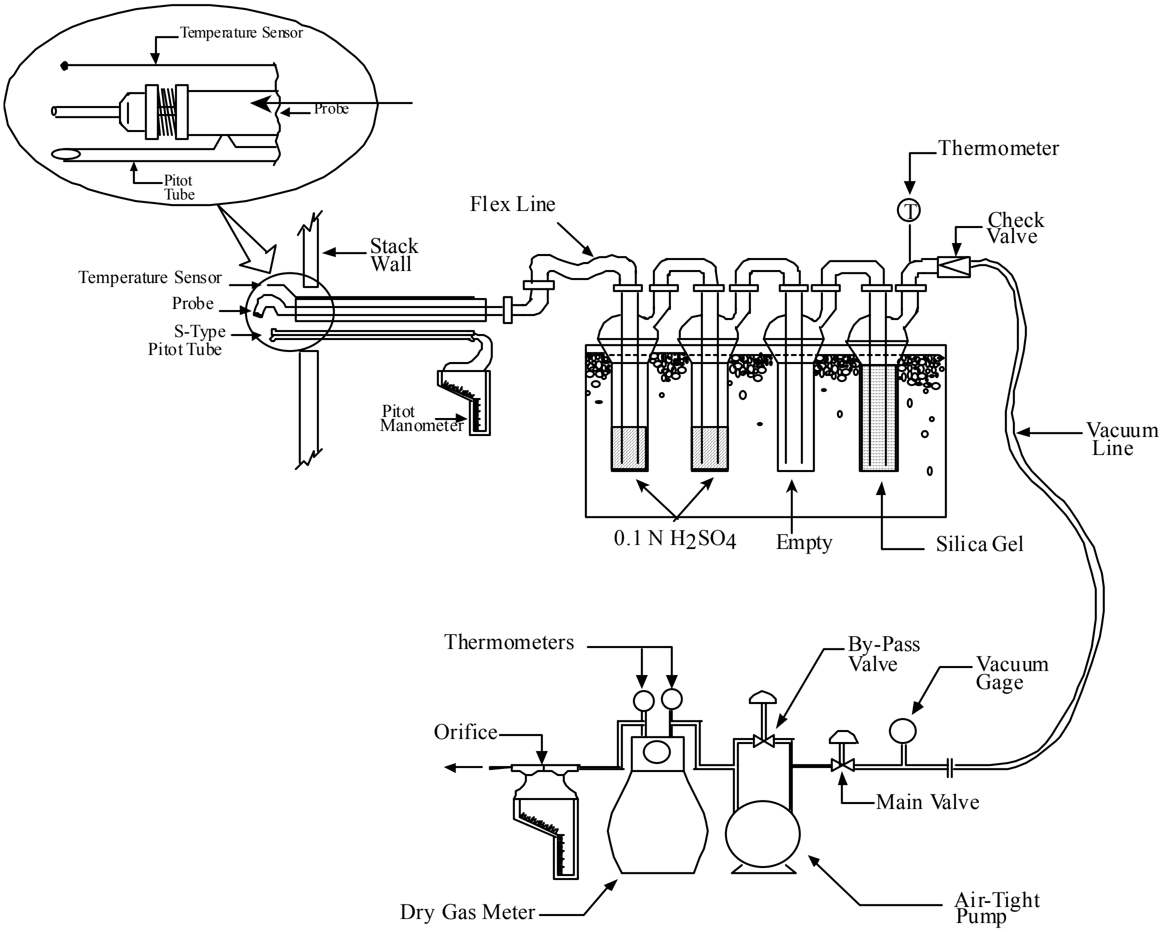


Figure 3-4. Ammonia Sample Train Configuration for SCAQMD Method 207.1.

connecting glassware. The combined sample is analyzed for NH_3 by Nessler colorimetry. A field blank was also submitted for analysis. Sampling occurred for six hours at a constant rate of 0.5 cfm. After the test, the train was purged for five minutes with ambient air. The recovery of the sampling train was performed on-site to reduce the probability of sample loss during shipment. During this recovery, all the impinger catches and glassware rinses were collected into a single bottle.

DILUTION SAMPLER TESTS

PM2.5 mass and chemical speciation in the stack gas was determined using a dilution sampler (Figure 3-5). A stainless steel probe with a buttonhook nozzle was used to withdraw the stack

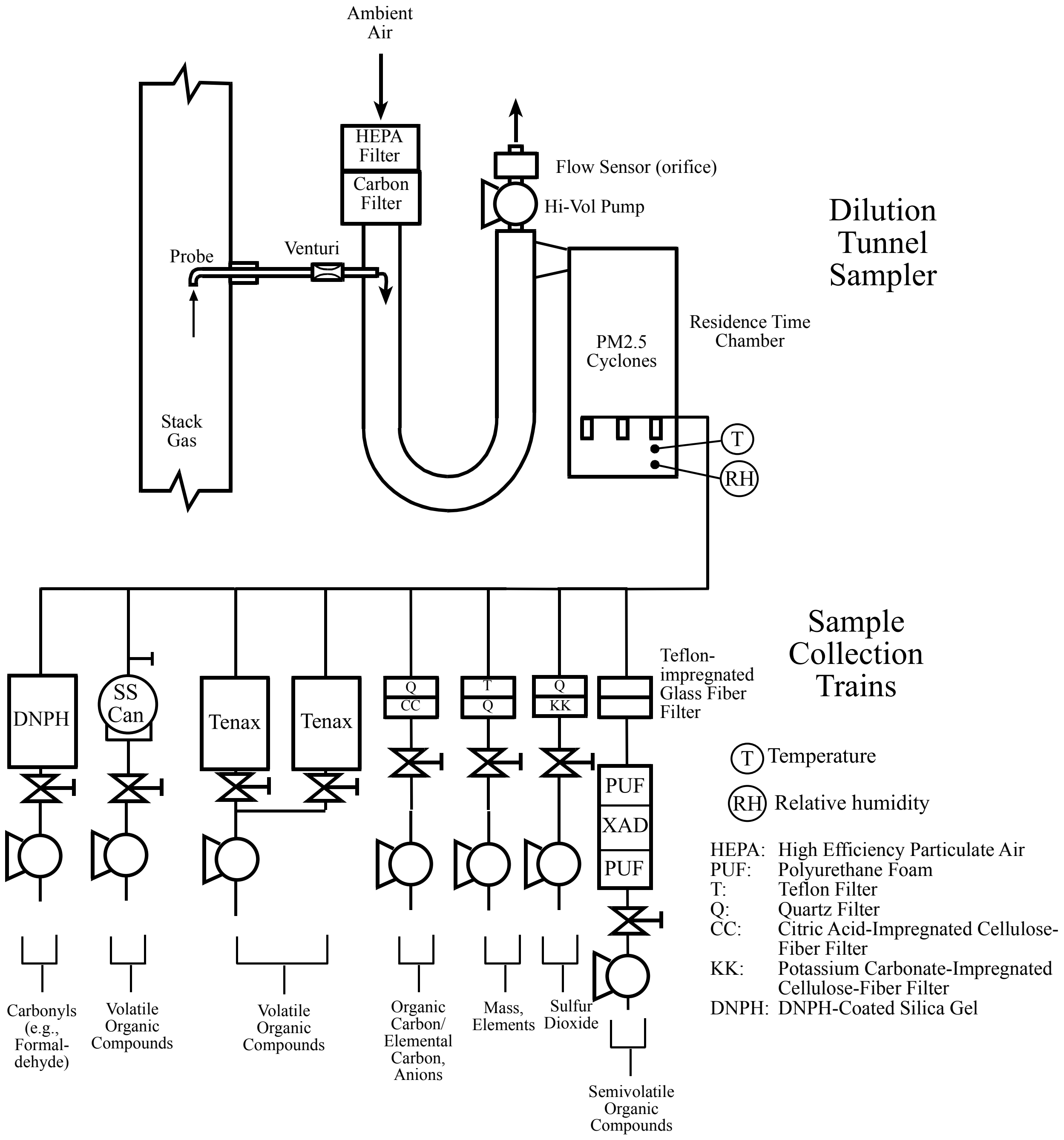


Figure 3-5. Dilution Sampling System.

gas sample at a rate of approximately 25 liters per minute (Lpm). The sample was transported through a heated copper line into the dilution sampler. The sample was mixed in the sampler with purified ambient air under turbulent flow conditions to cool and dilute the sample to near-ambient conditions. The ambient air used for dilution was purified using a HEPA filter to remove particulate matter and an activated carbon bed to remove gaseous organic compounds. After passing through a sampler length equal to 10 sampler diameters, approximately 50 percent of the diluted sample was withdrawn into a large chamber, where the sample aged for approximately 70 seconds to allow low-concentration aerosols (especially organic aerosols) to fully form. The aged sample was withdrawn through a sampling manifold of three cyclone separators to remove particles larger than 2.5 microns (μm) into a sampling module to provide a uniform gas stream for the sample collection media (TMF, quartz filter, potassium carbonate (K_2CO_3)-impregnated cellulose fiber filter, citric acid-impregnated cellulose fiber filter, Tenax tubes, DNPH-coated silica gel cartridges, stainless steel canisters and TIGF/PUF/XAD-4/PUF cartridge). The sample flow rate through the probe was monitored using a venturi flow meter and thermocouple. The venturi velocity head was measured continuously during the test using a pressure transducer and a Magnehelic® gauge. An S-type Pitot tube with electronic pressure transducer and thermocouple were used to monitor the velocity in the stack. The thermocouples and pressure transducers were connected to a laptop computer data acquisition system. The dilution airflow and backpressure were adjusted to maintain the target dilution ratio and sample flow rates. Total sampling time for each test run was six hours.

For these tests, flow rates were set in the field to achieve a target dilution ratio of approximately 36:1 (air:undiluted sample). 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 20:1 in this design. This program is evaluating and optimizing design parameters, including dilution ratio, in a separate pilot scale evaluation of the dilution sampling method, with results to be presented in a separate report.

A single ambient air sample was collected using the dilution sampler. The sampling setup was modified by attaching a three-cyclone manifold (similar to the one inside the residence time chamber) directly to the sampling module without the use of the dilution sampler. The ambient air sample was drawn into the module without dilution or filtration for a sampling period of six hours. The same sampling media were used as described below and in Figure 3-6. Ambient air was sampled at a location at ground level, near the combustion air intake for the heater. Dilution sampler operating conditions during the test are listed in Table 3-2.

Table 3-2. Dilution Sampler Operating Conditions.

Parameter	Units	Char-Run 1 06-Dec-01	Char-Run 2 07-Dec-01	Char-Run 3 10-Dec-01	Char-Run 4 11-Dec-01	Char-Amb 12-Dec-01	Char-TB 05-Dec-01
Ambient Air Temp.	oC	26.0	29.9	16.1	18.8	18.4	16.4
Ambient RH	%	21.1	15.1	44.4	26.2	44.6	56.0
Dilution Chamber Temp.	oC	33.7	35.8	26.0	25.3	50.0	23.8
Dilution Chamber RH	%	21.0	16.9	36.1	30.6	NA	35.4
Stack Sample Flow Rate	dry slpm	16.8	14.9	16.7	16.7	NA	NA
Dilution Ratio	--	36.4	39.6	33.2	33.0	NA	NA
Teflon Filter Flow Rate (mass, elements)	dry slpm	73.5	72.8	72.3	72.8	73.5	71.2
Quartz Filter Flow Rate (ions, OC/EC)	dry slpm	76.9	64.4	65.1	74.1	73.3	68.3
Citric Acid Filter Flow Rate (NH_3)	dry slpm	76.9	64.4	65.1	74.1	73.3	68.3
K_2CO_3 Filter Flow Rate (SO_2)	dry slpm	72.9	69.8	70.6	74.4	74.0	70.8

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 at a target rate of 75 standard liters per minute (sLpm) with a needle valve and monitored during sampling using a Thermo Scientific Incorporated (TSI) Model 4043 mass flow meter. Weighing was performed on a Cahn 31 electro-microbalance with a 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 x-ray fluorescence (XRF) analyses were conducted on each sample to optimize the detection limits for the specified elements. The filters were removed from their petri slides and placed with their deposit sides downward into polycarbonate filter cassettes. A polycarbonate retainer ring kept the filter flat against the bottom of the cassette. The cassettes were loaded into a carousel in the x-ray chamber. The sample chamber was evacuated to 10^{-3} Torr. A computer program controlled the positioning of the samples and the excitation conditions. Complete analysis of 16 samples using five excitation conditions required approximately 6 hours.

Sulfate, Nitrate, Chloride and Ammonium

Samples for determining water-soluble chloride (Cl^-), nitrate (NO_3^-), and sulfate ($SO_4^=$) were collected on quartz fiber filters. The flow rate through the filter was set prior to sample collection at a target rate of 75 sLpm with a needle valve and monitored during sampling using a TSI Model 4043 mass flow meter.

For analysis, 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. Cl^-, NO_3^-, and $SO_4^=$ were measured with a Dionex 2020i ion chromatograph (IC). Approximately 2 milliliters (mL) of the filter extract was injected into the IC.

A Technicon TRAACS 800 Automated Colorimetric System (AC) was used to measure ammonium (NH_4^+) concentrations by the indolphenol method. Sample vials containing 2 mL aliquots were placed in the computer-controlled autosampler. Each sample was mixed with reagents and subjected to appropriate reaction periods before analysis according to Beer's Law. Absorbency was measured using a NH_4^+-complex specific filter and a photomultiplier tube. Technicon software operating on a microcomputer controlled the sample throughput, calculated concentrations, and recorded data.

Organic and Elemental Carbon

Quartz fiber filters (Pallflex Tissuequartz 2500QAT-UP- 47 mm) 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 degrees Celsius (°C) prior to use. Pre-acceptance testing was performed on each lot of filters. Filters with levels exceeding 1.5 micrograms per square centimeter ($\mu g/cm^2$) of OC and 0.5 $\mu g/cm^2$ 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 using the IMPROVE protocol 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 sets of Tenax tubes (a front tube followed by a backup to check for breakthrough) were sampled in parallel for each test run due to the low concentrations expected in the sample. Each tube contained approximately 0.2 grams of Tenax resin. A sample rate of approximately 0.1 Lpm through each Tenax tube was used. The flow rate through the Tenax cartridges was controlled and monitored with a mass flow controller during sampling.

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

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

For analysis, a known volume of gaseous sample is passed through a cryogenically cooled trap, cooled with liquid argon, cryogenically trapping out C_2 and heavier VOCs without trapping methane. The trap containing the condensed VOC is warmed with hot water and its contents injected into a gas chromatograph (GC) capillary column where separation of the VOC takes place. Detection of the hydrocarbons and oxygenated hydrocarbons is by FID while detection of the halogenated compounds is by electron capture detection (ECD), and the resultant peaks are quantified and recorded by an electronic integrator and by the chromatographic data system

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 mass flow meter 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 the sample gas were collected by drawing sample through a cartridge containing DNPH-impregnated silica gel, 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 the sample. Typically C_1-C_6 carbonyl compounds, including benzaldehyde, are measured effectively by this technique. The target flow rate used for this sample was 0.4 Lpm.

Sulfur dioxide

Filter packs containing a quartz filter followed by a potassium carbonate-impregnated cellulose fiber filters were used to collect SO_2 gas downstream of the dilution sampler. The target flow rate used for this sample was 75 Lpm. 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 NH_3gas downstream of the dilution sampler. The target flow rate used for this sample was 75 Lpm. These filters were extracted with DI water and then analyzed using automated colorimetry.

Section 4

TEST RESULTS

All stack emission results are presented in units of milligrams per dry standard cubic meter (mg/dscm) and pounds per hour (lb/hr). Concentrations are corrected to a standard temperature of 68°F and a standard pressure of 29.92 inches of mercury unless otherwise indicated. See the conversion factors presented in Appendix B of this report to convert to Système Internationale (SI) units. Substances that were undetected in all four test runs generally are not listed on the tables. Where shown, undetected data are flagged "ND", treated as zeroes in sums, and excluded from average calculations. Data with one or more, but not all, constituents less than the detection limit are flagged with a "<" symbol. The approximate minimum in-stack detection limits achieved for all measured substances are given in Table 4-1. These detection limits are calculated from the analytical detection limits, an average sample volume and an average dilution ratio.

PROCESS OPERATING CONDITIONS

The process heater operating conditions during testing are summarized in Table 4-2. The heater operated at close to its normal firing rate ranging from 95 to 100 percent of full capacity (300 MMBtu/hr) over the four runs. The average heat input to the heater during the tests was calculated from the plant process data for fuel flow rate, in thousand standard cubic feet per hour (Mscfh) and fuel heating value in British thermal units per dry standard cubic foot (Btu/dscf). The average heat input was used to convert in-stack emission rates (lb/hr) to emission factors (lb/MMBtu), which are presented in Section 5.

PRELIMINARY TEST RESULTS

Preliminary tests were conducted to establish a single point in the stack for sample collection. Traversing the stack with the Pitot probe before and after each test run produced a velocity profile that was used to calculate the overall average stack velocity and flow rate.

Table 4-1. Approximate In-Stack Detection Limits Achieved for Gas Fired Heater Tests (Site Charlie).

Substance	Dilution Tunnel mg/dscm	In-stack methods mg/dscm	Substance	Dilution Tunnel mg/dscm	Substance	Dilution Tunnel mg/dscm	Substance	Dilution Tunnel mg/dscm
Total PM mass	--	2.5E-03	U	4.1E-5	Acenaphthylene	2.0E-4	1-methylpyrene	1.5E-5
PM10 mass	--	2.5E-03	V	4.5E-5	Acenaphthene	5.0E-5	Benzo(c)phenanthrene	2.1E-5
PM2.5 mass	1.4E-03	2.5E-03	Y	2.3E-5	Fluorene	2.3E-4	Benz(a)anthracene	1.2E-5
Ag	2.2E-4	--	Zn	2.0E-5	Phenanthrene	1.5E-5	7-methylbenz(a)anthracene	1.2E-5
Al	1.8E-4	--	Zr	3.1E-5	A-methylfluorene	2.0E-4	Chrysene	3.9E-6
As	2.9E-5	--	SO4=	2.2E-3	1-methylfluorene	1.3E-4	Benzanthrone	1.7E-5
Au	5.6E-5	--	NO3-	2.2E-3	B-methylfluorene	1.3E-4	Benz(a)anthracene-7,12-dionene	7.2E-5
Ba	9.3E-4	--	NH4+	2.2E-3	9-fluorenone	2.6E-4	5+6-methylchrysene	0.0E+0
Br	1.8E-5	--	Cl-	2.2E-3	Xanthone	7.7E-6	chryq14	0.0E+0
Ca	8.1E-5	--	Soluble Na	2.2E-4	Acenaphthenequinone	1.2E-5	Benzo(b+j+k)fluoranthene	1.9E-6
Cd	2.2E-4	--	Soluble K	4.3E-4	Perinaphthenone	1.9E-3	7-methylbenzo(a)pyrene	1.4E-5
Cl	1.8E-4	--	NH3	5.8E-4	A-methylphenanthrene	9.3E-5	Benzo(e)pyrene	1.2E-5
Co	1.6E-5	--	SO2	1.4E-3	2-methylphenanthrene	3.9E-6	Perylene	3.9E-6
Cr	3.4E-5	--	OC	1.6E-2	B-methylphenanthrene	2.1E-5	Benzo(a)pyrene	1.2E-5
Cu	2.0E-5	--	EC	3.8E-3	C-methylphenanthrene	5.4E-5	Indeno[123-cd]pyrene	1.2E-5
Fe	2.7E-5	--	Naphthalene	1.9E-3	1-methylphenanthrene	4.3E-5	Benzo(ghi)perylene	1.2E-5
Ga	3.4E-5	--	2-methylnaphthalene	1.2E-4	Anthrone	1.9E-6	Dibenzo(ah+ac)anthracene	1.2E-5
Hg	4.7E-5	--	1-methylnaphthalene	7.4E-5	Anthraquinone	1.0E-4	Coronene	1.2E-5
In	2.3E-4	--	Biphenyl	1.3E-4	2,3-Benzofluorene	0.0E+0	Dibenzo(ah+ac)anthracene	1.2E-5
K	1.1E-4	--	1+2-ethylnaphthalene	2.5E-4	3,6-dimethylphenanthrene	9.1E-5	Coronene	1.2E-5
La	1.1E-3	--	2,6+2,7-dimethylnaphthalene	2.1E-4	A-dimethylphenanthrene	9.1E-5	Volatile Organic Compounds	1.1E-03
Mg	n/a	--	1,3+1,6+1,7-dimethylnaphthalene	4.4E-4	B-dimethylphenanthrene	6.4E-5	Formaldehyde	4.2E-3
Mn	2.9E-5	--	1,4+1,5+2,3-dimethylnaphthalene	2.0E-4	C-dimethylphenanthrene	6.4E-5	Acetaldehyde	1.3E-2
Mo	4.9E-5	--	1,2-dimethylnaphthalene	1.3E-4	1,7-dimethylphenanthrene	6.4E-5	Acetone	5.1E-2
Na	n/a	--	2-Methylbiphenyl	3.1E-4	D-dimethylphenanthrene	5.8E-5	Acrolein	4.2E-3
Ni	1.6E-5	--	3-Methylbiphenyl	4.4E-4	E-dimethylphenanthrene	2.9E-5	Propionaldehyde	3.5E-3
P	1.0E-4	--	4-Methylbiphenyl	3.7E-5	Anthracene	0.0E+0	Crotonaldehyde	5.0E-3
Pb	5.4E-5	--	Dibenzofuran	1.2E-4	9-methylanthracene	8.9E-5	MEK	1.0E-2
Pd	2.0E-4	--	Bibenzyl	4.8E-3	Fluoranthene	3.9E-6	Methacrolein	5.0E-3
Rb	1.8E-5	--	A-trimethylnaphthalene	3.7E-6	Pyrene	7.7E-6	Butyraldehyde	3.1E-3
S	9.0E-5	--	B-trimethylnaphthalene	1.9E-6	9-Anthraldehyde	5.2E-5	Benzaldehyde	6.7E-3
Sb	3.2E-4	--	C-trimethylnaphthalene	1.5E-5	Retene	1.2E-4	Glyoxal	2.6E-3
Se	2.2E-5	--	E-trimethylnaphthalene	1.9E-6	Benzonaphthothiophene	3.9E-6	Valeraldehyde	5.8E-3
Si	1.1E-4	--	F-trimethylnaphthalene	1.8E-6	1-MeFl+C-MePy/Fl	3.1E-5	M-Tolualdehyde	7.2E-3
Sn	3.1E-4	--	2,3,5+I-trimethylnaphthalene	5.8E-6	B-MePy/MeFl	1.9E-6	Hexanaldehyde	6.4E-3
Sr	2.0E-5		2,4,5-trimethylnaphthalene	1.5E-5	C-MePy/MeFl	1.9E-6		
Ti	5.2E-5		J-trimethylnaphthalene	1.6E-5	D-MePy/MeFl	1.9E-6		
Tl	4.5E-5		1,4,5-trimethylnaphthalene	1.8E-4	4-methylpyrene	3.9E-6		

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

Parameter	Units	Run 1	Run 2	Run 3	Run 4	Average	RSD
Date	dd-mmm-yy	6-Dec-01	7-Dec-01	10-Dec-01	11-Dec-01	--	--
Start time	hh:mm	10:15	9:00	9:30	9:00	--	--
End time	hh:mm	16:15	15:00	15:30	15:00	--	--
Natural gas flowrate	Mscfh	219	211	203	208	210	3.2%
Firing Rate	MMBtu/hr	299	293	289	284	291	2.3%
Fuel heat content	Btu/dscf	1305	1318	1424	1298	1336	4.4%
Fuel gas specific gravity	--	0.80	0.81	0.87	0.79	0.82	4.5%
Stack O_2	%	7.7	8.1	8.5	8.0	8.1	4.1%
Stack flow	MMdscfh	3.3	3.3	3.3	3.2	3.3	1.1%
Preheater O_2	%	7.2	7.6	10.0	10.0	8.7	17%

STACK GAS CONDITIONS AND FLOW RATE

A summary of the stack conditions measured during testing is presented in Table 4-3. Stack gas temperature during the tests ranged from 335 to 351°F.

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

Parameter	Units	Run 1	Run 2	Run 3	Run 4	Average	RSD
Date		6-Dec-01	7-Dec-01	10-Dec-01	11-Dec-01	--	--
Stack Temperature	°F	345	351	342	335	343	2.0%
Moisture	%v	13.2	13.0	12.8	12.8	12.9	1.4%
Velocity	ft/s	25	25	24	24	25	2.1%
	m/s	7.7	7.7	7.5	7.4	7.6	2.1%
Flow Rate	acfm	115,400	114,900	111,400	110,700	113,100	2.1%
	dscfm	65,900	65,400	64,300	63,800	64,850	1.5%
	dscmm	1,870	1,850	1,820	1,810	1,838	1.5%

IN-STACK AND IMPINGER METHOD RESULTS

Particulate Mass

FPM. FPM results as measured by Method PRE-4 are presented in Table 4-4. The acetone rinse results have been blank corrected for the acetone reagent blank, which was significant relative to the raw sample results. Total FPM, which includes all PM collected in the in-stack nozzle/cyclone assembly and on the in-stack filter, ranged from 0.13 to 0.42 mg/dscm. FPM less than 10 micrometers, which includes the portion of total FPM collected downstream of the PM10 cyclone, was 0.03 to 0.23 milligrams per dry standard cubic meter (mg/dscm). FPM less than 2.5 micrometers, which includes the portion of FPM collected downstream of the PM2.5 cyclone and on the in-stack filter, ranged from 0.01 to 0.15 mg/dscm. These in-stack concentrations correspond to total weight gains in the sampling train of 0.5 to 1.5 milligrams (mg), with uncorrected net weights in each fraction of –0.9 to 1.8 mg. Negative in-stack filter weights for Runs 1 and 2 were flagged as non-detects and set to zero for total mass calculations. These results reflect the extremely low PM loading in the stack and suggest that, during these tests, the PM loading was at or below the practical limits of the overall method.

Table 4-4. Filterable Particulate Matter Results (EPA Method PRE-4; Site Charlie).

Parameter	Units	Results					
Run Number	-	1	2	3	4	Average	RSD
Date	-	6-Dec-01	7-Dec-01	10-Dec-01	11-Dec-01		
Total FPM	mg/dscm	0.19	0.13	0.37	0.42	0.28	50%
	lb/hr	0.05	0.03	0.09	0.10	0.07	49%
FPM <10 µm	mg/dscm	0.10	0.03	0.15	0.23	0.13	68%
	lb/hr	0.02	0.006	0.04	0.05	0.03	67%
FPM <2.5 µm	mg/dscm	0.10	0.013	0.006	0.15	0.07	105%
	lb/hr	0.02	0.003	0.001	0.04	0.02	104%

RSD - relative standard deviation

CPM. CPM results as measured by Method 202 are presented in Table 4-5. Note that for the organic CPM, two runs were below detection limits; Run 1 was invalidated by the lab due to a high mass coupled with an anomalous residue observed in the sample upon inspection.

The average total CPM, which is the sum of the evaporated organic extract (corrected for dichloromethane reagent blank), the inorganic residue (corrected for addition of ammonium hydroxide (NH_4OH) and water reagent blank) and the back-half filter, is 1.2 mg/dscm. The total inorganic CPM is 1.1 mg/dscm, approximately 70 percent of which is accounted for by sulfate, with an average concentration of 0.73 mg/dscm. This sulfate concentration reported in Table 4-5 was determined from the aliquot taken from the impinger catch and rinse before it is extracted with the organic

Table 4-5. Condensable Particulate Matter (EPA Method 202) Results (Site Charlie).

Parameter	Units	Value					
Run Number Date	- -	1 6-Dec-01	2 7-Dec-01	3 10-Dec-01	4 11-Dec-01	Average	RSD
Inorganic CPM	mg/dscm	0.70	1.04	1.38	1.29	1.10	28%
	lb/hr	0.17	0.25	0.33	0.31	0.27	27%
Organic CPM	mg/dscm	NV	0.34	ND	ND	0.34	n/a
	lb/hr	NV	0.08	ND	ND	0.08	n/a
Total CPM	mg/dscm	0.70	1.46	1.42	1.37	1.23	29%
(corrected for NH_4^+ and H_2O)	lb/hr	0.17	0.36	0.34	0.33	0.30	29%
Sulfate (as $SO_4^=$) in Impingers	mg/dscm	0.62	0.53	0.92	0.84	0.73	25%
	lb/hr	0.15	0.13	0.22	0.20	0.18	24%

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

solvent. The average organic CPM concentration is 0.34 mg/dscm, with two runs being below detection limits and one run being invalid. CPM concentration was more than an order of magnitude greater than FPM2.5 on average. On average, approximately 91 percent of the CPM was found in the inorganic fraction, while 6 percent was found in the organic fraction; the remaining mass (3 percent) is accounted for in the impinger filter that was not speciated. The inorganic CPM results are somewhat variable from run to run, with a standard deviation equal to 28 percent of the average result; organic CPM was only found at detectable levels in one run. CPM results have been corrected for dichloromethane and water recovery blank results. The inorganic CPM data are also corrected for ammonium ion retained and combined water released in the acid base titration, as described in Method 202. The water reagent blank mass was significant compared to the masses in the samples, accounting for from 58 to 74 percent of the uncorrected net weight of inorganic CPM. Further discussion of the data is provided in Section 7.

Additionally, the resuspended inorganic residues of the Method 202 train were analyzed for a broader range of elements and ions to more fully speciate the mass. The results (Table 4-6) have been corrected by subtracting the reagent blank, adjusted for relative volume. The mass in the blank was significant for many compounds, ranging from 4 to 500 percent of the uncorrected net weight; in cases where the blank was greater than the sample mass, the data were set to zero and flagged as not detected. $SO_4^=$, Cl^-, Na, S, Ca and NO_3^- are the six most abundant compounds in the inorganic CPM fraction. $SO_4^=$, Cl^-, and Na account for 97 percent of the inorganic CPM mass as presented in Table 4-5. The remaining elements that were detected account for the remaining 3 percent, of the average inorganic CPM mass. Agreement between the speciated mass and the gravimetric number is fairly good; the sum of species accounts for approximately 1.3 times the inorganic CPM mass, on average. Note that S was not included in the sum of the species because it is assumed to be accounted for in the $SO_4^=$ measurement. The $SO_4^=$ results for the impinger aliquot reported in Table 4-5 and for the residue reported in Table 4-6 are in excellent agreement, indicating that $SO_4^=$ in the impingers was preserved during the Method 202 extraction, titration, drying and weighing procedures. It is believed the majority of $SO_4^=$ found in the impinger contents is an artifact resulting from gaseous SO_2 in the stack gas. These results and issues are discussed further in Section 7.

Table 4-6. Speciation (mg/dscm) of Method 202 Inorganic Reaction Residue (Site Charlie).

Substance	Run 1		Run 2		Run 3		Run 4		Average		RSD
F-		5.86E-03		7.27E-03		1.18E-03		9.13E-03		5.86E-03	58%
Cl-		2.66E-01		3.23E-01		3.89E-01	ND		<	3.26E-01	19%
NO3-	ND		ND		ND			2.53E-02	<	2.53E-02	n/a
SO4=		6.02E-01		5.47E-01		9.52E-01		9.06E-01		7.52E-01	28%
Ba		1.99E-04		3.15E-04		1.40E-04		3.96E-04		2.63E-04	44%
Cd		1.01E-04	ND		ND			1.24E-04	<	1.12E-04	n/a
Ca		3.75E-02		3.70E-02		3.87E-02		1.91E-02		3.31E-02	28%
Cu		3.20E-04		5.73E-04		9.02E-05		2.59E-04		3.11E-04	n/a
Fe	ND		ND			4.39E-04	ND		<	4.39E-04	n/a
Mg		8.11E-03		6.05E-03		8.09E-03		3.68E-03		6.48E-03	32%
Mn		8.61E-04		2.30E-03		2.83E-04		2.81E-04		9.32E-04	n/a
Ni	ND			3.31E-04	ND		ND		<	3.31E-04	n/a
Na		1.70E-01		2.79E-01		4.64E-01		3.29E-01		3.11E-01	39%
Sr		4.14E-04		3.82E-04		3.86E-04		2.35E-04		3.54E-04	23%
S		2.05E-01		1.88E-01		3.36E-01		3.12E-01		2.60E-01	29%
Zn		8.64E-03		9.59E-03		6.11E-03		3.41E-03		6.94E-03	40%

< - one or more blank corrected values less than zero
n/a-not applicable. Only one rune within detectable limits
ND - blank corrected value less than zero

DILUTION SAMPLER RESULTS

Particulate Mass

PM2.5 mass measurements using the dilution sampler include both solid aerosols that are directly emitted and those that condense under simulated stack plume conditions in the residence chamber. The dilution sampler determines only the PM2.5 fraction of PM emissions; particles larger than 2.5 micrometers aerodynamic diameter in the stack or those that form and grow to be larger than 2.5 micrometers aerodynamic diameter in the dilution sampler are excluded. Results from these measurements show that PM2.5 concentrations and emission rates average 0.19 mg/dscm and 0.048 lb/hr, respectively, with a relative standard deviation of 84 percent, based on TMF weight (Table 4-7). The filter weight for Run 3 was negative due to a damaged filter; it is flagged as not valid. These results are approximately an order of magnitude lower than the sum of FPM2.5 and CPM measured by EPA Methods PRE-4 and 202. PM2.5 concentration measured by the dilution sampler in the heater stack gas was approximately five times higher than the concentration measured in the ambient air.

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

	Units	Results						
Run Number	-	Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average	RSD	Char-Amb
Date	-	06-Dec-01	07-Dec-01	10-Dec-01	11-Dec-01		(%)	12-Dec-01
PM2.5	mg/dscm	2.0E-01	3.5E-01	NV	3.0E-02	1.9E-01	84	4.1E-02
	lb/hr	4.9E-02	8.7E-02	NV	7.1E-03	4.8E-02	84	n/a

n/a-not applicable

NV - Not valid, filter damaged

RSD- Relative standard deviation

The concentration of PM2.5 using the dilution sampler is almost three times higher than FPM <2.5 micrometers measured using Method PRE-4 and approximately an order of magnitude lower than CPM measured using Method 202. This relative distribution of PM mass is the expected result. From low emission sources, such as this gas-fired heater, very little of the PM is expected to exist in solid, filterable form in the hot exhaust. Semivolatile material present in the stack will not condense until it is cooled, and if this cooling process occurs without dilution, as in the Method 202 train, more material will condense than would in a real world plume, where cooling occurs at the same time as the stack gases are diluted. Also, the CPM measured by Method 202 is believed to be biased high due to conversion of gaseous SO_2 to $SO_4^=$ in the impingers (see Section 7). Due to these suspected artifacts associated with Method 202, it is believed the dilution sampler results are more representative of the true primary PM2.5 emissions.

Sulfate, Nitrate, Chloride, Ammonium and Soluble Sodium

Quartz filters were analyzed for $SO_4^=$, Cl^-, NO_3^-, NH_4^+ and sodium ion (Na^+). Of these, $SO_4^=$ had the highest average concentration at 0.0083 mg/dscm, followed by NO_3^- at 0.0074 mg/dscm (Table 4-8). All ions in the field blank were present below detectable levels (see Section 6 for additional discussion of blanks).

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

Parameter	Units	Value						
Run Number	-	Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average	RSD	Char-Amb
Date	-	06-Dec-01	07-Dec-01	10-Dec-01	11-Dec-01		(%)	12-Dec-01
Sulfate	mg/dscm	1.5E-2	1.0E-2	3.9E-3	4.8E-3	8.3E-3	60	1.4E-03
	lb/hr	3.6E-3	2.5E-3	9.3E-4	1.1E-3	2.0E-3	61	n/a
Nitrate	mg/dscm	1.0E-2	9.0E-3	3.2E-3	ND	< 7.4E-3	50	5.0E-03
	lb/hr	2.5E-3	2.2E-3	7.6E-4	ND	< 1.8E-3	51	n/a
Chloride	mg/dscm	ND	2.7E-3	ND	ND	< 2.7E-3	n/a	6.5E-04
	lb/hr	ND	6.7E-4	ND	ND	< 6.7E-4	n/a	n/a
Ammonium	mg/dscm	5.1E-3	2.6E-3	ND	ND	< 3.9E-3	46	8.5E-04
	lb/hr	1.3E-3	6.4E-4	ND	ND	< 9.6E-4	46	n/a
Soluble Na	mg/dscm	1.0E-3	1.8E-3	3.9E-4	2.8E-4	8.9E-4	81	8.7E-05
	lb/hr	2.6E-4	4.5E-4	9.5E-5	6.8E-5	2.2E-4	81	n/a

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

The average $SO_4^=$ concentration from the dilution sampler is about two orders of magnitude lower than the average concentration reported above for Method 202. This difference lends further support to the possibility of significant sampling artifacts in Method 202 due to gaseous SO_2 in the stack gas and/or excessive nucleation of condensable aerosols. Concentrations of $SO_4^=$, NO_3^-, NH_4^+ and Cl^- measured in the stack gas are within an order of magnitude of the concentrations measured in the ambient air.

OC, EC and Organic Species

OC and EC were measured on quartz filters from the dilution sampler. OC concentration ranged from 0.11 to 0.38 mg/dscm. EC concentration ranged from undetected (detection limit of 0.0038 mg/dscm) up to 0.057 mg/dscm (Table 4-9). OC accounts for approximately 90 percent of the total carbon mass. Average EC and OC concentrations measured in the stack gas are greater than an order of magnitude greater than the ambient sample concentrations. EC concentrations were below detection limits in the field blank, however the OC concentrations in the field blank and trip blank were both within an order of magnitude of the average in-stack concentration (see Section 6 for additional discussion of blank results).

The quartz filters used for OC/EC analysis have the potential for positive OC bias due to absorption of VOCs on the filter. A backup quartz filter sampled behind the TMF to indicate the magnitude of this absorptive bias showed a high concentration of OC, approximately 50 to 115 percent of that in the sample. Some VOCs were present in the sample at concentrations similar to OC and the sum of measured VOCs is somewhat higher than OC. Therefore the magnitude of any bias is potentially significant. Please refer to section 7 for further discussion of the OC artifact.

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

Parameter	Units	Value						
Run Number	-	Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average*	RSD (%)	Char-Amb
Date	-	05-Dec-97	06-Dec-97	09-Dec-97	10-Dec-97			11-Dec-97
Organic Carbon (OC)**	mg/dscm	3.8E-1	3.0E-1	1.2E-1	1.1E-1	2.3E-1	58	1.3E-2
	lb/hr	9.3E-2	7.3E-2	2.9E-2	2.7E-2	5.6E-2	59	n/a
Elemental Carbon (EC)	mg/dscm	5.7E-2	4.7E-2	ND	2.5E-2	< 4.3E-2	37	2.8E-3
	lb/hr	1.4E-2	1.1E-2	ND	6.1E-3	< 1.0E-2	38	n/a
Total Carbon (TC)	mg/dscm	4.3E-1	3.4E-1	1.2E-1	1.4E-1	2.6E-1	59	1.5E-2
	lb/hr	1.1E-1	8.4E-2	2.9E-2	3.4E-2	6.3E-2	61	n/a
Backup Filter OC ***	mg/dscm	1.9E-1	2.0E-1	1.4E-1	8.3E-2	1.5E-1	35	4.3E-3

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

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

*** OC measured on back up filter. Refer to Section 7 for further discussion.

n/a - not applicable

ND - not detected

RSD- Relative standard deviation

SVOCs. SVOCs were captured on the combined TIGF/PUF/XAD-4/PUF cartridge used with the dilution sampler, allowing for determination of both aerosol and vapor phase SVOCs together. Results of the stack emissions and ambient air sample are presented in Table 4-10. Naphthalene is the most abundant SVOC in the diluted exhaust samples with an average concentration of 0.009 mg/dscm. Approximately 80 percent of the SVOC compounds at detectable levels in the stack gas are more than an order of magnitude greater than their concentrations in the ambient air. The high variability among runs for many of the SVOC compounds results in high uncertainties for their respective emission factors, presented in Section 5.

Table 4-10. SVOC Results (mg/dscm) (Site Charlie).

Parameter	Value							
Run Number	Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average	RSD (%)	Char-Amb	MDL
Date	06-Dec-01	07-Dec-01	10-Dec-01	11-Dec-01			12-Dec-01	
Naphthalene	7.3E-3	1.5E-2	4.4E-3	ND	< 8.9E-3	62	4.5E-4	1.9E-3
2-methylnaphthalene	7.0E-3	7.4E-3	9.1E-4	3.4E-4	3.9E-3	97	4.1E-4	1.2E-4
2-Methylbiphenyl	1.2E-3	2.4E-3	7.1E-3	3.4E-3	3.5E-3	73	1.6E-4	3.1E-4
1,3+1,6+1,7-dimethylnaphthalene	4.5E-3	3.4E-3	6.2E-4	ND	< 2.8E-3	70	5.5E-4	4.4E-4
1-methylnaphthalene	3.7E-3	3.9E-3	5.1E-4	2.1E-4	2.1E-3	96	2.5E-4	7.3E-5
3-Methylbiphenyl	1.1E-3	1.6E-3	3.4E-3	1.6E-3	1.9E-3	52	7.5E-5	4.4E-4
2,6+2,7-dimethylnaphthalene	2.3E-3	1.7E-3	3.0E-4	ND	< 1.4E-3	72	3.0E-4	2.1E-4
1,4+1,5+2,3-dimethylnaphthalene	1.2E-3	2.3E-3	2.0E-4	ND	< 1.2E-3	84	1.2E-4	2.0E-4
1+2-ethylnaphthalene	1.3E-3	1.2E-3	5.1E-4	ND	< 9.9E-4	43	1.3E-4	2.5E-4
2,3,5+I-trimethylnaphthalene	1.6E-3	1.7E-3	5.0E-5	4.0E-4	9.2E-4	89	4.3E-5	5.8E-6
4-Methylbiphenyl	5.3E-4	6.7E-4	1.5E-3	6.3E-4	8.3E-4	54	3.1E-5	3.7E-5
Biphenyl	6.2E-4	7.7E-4	ND	ND	< 7.0E-4	14	2.0E-5	1.3E-4
1-methylfluorene	5.5E-4	1.4E-3	ND	1.3E-4	< 6.9E-4	93	4.3E-6	1.3E-4
A-trimethylnaphthalene	1.2E-3	6.1E-4	8.9E-5	5.7E-5	5.0E-4	111	6.1E-5	3.6E-6
Acenaphthenequinone	5.8E-4	6.6E-4	3.1E-4	3.4E-4	4.7E-4	37	1.3E-5	1.2E-5
Fluorene	7.4E-4	3.1E-4	ND	2.4E-4	< 4.3E-4	63	1.8E-5	2.3E-4
1,2-dimethylnaphthalene	4.2E-4	3.1E-4	ND	ND	< 3.6E-4	21	4.5E-5	1.3E-4
B-trimethylnaphthalene	8.0E-4	5.1E-4	6.5E-5	3.0E-5	3.5E-4	106	4.3E-5	1.9E-6
Phenanthrene	6.5E-4	5.3E-4	2.1E-4	2.4E-5	3.5E-4	81	3.7E-5	1.5E-5
Acenaphthylene	ND	3.4E-4	ND	ND	< 3.4E-4	n/a	ND	2.0E-4
9-Anthraldehyde	7.0E-4	1.2E-4	1.7E-4	ND	< 3.3E-4	97	ND	5.2E-5
C-trimethylnaphthalene	7.1E-4	3.9E-4	9.5E-5	4.1E-5	3.1E-4	100	3.4E-5	1.5E-5
Acenaphthene	2.1E-4	3.3E-4	ND	ND	< 2.7E-4	32	2.1E-5	5.0E-5
B-methylfluorene	2.6E-4	ND	ND	ND	< 2.6E-4	n/a	ND	1.3E-4
J-trimethylnaphthalene	2.7E-4	1.3E-4	ND	ND	< 2.0E-4	51	1.0E-5	1.5E-5
E-trimethylnaphthalene	4.1E-4	2.9E-4	3.3E-5	2.4E-5	1.9E-4	101	2.4E-5	1.9E-6
F-trimethylnaphthalene	3.9E-4	2.6E-4	5.2E-5	2.2E-5	1.8E-4	96	2.2E-5	1.8E-6
A-methylphenanthrene	1.3E-4	1.2E-4	ND	ND	< 1.3E-4	8	1.1E-5	9.3E-5
C-dimethylphenanthrene	1.5E-4	1.1E-4	1.1E-4	ND	< 1.2E-4	17	7.8E-6	6.4E-5
C-methylphenanthrene	1.2E-4	ND	ND	ND	< 1.2E-4	n/a	9.3E-6	5.4E-5
3,6-dimethylphenanthrene	ND	1.1E-4	ND	ND	< 1.1E-4	n/a	3.1E-6	9.1E-5
2-methylphenanthrene	1.8E-4	1.7E-4	6.6E-5	1.4E-5	1.1E-4	75	1.3E-5	3.9E-6
1-methylphenanthrene	8.5E-5	1.6E-4	6.9E-5	ND	< 1.0E-4	46	7.9E-6	4.2E-5
B-methylphenanthrene	ND	9.3E-5	ND	ND	< 9.3E-5	n/a	ND	2.1E-5
E-dimethylphenanthrene	1.4E-4	ND	ND	3.4E-5	< 8.7E-5	86	1.4E-6	2.9E-5

Table 4-10. SVOC Results (mg/dscm) (Site Charlie) (Continued).

Parameter	Value							
Run Number	Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average	RSD	Char-Amb	MDL
Date	06-Dec-01	07-Dec-01	10-Dec-01	11-Dec-01		(%)	12-Dec-01	
2,4,5-trimethylnaphthalene	1.8E-4	1.1E-4	1.6E-5	2.8E-5	8.3E-5	94	6.6E-6	1.5E-5
Pyrene	8.9E-5	1.0E-4	1.0E-4	1.9E-5	7.8E-5	51	2.2E-6	7.7E-6
Benz(a)anthracene	7.6E-5	ND	ND	ND	< 7.6E-5	n/a	8.0E-7	1.2E-5
Fluoranthene	9.7E-5	1.1E-4	7.3E-5	1.1E-5	7.2E-5	60	2.5E-6	3.9E-6
Benzo(c)phenanthrene	ND	5.4E-5	ND	ND	< 5.4E-5	n/a	ND	2.1E-5
Xanthone	6.8E-5	ND	2.9E-5	ND	< 4.9E-5	57	2.2E-7	7.7E-6
Anthrone	ND	4.1E-5	5.7E-5	2.4E-5	< 4.1E-5	41	9.0E-7	1.9E-6
Anthracene	6.8E-5	6.1E-5	1.5E-5	1.7E-6	3.6E-5	91	1.3E-6	0.0E+0
B-MePy/MeFl	4.5E-5	3.4E-5	2.2E-5	ND	< 3.4E-5	34	1.0E-7	1.9E-6
7-methylbenzo(a)pyrene	ND	4.1E-5	2.0E-5	ND	< 3.1E-5	48	7.2E-7	1.4E-5
Benzo(a)pyrene	3.8E-5	3.6E-5	2.4E-5	1.7E-5	2.9E-5	35	1.6E-6	1.2E-5
Benzo(e)pyrene	4.2E-5	2.4E-5	2.7E-5	1.3E-5	2.7E-5	45	1.7E-6	1.2E-5
1-methylpyrene	1.7E-5	ND	3.0E-5	ND	< 2.3E-5	40	ND	1.5E-5
4-methylpyrene	3.2E-5	1.4E-5	3.2E-5	4.2E-6	2.1E-5	67	4.0E-7	3.9E-6
D-MePy/MeFl	2.1E-5	1.8E-5	2.1E-5	ND	< 2.0E-5	9	2.5E-7	1.9E-6
Benzo(b+j+k)fluoranthene	3.2E-5	ND	ND	5.9E-6	< 1.9E-5	97	3.0E-7	1.9E-6
Benzo(ghi)perylene	1.2E-5	1.9E-5	ND	ND	< 1.6E-5	32	ND	1.2E-5
Benzonaphthothiophene	8.4E-6	2.4E-5	4.3E-6	5.1E-6	1.0E-5	89	3.2E-7	3.9E-6
Chrysene	1.1E-5	ND	5.1E-6	1.0E-5	< 8.8E-6	37	8.7E-7	3.9E-6
Perylene	4.7E-6	ND	1.4E-5	5.9E-6	< 8.1E-6	60	ND	3.9E-6
C-MePy/MeFl	5.6E-6	6.1E-6	4.3E-6	3.4E-6	4.8E-6	25	7.5E-8	1.9E-6
5+6-methylchrysene	4.7E-6	ND	1.7E-6	7.6E-6	< 4.7E-6	63	ND	0.0E+0
A-methylfluorene	ND	ND	ND	ND	ND	n/a	1.1E-5	2.0E-4
9-fluorenone	ND	ND	ND	ND	ND	n/a	9.2E-6	2.6E-4
A-dimethylphenanthrene	ND	ND	ND	ND	ND	n/a	3.1E-6	9.1E-5
1,7-dimethylphenanthrene	ND	ND	ND	ND	ND	n/a	2.1E-6	6.4E-5
D-dimethylphenanthrene	ND	ND	ND	ND	ND	n/a	3.4E-6	5.8E-5

n/a- Not applicable. Only one run was within detectable limits.
ND - not detected
MDL - Method Detection Limit

VOCs – Tenax. Tenax sorbent was used to collect VOCs, focusing the analysis on VOCs with a carbon number greater than seven, which are considered precursors of secondary organic aerosols. Discussions with the organic lab indicate that the Tenax sample material is susceptible to degradation from components in the sample stream, making it difficult to differentiate true emissions from those due to Tenax decomposition. In light of this observation, the Tenax results should be viewed as highly uncertain, in particular for benzaldehyde, benzoic acid, hexadecanoic acid, phenol and acetophenone, which are all potential Tenax degradation products. Excluding these compounds, the most abundant VOC detected during sampling was m- & p-xylenes, with an average concentration of 0.058 mg/dscm (Table 4-11).

Table 4-11. VOC Results from Tenax (Site Charlie).

Parameter	Value						
Units	mg/dscm					%	
Run Number Date	Char-Run 1 12/06/01	Char-Run 2 12/07/01	Char-Run 3 12/10/01	Char-Run 4 12/11/01	Average	RSD	Char-Ambient 12/12/01
Benzoic acid	1.0E+0	* 9.6E-1	5.8E+0	3.3E-1	2.0E+0	125	1.7E-02
Hexadecanoic acid	6.6E-1	6.6E-1	7.6E-1	2.4E+0	1.1E+0	76	1.1E-02
Benzaldehyde	2.3E-1	3.2E-1	4.5E-1	3.3E-1	3.3E-1	27	3.2E-03
Acetophenone	1.5E-1	1.9E-1	2.2E-1	1.6E-1	1.8E-1	18	1.4E-03
Phenol	5.8E-2	5.3E-2	9.5E-2	8.8E-2	7.3E-2	29	1.4E-03
m & p-xylene	6.6E-2	9.5E-2	5.9E-2	1.3E-2	5.8E-2	58	3.4E-03
Nonane	6.3E-2	4.2E-2	3.4E-2	1.9E-2	3.9E-2	46	2.2E-03
Decane	4.5E-2	2.7E-2	1.8E-2	1.1E-2	2.5E-2	59	7.4E-04
p-isopropyltoluene	4.3E-2	3.2E-2	5.5E-3	4.6E-3	2.1E-2	91	2.0E-04
Undecane	3.0E-2	2.5E-2	1.1E-2	5.5E-3	1.8E-2	64	5.4E-04
o-xylene	2.0E-2	2.6E-2	1.8E-2	3.7E-3	1.7E-2	57	1.0E-03
Nonanal	ND	ND	1.6E-2	ND	< 1.6E-2	n/a	ND
Pentadecane	1.8E-2	1.6E-2	ND	1.5E-2	< 1.6E-2	10	3.7E-04
1,2,4-trimethylbenzene	1.5E-2	2.7E-2	1.7E-2	3.5E-3	1.6E-2	61	6.9E-04
m-ethyltoluene	1.6E-2	2.1E-2	1.7E-2	3.5E-3	1.4E-2	53	5.8E-04
Ethylbenzene	1.5E-2	2.0E-2	1.5E-2	3.4E-3	1.3E-2	52	7.8E-04
Dodecane	1.5E-2	1.5E-2	6.9E-3	3.0E-3	1.0E-2	60	3.0E-04
Tetradecane	1.3E-2	1.1E-2	3.2E-3	9.2E-3	9.1E-3	47	3.8E-04
p-ethyltoluene	7.2E-3	1.3E-2	1.0E-2	1.8E-3	8.1E-3	60	2.9E-04
Octanal	ND	1.1E-2	4.1E-3	ND	< 7.7E-3	66	ND
1-methylindan	9.4E-3	6.3E-3	6.7E-3	ND	< 7.5E-3	23	1.1E-04
Styrene	1.3E-2	1.5E-3	ND	6.0E-3	< 6.7E-3	83	5.6E-04
3-methyloctane	8.4E-3	8.8E-3	7.4E-3	2.0E-3	6.6E-3	48	3.8E-04
Hexadecane	1.0E-2	9.1E-3	1.3E-3	4.7E-3	6.3E-3	65	1.7E-04
Naphthalene	5.7E-3	1.1E-2	5.9E-3	2.1E-3	6.2E-3	59	3.5E-04
1,3,5-trimethylbenzene	7.0E-3	8.8E-3	6.7E-3	1.5E-3	6.0E-3	52	2.7E-04
o-ethyltoluene	4.9E-3	7.2E-3	4.4E-3	ND	< 5.5E-3	28	1.9E-04
Tridecane	5.7E-3	8.1E-3	4.2E-3	2.8E-3	5.2E-3	44	3.3E-04
B-dimethylindane	ND	4.8E-3	5.2E-3	ND	< 5.0E-3	5	ND
Heptadecane	7.3E-3	4.7E-3	ND	2.5E-3	< 4.8E-3	50	6.6E-05
Propylbenzene	5.1E-3	6.7E-3	4.9E-3	1.8E-3	4.6E-3	45	1.7E-04
2-methylnaphthalene	4.2E-3	5.1E-3	2.6E-3	ND	< 4.0E-3	32	2.7E-04
2-methyloctane	4.7E-3	3.3E-3	3.8E-3	ND	< 3.9E-3	18	2.0E-04
Indan	ND	5.0E-3	2.1E-3	ND	< 3.5E-3	59	6.0E-05
1,3-dichlorobenzene	3.2E-3	4.7E-3	2.6E-3	ND	< 3.5E-3	30	9.8E-05
Octadecane	1.9E-3	4.2E-3	ND	ND	< 3.0E-3	54	ND
Dimethyloctane	3.7E-3	2.1E-3	2.8E-3	ND	< 2.9E-3	29	1.2E-04
4-ethyl-o-xylene	2.0E-3	4.6E-3	1.9E-3	ND	< 2.8E-3	55	8.9E-05
2-methylindan	2.2E-3	3.4E-3	ND	ND	< 2.8E-3	29	3.1E-05
1,2,3,4-tetramethylbenzene	2.6E-3	ND	ND	ND	< 2.6E-3	n/a	3.2E-05
C-dimethylindane	ND	ND	2.5E-3	ND	< 2.5E-3	n/a	ND
5-ethyl-m-xylene	1.6E-3	3.0E-3	ND	ND	< 2.3E-3	44	4.6E-05
2-ethyl-p-xylene	ND	2.1E-3	1.4E-3	ND	< 1.7E-3	26	6.2E-05
1,2,4,5-tetramethylbenzene	ND	1.7E-3	ND	ND	< 1.7E-3	n/a	ND
1-methylnaphthalene	1.4E-3	1.9E-3	1.6E-3	ND	< 1.6E-3	13	1.4E-04
1,2,3,5-tetramethylbenzene	ND	2.0E-3	1.1E-3	ND	< 1.5E-3	44	4.9E-05
2-heptanone	ND	1.4E-3	ND	ND	< 1.4E-3	n/a	1.0E-04
Biphenyl	1.2E-3	ND	ND	ND	< 1.2E-3	n/a	ND
4-n-propyltoluene + 1,4-diethylbenzene	ND	ND	ND	ND	ND	n/a	4.5E-05
Isopropylbenzene	ND	ND	ND	ND	ND	n/a	5.5E-05
2-n-propyltoluene	ND	ND	ND	ND	ND	n/a	5.9E-05
Propylcyclohexane	ND	ND	ND	ND	ND	n/a	9.2E-05
2,6+2,7-dimethylnaphthalene	ND	ND	ND	ND	ND	n/a	2.0E-04

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

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

n/a- not applicable. Less than two runs within detectable limits.

RSD - relative standard deviation

In general, the average VOC compounds concentrations in the stack gas were between one to two orders of magnitude greater than their concentrations in the ambient air.

VOCs – Canisters. Stainless steel canisters were used to collect VOCs and the analysis of the sample obtained from the canisters allows for detection of organic species with carbon numbers as low as two. Results from the canister samples are presented in Table 4-12. Propane and n-butane were the two highest detected compounds with concentrations of 0.74 mg/dscm and 0.72 mg/dscm respectively. All concentrations at detectable levels in the stack samples are at least 2 times larger than concentrations in the ambient sample, with most being at least an order of magnitude larger; however most compounds have average sample concentrations of the same order of magnitude as the sampler blank concentrations, when expressed as in-stack equivalent concentrations. Blank results are discussed further in Section 6.

Elements

Element concentrations were determined by XRF analysis of the TMFs used in the dilution sampler. On average Si, Fe, Al, Ca, and S are the most abundant elements in the stack gas (Table 4-13). The sulfur results are approximately one third of the dilution sampler $SO_4^=$ results presented earlier, as expected based on relative molecular weights. Mg and Na results are considered semi-quantitative because of analytical limitations. Ag, As, Au, Ba, Cd, Ga, Hg, In, La, Pd, Sb, Se, Sn, Tl, U and Y were below detectable levels for all sample runs. About half of the average in-stack concentrations are within an order of magnitude of their ambient concentrations.

Carbonyls

Aldehydes were captured in two DNPH-impregnated silica gel cartridges assembled in series. The second cartridges were used to check for breakthrough, and the results presented in Table 4-14 are the sum of the two cartridges. Acetone, acetaldehyde, formaldehyde, and methyl ethyl ketone (MEK) were present in the highest concentrations in the stack samples. The data have been blank corrected based on an average of the field blank values. Formaldehyde was only detected in one of the five field blanks. A sampler blank was also performed, where the sample

Table 4-12. VOC Results from Canisters (Site Charlie).

Parameter	Value						
Units	mg/dscm					(%)	mg/dscm
Run Number	Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average	RSD	Char-Amb
Date	12/06/01	12/07/01	12/10/01	12/11/01			12/12/01
Propane	5.7E-1	1.3E+0	6.7E-1	4.9E-1	7.4E-1	47	3.0E-2
n-butane	3.6E-1	1.8E+0	4.9E-1	2.5E-1	7.2E-1	100	5.6E-2
Isobutane	2.1E-1	9.1E-1	3.4E-1	1.4E-1	4.0E-1	88	3.2E-2
Ethane	3.9E-1	5.9E-1	3.4E-1	2.6E-1	4.0E-1	36	1.4E-2
Isopentane	2.9E-1	5.7E-1	3.3E-1	1.6E-1	3.4E-1	51	3.2E-2
Toluene	4.0E-1	4.9E-1	3.2E-1	9.2E-2	3.3E-1	52	1.7E-2
Acetone	4.2E-1	5.3E-1	1.0E-1	1.6E-1	3.0E-1	68	9.7E-2
Propene	1.1E-1	3.9E-1	2.3E-1	1.2E-1	2.1E-1	62	2.5E-3
Methylene chloride	2.8E-1	2.6E-1	1.7E-1	1.3E-1	2.1E-1	34	2.5E-2
n-pentane	1.6E-1	2.2E-1	2.8E-1	6.8E-2	1.8E-1	50	2.6E-2
2-methylpentane	1.1E-1	2.8E-1	2.1E-1	4.2E-2	1.6E-1	65	1.5E-2
Ethene	1.8E-1	2.8E-1	8.2E-2	7.0E-2	1.5E-1	63	3.6E-3
Chloromethane	1.2E-1	1.9E-1	1.5E-1	1.2E-1	1.4E-1	23	3.7E-3
Acetylene	1.4E-1	2.6E-1	7.2E-2	6.8E-2	1.4E-1	66	2.9E-3
1-decene	1.3E-1	1.2E-1	7.0E-2	1.1E-1	1.1E-1	24	3.9E-3
m- & p-xylene	1.2E-1	1.7E-1	7.4E-2	3.3E-2	1.0E-1	60	5.8E-3
Acetaldehyde	1.3E-1	1.2E-1	6.9E-2	5.3E-2	9.4E-2	41	4.3E-3
2,2,4-trimethylpentane	1.2E-1	1.6E-1	6.9E-2	1.7E-2	9.4E-2	69	7.3E-3
n-hexane	1.1E-1	1.3E-1	7.8E-2	4.0E-2	9.1E-2	45	9.0E-3
Methylcyclopentane	7.7E-2	1.1E-1	7.3E-2	2.8E-2	7.2E-2	47	6.3E-3
3-methylpentane	6.8E-2	1.0E-1	7.0E-2	2.5E-2	6.7E-2	49	6.5E-3
2,3,5-trimethylhexane	7.5E-2	4.6E-2	3.9E-2	1.0E-1	6.5E-2	44	2.3E-3
Ethanol + ACN	4.4E-2	4.8E-2	2.1E-2	1.2E-1	5.9E-2	75	2.8E-3
Cyclohexane	5.2E-2	6.9E-2	4.9E-2	3.1E-2	5.0E-2	31	3.8E-3
Methylcyclohexane	6.2E-2	7.4E-2	3.9E-2	2.1E-2	4.9E-2	48	3.5E-3
Benzene	5.0E-2	8.5E-2	3.8E-2	2.1E-2	4.9E-2	56	3.6E-3
n-heptane	5.9E-2	6.8E-2	3.9E-2	1.8E-2	4.6E-2	48	3.7E-3
Iso-butene	4.2E-2	9.8E-2	2.7E-2	1.7E-2	4.6E-2	79	3.0E-3
3-methylhexane + pentanal	4.8E-2	6.5E-2	4.6E-2	1.5E-2	4.3E-2	48	3.7E-3
1-butene	3.6E-2	8.5E-2	2.0E-2	1.5E-2	3.9E-2	82	3.1E-3
2-methylhexane	4.0E-2	5.6E-2	3.9E-2	1.2E-2	3.7E-2	50	3.2E-3
o-xylene	4.1E-2	6.0E-2	2.6E-2	1.2E-2	3.5E-2	60	2.0E-3
2,3,-trimethylpentane	4.6E-2	5.7E-2	2.4E-2	7.0E-3	3.4E-2	67	9.2E-5
Hexanal	4.2E-2	4.1E-2	2.7E-2	2.0E-2	3.2E-2	33	1.6E-3
2,3-dimethylbutane	3.2E-2	5.4E-2	3.2E-2	1.1E-2	3.2E-2	54	3.1E-3
t-2-butene	2.5E-2	7.5E-2	1.7E-2	1.2E-2	3.2E-2	90	2.7E-3
F 12	3.4E-2	4.8E-2	1.9E-2	2.6E-2	3.2E-2	39	8.6E-4
2,2-dimethylbutane	3.2E-2	4.8E-2	3.7E-2	9.1E-3	3.1E-2	52	2.4E-3
n-octane	4.4E-2	4.5E-2	2.0E-2	1.3E-2	3.1E-2	53	2.1E-3
n-nonane	4.4E-2	4.2E-2	1.4E-2	1.3E-2	2.8E-2	59	1.2E-3
Ethylbenzene	3.5E-2	5.0E-2	2.0E-2	8.0E-3	2.8E-2	64	1.8E-3
2,3-dimethylpentane	3.0E-2	4.3E-2	2.2E-2	7.7E-3	2.6E-2	58	2.1E-3
c-2-butene	2.0E-2	5.6E-2	1.3E-2	1.0E-2	2.5E-2	85	2.2E-3
n-decane	3.8E-2	3.5E-2	1.1E-2	1.2E-2	2.4E-2	61	9.2E-4
m-ethyltoluene	3.1E-2	4.1E-2	1.6E-2	8.0E-3	2.4E-2	62	1.3E-3
2-methylheptane	2.7E-2	3.2E-2	1.9E-2	7.0E-3	2.1E-2	51	1.8E-3
Styrene + heptanal	3.0E-2	2.4E-2	1.6E-2	1.4E-2	2.1E-2	35	1.1E-3
Cyclopentane	2.1E-2	3.0E-2	2.1E-2	9.1E-3	2.0E-2	43	2.1E-3
2,4-dimethylpentane	2.0E-2	3.6E-2	1.5E-2	5.6E-3	1.9E-2	67	1.6E-3
alpha-pinene	6.5E-3	4.4E-2	7.8E-3	1.8E-2	1.9E-2	91	5.6E-4
Chlorobenzene	2.8E-2	2.9E-2	1.3E-2	5.9E-3	1.9E-2	60	1.1E-3
1-pentene	1.6E-2	2.0E-2	ND	ND	< 1.8E-2	17	5.9E-4
3-methylheptane	2.1E-2	2.5E-2	1.7E-2	6.3E-3	1.7E-2	47	1.4E-3
3-ethylpentane	1.8E-2	2.6E-2	1.9E-2	5.6E-3	1.7E-2	49	1.4E-3

Table 4-12. VOC Results from Canisters (Site Charlie) (Continued).

Parameter	Value						
Units	mg/dscm					(%)	mg/dscm
Run Number Date	Char-Run 1 12/06/01	Char-Run 2 12/07/01	Char-Run 3 12/10/01	Char-Run 4 12/11/01	Average	RSD	Char-Amb 12/12/01
1,2,3-trimethylbenzene	2.3E-2	2.8E-2	1.1E-2	4.9E-3	1.7E-2	65	7.0E-4
Methanol	3.5E-3	2.1E-2	1.4E-3	3.9E-2	1.6E-2	109	1.8E-4
2-methyl-2-butene	1.4E-2	2.9E-2	1.4E-2	8.4E-3	1.6E-2	54	1.0E-3
n-undecane	2.5E-2	2.2E-2	9.2E-3	6.6E-3	1.6E-2	58	6.9E-4
1,3-dimethylcyclopentane	1.6E-2	2.4E-2	1.6E-2	6.3E-3	1.5E-2	46	1.2E-3
F 113	1.6E-2	2.3E-2	1.3E-2	8.0E-3	1.5E-2	40	1.0E-3
t-2-pentene	1.2E-2	2.5E-2	1.1E-2	7.0E-3	1.4E-2	56	6.9E-4
1,3,5-trimethylbenzene	1.9E-2	2.3E-2	8.8E-3	4.9E-3	1.4E-2	60	6.4E-4
Unidentified C9 paraffins	6.5E-3	1.1E-2	3.5E-3	3.2E-2	1.3E-2	97	1.6E-4
Propanal + F11	1.7E-2	1.5E-2	1.1E-2	1.0E-2	1.3E-2	24	ND
2-methyl-1-butene	1.1E-2	2.2E-2	8.8E-3	6.3E-3	1.2E-2	57	5.7E-4
Isopropylcyclohexane	2.2E-2	1.8E-2	5.3E-3	2.1E-3	1.2E-2	81	6.0E-4
2,5-diemthylhexane	1.5E-2	1.8E-2	9.2E-3	2.8E-3	1.1E-2	60	8.3E-4
Unidentified C8 paraffins	1.3E-2	1.7E-2	1.2E-2	3.8E-3	1.1E-2	48	9.4E-4
Unidentified C10 aromatics	1.4E-2	1.8E-2	6.3E-3	3.8E-3	1.0E-2	62	3.8E-4
p-ethyltoluene	1.2E-2	1.8E-2	7.0E-3	2.4E-3	9.8E-3	67	4.7E-4
1,4-diethylbenzene	1.2E-2	1.5E-2	6.3E-3	4.5E-3	9.7E-3	53	3.2E-4
Unidentified C9 olefins	3.5E-3	2.5E-2	7.4E-3	3.1E-3	9.6E-3	105	2.0E-4
2,2,5-trimethylhexane	1.3E-2	1.5E-2	6.0E-3	1.0E-3	8.8E-3	74	6.8E-4
3,3-dimethylheptane	ND	8.8E-3	ND	ND	< 8.8E-3	n/a	3.1E-5
n-propylbenzene	1.2E-2	1.3E-2	5.6E-3	3.5E-3	8.4E-3	54	4.3E-4
c-2-pentene	7.3E-3	1.4E-2	7.0E-3	5.2E-3	8.3E-3	45	4.2E-4
o-ethyltoluene	1.1E-2	1.3E-2	4.9E-3	1.7E-3	7.7E-3	68	3.5E-4
Limonene	9.6E-3	9.2E-3	7.8E-3	2.8E-3	7.3E-3	43	5.4E-4
Indan	6.9E-3	1.0E-2	6.3E-3	5.2E-3	7.2E-3	31	4.8E-4
4-methylheptane	8.8E-3	1.0E-2	6.3E-3	2.1E-3	6.9E-3	52	5.9E-4
MTBE	4.2E-3	1.0E-2	6.3E-3	6.3E-3	6.8E-3	38	3.3E-4
Octanal	4.2E-3	4.2E-3	6.0E-3	1.1E-2	6.4E-3	52	2.2E-4
n-dodecane	5.8E-3	1.2E-2	4.6E-3	2.1E-3	6.1E-3	69	2.6E-4
Unidentified C10 paraffins	6.9E-3	8.3E-3	4.2E-3	2.4E-3	5.5E-3	48	2.9E-4
Isopropyltoluene	7.3E-3	9.2E-3	3.9E-3	1.4E-3	5.4E-3	64	2.5E-4
Benzaldehyde	5.0E-3	7.1E-3	3.9E-3	4.9E-3	5.2E-3	26	2.1E-4
Isopropylbenzene	7.7E-3	7.9E-3	2.8E-3	1.7E-3	5.0E-3	64	2.3E-4
Mechloroform	ND	ND	1.8E-3	7.7E-3	< 4.7E-3	89	ND
2,4,4-trimethyl-1-pentene	5.0E-3	4.2E-3	3.2E-3	4.9E-3	4.3E-3	20	1.4E-4
Nonene-1	6.9E-3	5.4E-3	2.5E-3	1.4E-3	4.1E-3	63	2.8E-4
1,1-dimethylcyclohexane	5.4E-3	7.1E-3	3.2E-3	3.5E-4	4.0E-3	73	2.6E-4
2-methyl-2-pentene	3.1E-3	8.3E-3	3.5E-3	1.0E-3	4.0E-3	77	2.6E-4
Naphthalene	1.5E-3	1.0E-2	2.5E-3	1.4E-3	4.0E-3	110	1.5E-4
Cyclohexene	4.2E-3	6.3E-3	4.2E-3	1.0E-3	3.9E-3	55	3.7E-4
1,3-butadiene	4.6E-3	7.5E-3	2.1E-3	1.4E-3	3.9E-3	71	2.4E-4
2,4-diemthylhexane	5.8E-3	5.8E-3	2.5E-3	7.0E-4	3.7E-3	69	2.9E-4
1,2,3,5-tetramethylbenzene	5.4E-3	5.8E-3	2.1E-3	1.4E-3	3.7E-3	61	1.7E-4
t-2-hexene	3.5E-3	5.8E-3	4.2E-3	1.0E-3	3.6E-3	55	2.6E-4
3-methyl-1-butene	3.5E-3	6.7E-3	2.5E-3	1.7E-3	3.6E-3	61	1.5E-4
1-hexene	5.4E-3	5.4E-3	2.1E-3	1.4E-3	3.6E-3	59	1.3E-4
Isobutylbenzene	1.9E-3	7.9E-3	3.2E-3	1.0E-3	3.5E-3	87	2.0E-4
1,2,4,5-tetramethylbenzene	4.6E-3	5.4E-3	1.8E-3	2.1E-3	3.5E-3	52	1.8E-4
1,3-diethylbenzene	3.8E-3	5.0E-3	3.5E-3	1.4E-3	3.4E-3	44	2.5E-4
1,2,4-trimethylbenzene	1.9E-3	2.1E-3	8.1E-3	1.4E-3	3.4E-3	94	9.2E-5
Nonanal	2.3E-3	4.2E-3	1.1E-3	5.9E-3	3.4E-3	63	5.1E-5
1,2-diethylbenzene	4.6E-3	5.4E-3	1.8E-3	1.4E-3	3.3E-3	61	1.6E-4
3,6-dimethyloctane	4.6E-3	4.6E-3	1.1E-3	2.4E-3	3.2E-3	55	1.7E-4
3,3-dimethylpentane	3.1E-3	4.2E-3	3.2E-3	1.7E-3	3.0E-3	33	2.9E-4

Table 4-12. VOC Results from Canisters (Site Charlie) (Continued).

Parameter	Value						
Units	mg/dscm					(%)	mg/dscm
Run Number	Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average	RSD	Char-Amb
Date	12/06/01	12/07/01	12/10/01	12/11/01			12/12/01
2,2,3-trimethylbutane	3.1E-3	4.6E-3	2.5E-3	1.7E-3	3.0E-3	41	2.1E-4
Unidentified C11 paraffins	5.0E-3	3.3E-3	1.8E-3	1.0E-3	2.8E-3	63	2.1E-4
2-methyl-1-pentene	1.9E-3	3.8E-3	2.1E-3	3.1E-3	2.7E-3	32	1.4E-4
Cyclopentene	2.7E-3	4.6E-3	2.5E-3	7.0E-4	2.6E-3	61	1.6E-4
trans-3-methyl-2-pentene	2.3E-3	4.2E-3	3.2E-3	7.0E-4	2.6E-3	57	2.1E-4
Unidentified C8 olefins	2.3E-3	2.9E-3	2.5E-3	ND	< 2.6E-3	12	1.3E-4
Isoprene	4.2E-3	3.3E-3	1.8E-3	7.0E-4	2.5E-3	63	1.2E-4
2-propyl toluene	1.2E-3	3.8E-3	2.8E-3	1.4E-3	2.3E-3	54	1.5E-4
beta-pinene	3.8E-3	3.3E-3	1.1E-3	7.0E-4	2.2E-3	71	1.1E-4
t-3-hexene + chloroform	1.9E-3	5.4E-3	3.5E-4	1.0E-3	2.2E-3	103	1.4E-4
1,2,3,4-trimethylbenzene	2.7E-3	2.9E-3	1.4E-3	1.4E-3	2.1E-3	39	8.2E-5
cis-3-methyl-2-pentene	1.5E-3	2.9E-3	2.1E-3	7.0E-4	1.8E-3	52	1.7E-4
t-3-heptene	1.5E-3	1.7E-3	1.4E-3	ND	< 1.5E-3	8	8.2E-5
2,5-dimethylheptane	1.2E-3	2.5E-3	1.8E-3	3.5E-4	1.4E-3	63	9.2E-5
c-2-hexene	1.2E-3	2.5E-3	1.8E-3	3.5E-4	1.4E-3	63	1.1E-4
3-methyloctane	7.7E-4	2.1E-3	7.0E-4	ND	< 1.2E-3	66	5.1E-5
2,3-dimethylhexane	7.7E-4	1.7E-3	1.1E-3	ND	< 1.2E-3	39	1.1E-4
1-methylindan	1.5E-3	1.7E-3	7.0E-4	7.0E-4	1.2E-3	45	5.1E-5
4-methylhexene	7.7E-4	1.7E-3	7.0E-4	ND	< 1.0E-3	51	6.2E-5
4-methyl-1-pentene	1.5E-3	8.3E-4	7.0E-4	ND	< 1.0E-3	44	6.2E-5
sec-butylbenzene	1.5E-3	1.3E-3	3.5E-4	7.0E-4	9.6E-4	56	4.1E-5
2,6-dimethyloctane	ND	ND	7.0E-4	1.0E-3	< 8.8E-4	28	8.2E-5
Unidentified C11 aromatics	7.7E-4	1.3E-3	7.0E-4	7.0E-4	8.6E-4	31	2.1E-5
Octene-1	1.2E-3	8.3E-4	7.0E-4	7.0E-4	8.5E-4	25	2.3E-4
Unidentified C7 olefins	3.8E-4	8.3E-4	1.4E-3	3.5E-4	7.4E-4	67	6.2E-5
1-methylcyclopentene	ND	ND	ND	7.0E-4	< 7.0E-4	n/a	ND
2,6-dimethylheptane	7.7E-4	8.3E-4	3.5E-4	ND	< 6.5E-4	40	3.1E-5
2,4-dimethylheptane	ND	8.3E-4	3.5E-4	ND	< 5.9E-4	57	ND
4,4-dimethylheptane	ND	8.3E-4	3.5E-4	ND	< 5.9E-4	57	2.1E-5
c-3-hexene	ND	8.3E-4	3.5E-4	ND	< 5.9E-4	57	5.1E-5
Indene	3.8E-4	4.2E-4	ND	ND	< 4.0E-4	6	2.1E-5
Total Identified NMHC	4.9E+0	9.7E+0	4.7E+0	2.6E+0	5.5E+0	55	3.4E-1
Unidentified	6.8E-1	9.5E-1	4.3E-1	3.0E-1	5.9E-1	49	3.3E-2
Identified oxygenated (ppbv	4.6E-1	5.4E-1	1.7E-1	2.5E-1	3.5E-1	50	7.5E-2
Identified other compounds	6.4E-2	7.1E-2	4.7E-2	3.8E-2	5.5E-2	28	4.7E-3

ND - Not Detected

n/a- not applicable. Less than two runs within detectable limits.

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

Parameter	Value							
Units	mg/dscm					%	mg/dscm	
Run	Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average	RSD	Char-Amb	MDL
Date	12/06/01	12/07/01	12/10/01	12/11/01			12/12/2001	(2)
Al	2.0E-03	1.0E-2	ND	ND	< 6.1E-3	96	3.3E-4	1.8E-4
Ba	ND	ND	ND	ND	ND	n/a	3.3E-5	9.3E-4
Br	2.9E-05	3.5E-5	ND	ND	< 3.2E-5	14	7.3E-6	1.8E-5
Ca	3.7E-03	1.6E-2	7.9E-4	5.9E-4	5.2E-3	138	7.7E-4	8.1E-5
Cl	5.5E-04	2.4E-3	4.3E-4	ND	< 1.1E-3	99	7.3E-4	1.8E-4
Co	4.8E-05	8.6E-5	ND	ND	< 6.7E-5	40	3.1E-6	1.6E-5
Cr	1.7E-04	5.0E-4	9.3E-5	6.0E-5	2.1E-4	98	5.5E-6	3.4E-5
Cu	3.0E-04	7.3E-4	7.2E-5	2.8E-5	2.8E-4	114	1.3E-5	2.0E-5
Fe	6.9E-03	2.3E-2	1.8E-3	1.2E-3	8.2E-3	124	9.2E-4	2.7E-5
K	1.5E-03	5.2E-3	2.8E-4	2.2E-4	1.8E-3	131	2.6E-4	1.1E-4
Mg	3.7E-04	1.9E-3	2.5E-4	ND	< 8.3E-4	109	6.2E-5	(1)
Mn	1.7E-04	5.2E-4	4.9E-5	3.1E-5	1.9E-4	118	1.7E-5	2.9E-5
Mo	ND	7.4E-5	ND	ND	< 7.4E-5	n/a	1.6E-6	4.9E-5
Na	3.8E-03	7.2E-4	3.0E-3	6.4E-4	2.0E-3	79	9.0E-4	(1)
Ni	1.1E-04	3.6E-4	7.8E-5	4.3E-5	1.5E-4	97	7.0E-6	1.6E-5
P	ND	1.6E-4	ND	ND	< 1.6E-4	n/a	ND	1.0E-4
Pb	1.0E-04	1.9E-4	5.2E-5	ND	< 1.1E-4	60	1.6E-5	5.4E-5
Rb	ND	2.2E-5	ND	ND	< 2.2E-5	n/a	1.1E-6	1.8E-5
S	5.3E-03	4.2E-3	9.6E-4	1.7E-3	3.0E-3	68	5.4E-4	9.0E-5
Si	8.1E-03	3.4E-2	3.2E-3	1.4E-3	1.2E-2	130	1.5E-3	1.1E-4
Sr	4.0E-05	1.4E-4	ND	ND	< 8.9E-5	78	6.8E-6	2.0E-5
Ti	5.5E-04	1.5E-3	1.1E-4	9.1E-5	5.6E-4	117	6.1E-5	5.2E-5
V	4.6E-05	1.2E-4	4.9E-5	ND	< 7.1E-5	58	1.3E-5	4.5E-5
Zn	8.0E-04	1.8E-3	1.9E-4	1.4E-4	7.3E-4	105	8.9E-5	2.0E-5
Zr	1.0E-04	5.7E-5	ND	ND	< 8.0E-5	40	2.5E-6	3.1E-5

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

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

MDL- Method Detection Limit

ND- Not detected

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

RSD- Relative standard deviation

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

Run		Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average	RSD (%)	Char-DSB	Char-Amb
Date	Units	12/06/01	12/07/01	12/10/01	12/11/01			12/05/01	12/12/01
Formaldehyde	mg/dscm	9.0E-2	1.3E-1	8.0E-2	4.1E-2	8.6E-2	43	4.2E-2	4.7E-3
	ppb	72	106	64	33	69	43	34	4
Acetaldehyde	mg/dscm	1.2E-1	1.7E-1	5.8E-2	7.1E-2	1.0E-1	48	1.7E-2	2.7E-3
Acetone	mg/dscm	4.8E-1	4.8E-1	ND	1.7E-1	< 3.7E-1	48	1.5E-1	6.2E-3
Propionaldehyde	mg/dscm	1.8E-2	2.7E-2	1.2E-2	1.3E-2	1.7E-2	40	ND	7.5E-4
MEK	mg/dscm	3.5E-2	5.8E-2	2.4E-2	2.5E-2	3.5E-2	45	ND	1.6E-3
Butyraldehyde	mg/dscm	ND	2.2E-2	ND	ND	< 2.2E-2	n/a	5.8E-3	6.4E-4
Benzaldehyde	mg/dscm	1.6E-2	2.6E-2	8.8E-3	1.2E-2	1.6E-2	47	ND	6.8E-4
Glyoxal	mg/dscm	3.2E-2	2.2E-2	1.0E-2	1.1E-2	1.9E-2	55	1.2E-2	8.9E-4
M-Tolualdehyde	mg/dscm	ND	ND	ND	9.6E-3	< 9.6E-3	n/a	ND	ND
Hexanaldehyde	mg/dscm	ND	ND	1.4E-2	1.2E-2	< 1.3E-2	9	ND	ND

ND - not detected
n/a- not applicable; only one run within detectable limits.
RSD - relative standard deviation

inlet was capped and an ambient sample was taken through the inlet filters and the dilution sampler; the sampler blank data are presented as in-stack equivalents, using the average dilution ratio. Sampler blank in-stack equivalent concentrations of formaldehyde are within an order of magnitude of the stack sample concentrations, indicating the stack sample results may be subject to positive bias. Formaldehyde concentrations detected in the second cartridge range from 9 to 28 percent of the total, indicating that some breakthrough may have occurred.

Gaseous PM2.5 Precursors

Gaseous PM2.5 precursors characterized in this program include SO_2, NO_X, NH_3, and VOC with carbon number greater than 7. VOC results were presented earlier (Table 4-11). Gaseous NH_3 was captured on a citric acid-impregnated cellulose-fiber filter downstream of the quartz filter used for ions and OC/EC analysis. Sulfur dioxide was captured on a potassium carbonate impregnated cellulose-fiber filter downstream of a quartz filter (Table 4-15). Note, SO_3 and H_2SO_4(g) that may be present in the sample also would be captured on the potassium carbonate filter, but these are typically very minor constituents in flue gas exhaust (typically 2-4 percent of SO_2 concentration). NH_3 was also measured using SCAQMD Method 207.1 (Table 4-15). NH_3 measurements by both methods showed NH_3 concentrations below 1 ppm, far below the permit limit of 20 ppm. These results are consistent with previous tests on this unit. The ammonia levels measured by the dilution sampler are approximately four times higher than the SCAQMD Method 207.1 results, on average. This difference is probably due to the higher resolution of the dilution sampler method, which has a detection limit that is an order of magnitude lower. NO_x was measured by a continuous emissions monitor and is expressed as NO_2.

Table 4-15. Secondary PM2.5 Gaseous Precursor Results (Site Charlie).

Parameter	Units	Value						
Run Number	-	Char-Run 1	Char-Run 2	Char-Run 3	Char-Run 4	Average	RSD	Char-Amb
Date	-	12/6/2001	12/7/2001	12/10/2001	12/11/2001		(%)	12/12/2001
Ammonia (DS)	mg/dscm	5.4E-1	1.2E+0	4.2E-1	3.1E-1	6.1E-1	62	2.2E-2
	ppm	7.7E-1	1.6E+0	6.0E-1	4.4E-1	8.6E-1	62	3.2E-2
	lb/hr	1.3E-1	2.8E-1	1.0E-1	7.4E-2	1.5E-1	62	n/a
Ammonia (SCAQMD 207.1)	mg/dscm	2.3E-1	1.4E-1	1.1E-1	1.1E-1	1.5E-1	39	--
	ppm	3.2E-1	1.9E-1	1.5E-1	1.5E-1	2.0E-1	39	--
	lb/hr	6.0E-2	3.0E-2	3.0E-2	3.0E-2	4.0E-2	41	--
Sulfur Dioxide (DS)	mg/dscm	7.7E-1	5.9E-1	3.0E-1	2.8E-1	4.8E-1	48	1.2E-2
	ppm	2.9E-1	2.2E-1	1.1E-1	1.1E-1	1.8E-1	48	4.7E-3
	lb/hr	1.9E-1	1.4E-1	7.3E-2	6.8E-2	1.2E-1	50	n/a
NOx (as NO2) (CEMS)	mg/dscm	1.6E+1	1.8E+1	1.8E+1	1.7E+1	1.7E+1	6	--
	ppm	8.2E+0	9.3E+0	9.2E+0	8.7E+0	8.8E+0	6	--
	lb/hr	3.9E+0	4.4E+0	4.2E+0	4.0E+0	4.1E+0	6	--

n/a - not applicable
CEMS - Continuous emissions monitoring system
DS - Dilution sampler
ND - not detected
RSD- Relative standard deviation

Section 5

EMISSION FACTORS AND SPECIATION PROFILES

Emission factors were determined by dividing the emission rate, in lb/hr, by the measured heat input, in MMBtu/hr, to give pounds per million British thermal units (lb/MMBtu). Heat input is the product of the measured fuel flow rate and the fuel heating value given by the plant monitor. Average emission factors were determined by averaging detected data. Undetected data were excluded.

UNCERTAINTY

An uncertainty analysis was performed to determine the 95 percent confidence interval and to estimate the upper limit of the measured emission factor and the mass speciation results (American Society of Mechanical Engineers (ASME), 1990). In the tables that follow, the reported results, the total uncertainty (at the 95% confidence level), a 95 percent confidence upper bound, and the number of detected sample runs are given for each of the substances of interest. The total uncertainty represents the 95 percent confidence interval based on a two-tailed Student "t" distribution. The 95 percent confidence upper bound estimate is based on the single-tailed Student "t" distribution at the 95 percent confidence level.

EMISSION FACTORS

Table 5-1 presents emission factors for primary emissions, including FPM and CPM as measured with in-stack methods, and PM2.5, elements and ions as measured on the dilution sampler filters. The dilution sampler data exclude substances with only one detected run and substances with average concentrations less than the dilution sampler blank or field blank levels. FPM includes all PM captured in the in-stack cyclones, probe and filter with Method PRE-4. Total CPM is blank corrected in accordance with Method 202 guidelines. The average emission factor for total PM2.5 (including CPM) measured using in-stack impinger train methods is approximately an order of magnitude higher than the emission factor for PM2.5 by the dilution sampler. As noted previously, this difference is believed to be largely due to sampling and analytical artifacts associated with the CPM measurement methods (i.e., conversion of SO_2 to CPM in the impinger

Table 5-1. Primary Emissions – Particulate Mass, Elements, and Ions (Site Charlie).

		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	No. of Detected Sample Runs
Particulate Mass	Organic CPM (Method 202)	2.8E-4	n/a	n/a	1
	Inorganic CPM (Method 202)	9.2E-4	48	1.3E-3	4
	Total CPM (Method 202)	1.0E-3	50	1.4E-3	4
	Total Filterable PM (Method PRE-4/202 train)	2.3E-4	82	3.8E-4	4
	Filterable PM10 (Method PRE-4/202 train)	1.0E-4	110	1.9E-4	4
	Filterable PM2.5 (Method PRE-4/202 train)	5.5E-5	170	1.2E-4	4
	PM2.5 mass (Dilution System)	< 1.6E-4	210	3.9E-4	3
Elements (Dilution Sampler)	Si	9.8E-6	210	2.5E-5	4
	Fe	6.8E-6	200	1.7E-5	4
	Ca	4.3E-6	220	1.1E-5	4
	K	1.5E-6	210	3.8E-6	4
	Cl	< 9.5E-7	250	2.5E-6	3
	Mg	< 6.9E-7	270	2.0E-6	3
	Zn	6.1E-7	170	1.4E-6	4
	Ti	4.7E-7	190	1.1E-6	4
	Cu	2.3E-7	180	5.5E-7	4
	Mn	1.6E-7	190	3.8E-7	4
	Pb	< 9.5E-8	150	1.9E-7	3
	Al	< 5.1E-6	860	2.7E-5	2
	Co	< 5.6E-8	640	3.7E-7	2
	Sr	< 7.4E-8	700	3.3E-7	2
	Zr	< 6.6E-8	360	1.8E-7	2
Ions (Dilution Sampler)	NO_3^-	< 6.2E-6	130	1.2E-5	3
	Soluble Na	7.4E-7	130	1.5E-6	4
	NH_4^+	< 3.2E-6	420	9.9E-6	2

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

train and over saturation of vapor phase species leading to excessive nucleation compared to the stack plume, discussed further in Section 7). As a result of this hypothesis, the emission factor derived from the dilution sampler results is considered more representative of the source at this time. However, the relatively high uncertainty of the dilution sampler result, primarily due to the imprecision in this limited data set and the low emission rates, indicates the need for caution in applying the dilution sampler PM2.5 emission factor derived from this single test. Other emission factors with an uncertainty greater than 100 percent shown in Table 5-1 also should be used with appropriate caution. Further development work is being undertaken, and future results from a pilot scale evaluation and subsequent field tests should help to validate this hypothesis.

Table 5-2 presents emission factors for OC, EC, total carbon, and SVOCs as measured by the dilution sampler. The data exclude substances with only one detected run, uncertainty greater than 100%, and average concentrations less than the dilution sampler blank or field blank levels.

Table 5-2. Primary Emissions – Carbon and SVOCs (Site Charlie).

Substance		Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	No. of Detected Sample Runs
Organic Carbon*		1.9E-4	93	3.2E-4	4
Elemental Carbon	<	3.6E-5	95	5.9E-5	3
Total Carbon**		2.2E-4	96	3.7E-4	-
Semi-Volatile Organic Compounds					
3-Methylbiphenyl		1.6E-6	85	2.6E-6	4
4-Methylbiphenyl		6.9E-7	88	1.2E-6	4
Acenaphthenequinone		3.9E-7	61	5.8E-7	4
C-dimethylphenanthrene	<	1.0E-7	48	1.4E-7	3
Pyrene		6.5E-8	86	1.1E-7	4
B-MePy/MeFl	<	2.8E-8	97	4.9E-8	3
Benzo(e)pyrene		2.2E-8	89	3.9E-8	4
D-MePy/MeFl	<	1.7E-8	80	3.0E-8	3
A-methylphenanthrene	<	1.0E-7	81	1.5E-7	2
Backup Filer OC***		1.3E-4	59	1.8E-4	4

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

* OC measurements are subject to a potential positive bias from adsorption of VOC species. Refer to Section 7 for further discussion of OC artifact.

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

*** OC measured on back up filter. Refer to Section 7 for further discussion.

3-methylbiphenyl has the highest value, with an emission factor of 1.6×10^{-6} lb/MMBtu. SVOC emission factors are extremely low. The average sum of all SVOCs (including compounds excluded from Table 5-2 but listed in Table 4-10) equals 3.1×10^{-5} lb/MMBtu; the carbon mass associated with this SVOC sum comprises approximately 12 percent of the total OC. The high variability among runs and low emission rates for many of the SVOC compounds result in high uncertainties for their respective emission factors. The average sum of the SVOCs listed in Table 5-2 is 3.0×10^{-6} lb/MMBtu . As noted in Section 4, the quartz filters used for OC/EC analysis have the potential for positive OC bias due to absorption of VOCs on the filter. A backup quartz filter sampled behind the TMF to indicate the magnitude of this absorptive bias showed a high concentration of OC, on average approximately 67 percent of that in the sample. Please refer to section 7 for further discussion of the OC bias.

Emission factors for VOCs with carbon number greater than seven, which are secondary organic aerosol precursors, were obtained from the Tenax samples (Table 5-3). Known Tenax degradation products (benzaldehyde, benzoic acid, hexadecanoic acid, phenol and acetophenone) are not included on the table because the potential for significant bias is high. The data also exclude substances with only one detected run, uncertainty greater than 100%, and average concentrations less than the dilution sampler blank or field blank levels. All VOCs are present at low levels, with m- & p-xylenes and nonane being the most abundant: 4.9×10^{-5} lb/MMBtu and 3.3×10^{-5} lb/MMBtu, respectively. The average sum of all VOCs (including compounds excluded from Table 5-3 but listed in Table 4-11) equals 3.5×10^{-3} lb/MMBtu. The high variability among runs and low emission rates for many of the VOC compounds result in high uncertainties for their respective emission factors. The average sum of the VOCs listed in Table 5-3 is 2.2×10^{-4} lb/MMBtu .

Table 5-3. Secondary Organic Aerosol Precursors (VOCs) – Tenax (Site Charlie).

Substance	Average (lb/MMBtu	Uncertainty	95% Confidence Upper Bound	No. of Detected Sample Runs
m & p-xylene	4.9E-5	94	8.3E-5	4
Nonane	3.3E-5	75	5.1E-5	4
Decane	2.1E-5	96	3.6E-5	4
o-xylene	1.4E-5	91	2.4E-5	4
1,2,4-trimethylbenzene	1.3E-5	99	2.3E-5	4
m-ethyltoluene	1.2E-5	86	2.0E-5	4
Ethylbenzene	1.1E-5	85	1.8E-5	4
Dodecane	8.4E-6	98	1.5E-5	4
p-ethyltoluene	6.7E-6	97	1.2E-5	4
Naphthalene	5.2E-6	96	8.9E-6	4
1-methylindan	6.2E-6	59	8.8E-6	3
3-methyloctane	5.5E-6	78	8.8E-6	4
1,3,5-trimethylbenzene	5.0E-6	84	8.2E-6	4
o-ethyltoluene	4.6E-6	71	6.9E-6	3
Tridecane	4.3E-6	72	6.7E-6	4
Propylbenzene	3.9E-6	73	6.0E-6	4
2-methylnaphthalene	3.3E-6	80	5.1E-6	3
1,3-dichlorobenzene	2.9E-6	76	4.5E-6	3
2-methyloctane	3.3E-6	48	4.4E-6	3
Dimethyloctane	2.4E-6	73	3.6E-6	3
1-methylnaphthalene	1.4E-6	37	1.7E-6	3
B-dimethylindane	4.2E-6	55	5.4E-6	2

Emission factors for VOCs with carbon number greater than two obtained from the canister samples are presented in Table 5-4. The data exclude substances with only one detected run, uncertainty greater than 100%, and average concentrations less than the dilution sampler blank level. All VOCs are present at low levels, with toluene being the most abundant (2.7×10^{-4} lb/MMBtu). The average sum of all VOCs (including compounds excluded from Table 5-4 but listed in Table 4-12) equals 5.5×10^{-3} lb/MMBtu. The high variability among runs and low emission rates for many of the VOC compounds result in high uncertainties for their respective emission factors. The average sum of the VOCs listed in Table 5-3 is 7.6×10^{-4} lb/MMBtu .

Carbonyl emission factors are presented in Table 5-5. Acetone is used to clean the dilution tunnel; thus, acetone measurements are not considered reliable and are excluded from the table. The data also exclude substances with only one detected run, uncertainty greater than 100%, and average concentrations less than the dilution sampler blank level. Formaldehyde and acetaldehyde are present at approximately the same levels, 7.2×10^{-5} lb/MMBtu and 8.6×10^{-5} lb/MMBtu, respectively. The high variability among runs and low emission rates for many of the carbonyls result in high uncertainties for their respective emission factors. The emission factor for formaldehyde (7.2×10^{-5} lb/MMBtu) is higher than that found in the found in the EPA FIRE 4.23 database (5.5×10^{-5} lb/MMBtu) for a process gas-fired process heater with no emission controls but within the 95 percent confidence interval for the Charlie emission factor; therefore, the Charlie and EPA FIRE emission factors are likely not significantly different .

Emission factors for NO_X, SO_2 and NH_3 are presented in Table 5-6. The NO_X data are derived from the plant CEMS data, while the SO_2 data are derived from dilution sampler measurements and the NH_3 data are derived from dilution sampler measurements and SCAQMD 207.1 measurements. The plant CEMS was assumed to have a bias of 10 percent, which is the relative accuracy required by local regulations, for uncertainty calculations.

Table 5-4. VOCs – Canisters (Site Charlie).

Substance		Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	No. of Detected Sample Runs
Toluene		2.7E-4	88	4.5E-4	4
Methylene chloride		1.7E-4	61	2.6E-4	4
Chloromethane		1.2E-4	45	1.6E-4	4
Identified other compounds		4.6E-5	51	6.5E-5	4
F 12		2.6E-5	67	4.0E-5	4
n-nonane		2.4E-5	98	4.1E-5	4
Chlorobenzene		1.6E-5	99	2.8E-5	4
n-undecane		1.3E-5	96	2.3E-5	4
1,3,5-trimethylbenzene		1.1E-5	99	2.0E-5	4
2,5-diemthylhexane		9.4E-6	100	1.7E-5	4
1,4-diethylbenzene		8.0E-6	88	1.3E-5	4
n-propylbenzene		7.0E-6	90	1.2E-5	4
Limonene		6.1E-6	73	9.6E-6	4
Unidentified C10 paraffins		4.6E-6	81	7.4E-6	4
1-hexene		3.0E-6	98	5.2E-6	4
1,2,4,5-tetramethylbenzene		2.9E-6	87	4.8E-6	4
1,3-diethylbenzene		2.9E-6	74	4.5E-6	4
3,6-dimethyloctane		2.6E-6	91	4.5E-6	4
2-methyl-1-pentene		2.3E-6	57	3.3E-6	4
trans-3-methyl-2-pentene		2.2E-6	94	3.7E-6	4
Unidentified C8 olefins	<	2.1E-6	41	2.8E-6	3
2-propyl toluene		1.9E-6	89	3.2E-6	4
1,2,3,4-trimethylbenzene		1.8E-6	67	2.7E-6	4
t-3-heptene	<	1.3E-6	34	1.7E-6	3
1-methylindan		9.6E-7	77	1.5E-6	4
sec-butylbenzene		8.0E-7	92	1.4E-6	4
Unidentified C11 aromatics		7.1E-7	56	1.0E-6	4

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

Table 5-5. Carbonyl Emission Factors (Site Charlie).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	No. of Detected Sample Runs
Formaldehyde	7.2E-5	75	1.1E-04	4
Acetaldehyde	8.6E-5	86	1.5E-04	4
Propionaldehyde	1.4E-5	72	2.3E-05	4
MEK	3.0E-5	82	4.9E-05	4
Benzaldehyde	1.3E-5	91	2.3E-05	4
Glyoxal	1.5E-5	93	2.7E-05	4
Hexanaldehyde	< 1.1E-5	93	1.7E-05	2

Table 5-6. Secondary PM2.5 Precursors- NO_X, NH_3 and SO_2 (Site Charlie).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	No. of Detected Sample Runs
NH_3 (DS)	5.1E-4	99	8.8E-4	4
NH_3 (SCAQMD 207.1)	1.2E-4	65	1.8E-4	4
SO_2 (DS)	4.0E-4	78	6.4E-4	4
NOx as NO_2 (CEMS)	1.4E-2	18	1.7E-1	4

DS - dilution sampler

CEMS - continous emissions monitoring system.

PM2.5 SPECIATION PROFILES

Dilution Sampler

The speciation profile for PM2.5, based on dilution sampler results, is given in Table 5-7. This table includes all results from the ED-XRF analysis of the dilution sampler TMFs (Table 5-1), the ion analysis of the dilution sampler quartz filters (Table 5-1) and the OC/EC analysis of the dilution sampler quartz filters (Table 5-2) with mass fractions of 0.01% or greater. The mass fractions presented are the ratio of the emission factor of the emitted compound over the sum of the species emission factors, assuming the highest stable oxide for the metallic species and correcting OC for hydrogen and oxygen in SVOCs.

The average emission factor for the sum of species ($2.9x10^{-4}$ lb/MMBtu) is comparable to the average emission factor for total PM2.5 mass ($1.6x10^{-4}$ lb/MMBtu, measured gravimetrically). The difference between the two emission factors is less than the 95% confidence interval uncertainties for both the PM2.5 and the sum of species. Any difference is most likely due to the

Table 5-7. Speciation Profile for Primary Emissions- Dilution Sampler Results (Site Charlie).

Substance	Average Mass Fraction (1) (2) (%)	Uncertainty (%) (a)	95% Confidence Upper Bound (%) (b)
OC*	74	28	89
EC	8.6	120	16
Si	5.6	140	11
Fe	2.6	130	5.1
Ca	2.0	170	4.3
NO3-	1.4	110	2.6
Al	1.0	250	2.9
K	0.69	150	1.5
Soluble Na	0.57	51	0.80
NH4+	0.35	230	0.98
Zn	0.25	95	0.43
Ti	0.21	140	0.43
Mn	0.09	120	0.16
Cu	0.08	120	0.15
Pb	0.02	120	0.05
Sr	0.01	230	0.03
Zr	0.01	200	0.02
Co	0.01	600	0.06
Backup Filter OC **	58	81	93

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

** OC measured on a "backup" quartz fiber filter placed downstream of Teflon membrane filter - not included in sum of species calculations. Refer to Sections 6 & 7 for further discussion.

1- Mass fraction is emission factor (EMF) of species divided by EMF of sum of species - calculated from highest stable oxide form of elements for runs 1 - 4 and OC corrected for C, H in SVOC. NDs assumed to be zero for speciation calculations. The average sum of species EMF (3.0E-4 lb/MMBtu) is greater than average PM2.5 EMF (1.6E-4 lb/MMBtu); the difference is less than the 95% CI of the measurements.

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

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

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

bias associated with the different analytical methods used to determine the speciation of the mass versus the gravimetric analysis used to measure total PM2.5 mass. In addition, two different types of filters were used: TMFs were used for the elemental analysis and PM mass, while quartz filters were used for OC/EC analysis and ionic analysis. It is possible, but unlikely, that variations in particle deposition occurred between the different filters, resulting in a bias.

Figure 5-1 shows the data presented in Table 5-7. The majority of the mass (73 percent) is composed of OC, with EC being the next most abundant constituent (9.1 percent). S, Cl^-, Na and Mg were all measured at detectable levels, but are not included in the sum of species. S and Cl^- were not included to avoid duplicated counts with $SO_4^=$ and Cl. Na and Mg were not included because there results were semi-quantitative due to analytical limitations. The error bars on the chart show the 95% confidence upper bounds for the mass fractions. As noted previously, the quartz filters used for OC/EC analysis have the potential for positive OC bias due to absorption of VOCs on the filter. A backup quartz filter sampled behind the TMF to indicate the magnitude of this absorptive bias showed an average an average backup filter OC concentration equal to approximately 57 percent of the sum of species. Please refer to section 7 for further discussion of the OC VOC adsorption bias. These data were collected using a dilution sampler; therefore, these speciation profiles should only be applied to PM2.5 mass results measured with a dilution sampler. They should not be applied to PM emissions factors measured by other methods (e.g. hot filter, wet impinger).

<u>Organic Aerosols</u>

Table 5-8 shows the organic aerosol speciation profile, expressed as a mass fraction. This table includes all results from Table 5-2 with mass fractions of 0.01% or greater. Mass fraction are determined by dividing the average emission factor of the carbon mass in the emitted SVOC by the average emission factor of total OC, both in units of lb/MMBtu. As noted previously, the speciated OC, measured as SVOCs (including compounds excluded from Table 5-2), accounts for approximately 12 percent of the average total OC as measured on the quartz filters. The most abundant fraction of the speciated organic aerosol is 3-methylbiphenyl (1.2%). This profile is calculated using the OC emission factor and thus would be impacted by the OC VOC adsorption bias. Please refer to section 7 for further discussion of the OC VOC adsorption bias.

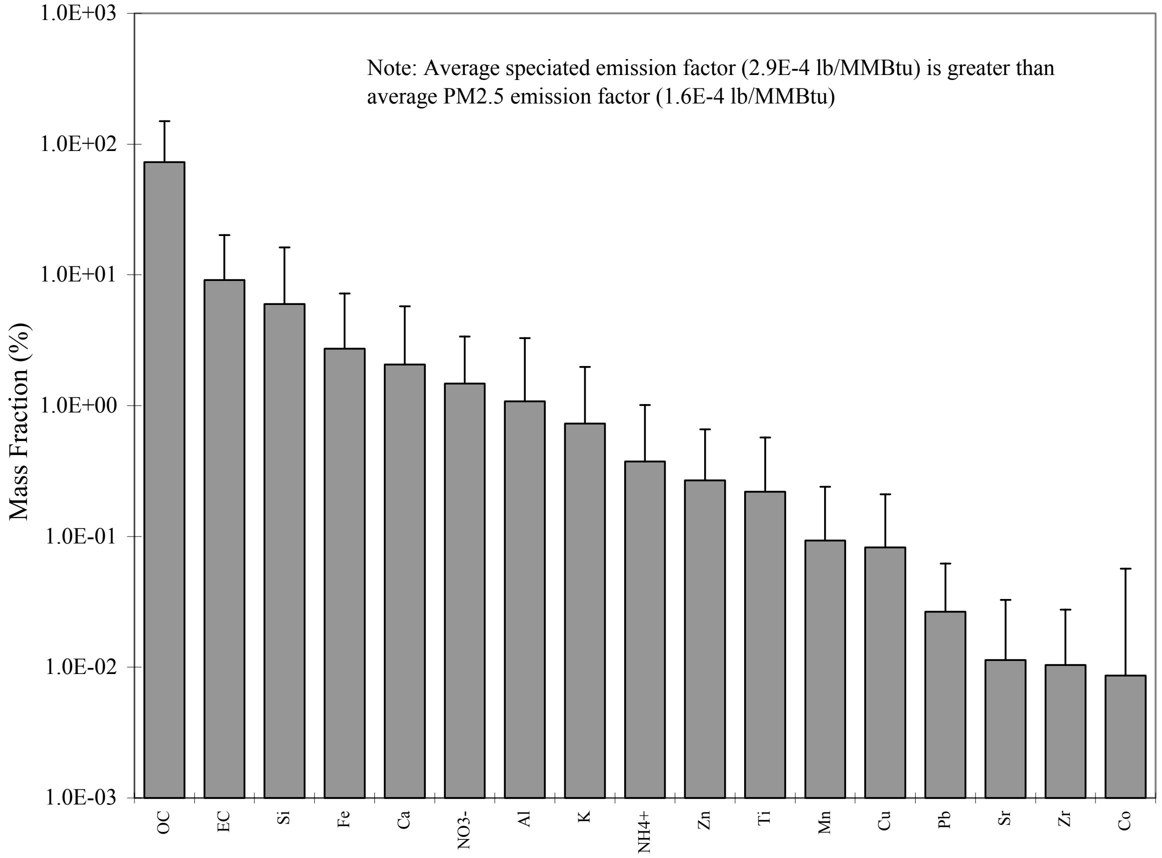


Figure 5-1. PM2.5 Speciation, as Measured by the Dilution Sampler (Site Charlie).

Method PRE-4/202

Table 5-9 shows the speciation profile of the PM2.5 mass as measured by Method PRE-4/202. Mass fraction is the ratio of the measured quantity to the total PM2.5 mass (FPM and CPM). In this table, total CPM has been subdivided into its respective organic and inorganic fractions for illustrative purposes. Inorganic CPM has been further subdivided to show the amount of PM2.5 mass accounted for by $SO_4^=$.

The data from Table 5-9 are shown in Figure 5-2. As can be seen from the figure, most of the PM2.5 mass comes from CPM (94 percent). The large majority of CPM is contained in the inorganic fraction, which accounts for 85 percent of the total PM2.5 mass.

Table 5-8. Organic Aerosol Speciation Profile (Site Charlie).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%) (a)	95% Confidence Upper Bound (%) (b)
3-Methylbiphenyl	1.2	140	2.4
4-Methylbiphenyl	0.50	150	1.1
Acenaphthenequinone	0.18	44	0.25
A-trimethylnaphthalene	0.15	130	0.29
C-dimethylphenanthrene	0.04	150	0.08
Pyrene	0.04	120	0.07
Benzo(e)pyrene	0.01	98	0.02
B-MePy/MeFl	0.01	130	0.02
D-MePy/MeFl	0.01	180	0.02

1- SVOC carbon mass expressed as a percent of total organic carbon mass.

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

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

Table 5-9. Speciation Profile for PM2.5 Measured by Method PRE-4/202 (Site Charlie).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound
Filterable PM2.5	5.9E+0	180	1.3E+1
Total Condensable PM	9.4E+1	68	1.4E+2
Organic CPM	5.7E+0	n/a	n/a
Inorganic CPM	8.5E+1	66	1.3E+2
Sulfate (as $SO_4^{=}$)	5.9E+1	63	8.7E+1

(1) Mass fraction is percent of total PM2.5 (filterable and condensable).

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

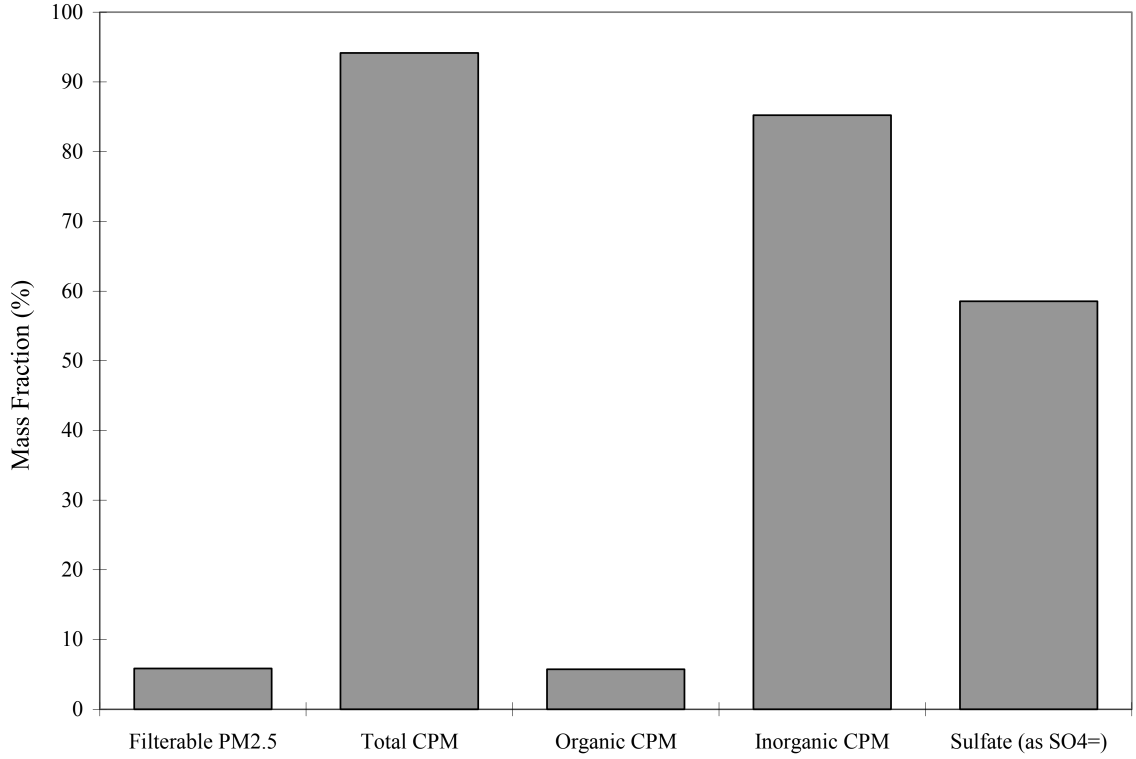


Figure 5-2. Method PRE-4/202 PM2.5 Mass Speciation Profile (Site Charlie).

Section 6

QUALITY ASSURANCE

SAMPLE STORAGE AND SHIPPING

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

METHOD 202 AND METHOD PRE-4 SAMPLES

Gravimetric Analysis

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

Table 6-1 presents the results of the methylene chloride, water and acetone rinse blanks. The acetone blank values were used to correct the EPA Method PRE-4 particulate data. Results of the filter blank weights are also presented in Table 6-2. All negative filter weights were treated as a zero in final calculations.

Table 6-1. Filter and Reagent Blank Results.

Sample	Volume (mL)	Mass (mg)
Method 202 Water Reagent Blank	500	3.9
Method 202 Dichloromethane Reagent Blank	250	ND (1)
Acetone Recovery Blank	67	0.6
Method 202 Impinger Filter Blank	n/a	0.49
Method PRE-4 Filter Blank	n/a	0.02
Dilution Tunnel Filter Field Blank	n/a	-0.016
Dilution Tunnel Filter Trip Blank	n/a	-0.025

(1) Detection limit = 1 mg

An analysis of the acetone rinse blanks is presented in Table 6-2. The particulate mass minimum detection limit was calculated as three times the standard deviation of the results of the field blank acetone rinses and the acetone recovery blank. The resulting minimum detection limit of approximately 0.7 mg further indicates that the filterable particulate levels at the heater were near detection limits. Therefore, the filterable particulate data from Method PRE-4 presented in Section 5 should be considered qualitative.

Table 6-2. Results from Acetone Blank Rinses.

Sample Fraction	Volume (mL)	Mass (mg)
PM10 cyclone catch rinse	16	0.6
PM2.5 cyclone catch rinse (2.5-10 µm)	23	0.5
<PM2.5 rinse (<2.5 µm)	23	0.5
Acetone Recovery Blank	67	0.6
Method 202 Impinger Filter Blank	n/a	0.49
Method PRE-4 Filter Blank	n/a	0.02
Detection Limit (3*standard deviation)		0.7

Inorganic Residue Analysis

A reagent blank was analyzed in the same manner as the Method 202 field samples, as described previously. The results are presented in Table 6-3. Ba, S, Zn and sulfate are the only compounds with stack concentrations more than an order of magnitude greater than the reagent blank concentration. The average sample concentrations of B and Si are less than the concentrations in the reagent blank; ortho-phosphate, Be, Cr, Co, Pb, Mo, P, K, Ag, Tl, Sn, Ti, V and Zr average sample concentrations are approximately equal to their blank concentrations.

Table 6-3. Method 202 Water Reagent Blank Results (mg/dscm).

Compound		mg/dscm
Fluoride		2.6E-3
Chloride		7.7E-2
Nitrate (as N)		4.4E-2
ortho-phosphate (as P)		1.4E-2
Sulfate (as SO4=)		2.6E-2
Al	<	9.1E-4
Ba	<	3.0E-5
Be	<	3.0E-5
B		4.1E-3
Cd	<	6.1E-5
Ca		5.0E-2
Cr	<	1.2E-4
Co	<	3.0E-4
Cu	<	1.8E-4
Fe	<	6.1E-4
Pb	<	6.1E-4
Mg		5.3E-3
Mn	<	1.5E-4
Mo	<	1.5E-4
Ni	<	6.1E-4
P	<	1.8E-3
K	<	3.0E-2
Si		6.9E-2
Ag	<	3.0E-4
Na		1.9E-1
Sr		2.7E-4
S		1.4E-2
Tl	<	1.8E-3
Sn	<	1.5E-3
Ti	<	3.0E-4
V	<	3.0E-4
Zn	<	3.0E-4
Zr	<	3.0E-4

< - below limit of quantitation (Detection limit x 3.33)

DILUTION SAMPLER SAMPLES

Dilution sampler blank, field blank, Trip blank and ambient air quality assurance (QA) samples were collected and analyzed. The dilution sampler blanks were collected after the emissions sampling, before the dilution sampler was cleaned. The dilution sampler blanks were conducted by drawing filtered air through the dilution sampler and collecting samples per the normal procedures. Dilution sampler blank results are an indication of the background levels in the dilution sampler, likely from deposition of species on dilution sampler surfaces during sampling or HEPA and/or carbon filter breakthrough. Field blanks were collected by setting up and breaking down the dilution sampler sampling equipment without drawing gas through the sampling media. Field blank results are an indication of the species collected on the sampling media during the handling and transport of the materials. Trip blanks are sampling media that are shipped from the lab to the test site and back but are not opened. Trip blank results are an indication of the species collected on the sampling media during the transport of the materials. Ambient air samples were collected by drawing air directly into the sampling media. The dilution sampler is bypassed. The following tables and discussion present the results of the dilution sampler blank, field blank, trip blank, and ambient air samples. The dilution sampler blank, field blank, and trip blank are presented as in-stack equivalents using the average dilution factor of the sampling runs. Ambient air samples are as measured. The average of the test series is also included in each table. Each blank is compared to the 95 percent confidence lower bound of the average. The procedures used for calculating the confidence intervals were described in Section 5. If the blank or ambient level is greater than the 95 percent lower bound the data is flagged. Flags suggest the field data may not be significantly different than the blank data. Further discussion on these results is presented in Section 7.

Gravimetric Analysis

Prior to testing, unused filters were stored for at least one month in a controlled environment, followed by one week of equilibration in the weighing environment, to achieve stable filter tare weights. New and used filters were equilibrated at 20 ±5°C and a relative humidity of 30 ±5 percent for a minimum of 24 hours prior to weighting. Weighing was performed on a Cahn 31 electro-microbalance with ±1 microgram sensitivity. The electrical charge on each filter was neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance was calibrated with a 20 mg Class M weight and the tare was set prior to weighing each batch of filters. After every 10 filters were weighed, the calibration and tare were rechecked. If the results of these performance tests deviated by more than ±5 μg, the balance was recalibrated. If the difference exceeded ±15 μg, the balance was recalibrated and the previous 10 samples were reweighed. One hundred percent of initial weights and at least 30 percent of exposed weights were checked by an independent technician and samples were reweighed if these check-weights did not agree with the original weights within ±0.015 mg. Pre- and post-weights, check weights and reweights (if required) were recorded on data sheets, as well as being directly entered into a database via an RS232 connection. Table 6-4 lists the PM2.5 blanks concentrations. The average stack sample level was greater than the dilution sampler blank and ambient concentrations; however, the dilution sampler blank and the ambient concentrations were greater than the 95 percent confidence lower bound of the average. PM2.5 was not detected in the field blank or the trip blank.

Table 6-4. PM Results (Site Charlie).

	mg/dscm			
	Average	Char-DSB	Char-FB	Char-Amb
PM2.5 mass	< 1.9E-1	6.7E-2 a	ND	4.1E-2 c

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

Ions and Secondary PM Gaseous Precursors Analysis

The primary standard solutions were prepared with reagent grade salts, that were dried in an oven at 105 °C for one hour and then brought to room temperature in a desiccator. These anhydrous salts were weighed to the nearest 0.10 mg on a routinely calibrated analytical balance under controlled temperature (approximately 20 °C) and relative humidity (±30 percent) conditions. These salts were diluted in precise volumes of DI water. Calibration standards were prepared at least once within each month by diluting the primary standard solution to concentrations covering the range of concentrations expected in the filter extracts and stored in a refrigerator. The calibration concentrations prepared were at 0.1, 0.2, 0.5, 1.0, and 2.0 micrograms per milliliter (μg/ml) for each of the analysis species. Calibration curves were performed weekly. Chemical compounds were identified by matching the retention time of each peak in the unknown sample with the retention times of peaks in the chromatograms of the standards. A DI water blank was analyzed after every 20 samples and a calibration standard was analyzed after every 10 samples. These quality control checks verified the baseline and calibration, respectively. Environmental Research Associates (ERA, Arvada, CO) standards were used daily as an independent quality assurance (QA) check. These standards (ERA Wastewater Nutrient and ERA Mineral WW) were traceable to NIST simulated rainwater standards. If the values obtained for these standards did not coincide within a pre-specified uncertainty level (typically three standard deviations of the baseline level or ±5 percent), the samples between that standard and the previous calibration standards were reanalyzed.

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

Table 6-5 lists the blanks and ambient sample concentrations for ions and the secondary PM gaseous precursors. The dilution sampler blank levels were greater than the 95 percent confidence lower bound for the stack sample average for all substances except SO_2. No substances were measured in the field blank at concentrations greater than the 95 percent confidence lower bound for the stack sample average. NO_3^-, NH_4^+, and soluble Na were present in the dilution sampler blank and ambient sample at levels greater than the 95 percent lower bound for the stack sample average.

Elemental (XRF) Analysis

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

(SRM 1833). A separate Micromatter thin-film standard was used to calibrate the system for each element.

Table 6-5. Ions and Secondary PM Gaseous Precursors Blank Results (Site Charlie).

	mg/dscm							
	Average		Char-DSB		Char-FB		Char-Amb	
Cl-	<	2.7E-3	ND	d	ND	d	6.5E-4	d
NO3-	<	7.4E-3	4.7E-3	a	ND		5.0E-3	c
SO4=		8.3E-3	1.0E-2	a	ND		1.4E-3	
NH4+	<	3.9E-3	3.8E-3	a	ND		8.5E-4	c
NH3		6.1E-1	3.9E-1	a	6.0E-3		2.2E-2	
SO2		4.8E-1	1.0E-1		ND		1.2E-2	
Soluble Na		8.9E-4	3.8E-4	a	ND		8.7E-5	c

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

A quality control standard and a replicate from a previous batch were analyzed with each set of 14 samples. When a quality control value differed from specifications by more than ±5 percent or when a replicate concentration differed from the original value (when values exceed 10 times the detection limits) by more than ±10 percent, the samples were reanalyzed. If further tests of standards showed that the system calibration had changed by more than ±2 percent, the instrument was recalibrated as described above. All XRF results were entered directly into the analytical laboratory’s database.

Table 6-6 lists the blanks and ambient concentrations for elements. Most elements were present in the dilution sampler blank sample and the ambient sample at concentrations greater than the 95 percent confidence lower bound for the stack sample average. Only magnesium and sodium were present at detectable levels in the field blank. Mg and Na were also the only substances detected in the trip blank.

Table 6-6. Elements Blank Results (Site Charlie).

	mg/dscm						
	Average	Char-DSB		DC-FB		Char-Amb	
Al	< 6.1E-3	4.8E-4	a	ND		3.3E-4	c
Br	< 3.2E-5	3.3E-5	a	ND		7.3E-6	
Ca	5.2E-3	7.6E-4	a	ND		7.7E-4	c
Cl	< 1.1E-3	3.6E-4	a	ND		7.3E-4	c
Co	< 6.7E-5	ND		ND		3.1E-6	c
Cr	2.1E-4	2.5E-4	a	ND		5.5E-6	c
Cu	2.8E-4	4.9E-5	a	ND		1.3E-5	c
Fe	8.2E-3	2.2E-3	a	ND		9.2E-4	c
K	1.8E-3	4.1E-4	a	ND		2.6E-4	c
Mg	< 8.3E-4	4.3E-4	a	6.1E-4	b	6.2E-5	c
Mn	1.9E-4	5.1E-5	a	ND		1.7E-5	c
Mo	< 7.4E-5	ND	d	ND	d	1.6E-6	d
Na	2.0E-3	5.4E-3	a	2.2E-3	b	9.0E-4	c
Ni	1.5E-4	3.0E-4	a	ND		7.0E-6	c
P	< 1.6E-4	ND	d	ND	d	ND	d
Pb	< 1.1E-4	ND		ND		1.6E-5	c
Rb	< 2.2E-5	ND	d	ND	d	1.1E-6	d
S	3.0E-3	3.6E-3	a	ND		5.4E-4	
Si	1.2E-2	1.9E-3	a	ND		1.5E-3	c
Sr	< 8.9E-5	ND		ND		6.8E-6	c
Ti	5.6E-4	8.3E-5	a	ND		6.1E-5	c
V	< 7.1E-5	9.9E-5	a	ND		1.3E-5	c
Zn	7.3E-4	2.3E-4	a	ND		8.9E-5	c
Zr	< 8.0E-5	6.1E-5	a	ND		2.5E-6	c

DSB - Dilution Sampler Blank

FB - Field Blank

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

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

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

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

e - QA/QC sample not collected

Organic and Elemental Carbon Analysis

The TOR system was calibrated by analyzing samples of known amounts of methane, carbon dioxide, and potassium hydrogen phthalate (KHP). The FID response was compared to a reference level of methane injected at the end of each sample analysis. Performance tests of the instrument calibration were conducted at the beginning and end of each day's operation. Intervening samples were reanalyzed when calibration changes of more than ±10 percent were found.

Known amounts of American Chemical Society (ACS) certified reagent-grade crystal sucrose and KHP were committed to TOR as a verification of the OC fractions. Fifteen different standards were used for each calibration. Widely accepted primary standards for EC and/or OC are still lacking.

Table 6-7 lists the blanks and ambient concentrations for organic and elemental carbon. EC was present in the dilution sampler blank sample at concentrations greater than the 95 percent confidence lower bound for the stack sample average. OC was present in the dilution sampler blank sample at concentrations greater than the stack sample average. Field blank, trip blank (2.5E-2 mg/dscm), and ambient concentrations were less than the 95 percent lower bound. The quartz filters used for OC/EC analysis have the potential for positive OC bias due to absorption of VOCs on the filter. A backup quartz filter sampled behind the TMF to indicate the magnitude of this absorptive bias showed high concentrations of OC. The average backup filter OC concentration was approximately 67 percent of the average OC measured in the field samples. The ratios of the backup filter OC to the sample OC were 0.83, 1.34, and 0.32 for the dilution sampler blank, field blank, and ambient sample, respectively. Please refer to section 7 for further discussion of the OC VOC adsorption bias.

Table 6-7. Organic and Elemental Carbon Blank Results (Site Charlie).

	mg/dscm			
	Average	Char-DSB	Char-FB	Char-Amb
OC	2.3E-1	2.7E-1 a	6.9E-2	1.3E-2
EC	< 4.3E-2	2.2E-2 a	ND	2.8E-3
Backup Filter OC *	1.5E-1	2.3E-1 a	9.3E-2 b	4.3E-3

DSB - Dilution Sampler Blank
FB - Field Blank
a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.
b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.
c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.
d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.
e - QA/QC sample not collected
* OC measurements are subject to a potential positive bias from adsorption of VOC species.
OC measured on back up filter. Refer to Section 7 for further discussion.

SVOC Analysis

Prior to sampling, the XAD-4 resin was Soxhlet extracted with methanol, followed by dichloromethane, each for 24 hours. The cleaned resin was dried in a vacuum oven heated to

40°C and stored in sealed glass containers in a clean freezer. The PUF plugs were Soxhlet extracted with acetone, followed by 10 percent diethyl ether in hexane. The TIGF filters were cleaned by sonification in dichloromethane for 30 minutes followed by another 30-minute sonification in methanol. Then they were dried, placed in aluminum foil, and labeled. Each batch of precleaned XAD-4 resin and approximately 10 percent of the precleaned TIGF filters and PUF plugs were checked for purity by solvent extraction and GC/MS analysis of the extracts. The PUF plugs and XAD-4 resins were assembled into glass cartridges (10 g of XAD between two PUF plugs), wrapped in hexane-rinsed aluminum foil and stored in a clean freezer prior to shipment to the field.

Prior to extraction, the following deuterated internal standards were added to each filter-sorbent pair:

naphthalene-d8	9.76	nanograms per microliter (ng/μl)	
acenaphthene-d8	10.95	ng/μl	(for acenapththene and acenaphthylene)
biphenyl-d10	7.56	ng/μl	
phenanthrene-d10	4.61	ng/μl	
anthracene-d10	3.5	ng/μl	
pyrene-d10	5.28	ng/μl	(for fluoranthene and pyrene)
chrysene-d12	3.54	ng/μl	(for benz[a]anthracene and chrysene)
benzo[e]pyrene-d12	4.20	ng/μl	
benzo[a]pyrene-d12	4.68	ng/μl	
benzo[k]fluoranthene-d12	2.0	ng/μl	
benzo[g,h]perylene-d12	1.0	ng/μl	(for indeno[1,2,3-cd]pyrene, dibenzo[ah+ac]anthracne, benzo[ghi]perylene and coronene)

Calibration curves for the GC/MS/MID quantification were made for the molecular ion peaks of the PAH and all other compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. NIST SRM 1647 (certified PAH), with the addition of deuterated internal standards and compounds not present in the SRM, was used to make calibration solutions. Three concentration levels for each analyte were employed, and each calibration solution was injected twice. After the three-level calibration was completed, a standard solution was injected to perform calibration checks. If deviation from the true value exceeded 20 percent, the system was recalibrated. The mass selective detector (MSD) was tuned daily for mass sensitivity using perfluorotributylamine. In addition, one level calibration solution was run daily. If the difference between true and measured concentrations exceeded 20 percent, the system was recalibrated.

Table 6-8 lists the blanks and ambient concentrations for SVOCs. About 67 percent of the detected SVOCs were present in the dilution sampler blank sample at concentrations greater than the 95 percent confidence lower bound for the stack sample average. About 37 percent of the detected SVOCs were measured in the field blank at concentrations greater than the 95 percent confidence lower bound. About 50 percent of the detected SVOCs were measured in the ambient sample at concentrations greater than the 95 percent confidence lower bound.

VOC Analysis

Calibration curves were performed weekly. Volatile organic compounds were identified by matching the response factors of each unknown sample with the response factors of the standards. Tenax cartridges spiked with a mixture of paraffinic (in the C9-C20 range) and aromatic (C4, C5, and C6 benzenes) hydrocarbons were periodically analyzed by GC/FID to verify quantitative recovery from the cartridges. Three to five different concentrations of the hydro carbon (HC) standard and one zero standard were injected, and the response factors obtained. If the percent difference of the response factor from the mean was more than 5 percent, the response factors were corrected before proceeding with the analysis.

Table 6-9 lists the blanks and ambient concentrations for VOCs measured using Tenax. About 35 percent the detected VOCs were present in the dilution sampler blank sample at concentrations greater than the 95 percent confidence lower bound for the stack sample average. Two (4percent) of the detected VOCs were measured in the field blank at concentrations greater than the 95 percent lower bound and about 17 percent of the detected VOCs were measured in the ambient sample at concentrations greater than the 95 percent lower bound.

Table 6-8. PUF/XAD Tunnel and Field Blank Results (mg/dscm) (Site Charlie).

Compound	NG-Average		DS Blank		Field Blank		Ambient	
Naphthalene	<	8.9E-3	3.0E-3	a	2.6E-3	b	4.5E-4	c
2-methylnaphthalene		3.9E-3	3.6E-3	a	ND		4.1E-4	c
2-Methylbiphenyl		3.5E-3	1.1E-3	a	2.1E-3	b	1.6E-4	
1,3+1,6+1,7-dimethylnaphthalene	<	2.8E-3	5.2E-3	a	ND		5.5E-4	c
1-methylnaphthalene		2.1E-3	1.9E-3	a	ND		2.5E-4	c
3-Methylbiphenyl		1.9E-3	9.6E-4	a	7.7E-4	b	7.5E-5	
2,6+2,7-dimethylnaphthalene	<	1.4E-3	1.9E-3	a	ND		3.0E-4	c
1,4+1,5+2,3-dimethylnaphthalene	<	1.2E-3	1.7E-3	a	ND		1.2E-4	c
1+2-ethylnaphthalene	<	9.9E-4	1.4E-3	a	ND		1.3E-4	
2,3,5+I-trimethylnaphthalene		9.2E-4	1.3E-3	a	5.9E-5	b	4.3E-5	c
4-Methylbiphenyl		8.3E-4	5.2E-4	a	2.0E-4		3.1E-5	
Biphenyl	<	7.0E-4	4.0E-4	a	ND		2.0E-5	
1-methylfluorene	<	6.9E-4	ND		4.7E-4	b	4.3E-6	c
A-trimethylnaphthalene		5.0E-4	8.4E-4	a	3.1E-5	b	6.1E-5	c
Acenaphthenequinone		4.7E-4	6.2E-4	a	4.4E-4	b	1.3E-5	
Fluorene	<	4.3E-4	5.9E-4	a	ND		1.8E-5	c
1,2-dimethylnaphthalene	<	3.6E-4	7.5E-4	a	ND		4.5E-5	c
B-trimethylnaphthalene		3.5E-4	6.8E-4	a	1.4E-5	b	4.3E-5	c
Phenanthrene		3.5E-4	4.0E-4	a	2.9E-5	b	3.7E-5	c
Acenaphthylene	<	3.4E-4	8.5E-4	d	ND	d	ND	d
9-Anthraldehyde	<	3.3E-4	1.0E-3	a	1.7E-4	b	ND	
C-trimethylnaphthalene		3.1E-4	5.3E-4	a	2.8E-5	b	3.4E-5	c
Acenaphthene	<	2.7E-4	5.4E-4	a	2.5E-4	b	2.1E-5	c
B-methylfluorene	<	2.6E-4	ND	d	1.4E-4	d	ND	d
J-trimethylnaphthalene	<	2.0E-4	8.6E-5	a	ND		1.0E-5	c
E-trimethylnaphthalene		1.9E-4	3.8E-4	a	2.0E-5	b	2.4E-5	c
F-trimethylnaphthalene		1.8E-4	2.4E-4	a	1.7E-5	b	2.2E-5	c
A-methylphenanthrene	<	1.3E-4	ND		ND		1.1E-5	
C-dimethylphenanthrene	<	1.2E-4	1.0E-4	a	ND		7.8E-6	
C-methylphenanthrene	<	1.2E-4	8.3E-5	d	ND	d	9.3E-6	d
3,6-dimethylphenanthrene	<	1.1E-4	ND	d	ND	d	3.1E-6	d
2-methylphenanthrene		1.1E-4	6.8E-5	a	1.5E-5	b	1.3E-5	c
1-methylphenanthrene	<	1.0E-4	5.9E-5	a	ND		7.9E-6	
B-methylphenanthrene	<	9.3E-5	ND	d	ND	d	ND	d
E-dimethylphenanthrene	<	8.7E-5	2.5E-4	a	1.1E-4	b	1.4E-6	c
2,4,5-trimethylnaphthalene		8.3E-5	1.2E-4	a	ND		6.6E-6	c
Pyrene		7.8E-5	1.3E-4	a	1.3E-5		2.2E-6	
Benz(a)anthracene	<	7.6E-5	7.3E-5	d	ND	d	8.0E-7	d
Fluoranthene		7.2E-5	1.6E-4	a	8.2E-6		2.5E-6	
Benzo(c)phenanthrene	<	5.4E-5	ND	d	2.3E-5	d	ND	d
Xanthone	<	4.9E-5	7.1E-5	a	3.9E-5	b	2.2E-7	c
Anthrone	<	4.1E-5	7.2E-5	a	4.5E-5	b	9.0E-7	
Anthracene		3.6E-5	3.5E-5	a	4.2E-5	b	1.3E-6	c
B-MePy/MeFl	<	3.4E-5	ND		8.2E-6		1.0E-7	
7-methylbenzo(a)pyrene	<	3.1E-5	ND		ND		7.2E-7	c
Benzo(a)pyrene		2.9E-5	1.9E-4	a	1.4E-5	b	1.6E-6	c
Benzo(e)pyrene		2.7E-5	1.9E-4	a	ND		1.7E-6	
1-methylpyrene	<	2.3E-5	ND		ND		ND	
4-methylpyrene		2.1E-5	4.5E-5	a	ND		4.0E-7	c
D-MePy/MeFl	<	2.0E-5	2.9E-5	a	ND		2.5E-7	
Benzo(b+j+k)fluoranthene	<	1.9E-5	1.4E-5	a	ND		3.0E-7	c
Benzo(ghi)perylene	<	1.6E-5	ND		ND		ND	
Benzonaphthothiophene		1.0E-5	4.6E-6	a	1.0E-4	b	3.2E-7	c
Chrysene	<	8.8E-6	ND		ND		8.7E-7	c
Perylene	<	8.1E-6	ND		ND		ND	
C-MePy/MeFl		4.8E-6	ND		ND		7.5E-8	c
5+6-methylchrysene	<	4.7E-6	ND		9.1E-7	b	ND	

MDL - method detection limit
DS - Dilution Sampler
FB - Field Blank
a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.
b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.
c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.
d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.
e - QA/QC sample not collected

Table 6-9. Tenax VOCs Blanks Results (Site Charlie).

	mg/dscm						
Substance	Average	Char-DSB		Char-FBavg		Char-Ambient	
Benzoic acid	2.0E+0	5.5E-1	a	2.8E-1	b	1.7E-2	c
Hexadecanoic acid	1.1E+0	ND		3.2E-1	b	1.1E-2	
Benzaldehyde	3.3E-1	1.4E-1		1.0E-2		3.2E-3	
Acetophenone	1.8E-1	8.5E-2		5.2E-3		1.4E-3	
Phenol	7.3E-2	2.3E-2		3.6E-3		1.4E-3	
m & p-xylene	5.8E-2	2.0E-2	a	ND		3.4E-3	
Nonane	3.9E-2	1.3E-2		ND		2.2E-3	
Decane	2.5E-2	1.3E-2	a	ND		7.4E-4	
p-isopropyltoluene	2.1E-2	5.3E-2	a	ND		2.0E-4	c
Undecane	1.8E-2	2.4E-2	a	ND		5.4E-4	
o-xylene	1.7E-2	5.4E-3		ND		1.0E-3	
Nonanal	< 1.6E-2	2.7E-2	d	ND	d	ND	d
Pentadecane	< 1.6E-2	2.0E-2	a	ND		3.7E-4	
1,2,4-trimethylbenzene	1.6E-2	4.6E-3	a	ND		6.9E-4	
m-ethyltoluene	1.4E-2	4.2E-3		ND		5.8E-4	
Ethylbenzene	1.3E-2	4.5E-3		ND		7.8E-4	
Dodecane	1.0E-2	8.0E-3	a	ND		3.0E-4	
Tetradecane	9.1E-3	1.3E-2	a	ND		3.8E-4	
p-ethyltoluene	8.1E-3	2.4E-3	a	ND		2.9E-4	
Octanal	< 7.7E-3	ND		ND		ND	
1-methylindan	< 7.5E-3	ND		ND		1.1E-4	
Styrene	< 6.7E-3	ND		ND		5.6E-4	c
3-methyloctane	6.6E-3	1.4E-3		ND		3.8E-4	
Hexadecane	6.3E-3	1.4E-2	a	ND		1.7E-4	
Naphthalene	6.2E-3	3.8E-3	a	ND		3.5E-4	
1,3,5-trimethylbenzene	6.0E-3	1.2E-3		ND		2.7E-4	
o-ethyltoluene	< 5.5E-3	1.4E-3		ND		1.9E-4	
Tridecane	5.2E-3	4.1E-3	a	ND		3.3E-4	
B-dimethylindane	< 5.0E-3	ND		ND		ND	
Heptadecane	< 4.8E-3	2.4E-3	a	ND		6.6E-5	
Propylbenzene	4.6E-3	ND		ND		1.7E-4	
2-methylnaphthalene	< 4.0E-3	2.5E-3	a	ND		2.7E-4	
2-methyloctane	< 3.9E-3	ND		ND		2.0E-4	
Indan	< 3.5E-3	ND		ND		6.0E-5	c
1,3-dichlorobenzene	< 3.5E-3	2.8E-3	a	ND		9.8E-5	
Octadecane	< 3.0E-3	2.7E-3	a	ND		ND	
Dimethyloctane	< 2.9E-3	ND		ND		1.2E-4	
4-ethyl-o-xylene	< 2.8E-3	ND		ND		8.9E-5	
2-methylindan	< 2.8E-3	ND		ND		3.1E-5	c
1,2,3,4-tetramethylbenzene	< 2.6E-3	ND	d	ND	d	3.2E-5	d
C-dimethylindane	< 2.5E-3	ND	d	ND	d	ND	d
5-ethyl-m-xylene	< 2.3E-3	ND		ND		4.6E-5	c
2-ethyl-p-xylene	< 1.7E-3	ND		ND		6.2E-5	c
1,2,4,5-tetramethylbenzene	< 1.7E-3	ND	d	ND	d	ND	d
1-methylnaphthalene	< 1.6E-3	ND		ND		1.4E-4	
1,2,3,5-tetramethylbenzene	< 1.5E-3	ND		ND		4.9E-5	c
2-heptanone	< 1.4E-3	ND	d	ND	d	1.0E-4	d
Biphenyl	< 1.2E-3	ND	d	ND	d	ND	d

DSB - Dilution Sampler Blank

FB - Field Blank

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

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

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

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

e - QA/QC sample not collected

Table 6-10 lists the blanks and ambient concentrations for VOCs measured using canisters. Almost all of the detected VOCs were present in the dilution sampler blank sample at concentrations greater than the 95 percent confidence lower bound for the stack sample average. About 14 percent of the detected VOCs were measured in the ambient sample at concentrations greater than the 95 percent lower bound.

Carbonyls Analysis

Table 6-11 lists the blanks and ambient concentrations for carbonyls. Formaldehyde, acetone, and glyoxal were present in the dilution sampler blank sample at concentrations greater than the 95 percent confidence lower bound for the stack sample average. None of the detected carbonyls were measured in the ambient sample at concentrations greater than the 95 percent lower bound.

Table 6-10. Canister Samples VOCs Blanks Results (Site Charlie).

	mg/dscm				
Substance	Average	Char-DSB		Char-Amb	
Propane	7.4E-1	1.5E+0	a	3.0E-2	
n-butane	7.2E-1	2.2E+0	a	5.6E-2	c
Isobutane	4.0E-1	9.6E-1	a	3.2E-2	c
Ethane	4.0E-1	5.9E-1	a	1.4E-2	
Isopentane	3.4E-1	1.1E+0	a	3.2E-2	
Toluene	3.3E-1	2.9E-1	a	1.7E-2	
Acetone	3.0E-1	4.7E-1	a	9.7E-2	c
Propene	2.1E-1	8.8E-2	a	2.5E-3	
Methylene chloride	2.1E-1	8.9E-2		2.5E-2	
n-pentane	1.8E-1	6.9E-1	a	2.6E-2	
2-methylpentane	1.6E-1	4.0E-1	a	1.5E-2	
Ethene	1.5E-1	1.1E-1	a	3.6E-3	
Chloromethane	1.4E-1	1.3E-1	a	3.7E-3	
Acetylene	1.4E-1	9.1E-2	a	2.9E-3	
1-decene	1.1E-1	1.5E-1	a	3.9E-3	
m- & p-xylene	1.0E-1	1.0E-1	a	5.8E-3	
Acetaldehyde	9.4E-2	1.6E-1	a	4.3E-3	
2,2,4-trimethylpentane	9.4E-2	1.1E-1	a	7.3E-3	
n-hexane	9.1E-2	2.3E-1	a	9.0E-3	
Methylcyclopentane	7.2E-2	1.6E-1	a	6.3E-3	
3-methylpentane	6.7E-2	1.6E-1	a	6.5E-3	
2,3,5-trimethylhexane	6.5E-2	1.0E-1	a	2.3E-3	
Ethanol + ACN	5.9E-2	6.9E-2	a	2.8E-3	
Cyclohexane	5.0E-2	7.9E-2	a	3.8E-3	
Methylcyclohexane	4.9E-2	7.2E-2	a	3.5E-3	
Benzene	4.9E-2	6.3E-2	a	3.6E-3	
n-heptane	4.6E-2	7.8E-2	a	3.7E-3	
Iso-butene	4.6E-2	4.7E-2	a	3.0E-3	c
3-methylhexane + pentanal	4.3E-2	6.8E-2	a	3.7E-3	
1-butene	3.9E-2	4.3E-2	a	3.1E-3	c
2-methylhexane	3.7E-2	5.5E-2	a	3.2E-3	
o-xylene	3.5E-2	3.9E-2	a	2.0E-3	
2,3,-trimethylpentane	3.4E-2	2.7E-2	a	9.2E-5	
Hexanal	3.2E-2	4.2E-2	a	1.6E-3	
2,3-dimethylbutane	3.2E-2	6.4E-2	a	3.1E-3	
t-2-butene	3.2E-2	3.1E-2	a	2.7E-3	c
F 12	3.2E-2	2.8E-2	a	8.6E-4	
2,2-dimethylbutane	3.1E-2	3.5E-2	a	2.4E-3	
n-octane	3.1E-2	3.4E-2	a	2.1E-3	
n-nonane	2.8E-2	1.9E-2	a	1.2E-3	
Ethylbenzene	2.8E-2	3.0E-2	a	1.8E-3	
2,3-dimethylpentane	2.6E-2	4.3E-2	a	2.1E-3	
c-2-butene	2.5E-2	2.5E-2	a	2.2E-3	c
n-decane	2.4E-2	1.8E-2	a	9.2E-4	
m-ethyltoluene	2.4E-2	2.3E-2	a	1.3E-3	
2-methylheptane	2.1E-2	3.0E-2	a	1.8E-3	
Styrene + heptanal	2.1E-2	3.3E-2	a	1.1E-3	
Cyclopentane	2.0E-2	5.9E-2	a	2.1E-3	
2,4-dimethylpentane	1.9E-2	2.8E-2	a	1.6E-3	

Table 6-10. Canister Samples VOCs Blanks Results: Site Charlie.(Continued)

Substance	mg/dscm					
		Average	Char-DSB		Char-Amb	
alpha-pinene		1.9E-2	3.0E-2	a	5.6E-4	c
Chlorobenzene		1.9E-2	1.6E-2	a	1.1E-3	
1-pentene	<	1.8E-2	1.1E-2	a	5.9E-4	
3-methylheptane		1.7E-2	2.0E-2	a	1.4E-3	
3-ethylpentane		1.7E-2	3.4E-2	a	1.4E-3	
1,2,3-trimethylbenzene		1.7E-2	1.4E-2	a	7.0E-4	
Methanol		1.6E-2	7.9E-3	a	1.8E-4	c
2-methyl-2-butene		1.6E-2	2.0E-2	a	1.0E-3	
n-undecane		1.6E-2	1.3E-2	a	6.9E-4	
1,3-dimethylcyclopentane		1.5E-2	3.1E-2	a	1.2E-3	
F 113		1.5E-2	2.1E-2	a	1.0E-3	
t-2-pentene		1.4E-2	1.7E-2	a	6.9E-4	
1,3,5-trimethylbenzene		1.4E-2	1.3E-2	a	6.4E-4	
Unidentified C9 paraffins		1.3E-2	1.9E-3	a	1.6E-4	c
Propanal + F11		1.3E-2	2.2E-2	a	ND	
2-methyl-1-butene		1.2E-2	1.4E-2	a	5.7E-4	
Isopropylcyclohexane		1.2E-2	1.1E-2	a	6.0E-4	c
2,5-diemthylhexane		1.1E-2	1.1E-2	a	8.3E-4	
Unidentified C8 paraffins		1.1E-2	1.5E-2	a	9.4E-4	
Unidentified C10 aromatics		1.0E-2	1.1E-2	a	3.8E-4	
p-ethyltoluene		9.8E-3	8.3E-3	a	4.7E-4	
1,4-diethylbenzene		9.7E-3	7.5E-3	a	3.2E-4	
Unidentified C9 olefins		9.6E-3	9.4E-3	a	2.0E-4	c
2,2,5-trimethylhexane		8.8E-3	7.5E-3	a	6.8E-4	
3,3-dimethylheptane	<	8.8E-3	ND	d	3.1E-5	d
n-propylbenzene		8.4E-3	7.9E-3	a	4.3E-4	
c-2-pentene		8.3E-3	9.8E-3	a	4.2E-4	
o-ethyltoluene		7.7E-3	8.6E-3	a	3.5E-4	
Limonene		7.3E-3	6.0E-3	a	5.4E-4	
Indan		7.2E-3	7.9E-3	a	4.8E-4	
4-methylheptane		6.9E-3	8.3E-3	a	5.9E-4	
MTBE		6.8E-3	8.3E-3	a	3.3E-4	
Octanal		6.4E-3	1.4E-2	a	2.2E-4	
n-dodecane		6.1E-3	7.1E-3	a	2.6E-4	
Unidentified C10 paraffins		5.5E-3	4.9E-3	a	2.9E-4	
Isopropyltoluene		5.4E-3	4.5E-3	a	2.5E-4	
Benzaldehyde		5.2E-3	5.3E-3	a	2.1E-4	
Isopropylbenzene		5.0E-3	4.9E-3	a	2.3E-4	
Mechloroform	<	4.7E-3	ND		ND	
2,4,4-trimethyl-1-pentene		4.3E-3	4.9E-3	a	1.4E-4	
Nonene-1		4.1E-3	5.3E-3	a	2.8E-4	
1,1-dimethylcyclohexane		4.0E-3	3.8E-4		2.6E-4	
2-methyl-2-pentene		4.0E-3	5.6E-3	a	2.6E-4	
Naphthalene		4.0E-3	4.5E-3	a	1.5E-4	c
Cyclohexene		3.9E-3	1.0E-2	a	3.7E-4	
1,3-butadiene		3.9E-3	3.4E-3	a	2.4E-4	
2,4-diemthylhexane		3.7E-3	3.4E-3	a	2.9E-4	
1,2,3,5-tetramethylbenzene		3.7E-3	3.0E-3	a	1.7E-4	
t-2-hexene		3.6E-3	6.4E-3	a	2.6E-4	
3-methyl-1-butene		3.6E-3	4.9E-3	a	1.5E-4	

Table 6-10. Canister Samples VOCs Blanks Results (Site Charlie).(Continued)

	mg/dscm					
Substance		Average	Char-DSB		Char-Amb	
1-hexene		3.6E-3	1.1E-3	a	1.3E-4	
Isobutylbenzene		3.5E-3	7.5E-4	a	2.0E-4	c
1,2,4,5-tetramethylbenzene		3.5E-3	3.4E-3	a	1.8E-4	
1,3-diethylbenzene		3.4E-3	3.0E-3	a	2.5E-4	
1,2,4-trimethylbenzene		3.4E-3	2.6E-3	a	9.2E-5	c
Nonanal		3.4E-3	1.0E-2	a	5.1E-5	
1,2-diethylbenzene		3.3E-3	2.6E-3	a	1.6E-4	
3,6-dimethyloctane		3.2E-3	3.0E-3	a	1.7E-4	
3,3-dimethylpentane		3.0E-3	4.1E-3	a	2.9E-4	
2,2,3-trimethylbutane		3.0E-3	3.4E-3	a	2.1E-4	
Unidentified C11 paraffins		2.8E-3	2.3E-3	a	2.1E-4	
2-methyl-1-pentene		2.7E-3	1.1E-3		1.4E-4	
Cyclopentene		2.6E-3	2.6E-3	a	1.6E-4	
trans-3-methyl-2-pentene		2.6E-3	2.3E-3	a	2.1E-4	
Unidentified C8 olefins	<	2.6E-3	7.5E-4		1.3E-4	
Isoprene		2.5E-3	1.9E-3	a	1.2E-4	
2-propyl toluene		2.3E-3	1.1E-3	a	1.5E-4	
beta-pinene		2.2E-3	1.1E-3	a	1.1E-4	
t-3-hexene + chloroform		2.2E-3	3.4E-3	a	1.4E-4	c
1,2,3,4-trimethylbenzene		2.1E-3	1.5E-3	a	8.2E-5	
cis-3-methyl-2-pentene		1.8E-3	3.0E-3	a	1.7E-4	
t-3-heptene	<	1.5E-3	7.5E-4		8.2E-5	
2,5-dimethylheptane		1.4E-3	3.8E-4	a	9.2E-5	
c-2-hexene		1.4E-3	1.9E-3	a	1.1E-4	
3-methyloctane	<	1.2E-3	1.1E-3	a	5.1E-5	c
2,3-dimethylhexane	<	1.2E-3	1.5E-3	a	1.1E-4	
1-methylindan		1.2E-3	1.1E-3	a	5.1E-5	
4-methylhexene	<	1.0E-3	7.5E-4	a	6.2E-5	
4-methyl-1-pentene	<	1.0E-3	1.1E-3	a	6.2E-5	
sec-butylbenzene		9.6E-4	7.5E-4	a	4.1E-5	
2,6-dimethyloctane	<	8.8E-4	1.1E-3	a	8.2E-5	c
Unidentified C11 aromatics		8.6E-4	ND		2.1E-5	
Octene-1		8.5E-4	2.3E-3	a	2.3E-4	
Unidentified C7 olefins		7.4E-4	3.8E-4	a	6.2E-5	
1-methylcyclopentene	<	7.0E-4	ND	d	ND	d
2,6-dimethylheptane	<	6.5E-4	ND		3.1E-5	
2,4-dimethylheptane	<	5.9E-4	7.5E-4	a	ND	
4,4-dimethylheptane	<	5.9E-4	3.8E-4	a	2.1E-5	c
c-3-hexene	<	5.9E-4	1.1E-3	a	5.1E-5	c
Indene	<	4.0E-4	1.5E-3	a	2.1E-5	
Total Identified NMHC		5.5E+0	1.0E+1	a	3.4E-1	
Unidentified		5.9E-1	9.7E-1	a	3.3E-2	
Identified oxygenated (ppbv)		3.5E-1	5.4E-1	a	7.5E-2	
Identified other compounds		5.5E-2	3.4E-2	a	4.7E-3	

DSB - Dilution Sampler Blank

FB - Field Blank

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

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

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

e - QA/QC sample not collected

Table 6-11. Carbonyls VOCs Blanks Results (Site Charlie).

Substance	mg/dscm					
		Average	Char-DSB		Char-Amb	
Formaldehyde		8.6E-2	4.2E-2	a	4.7E-3	
Acetaldehyde		1.0E-1	1.7E-2		2.7E-3	
Acetone	<	3.7E-1	1.5E-1	a	6.2E-3	
Acrolein		ND	ND	c	ND	c
Propionaldehyde		1.7E-2	ND		7.5E-4	
Crotonaldehyde		ND	ND	c	ND	c
MEK		3.5E-2	ND		1.6E-3	
Methacrolein		ND	ND	c	ND	c
Butyraldehyde	<	2.2E-2	5.8E-3	c	6.4E-4	c
Benzaldehyde		1.6E-2	ND		6.8E-4	
Glyoxal		1.9E-2	1.2E-2	a	8.9E-4	
Valeraldehyde		ND	6.6E-3	c	ND	c
M-Tolualdehyde	<	9.6E-3	ND	c	ND	c
Hexanaldehyde	<	1.3E-2	ND		ND	

DSB - Dilution Sampler Blank
FB - Field Blank
a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.
b - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.
c - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.
d - QA/QC sample not collected

Section 7

DISCUSSION AND FINDINGS

The objectives of this test were to develop emissions factors and speciation profiles for particulate emissions, including PM2.5, as well as gaseous secondary PM2.5 precursors. In addition to using the dilution sampler, samples were also collected according to EPA Method PRE-4/202. Before discussing the results, it is instructive to review the differences between these procedures.

DILUTION SAMPLER MEASUREMENTS

Dilution sampling is designed to capture filterable matter and any aerosols that condense under simulated stack plume conditions. The sample gas is cooled to near ambient temperatures, typically 60-85 °F in these tests as it mixes with dilution air in the dilution sampler. Samples for analyses are then collected from the diluted sample. Conventional in-stack methods are intended to collect particles that are filterable at the filter temperature and those that condense in a series of aqueous impingers placed in an ice bath. The gas temperature leaving the impingers is typically 55-65 °F; thus, both systems cool the sample gas to similar final temperatures. However the in-stack methods cool the sample rapidly without dilution by quenching the gas sample in water maintained at near freezing temperatures, while the dilution sampler cools and dilutes the sample more slowly by mixing it with purified ambient air. Since aerosol condensation depends on temperature, concentration, residence time and other factors, it is not surprising that the results of the two methods differ. However, mechanistic variations alone may not account for the magnitude of the difference observed in these tests.

As shown earlier in Table 5-1, dilution sampler PM2.5 ($1.6\text{x}10^{-4}$ lb/MMBtu) is approximately three times higher than the filterable PM 2.5 measured by the Method PRE-4/202 in-stack method ($5.5\text{x}10^{-5}$ lb/MMBtu). However, total PM2.5 (filterable plus condensable) measured by the in-stack method (1.1E-3 lb/MMBtu) is about seven times greater than the dilution sampler PM2.5; about 90 percent of the mass found by Method PRE-4/202 was contained in the condensable fraction collected in the impingers, a similar finding to that from earlier tests of gas-fired units (England et al., 2000). This relative distribution of PM mass is the expected result.

From low emission sources, such as this gas-fired heater, very little of the PM exists in solid, filterable form in the hot exhaust. Semivolatile material present in the stack will not condense until it is cooled, and if this cooling process occurs without dilution, as in the Method 202 train, more material will condense than would in a real world plume, where cooling occurs at the same time as the stack gases are diluted.

A review of those data led us to suspect the validity of the conventional CPM results and initiate a more extensive analysis of this fraction in this program than that prescribed by Method 202. Most of the inorganic CPM mass is composed of $SO_4^=$, Cl^- and Na, with small contributions from Ca, NO_3^-, Zn, Mg, and others. Figure 7-1 presents average inorganic CPM speciation results. 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 (presented in Section 4) of the impinger solutions does not show any significant levels of other elements. The agreement between the speciated mass and gravimetric measurements lead to further investigation of the sulfate measurements in an effort to understand the difference between the dilution sampler and Method PRE-4/202 emissions.

<u>Sulfate Comparison</u>

Table 7-1 presents a comparison of the $SO_4^=$ measurements, expressed as $SO_4^=$ ion in mg/dscm. The average $SO_4^=$ measured in the Method 202 aliquot equals the average SO_2 (as $SO_4^=$) measured by the K_2CO_3-impregnated cellulose-fiber filter downstream of the dilution sampler. Compared to the measured SO_2 value, the $SO_4^=$ levels measured by the dilution sampler account for approximately 1 percent of the SO_2 in the flue gas and are within an order of magnitude of $SO_4^=$ measured in the ambient sample.

The formation of artifact $SO_4^=$ caused by SO_2 absorption and conversion in the aqueous solutions is a known artifact with impinger methods. Both SO_2 and oxygen are soluble in water and the dissolved H_2SO_3 can slowly oxidize to $SO_4^=$. This is implicitly recognized by Method 202, which recommends purging the impingers with nitrogen (air is also acceptable) to minimize this bias. Method 202 also provides the option of omitting the post-test purge if the potential of

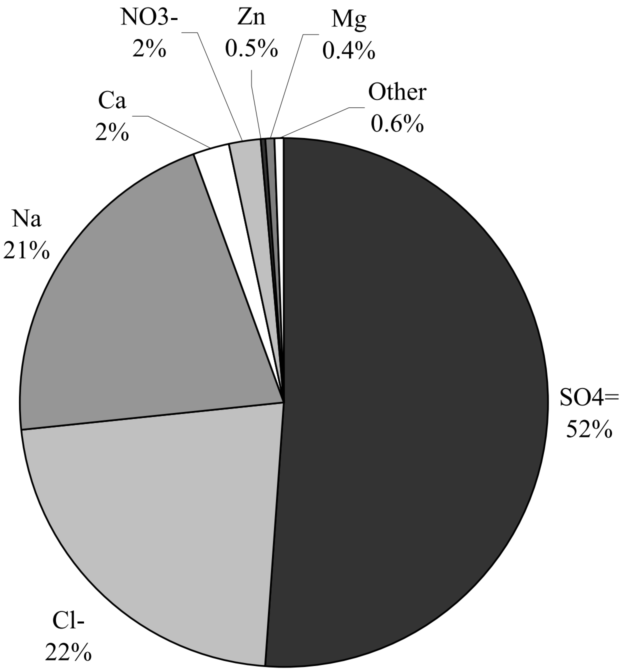


Figure 7-1. Inorganic CPM Residue Speciation Results.

Table 7-1. 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 sampler	0.015	0.010	0.0039	0.0048	0.0083
Ambient (1)	0.0014	--	--	--	0.0013
Dilution sampler SO_2 measurement (as $SO_4^=$)	1.15	0.88	0.45	0.42	0.73

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

hydrogen (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_2 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_2 concentrations, a laboratory scale study was conducted evaluating potential bias at these concentrations (GE EER, 1999; Wien et al., 2001). The experiments passed simulated combustion gas containing representative amounts of O_2, CO_2, nitrogen (N_2), NO_x, and SO_2 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_2. Significant amounts of $SO_4^=$, proportional to the SO_2 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 $SO_4^=$ 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_2 oxidation occurs within this period. This result shows that the $SO_4^=$, and hence most of the CPM collected by Method 202 in our field test results, comes from this mechanism of artifact $SO_4^=$ formation from dissolved SO_2. These results indicated that approximately 50 to 100 percent of the sulfate measured by Method 202 can be accounted for by this artifact.

Particulate OC

There is currently heightened interest in particulate carbon from gas-fired combustion sources due to PM10 and PM2.5 NAAQS and Regional Haze rules. Background work for development of PM2.5 State Implementation Plans has begun in several states in response to the 1997 PM2.5 NAAQS. In addition, atmospheric visibility is a key concern in Class 1 Areas, such as near National Parks. The National Park Service (NPS) must evaluate the visibility impact of new plants within 100 km of Class 1 Areas during permitting. Source emissions are evaluated for impact on regional haze and other criteria. Primary EC and OC, $SO_4^=$ and NO_3^- aerosols, and coarse (PM10-2.5) and fine (PM2.5) PM emissions are key factors in the visibility evaluation. Quartz filters were used to collect PM that was then analyzed for OC and EC by TOR using the IMPROVE protocol. Previous studies have shown that OC measurements on quartz filters are susceptible to biases: adsorption of VOCs onto the filter media and collected PM, and devolatilization of organic PM, with the adsorptive effect dominating and causing a positive bias (Winegar, 1993). In these tests, a quartz fiber filter was placed downstream of a TMF during sample collection and subsequently analyzed for OC and EC to determine the extent of this bias (Turpin, 1994). The OC collected on this filter may be used to evaluate the potential significance of the bias relative to the OC collected on the front-loaded quartz fiber filter. This is commonly referred to as “backup OC”. In some cases, this approach may overestimate the extent of the bias because the adsorptive capacity of the filter media itself and the collected particles can affect the amount of VOC adsorbed on the filter (Kirchstetter, 2001). Therefore, it is convention not to correct OC measurements for the backup filter results, but rather to present both sets of results and discuss the potential impact of the on the measured OC results.

Table 7-2 presents the data from the backup and front quartz filters used this test, as well as the equivalent OC concentration if the results are corrected for backup OC (i.e., the OC mass measured on the backup quartz filter is subtracted from the OC mass measured on the primary quartz filter). For this test, the backup OC ranged from 50 to 116 percent of the OC concentration measured on the primary quartz filter. These results are qualitatively similar to the results of Hildemann et al. (1991), who determined speciated PM emissions from gas-fired home appliances using methods identical to those used in this program. Hildemann found that OC accounted for 84.9 percent of PM mass and that the backup OC accounts for 73 percent of the measured OC emissions, on average. Hildemann's data are incorporated into EPA's SPECIATE database, and are currently the only PM speciation data available for gas-combustion. Thus, Hildemann's results provide validation of the OC results measured in this study, and also reinforce the need for caution when using the OC results.

Table 7-2. Organic Carbon and Backup Filter Carbon Results (mg/dscm) (Site Charlie)

	Run 1	Run 2	Run 3	Run 4	Average	DSB	FB	Ambient
OC	0.377	0.298	0.120	0.115	0.227	0.267	0.0693	0.0127
Backup Filter OC	0.188	0.201	0.139	0.083	0.153	0.229	0.093	0.0040
OC - Corrected for Backup Filter OC	0.189	0.097	-0.019	0.0317	0.075	0.046	-0.024	0.0087
Backup Filter OC/OC (%)	49.8	67.6	116	72.4	76.4	83.0	134	31.5

FB - Field Blank
DSB - Dilution sampler blank

Figure 7-2 shows the potential impact of the bias on the overall average sample concentration, and the levels in the field blank. Although the ambient result appears to be elevated above the stack samples, the data are presented in mass per sample and the OC results from the stack sample results have not been corrected for dilution ratio (approximately 36:1) in this graph. The high blank levels as well as the VOC adsorption associated with the quartz filters used to measure OC indicate a significant positive bias on the OC concentrations. These data indicate that the true carbon emissions are probably below measured results. Therefore, the OC results should be considered as an upper bound for the potential OC emissions, with significant uncertainty beyond the reported values.

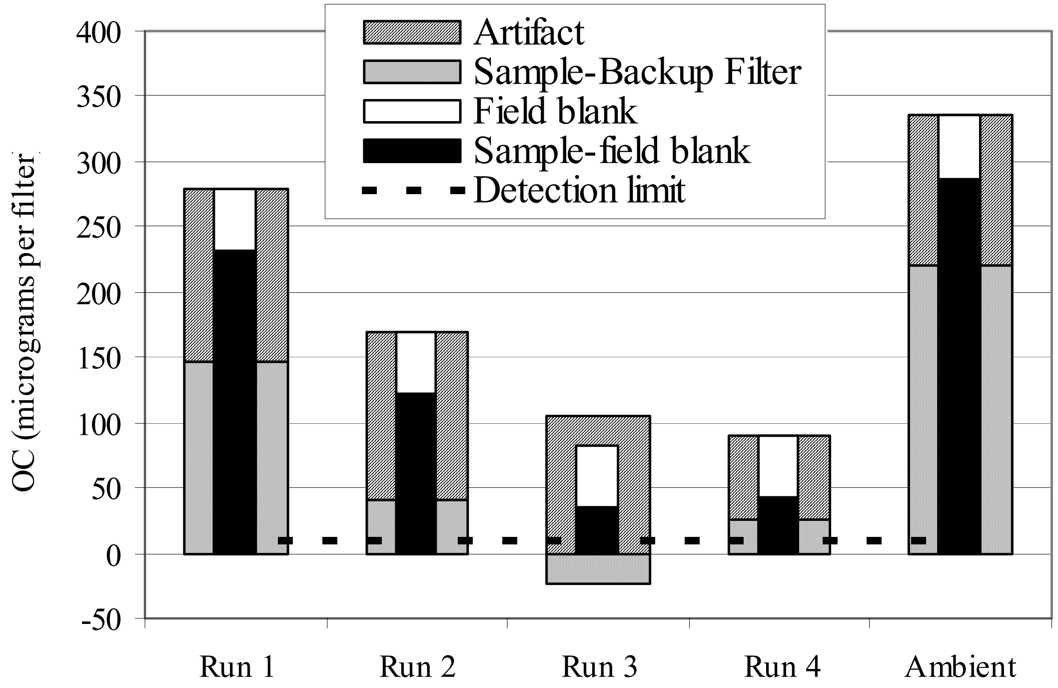


Figure 7-2. Site Charlie (Refinery Gas-Fired Process Heater) OC Results.

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 7-3 presents some of their data (Lakewood Cogeneration and Kamine Milford units) along with data collected in the current program (for DOE/CEC/NYSERDA/GRI/API) for gas-fired sources (Sites Alpha and Bravo) and its predecessor conducted for API/DOE/GRI (Sites A, B and C). These data compare results from the filterable and condensable PM fractions, along with the composition of CPM.

As shown in Table 7-3, the CPM data from Site Charlie presented in this report is slightly lower than, but comparable to the Lakewood Cogeneration data, and is the lowest of all sites from the current program to date. The filterable fraction is also lower than almost all the other gas-fired combustion units.

The total PM10 emission factor obtained using Method PRE-4/202 trains is lower than all other sites tested, but they are all within an order of magnitude (Table 7-4). The filterable PM10 emission factor for Site Charlie (0.00010 lb/MMBtu) is more than an order of magnitude lower

Table 7-3. Comparison of Data from Corio and Sherwell (2000) and Current Program Data.

Source (1)	Unit Type	Filterable PM		Condensable PM		Makeup of CPM			
						Inorganic Fraction		Organic Fraction	
		lb/ MMBtu	% of Total PM10	lb/ MMBtu	% of Total PM10	lb/ MMBtu	% of Total CPM	lb/ MMBtu	% of Total CPM
Lakewood Cogeneration	Natural Gas-fired Boiler	0.0019	46	0.0022	54	0.0015	66	0.00076	34
Lakewood Cogeneration – Unit #1	Natural Gas-fired Turbine	0.00021	14	0.0012	86	0.001	81	0.00023	19
Lakewood Cogeneration – Unit #2	Natural Gas-fired Turbine	0.00052	33	0.0011	67	0.00084	78	0.00024	22
Kamine Milford (2)	Natural Gas-fired Turbine	0.0132	56	0.011	44	0.0045	43	0.006	57
Kamine Milford (3)	Natural Gas-fired Turbine	0.0015	12	0.011	88	0.0067	60	0.0045	40
Kamine Milford (4)	Natural Gas-fired Turbine	0.0012	10	0.011	90	0.0079	74	0.0028	26
Kamine Milford (5)	Natural Gas-fired Turbine	0.0014	12	0.010	88	0.0066	66	0.0034	34
Site A	Refinery Gas-fired Boiler	0.00016	2	0.0097	98	0.0091	94	0.00064	6
Site B	Refinery Gas-fired Process Heater	0.00064	12	0.0046	88	0.0044	96(6)	0.00014	3(6)
Site C	Natural Gas-fired Steam Generator	0.00008	6	0.0012	94	0.00052	44(6)	0.00048	41(6)
Site Alpha	Refinery Gas-fired Process Heater	0.00059	7	0.0078	93	0.0066	86(6)	0.0011	14(6)
Site Bravo	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, SCR, and oxidation catalyst	0.00029	9	0.0030	91	0.0027	91(6)	0.00055	6(6)
Site Charlie	Natural Gas-fired Process Heater with SCR	0.00010	9	0.0010	91	0.00092	91(6)	0.00028	6(6)

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

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

[3] SI off, WHRB off.

[4] SI on, WHRB on.

[5] SI off, WHRB on.

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

than that given in EPA's AP-42 emission factor database for natural gas combustion (0.0019 lb/MMBtu) and the EPA CPM emission factor is more than 5 times higher than that for Site Charlie (EPA, 2000). Since the EPA results were obtained using the same manual methods used for testing at the program sites, a similar bias in the filterable and condensable catch was observed. Nevertheless, the correlation of our results with those presented in the EPA database provides additional confidence in the validity of the results found here.

Table 7-4. Comparison of EPA AP-42 Database and Current Program Data.

Source	Unit Type	Total PM10 (1)	Filterable PM		Condensable PM		PM2.5 by DS (2)
		lb/MMBtu	lb/MMBtu	% of Total PM10	lb/MMBtu	% of Total PM10	lb/MMBtu
AP-42	Natural Gas Combustion	0.0075	0.0019	25	0.0056	75	--
Site A	Refinery Gas-fired Boiler	0.0099	0.000160	2	0.0097	98	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	0.000077	6	0.0012	94	0.000056
Site Alpha	Refinery Gas-fired Process Heater	0.0084	0.00059	7	0.0078	93	0.000052
Site Bravo	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, SCR, and oxidation catalyst	0.0032	0.00029	9	0.0030	91	0.00025
Site Charlie	Natural Gas-fired Process Heater with SCR	0.0011	0.00010	9	0.0010	91	0.00016

(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.

The results for a number of gas-fired combustion units all show that regardless of the composition of the fuel gas, PM2.5 emissions are negligible relative to AP-42 estimates. In addition, Method PRE-4/202 also may overestimate the condensable organic fraction. 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 samplers provide conditions that simulate true atmospheric condensation conditions, as compared to impinger condensation, results obtained by this technique are more representative of the actual PM emissions from gas-fired combustion sources such as this heater.

FORMALDEHYDE AND ACETALDEHYDE

Formaldehyde and acetaldehyde emissions from the process heater were measured using DNPH cartridges downstream of the dilution sampler. A number of field blanks were taken during the test in addition to a sampler blank, which drew only ambient air through the sampler. Formaldehyde was detected in only one of the field blanks at about 0.00063 mg/dscm (0.5 ppbv) and acetaldehdye was detected in all field blanks at an average concentration of about 0.058 mg/dscm (32 ppbv). Sample run results were all field blank corrected by the analytical lab. There was also detectable levels of formaldehyde and acetaldehyde in the sampler blank. Figures 7-3 and 7-4 show the stack sample results (for formaldehyde and acetaldehyde, respectively) with the concentration in the sampler blank subtracted out, and the sampler blank

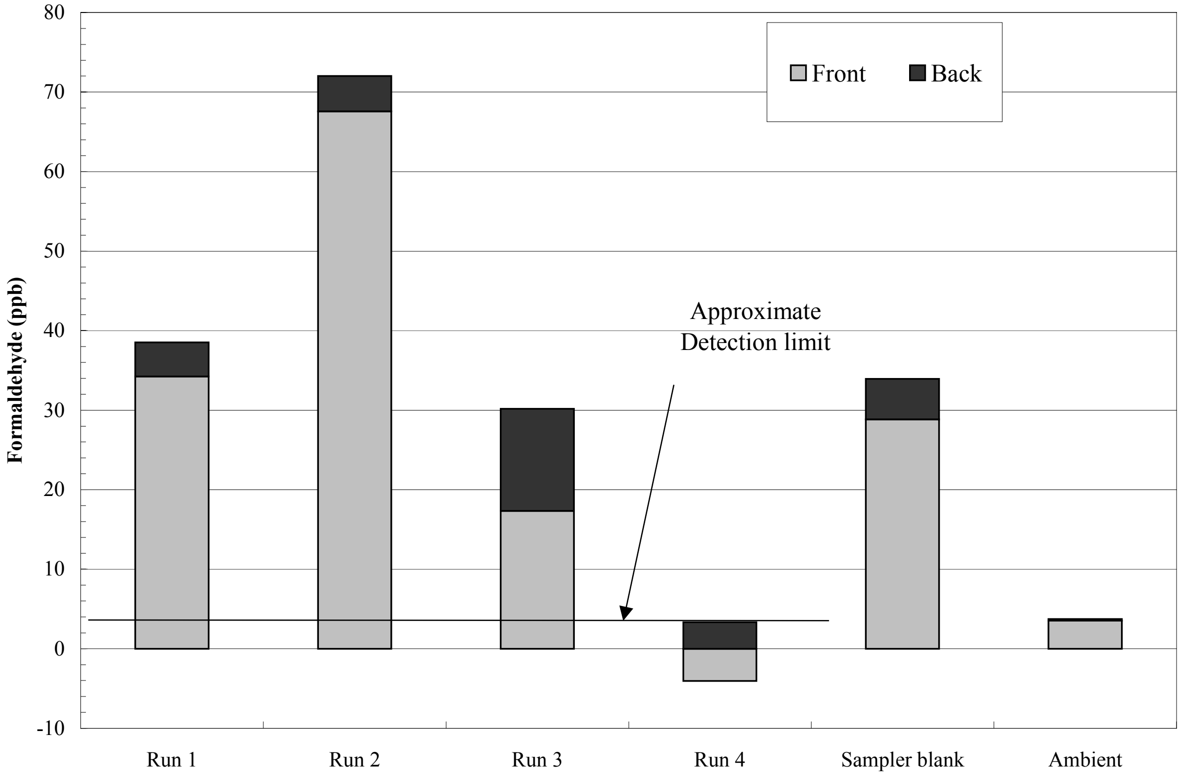


Figure 7-3. Sampler Blank-Corrected Formaldehyde Concentrations (Site Charlie).

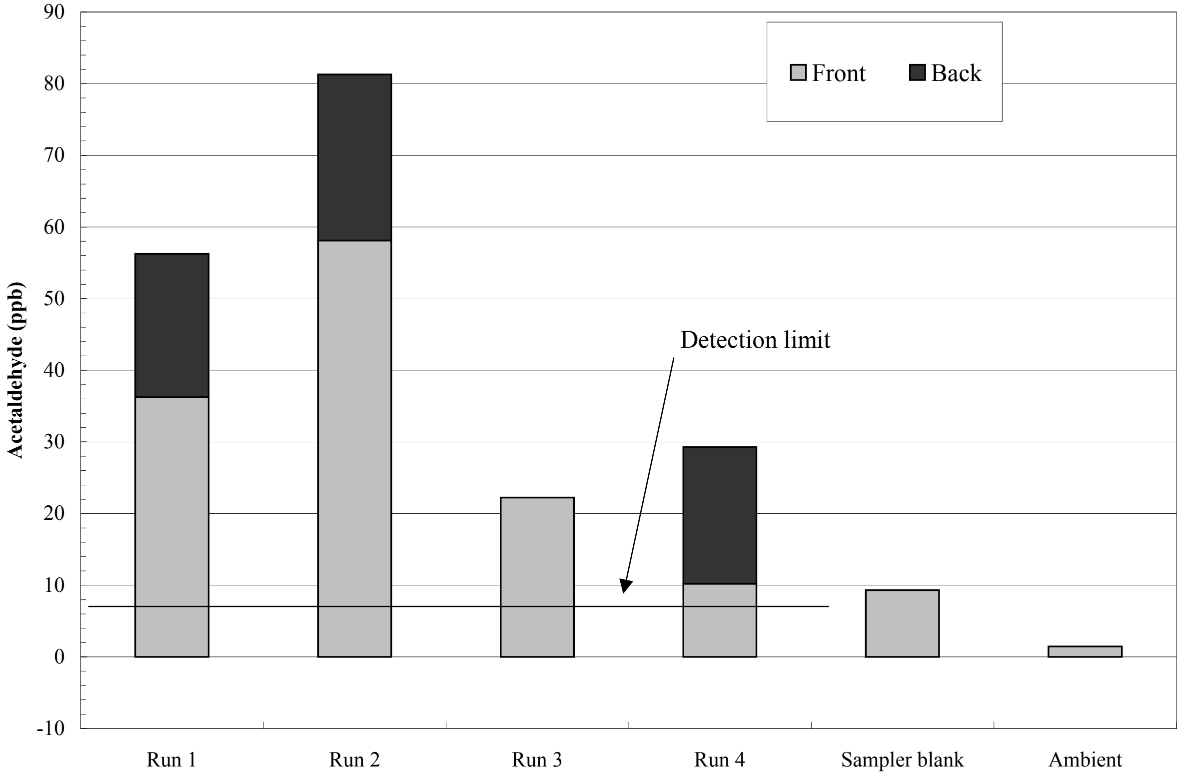


Figure 7-4. Sampler Blank-Corrected Acetaldehyde Concentrations (Site Charlie).

and ambient concentrations. All concentrations have been corrected for the dilution ratio, and are in-stack concentrations. The sampler blank concentration is an in-stack equivalent concentration using an average dilution ratio. In Run 4, the formaldehyde concentration in the sampler blank was greater than the sample concentration, causing the result to be negative. 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 and acetaldehyde emissions.

POTENTIAL EMISSIONS MARKER SPECIES

The results obtained using the dilution sampler are believed to provide the best representation of the chemical species present in the stack gas emissions. Ions, carbon, and other elements were detected in both stack and ambient air samples. A comparison of the observed concentrations of these species in ambient and stack samples (Figure 7-5) can provide an indication of which species are considered good markers of natural gas combustion for this source.

Ba was detected in the ambient air but not for the in-stack sample (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 PM2.5 mass, Br, Ca, Fe, K, Na, Pb, S, Si, Ti, V, Zn, Cl^-, NO_3^-, $SO_4^=$, NH_4^+ and EC are within a factor of ten of their respective ambient air concentrations. OC, Al, Co, Cr, Cu, Mg, Mn, Mo, Ni, Rb, Sr, 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.

However, some species cannot reliably be distinguished because their in-stack concentrations are within a factor of ten from the minimum method detection limits (Figure 7-6); these include: Br, Cl, Co, Cr, Mn, Mo, Ni, P, Pb, Rb, Sr, V, Zr, Cl^-, NO_3^-, $SO_4^=$, and NH_4^+. The above two criteria leave OC, Cu and Al as potential marker species.

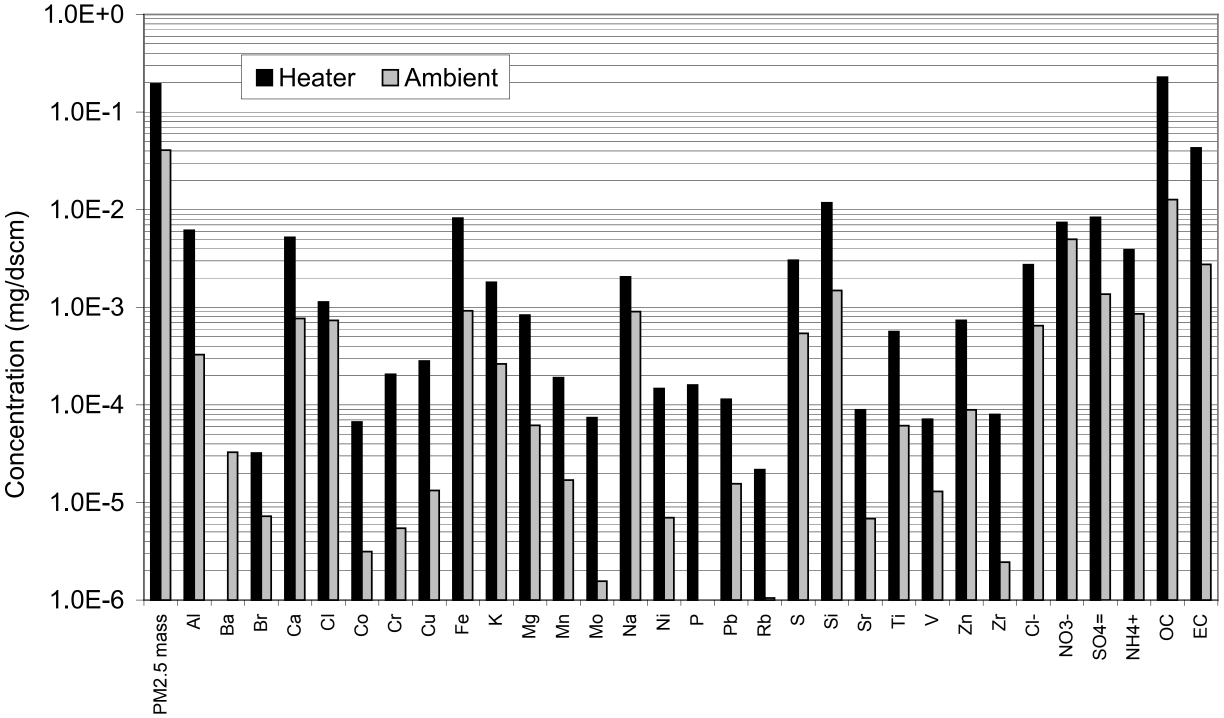


Figure 7-5. Mass Speciation for Dilution Sampler Ambient and Stack Samples (Site Charlie).

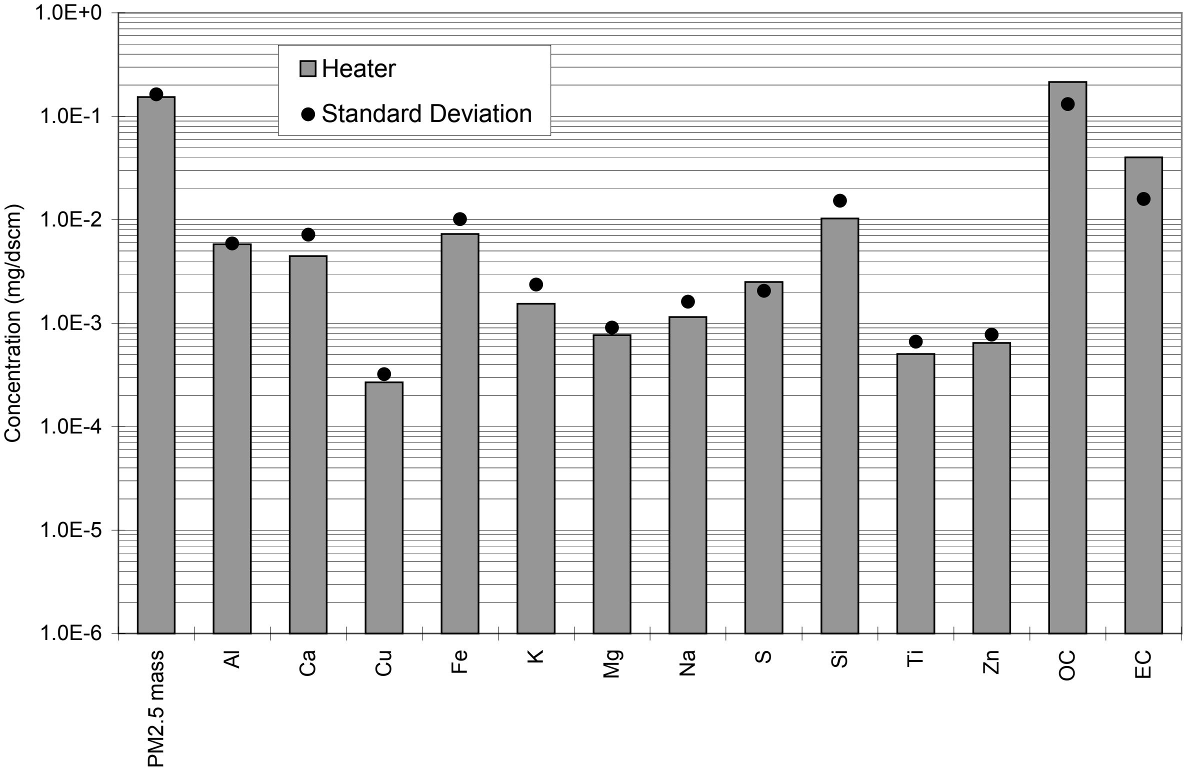


Figure 7-6. Comparison of Average Sample Concentration and Detection Limits (Site Charlie).

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 profile (Figure 7-7) suggests that these are OC and EC.

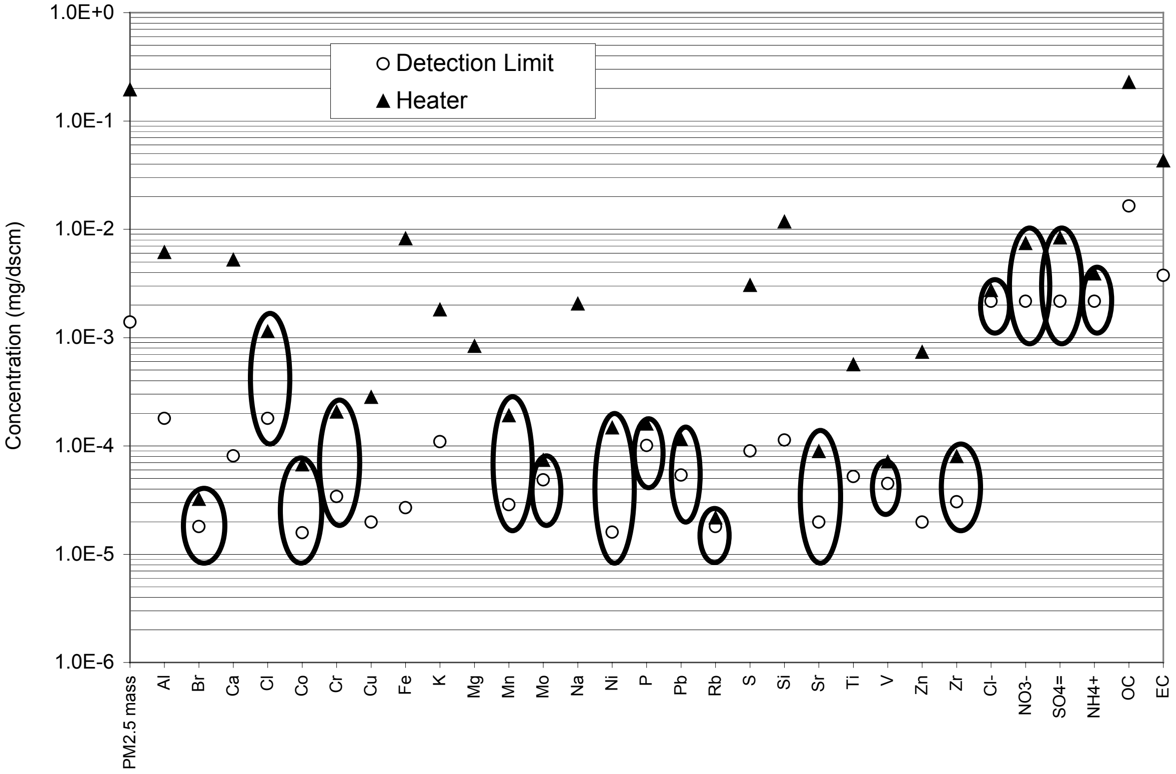


Figure 7-7. Average Sample Concentration Minus Ambient Concentration (Site Charlie).

The uncertainty of several of these values is large, as reflected in the high standard deviations, casting doubt on any of the species being definitively used as an emissions marker. Compounds with high uncertainties suggest that they may not be reliable markers.

Another potentially useful marker for source emissions is the organic emissions profile. All of the SVOCs detected were present at low concentrations. About 25 percent of the SVOC compounds at detectable levels in the stack gas are within a factor of ten of their concentration in the ambient air. Total SVOCs (including all compounds listed in Table 4-10) account for approximately 12 percent of the OC measured by the dilution sampler indicating the presence of unspeciated 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 quantifiable by the methods used in this study.

OC emissions for Site Charlie are slightly higher than those from Sites B and Alpha, but still within an order of magnitude of those sites (Table 7-5). OC emissions from Sites A and Bravo are approximately equal to those from Site Charlie. Measurable SVOC emissions at Site Charlie were slightly lower than those at Site A. VOC emissions from Site Charlie are the same order of magnitude as measured at all other sites to date, however this number may be biased high due to the high levels of potential Tenax degradation products detected in the samples.

Table 7-5. 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	9.3E-5	1.0E-5	1.0E-4	5.5E-6	3.6E-5
Site Bravo	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, SCR and oxidation catalyst	2.0E-4	1.9E-5	2.2E-4	9.1E-7	NI
Site Charlie	Refinery Gas-fired Heater	1.9E-4	3.6E-5	2.2E-4	3.0E-6	2.4E-4

* Sum of substances included in Table 5-2.

** Sum of substances measured on Tenax and included in Table 5-3.

NI - None of the measured species emission factors met the Table 5-3 inclusion critieria.

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 semivolatile organic compounds. For Site Charlie, of the species listed in Table 5-2, only B-MePy/MeFl and A-methylphenanthrene are significantly greater than their ambient and dilution sampler blank concentrations (greater than 2 standard deviations at a 95 percent confidence level), and might be potential marker species. However, the relative concentrations of these compounds may not be unique enough to clearly distinguish this source from other external combustion sources.

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.

FINDINGS

The main findings of these tests are:

- Particulate mass emissions from the heater were extremely low, consistent with levels expected for gaseous fuel combustion. Based on the gas fired sources comparison shown in Table 7-4, ammonia injection does not appear to impact PM2.5 emissions.

- Two methods for determining the average emission factor for primary PM2.5 mass gave results that differed by an order of magnitude: 0.00016 lb/MMBtu using the dilution sampler; and 0.0011 lb/MMBtu using conventional hot filter and iced impinger methods for filterable and condensable particulate. This difference is attributed to three likely causes:

    - Solid particle emissions are extremely low, below the capability of traditional hot filter methods to measure with high confidence. Over 90 percent of the total PM2.5 emission measured by the hot filter/iced impinger method was found in the impinger fraction (condensable particulate matter);

    - Traditional impinger methods are subject to significant positive bias, especially for gas-fired sources. Sampling and analytical artifacts principally caused by gaseous SO_2 in the stack gas sample are known to produce a relatively large positive bias in condensable particulate as measured by impinger methods. The large amount of $SO_4^=$ in the impinger residue compared to much smaller amounts of $SO_4^=$ in the dilution sampler found in these tests indicates this artifact was probably a significant factor.

    - Aerosol thermo-physics dictates that condensation of vapor phase substances in the impingers of traditional methods will be greater than condensation in the dilution sampler. Vapor phase substances in the stack gas will not condense until cooled, and if this cooling occurs without dilution, as in the impingers of the Method 202 train, more material will condense than in a real-world plume, where dilution occurs at the same time as the stack gases are cooled. Thus, the results obtained with impinger methods are positively biased, and dilution sampling results are considered more representative of true emissions.

- 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.

- OC and EC comprise approximately 85 percent of the total PM2.5 chemical species measured by the dilution sampler; however, the quartz filter used for ion and carbon speciation is subject to organic absorptive bias, especially in low load sources, such as gas-fired heaters, so a likely source of this difference is the high organic carbon value. A backup quartz filter sampled behind the TMF indicated that about three-quarters of the organic carbon might be due to adsorption bias.

- Most elements and organic compounds are not present at levels significantly above the background levels in the ambient air and blanks or above the minimum detection limits of the test methods. These extremely low levels are consistent with gaseous fuel combustion, and combined with the variability in the emission rates, result in large uncertainties for many of the reported emissions. The 95% confidence upper bounds for the emission factors provide conservative estimates of the PM emission factors that are much lower and more reliable than those determined by Method 202 and its gas absorption bias.

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Appendix A
LIST OF ABBREVIATIONS

$(Na)_2SO_4$	sodium sulfate
°C	degrees Celsius
°F	degrees Fahrenheit
$\mu g/cm^2$	micrograms per square centimeter
µg/ml	micrograms per milliliter
µm	micrometers
AC	automated colorimetric 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
Au	gold
B	boron
Ba	barium
Br	bromine
Btu/dscf	British thermal units per dry standard cubic foot
Ca	calcium
Cd	cadmium
CEC	California Energy Commission
CEMS	continuous emissions monitoring system
cfm	cubic feet per minute
Cl^-	chloride ion
Cl	chlorine
Co	cobalt
CO_2	carbon dioxide
CPM	condensible particulate matter
Cr	chromium
Cu	copper
DI	distilled deionized
DNPH	dinitrophenylhydrazine
DOE	United States Department of Energy
DRI	Desert Research Institute
dscfm	dry standard cubic feet per minute
dscmm	dry standard cubic meters per minute
EC	elemental carbon
ECD	electron capture detection
ED-XRF	energy dispersive x-ray fluorescence
EI	electron impact
EPA	Environmental Protection Agency
ERA	Environmental Research Associates

LIST OF ABBREVIATIONS
(Continued)

eV	electron volts
Fe	iron
FID	flame ionization detection
FPM	filterable particulate matter
Ga	gallium
GC	gas chromatography
GC/IRD/MSD	gas chromatography/infrared detector/mass selective detector
GC/MS	gas chromatography/mass spectrometry
GCS	gas chromatographic separation
GE EER	GE Energy and Environmental Research Corporation
GE MP	GE MostardiPlatt
GRI	Gas Research Institute
H_2O	water
H_2SO_4	hydrosulfate acid
HC	hydrocarbon
HEPA	high efficiency particulate air
Hg	mercury
HPLC	high performance liquid chromatography
IC	ion chromatography
ICP/MS	inductively coupled plasma/mass spectrometry
In	indium
K	potassium
K_2CO_3	potassium carbonate
keV	kilo electron volts
KHP	potassium hydrogen phthalate
La	lanthanum
lb/hr	pounds per hour
lb/MMBtu	pounds of pollutant per million British thermal units of gas fired
Lpm	liters per minute
MDL	method detection limit
MeFl	methylfluorene
MEK	methyl ethyl ketone
MePy	methylpyrene
Mg	magnesium
mg	milligram
mg/dscm	milligrams per dry standard cubic meter
MID	multiple ion detection
mL	milliliter
mm	millimeter
MMBtu/hr	million British thermal units per hour
MMdscfh	million dry standard cubic feet per hour
Mn	manganese
Mo	molybdenum

LIST OF ABBREVIATIONS
(Continued)

Mscfh	thousand standard cubic feet per hour
MSD	mass selective detector
MSD/FTIR	mass selective detector/Fourier transform infrared detection
n/a	not applicable
N_2	Nitrogen
Na	sodium
Na^+	sodium ion
NaCl	sodium chloride
$NaNO_3$	sodium nitrate
ND	not detected
ng/µl	nanograms per microliter
NH_3	ammonia
NH_4^+	ammonium ion
NH_4OH	ammonium hydroxide
Ni	nickel
NIST	National Institute of Standards and Technology
NMHC	non-methane hydrocarbons
NO_3^-	nitrate ion
NO_x	oxides of nitrogen
NV	not valid
NYSERDA	New York State Energy Research and Development Authority
O_2	molecular oxygen
OC	organic carbon
P	phosphorus
PAH	polycyclic aromatic hydrocarbon
Pb	lead
Pd	palladium
pH	potential of hydrogen
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 micrometers
PM2.5	particulate with aerodynamic diameter less than 2.5 micrometers
ppm	parts per million
PUF	polyurethane foam
QA	quality assurance
Rb	rubidium
RSD	relative standard deviation
S	sulfur
Sb	antimony
SCAQMD	South Coast Air Quality Management District
SCR	Selective catalytic reduction
Se	selenium
Si	silicon
SI	Système Internationale

LIST OF ABBREVIATIONS
(Continued)

sLpm	standard liters per minute
Sn	tin
SO_2	sulfur dioxide
$SO_4^=$	sulfate ion
Sr	strontium
SRM	standard reference material
SS	stainless steel
SVOC	semivolatile organic compound
Ti	titanium
TIGF	Teflon-impregnated glass fiber
Tl	thallium
TMF	Teflon-membrane filter
TOR	thermal/optical reflectance
TSI	Thermo Scientific Incorporated
U	uranium
V	vanadium
VOC	volatile organic compound
WHRB	waste heat-recovery boiler
XAD-4	Amberlite® sorbent resin (trademark)
XRF	x-ray fluorescence
Y	yttrium
Zn	zinc
Zr	zirconium

Appendix B

SI CONVERSION FACTORS

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