Energy Research and Development Division
INTERIM/FINAL PROJECT REPORT

EVALUATION & IMPROVEMENT OF PARTICULATE MATTER FROM NG POWER PLANTS

Prepared for: California Energy Commission
Prepared by: Center for Environmental Research and Technology

SEPTEMBER 2015
CEC-500-10-038

PREPARED BY:

Primary Author(s):

Wayne Miller
David Cocker
Bill Welch

Center for Environmental Research and Technology
1084 Columbia Ave
Riverside, CA 92501
Phone: 951-781-5791 | Fax: 951-781-5790
http://www.cert.ucr.edu/

Contract Number: 500-10-038

Prepared for:

California Energy Commission

Guido Franco
Contract Manager

Rachel Grant
Office Manager
Energy Commission Research Office

Laurie ten Hope
Deputy Director
ENERGY RESEARCH AND DEVELOPMENT DIVISION

Robert P. Oglesby
Executive Director

ACKNOWLEDGEMENTS

We would like to acknowledge Marla Mueller, the initial CEC project manager, and the assistance of UCI, UCR staff and students, particularly Nicholas Gysel, and the advisory board for their assistance in completion of this project.

PREFACE

The California Energy Commission Energy Research and Development Division supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The Energy Research and Development Division conducts public interest research, development, and demonstration (RD&D) projects to benefit California.

The Energy Research and Development Division strives to conduct the most promising public interest energy research by partnering with RD&D entities, including individuals, businesses, utilities, and public or private research institutions.

Energy Research and Development Division funding efforts are focused on the following RD&D program areas:

- Buildings End-Use Energy Efficiency
- Energy Innovations Small Grants
- Energy-Related Environmental Research
- Energy Systems Integration
- Environmentally Preferred Advanced Generation
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Transportation

Evaluaton & Improvement of Particulate Matter from NG Power Plant is the final report for the PIER project (contract number 500-10-038) conducted by Center for Environmental Research and Technology. The information from this project contributes to Energy Research and Development Division's Energy-Related Environmental Research Program.

For more information about the Energy Research and Development Division, please visit the Energy Commission's website at www.energy.ca.gov/research/ or contact the Energy Commission at 916-327-1551.

ABSTRACT

Extensive testing of three natural gas fired turbines using both existing protocol methods and the dilution methods yielded widely varying results. As documented in the report, PM emissions were well below measurable levels that these protocols were developed for. Further, the method of dilution (temperature, dilution ratio, residence time, and relative humidity) had significant (albeit varied test unit to test unit) impacts on measured particulate matter. While PM mass concentrations measured varied by several order of magnitude, in all cases the PM mass concentrations in the effluent after dilution were below the ambient NAAQS PM standard and were often well below that of the surrounding air ambient concentrations.

Development of an inexpensive electronic monitor or simplified test method requires determination of what the most appropriate dilution conditions to simulate the particle formation near a turbine. This requires additional measurements beyond the scope of this program such as PM mass concentration of the evolving plume near the exit of a turbine. This may be accomplished in future research programs through an ambient field campaign that allows for measurements at the near stack (perhaps weather balloon, drone, or small aircraft).

Keywords: Particulate Matter Mass and Number, Power plant emissions, Natural Gas Testing and Characterization

Please use the following citation for this report:

Miller, Wayne; Cocker, David; Welch, Bill. (California Energy Commission). 2015. ***Evaluation & Improvement of Particulate Matter from NG Power Plant.*** California Energy Commission. Publication number: CEC-500-10-038.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

Introduction

The problem of accurate particulate (PM) measurement needs resolution to ensure timely installation and appropriate costs for new natural gas (NG) power plants. Understanding analytical methods used to measure the PM emissions are a key element in determining how to apply them to the new NG plants. The current test methods need to be updated using the many recent advances in PM measurement methods to accurately reflect the low emission levels now being seen from NG power plants. The CEC, EPA and ARB are aware of the challenge to accurately measure low PM levels, which has promulgated this study to determine whether the current analytical methods provide the required data for measuring PM with an acceptable range, sensitivity, accuracy, and precision.

Project Purpose

The current methods and instrumentation used for measuring PM were first assessed in a literature review. The information from the review and input from a key advisory group was then used to develop an appropriate set of tests to determine if current, proposed, or available instruments and mechanisms exist for accurate testing of PM from natural gas power plants. One of the tested power plants is shown in Figure EX-1. A total of three power plants of varying sizes were planned and executed (Table EX-1).

Figure EX-1: A 50 MW, Peaker Power Plant Using GE's LM6000 Turbine with SCR

Table EX-1: List of NG Power Generation Units Tested

Test	Power Generator Description
1	Capstone C-65 microturbine (65kW)
2	Solar Titan™ 130 Turbine + SCR (13.5MW) on NG
3	Large NG Turbine (~50MW) + control

Project Results

A dilution sampling system was designed and constructed to carryout the unique testing in this project (Figure EX-2).

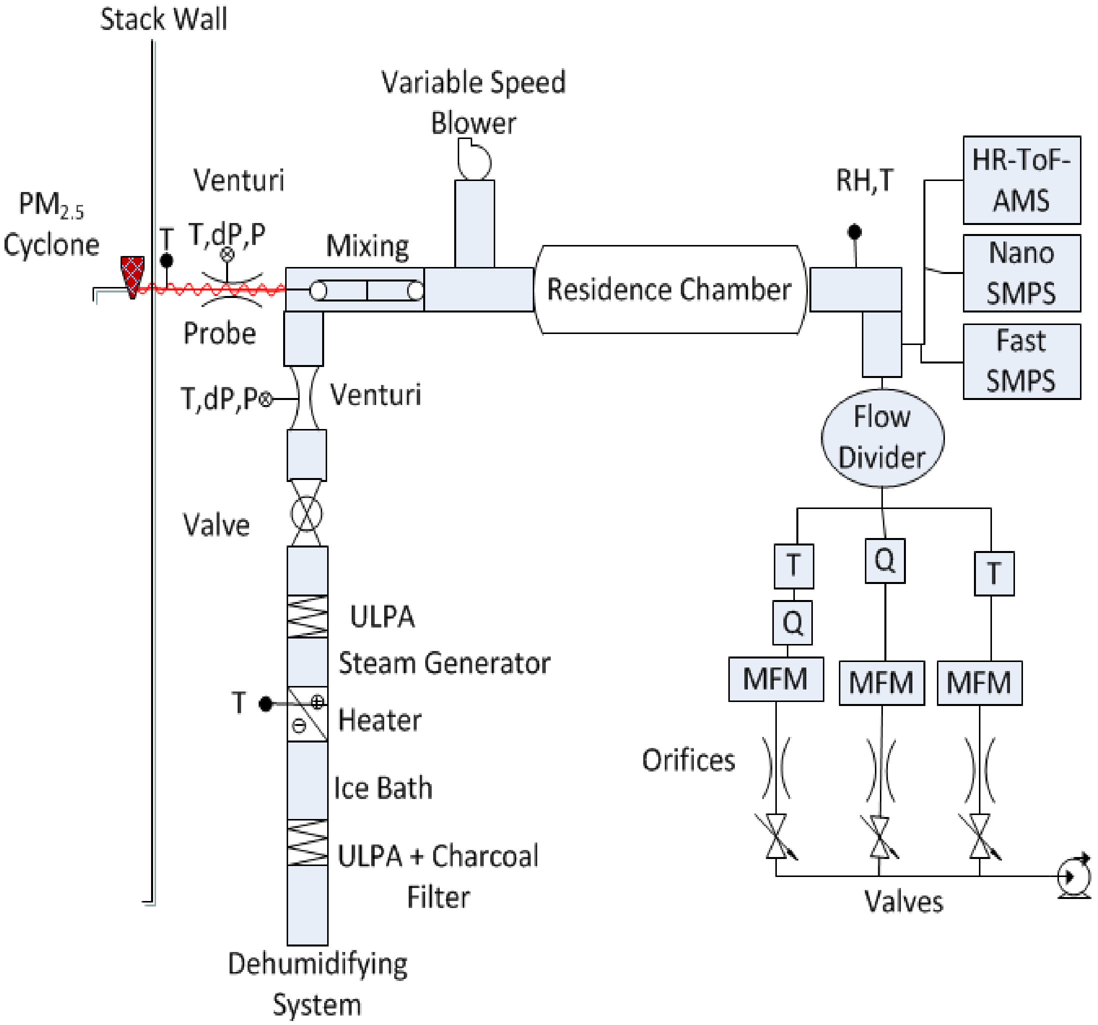


Figure EX-2: UCR Dilution System

The results yielded the following conclusions:

- Particles from NG power plants are extremely small in size (<15 nm) and can beorders of magnitude lower than currently used PM protocol measurement methods. Concentrations of particulate matter were typically well below that of the National Ambient Air Quality Standard (NAAQS) for PM mass (Figure EX-3).
- The protocol and dilution methods produce widely varying results, regardless of the size or type of power plant being tested. (Figure EX-3)
- Two variables are more important than others in varying the PM mass and number: these are the dilution ratio and the residence time. New methods should focus on ensuring these variables are highly controlled for any test method to be successful. (Figure EX-3)
- Each individual dilution method using system created as part of this program can produce consistent and repeatable PM mass and numbers. Emission levels are well below the workable range of the currently used stationary source protocol methods. (Figure EX-3)

Figure EX-3 compares the various measurement methods (both protocol listed in text box and dilution method). Clear findings within this work is that NG turbine emissions are far more sensitive to dilution parameters than has been observed for other emission systems (e.g., diesel exhaust). Decreasing dilution ratio, dilution temperature, dilution ratio and increasing residence time leads to increases in the PM measured, often by orders of magnitude. This is most likely due to the extremely low solid particle formation within the turbines reducing the surface area for condensational growth thereby increasing the impact of nucleation (new particle formation) processes. Due to the incredibly small size of the turbine particles (on the order of 10 – 15 nm), many gas-particle conversion effects are exacerbated as surface tension/energy effects become critical during particle growth.

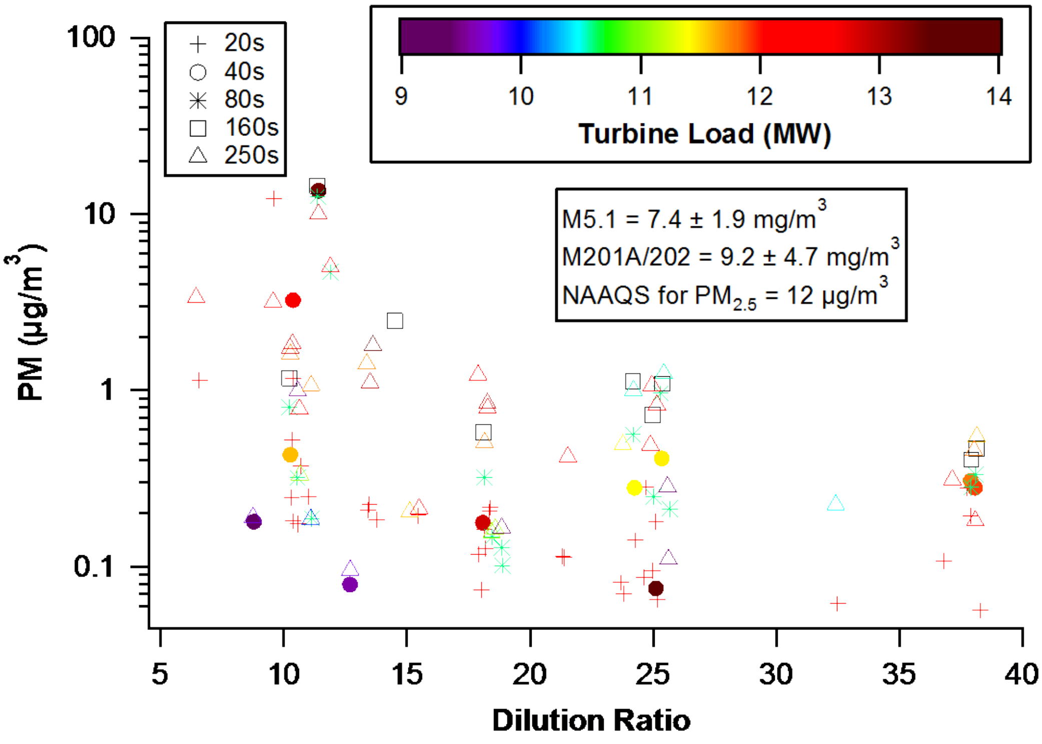


Figure EX-3. Comparison of Different PM Measurement Methods

Development of an inexpensive electronic monitor or simplified test method requires determination of what the most appropriate dilution conditions to simulate the particle formation near a turbine. This requires additional measurements beyond the scope of this program such as PM mass concentration of the evolving plume near the exit of a turbine. This may be accomplished in future research programs through an ambient field campaign that allows for measurements at the near stack (perhaps weather balloon, drone, or small aircraft).

Project Benefits

This project confirms the low levels of PM mass from various natural gas power generation units and provides guidance on the important considerations and next steps to develop new methods to improve our accuracy at these very low levels. Accurate test methods are important for ensuring our electricity production is not causing adverse health impacts and ensuring power plants are in compliance with regulations.

CHAPTER 1:
Literature Review and Data Summary

1.1 Data Summary

This literature review and data summary is prepared for PM emissions from stationary gas turbines and other related relevant literature and data.

The dilution and impinger methods used to measure low PM concentrations are highly variable preventing accurate and precise measurements from being attained. PM measured by these methods for low PM emission sources such as natural gas fired turbines is below the lower quantification limit and minimum detection limit, thereby leading to inaccurate measurements. Contributing to the PM emission rate discrepancies (in addition to PM measurements) from different measurement sites are the control technologies, the fuel, the operating conditions, plant size, plant design and the operating cycle.

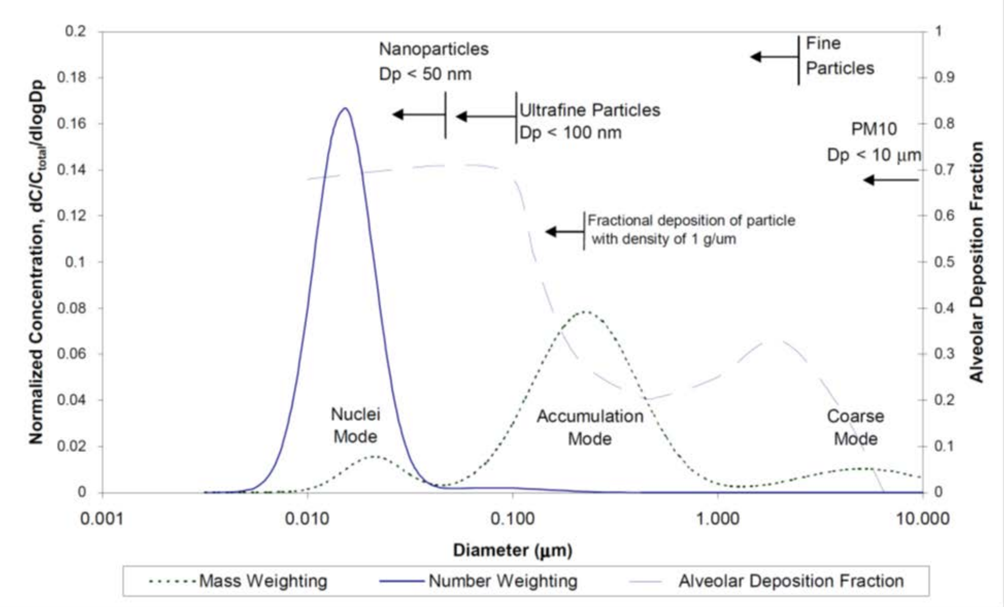
Impinger methods have been known to contribute a positive bias in condensable PM measurements. The oxidation of soluble gases such as SO_2 in the impinger solutions is the main contribution to this artifact in condensable PM measurements. A revised Method 202 has been implemented to minimize biases with dry impingers, a condenser and a condensable PM filter when compared to the standard wet impinger methods. Although results indicate that the revised Method 202 will minimize biases associated with condensable PM, artifact still remains. In response, dilution methods have been pursued, as they have been determined to provide a more accurate representation of atmospheric PM formation and condensation of semi-volatile compounds. The mechanisms of particle formation and physics as described by Kittelson are of a large importance to these methods. Particle formation is sensitive to varying dilution parameters which include residence time, relative humidity, dilution ratio and temperature. Results from the dilution method, CTM 039, indicate that both accurate and precise measurements are difficult to obtain indicating further testing and development is needed when measuring sources of low PM.

1.2 Literature Review of PM from Stationary Gas Turbines

Current methods of measurement for stationary gas turbines are limited by their lower detection limit, such that PM cannot be accurately quantified. Obtaining accurate emission measurements from natural gas power plants is difficult due to the low concentrations of PM emitted. Attaining both accurate and precise measurements is important for a number of reasons. Many regions in California have the title of non-attainment sectors meaning that emissions from newer power plants must offset the emissions from existing plants to meet the regulations placed on PM_{10} and $PM_{2.5}$ (particulates less than 10 micrometers and less than 2.5 micrometers, respectively) by EPA.

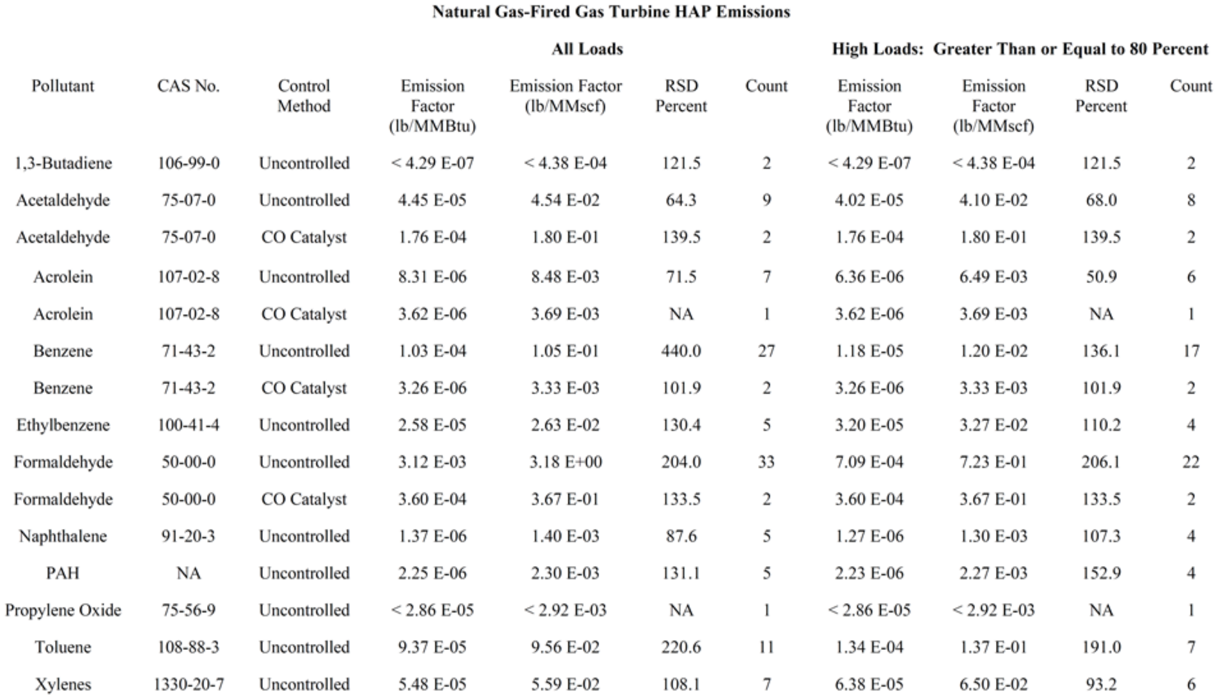
Additionally, the health effects associated with fine particulate matter have been well documented. As shown in Figure 1-1 below[1], the smaller the particles the higher the alveolar deposition rate, which will lead to adverse health effects. EPA regulates $PM_{2.5}$ and PM_{10} with the National Ambient Air Quality Standards (NAAQS) due to their associated health risks, which can include death caused by heart failure as well as other cardiovascular diseases [2].

Figure 1-1: PM Mass, PM Number and Health Effects from PM



Compliance for stationary turbines is provided in US EPA AP-42. The regulations are listed in Table 1-1 to Table 1-4. The filterable PM or FPM was measured with Method 5 or an equivalent method while the condensable particulate matter or CPM was measured with Method 202. All PM data provided for natural gas turbines in AP-42 are listed as “C” data quality or grade which refers to data which “tests that were based on an untested methodology or that lacked a significant amount of background data [3].” It is desired to develop a data set of “A” quality, which states “Multiple tests that were performed on the same source using sound methodology and reported in enough detail for adequate validation. These tests do not necessarily conform exactly to the methodology specified in EPA referenced test methods, but at least follow EPA methods in form and function [3].”

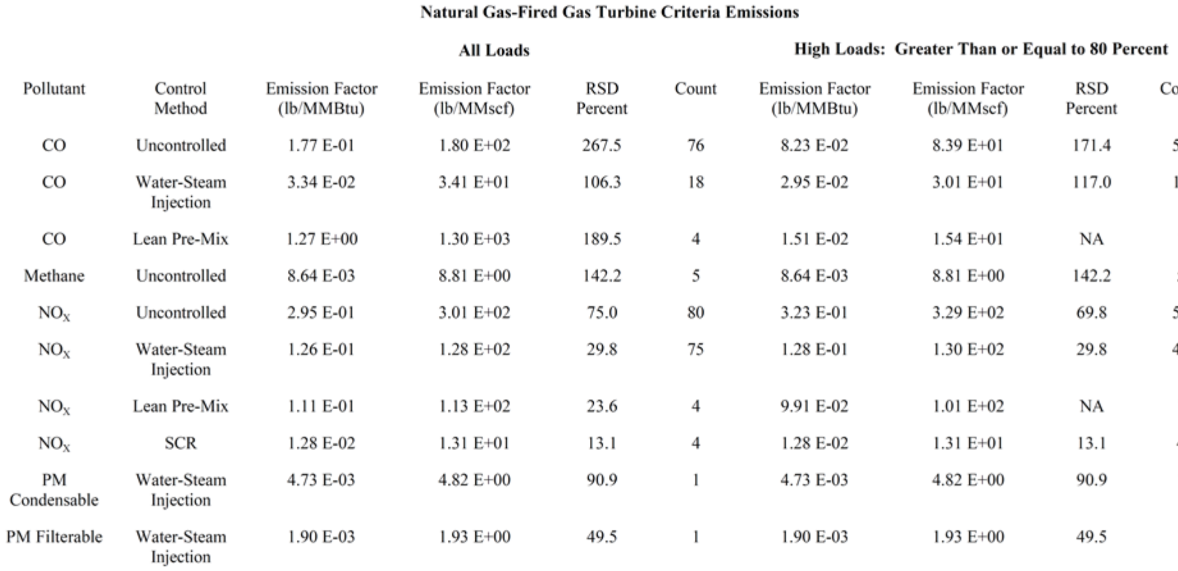
Table 1-1: AP-42 Natural Gas fired Stationary Turbines HAP Emissions



Natural Gas-Fired Gas Turbine HAP Emissions

			All Loads				**High Loads: Greater Than or Equal to 80 Percent**			
Pollutant	CAS No.	Control Method	Emission Factor (lb/MMBtu)	Emission Factor (lb/MMscf)	RSD Percent	Count	Emission Factor (lb/MMBtu)	Emission Factor (lb/MMscf)	RSD Percent	Count
1,3-Butadiene	106-99-0	Uncontrolled	< 4.29 E-07	< 4.38 E-04	121.5	2	< 4.29 E-07	< 4.38 E-04	121.5	2
Acetaldehyde	75-07-0	Uncontrolled	4.45 E-05	4.54 E-02	64.3	9	4.02 E-05	4.10 E-02	68.0	8
Acetaldehyde	75-07-0	CO Catalyst	1.76 E-04	1.80 E-01	139.5	2	1.76 E-04	1.80 E-01	139.5	2
Acrolein	107-02-8	Uncontrolled	8.31 E-06	8.48 E-03	71.5	7	6.36 E-06	6.49 E-03	50.9	6
Acrolein	107-02-8	CO Catalyst	3.62 E-06	3.69 E-03	NA	1	3.62 E-06	3.69 E-03	NA	1
Benzene	71-43-2	Uncontrolled	1.03 E-04	1.05 E-01	440.0	27	1.18 E-05	1.20 E-02	136.1	17
Benzene	71-43-2	CO Catalyst	3.26 E-06	3.33 E-03	101.9	2	3.26 E-06	3.33 E-03	101.9	2
Ethylbenzene	100-41-4	Uncontrolled	2.58 E-05	2.63 E-02	130.4	5	3.20 E-05	3.27 E-02	110.2	4
Formaldehyde	50-00-0	Uncontrolled	3.12 E-03	3.18 E+00	204.0	33	7.09 E-04	7.23 E-01	206.1	22
Formaldehyde	50-00-0	CO Catalyst	3.60 E-04	3.67 E-01	133.5	2	3.60 E-04	3.67 E-01	133.5	2
Naphthalene	91-20-3	Uncontrolled	1.37 E-06	1.40 E-03	87.6	5	1.27 E-06	1.30 E-03	107.3	4
PAH	NA	Uncontrolled	2.25 E-06	2.30 E-03	131.1	5	2.23 E-06	2.27 E-03	152.9	4
Propylene Oxide	75-56-9	Uncontrolled	< 2.86 E-05	< 2.92 E-03	NA	1	< 2.86 E-05	< 2.92 E-03	NA	1
Toluene	108-88-3	Uncontrolled	9.37 E-05	9.56 E-02	220.6	11	1.34 E-04	1.37 E-01	191.0	7
Xylenes	1330-20-7	Uncontrolled	5.48 E-05	5.59 E-02	108.1	7	6.38 E-05	6.50 E-02	93.2	6

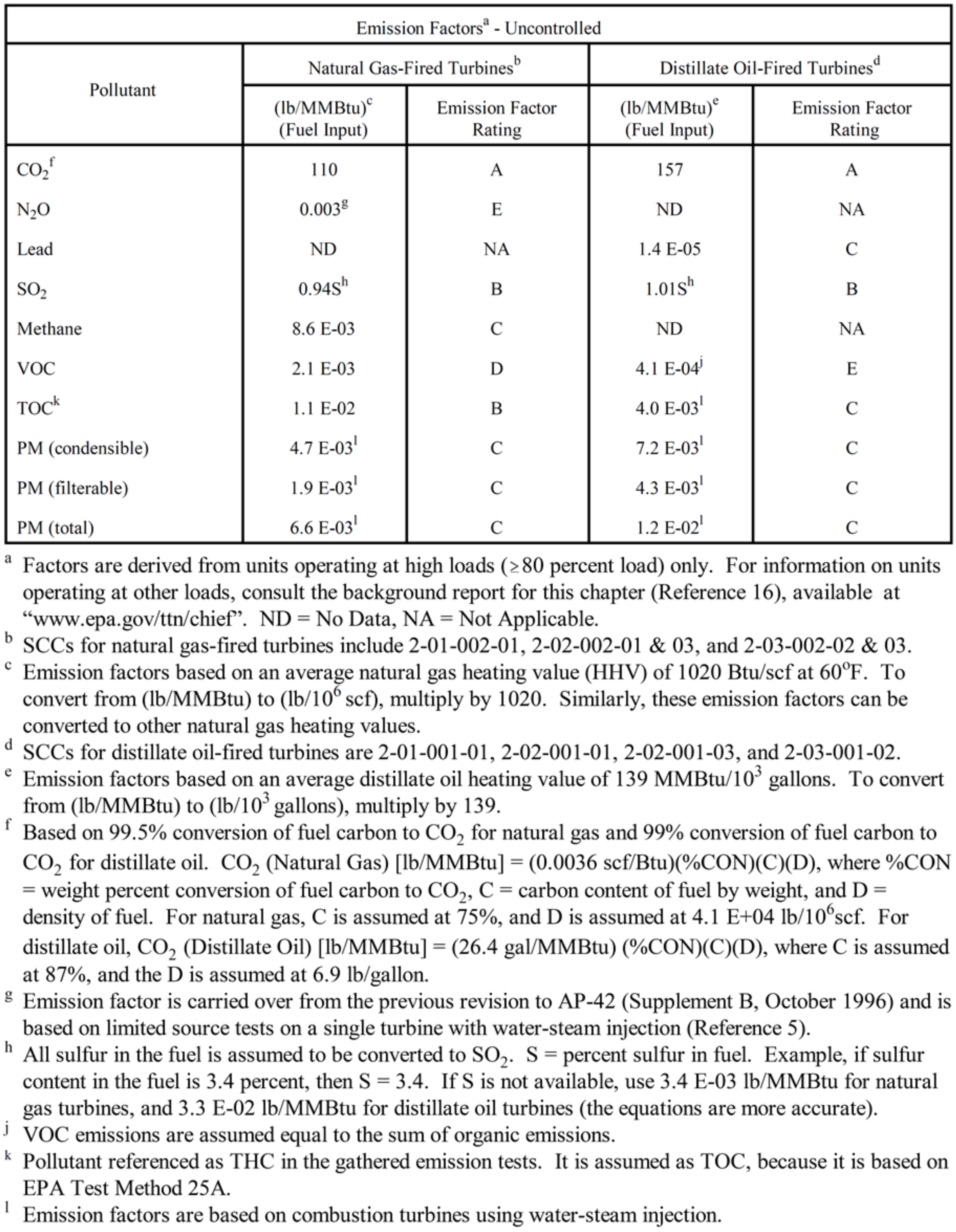
Table 1-2: AP-42 Natural Gas fired Stationary Turbines Criteria Emissions



Natural Gas-Fired Gas Turbine Criteria Emissions

		All Loads				**High Loads: Greater Than or Equal to 80 Percent**			
Pollutant	Control Method	Emission Factor (lb/MMBtu)	Emission Factor (lb/MMscf)	RSD Percent	Count	Emission Factor (lb/MMBtu)	Emission Factor (lb/MMscf)	RSD Percent	Count
CO	Uncontrolled	1.77 E-01	1.80 E+02	267.5	76	8.23 E-02	8.39 E+01	171.4	53
CO	Water-Steam Injection	3.34 E-02	3.41 E+01	106.3	18	2.95 E-02	3.01 E+01	117.0	16
CO	Lean Pre-Mix	1.27 E+00	1.30 E+03	189.5	4	1.51 E-02	1.54 E+01	NA	1
Methane	Uncontrolled	8.64 E-03	8.81 E+00	142.2	5	8.64 E-03	8.81 E+00	142.2	5
NO_X	Uncontrolled	2.95 E-01	3.01 E+02	75.0	80	3.23 E-01	3.29 E+02	69.8	56
NO_X	Water-Steam Injection	1.26 E-01	1.28 E+02	29.8	75	1.28 E-01	1.30 E+02	29.8	46
NO_X	Lean Pre-Mix	1.11 E-01	1.13 E+02	23.6	4	9.91 E-02	1.01 E+02	NA	1
NO_X	SCR	1.28 E-02	1.31 E+01	13.1	4	1.28 E-02	1.31 E+01	13.1	4
PM Condensable	Water-Steam Injection	4.73 E-03	4.82 E+00	90.9	1	4.73 E-03	4.82 E+00	90.9	1
PM Filterable	Water-Steam Injection	1.90 E-03	1.93 E+00	49.5	1	1.90 E-03	1.93 E+00	49.5	1

Table 1-3: AP-42 Natural Gas fired Stationary Turbines Criteria Emissions



Emission Factors[a] - Uncontrolled				
Pollutant	Natural Gas-Fired Turbines[b]		Distillate Oil-Fired Turbines[d]	
	(lb/MMBtu)[c] (Fuel Input)	Emission Factor Rating	(lb/MMBtu)[e] (Fuel Input)	Emission Factor Rating
CO_2[f]	110	A	157	A
N_2O	0.003[g]	E	ND	NA
Lead	ND	NA	1.4 E-05	C
SO_2	0.94S[h]	B	1.01S[h]	B
Methane	8.6 E-03	C	ND	NA
VOC	2.1 E-03	D	4.1 E-04[j]	E
TOC[k]	1.1 E-02	B	4.0 E-03[l]	C
PM (condensible)	4.7 E-03[l]	C	7.2 E-03[l]	C
PM (filterable)	1.9 E-03[l]	C	4.3 E-03[l]	C
PM (total)	6.6 E-03[l]	C	1.2 E-02[l]	C

[a] Factors are derived from units operating at high loads (≥80 percent load) only. For information on units operating at other loads, consult the background report for this chapter (Reference 16), available at "www.epa.gov/ttn/chief". ND = No Data, NA = Not Applicable.

[b] SCCs for natural gas-fired turbines include 2-01-002-01, 2-02-002-01 & 03, and 2-03-002-02 & 03.

[c] Emission factors based on an average natural gas heating value (HHV) of 1020 Btu/scf at 60°F. To convert from (lb/MMBtu) to (lb/10^6 scf), multiply by 1020. Similarly, these emission factors can be converted to other natural gas heating values.

[d] SCCs for distillate oil-fired turbines are 2-01-001-01, 2-02-001-01, 2-02-001-03, and 2-03-001-02.

[e] Emission factors based on an average distillate oil heating value of 139 MMBtu/10^3 gallons. To convert from (lb/MMBtu) to (lb/10^3 gallons), multiply by 139.

[f] Based on 99.5% conversion of fuel carbon to CO_2 for natural gas and 99% conversion of fuel carbon to CO_2 for distillate oil. CO_2 (Natural Gas) [lb/MMBtu] = (0.0036 scf/Btu)(%CON)(C)(D), where %CON = weight percent conversion of fuel carbon to CO_2, C = carbon content of fuel by weight, and D = density of fuel. For natural gas, C is assumed at 75%, and D is assumed at 4.1 E+04 lb/10^6scf. For distillate oil, CO_2 (Distillate Oil) [lb/MMBtu] = (26.4 gal/MMBtu) (%CON)(C)(D), where C is assumed at 87%, and the D is assumed at 6.9 lb/gallon.

[g] Emission factor is carried over from the previous revision to AP-42 (Supplement B, October 1996) and is based on limited source tests on a single turbine with water-steam injection (Reference 5).

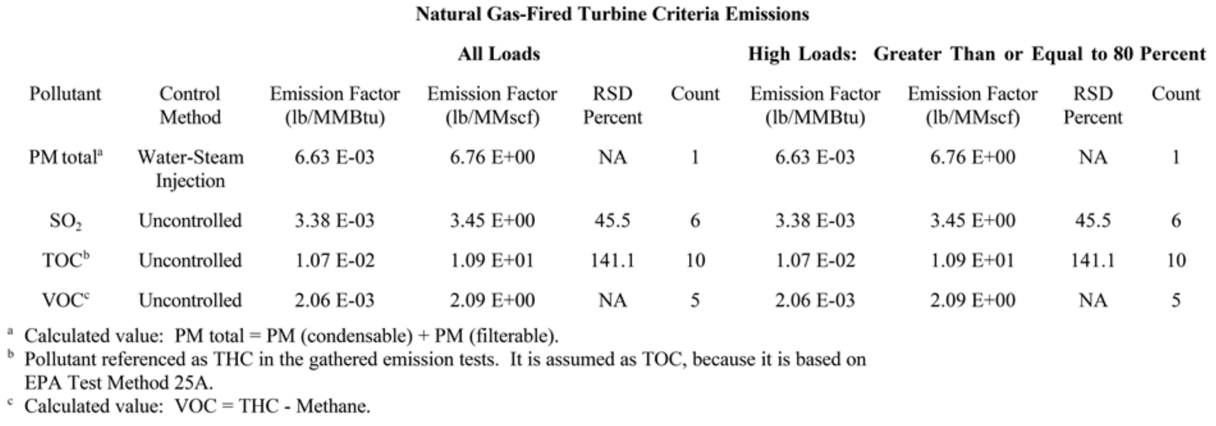
[h] All sulfur in the fuel is assumed to be converted to SO_2. S = percent sulfur in fuel. Example, if sulfur content in the fuel is 3.4 percent, then S = 3.4. If S is not available, use 3.4 E-03 lb/MMBtu for natural gas turbines, and 3.3 E-02 lb/MMBtu for distillate oil turbines (the equations are more accurate).

[j] VOC emissions are assumed equal to the sum of organic emissions.

[k] Pollutant referenced as THC in the gathered emission tests. It is assumed as TOC, because it is based on EPA Test Method 25A.

[l] Emission factors are based on combustion turbines using water-steam injection.

Table 1-4: AP-42 Natural Gas Fired Stationary Turbines Uncontrolled Emission Factors



Natural Gas-Fired Turbine Criteria Emissions

		All Loads				**High Loads: Greater Than or Equal to 80 Percent**			
Pollutant	Control Method	Emission Factor (lb/MMBtu)	Emission Factor (lb/MMscf)	RSD Percent	Count	Emission Factor (lb/MMBtu)	Emission Factor (lb/MMscf)	RSD Percent	Count
PM total[a]	Water-Steam Injection	6.63 E-03	6.76 E+00	NA	1	6.63 E-03	6.76 E+00	NA	1
SO_2	Uncontrolled	3.38 E-03	3.45 E+00	45.5	6	3.38 E-03	3.45 E+00	45.5	6
TOC[b]	Uncontrolled	1.07 E-02	1.09 E+01	141.1	10	1.07 E-02	1.09 E+01	141.1	10
VOC[c]	Uncontrolled	2.06 E-03	2.09 E+00	NA	5	2.06 E-03	2.09 E+00	NA	5

[a] Calculated value: PM total = PM (condensable) + PM (filterable).

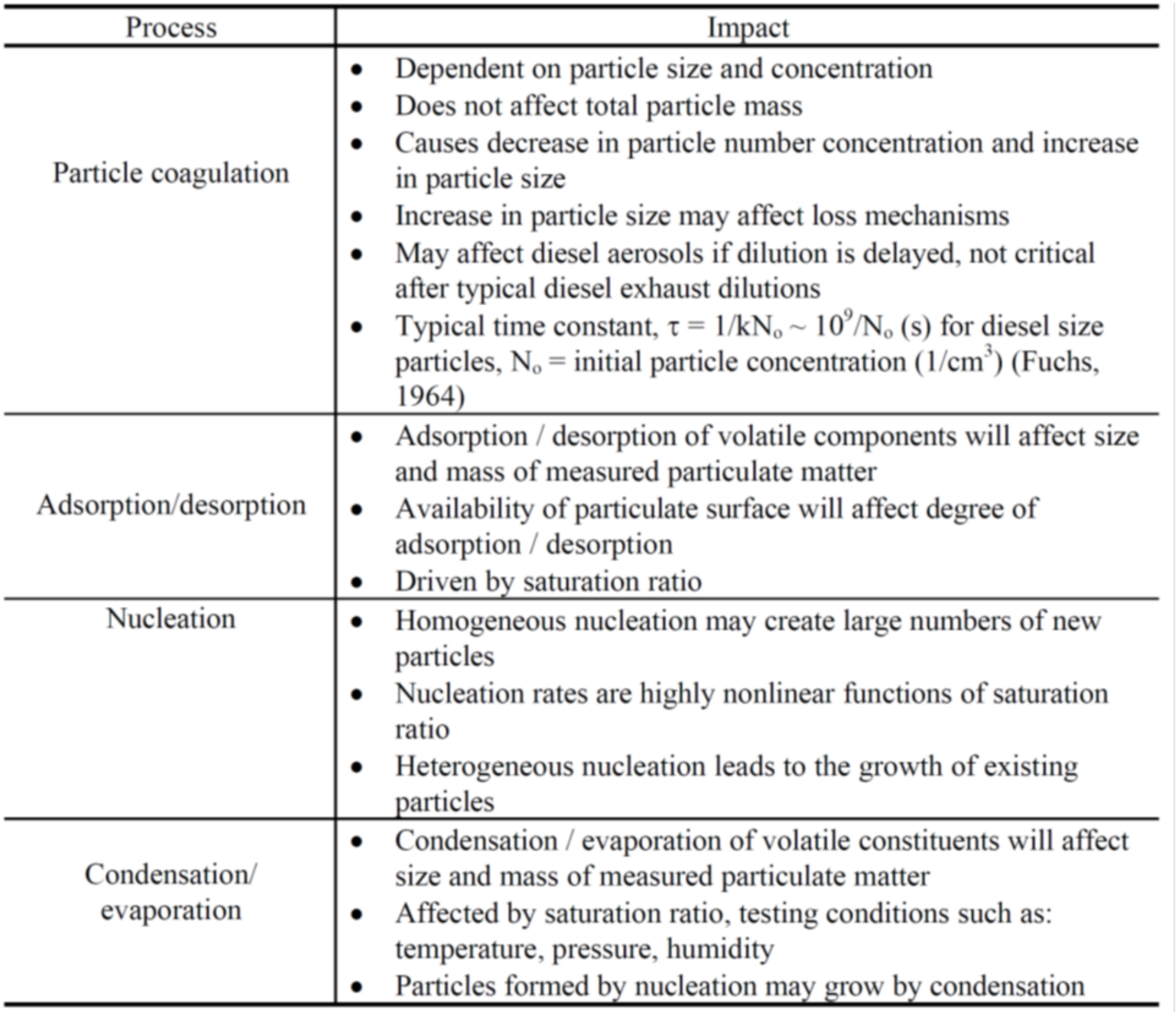
[b] Pollutant referenced as THC in the gathered emission tests. It is assumed as TOC, because it is based on EPA Test Method 25A.

[c] Calculated value: VOC = THC - Methane.

1.1.1 Particle Formation

The mechanisms and particle transformations for diesel exhaust as proposed by Kittelson are summarized in Table 1-5. For diesel fired engines, the majority of the larger particles are emitted at the higher temperatures, as depicted in Figure 1-2 below. As the temperature cools, the volatile and semi-volatiles emitted from the tailpipe or exhaust will undergo rapid dilution followed by nucleation and rapid condensational particle growth. Nucleation is dependent upon the semi-volatile concentration and the surface area of existing carbon agglomerates available for semi-volaties to condense. As noted by Kittelson, since the semi-volatiles are sensitive to the conditions outside the tailpipe (e.g., dilution rate, temperature, relative humidity), the dilution conditions will play a large role in particle formation [1]. Dilution can generate new particles from condensable gases through the following pathways. The first of which is cooling the sample gas to a low enough temperature to lower the vapor pressure of the semi-voltaile precursors to achieve a sufficiently high supersaturation ratio thereby promoting the semi-volatiles to nucleate and form new particles. The second pathway is to reduce the primary PM emissions such that there are fewer surfaces available for semi-volatiles to condense onto allowing for achievement of greater supersaturation ratios and therefore enhancing nucleation. Nucleation processes rapidly increases the number concentration; however, do to their small size, has only minor impacts on PM mass concentration. Alternatively, heterogeneous condensation increases PM mass concentration and shifts the PM size mode to a larger particle size [4]. As determined by studies conducted by Kittelson, the dilution temperature will affect the concentration of nuclei mode particulate by affecting the peak supersaturation ratio achieved with new particle nucleation increasing with decreasing dilution air temperature [1]. There is a tradeoff to which preferential particle mode will occur: the nucleation mode (fresh particles) or accumulation (through condensational or coagulation growth). If the emission source has many larger particles such as carbonaceous agglomerates (large surface area), the semi-volatiles will either adsorb onto the existing particles or coagulate forming a larger accumulation mode as the supersaturation ratio will be too low for nucleation to occur. Conversely, if the emissions have low particle surface area, nucleation will become the preferential mode as the supersaturation ratio will be high enough for nucleation to occur.

Table 1-5: Kittelson PM Drivers



Process	Impact
Particle coagulation	• Dependent on particle size and concentration • Does not affect total particle mass • Causes decrease in particle number concentration and increase in particle size • Increase in particle size may affect loss mechanisms • May affect diesel aerosols if dilution is delayed, not critical after typical diesel exhaust dilutions • Typical time constant, $\tau = 1/kN_o \sim 10^9/N_o$ (s) for diesel size particles, N_o = initial particle concentration ($1/cm^3$) (Fuchs, 1964)
Adsorption/desorption	• Adsorption / desorption of volatile components will affect size and mass of measured particulate matter • Availability of particulate surface will affect degree of adsorption / desorption • Driven by saturation ratio
Nucleation	• Homogeneous nucleation may create large numbers of new particles • Nucleation rates are highly nonlinear functions of saturation ratio • Heterogeneous nucleation leads to the growth of existing particles
Condensation/ evaporation	• Condensation / evaporation of volatile constituents will affect size and mass of measured particulate matter • Affected by saturation ratio, testing conditions such as: temperature, pressure, humidity • Particles formed by nucleation may grow by condensation

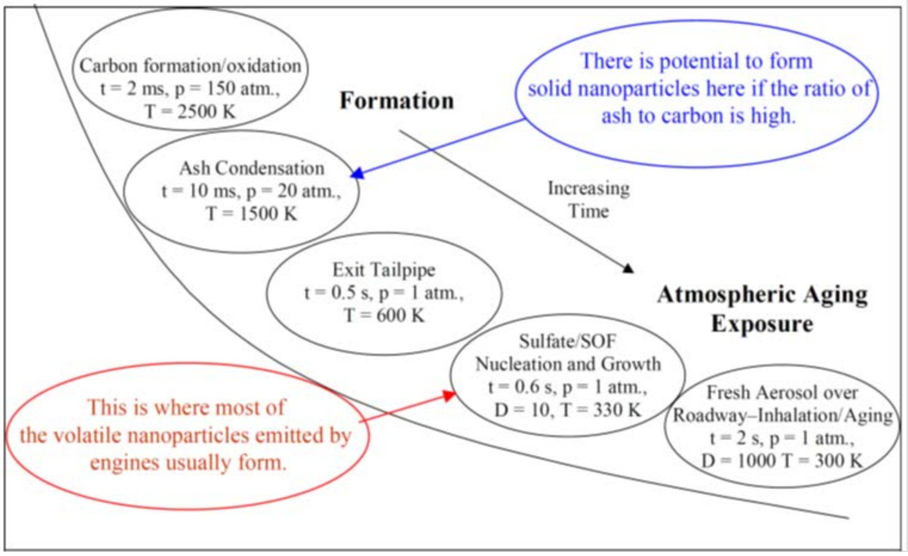


Figure 1-2: Kittelson Particle Formation from Diesel Engines

Important to the conventionally used methods in this project is the fuel sulfur content. Sulfur will oxidize during combustion to form mainly SO_2 with a small fraction converted to SO_3, which rapidly converts in the presence of water to sulfuric acid (H_2SO_4). Since sulfur deposits in the impingers have been known to cause gross overestimation of CPM in conventional methods [5,6,7], the formation of SO_2 and SO_3 is of great importance to this study. Previously, it was determined by Doyle in 1961 that homogeneous nucleation occurs between sulfuric acid and water at a small partial pressure of 10E-9 Torr and temperature of 298K and 50% relative humidity [8]. Kittelson and Khalek [8] studied the effect of solid particles on volatile matter condensation for diesel emissions. The test conditions included a temperature of 42 C, dilution ratio of 18 and 0.03% sulfur fuel content. Three modes were studied, which include zero solid particle background, moderate and heavy PM loading. They found that solid particles decrease nucleation by two orders of magnitude.

With cleaner fuel technologies, such as natural gas fueled power plants, nucleation will be the predominant mode. Additionally, with after treatment systems, the nucleation mode can be enhanced. Kittelson [1] determined that for a diesel operating at 50% load, the number concentration was much higher at low temperature and high residence time when compared to a case of high dilution temperature and low residence time. Although these studies were conducted on diesel engines, it shows the sensitivity of the nanoparticles to dilution conditions. Since smaller particle sizes are predominant in natural gas PM emissions, much can be learned and applied from the work of Kittelson and Khalek.

Ronkko et al. [9] measured nanoparticle formation and dilution effects on PM with a heavy-duty diesel vehicle. They found that lowering the dilution temperature would increase the particle concentration and size of the nanoparticles. Accordingly Vaaraslahti et al. [10] determined that nucleation will occur at both lower and higher operational loads. They proposed at higher loads (high temperature) with catalyst and a particulate filter that sulfur oxidation to SO_2 and SO_3 increases leading to increased H_2SO_4 nanoparticle formation. While at lower loads (low temperature) without any control technologies, hydrocarbons will become the predominant mechanism to particle formation as SO_3 concentration remains low.

1.1.2 Test Methods/Instrumentation and Literature Results

Each of the proceeding methods will be tested for their accuracy and precision when measuring PM. These methods include CARB Method 5, EPA Methods 201A and 202, and EPA Conditional Test Method (CTM) 039

1.1.2.1 CARB Method 5

CARB Method 5 is an in-stack method which measures the total suspended particulate (TSP), both filterable from a heated filter and condensable from liquid impinger trains. It is essentially a combination of EPA Method 5 and the EPA wet impinger Method 202. The sample train is shown in Figure 1-2. Liquid impingers measure the CPM by using a liquid medium to dissolve the particulate from the sample. The liquid medium is then analyzed and the CPM is determined from the total sample volume run through the impinger(determined by a dry gas meter). The PM collected is defined by CARB Method 5 as follows: “The particulate matter catch shall be itemized by weight as follows: (1) Filter Catch, (2) Probe Catch, (3) Impinger Catch, and (4) Solvent Extract to allow adjustment of the particulate matter determination to be consistent with the applicable regulation [11].” From previous studies conducted by EPA, it was determined that the CPM measured by liquid impingers led to a positive bias [5,6,7]. Since some noncondensable gases can oxidize in the water medium, forming pseudo-particulate (e.g., SO_2 to SO_4^{2-}), a positive CPM bias can occur with the noncondensable gases counted towards CPM. In this work , the direct or FPM from this method is compared to Method 201A, while the CPM is compared to the dry impinger Method 202.

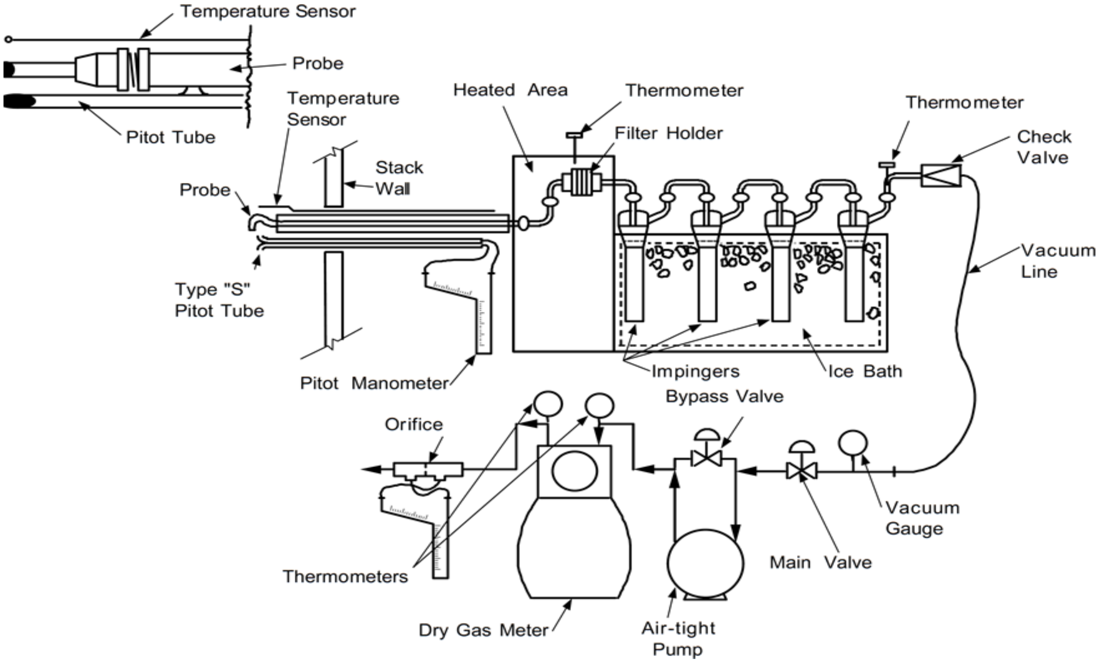


Figure 1-2 CARB Method 5 Sampling Train

1.1.2.2 EPA Method 201A and 202

Method 201A [12] is an in-stack method which measures filterable PM_{10} and/or $PM_{2.5}$ (Figure 1-3). A pre-determined stack gas flow rate is isokinetically withdrawn from the stack to the cyclones through a heated line and filter holder for FPM collection. The sample is then passed to a condenser. The condenser recirculates water from the impinger water bath to cool the sample gas flow. The first impinger known as the water droplet knockout impinger is used to separate the water from the sample gas, while the next empty backup impinger is used to further knockout water and ensure CPM formation. The CPM is then collected in the first two impingers and on the CPM filter. This back half portion of the sampling train (after FPM collection) is called Method 202 [13] which is shown in Figure 1-4. The revised Method 202 (condenser and dry impingers) are compared in this work with CARB Method 5, to determine the parameters, which leads to positive biases in CPM measurements; the direct PM will also be compared by both methods. The biases to be minimized are the pseudo-particulate formed due to the oxidation of soluble gases. These soluble gases will include SO_2 and NO_2 as well as others. Based on the study conducted by Richards et al. [14], it was determined that the conversion of sulfur dioxide to sulfuric acid is up to three times higher per hour in an aqueous setting compared to a dry setting. Although dry impingers will minimize the sulfur containing artifact, it will not completely rid the biases as sulfur oxidation begins immediately upon sampling. Having said this, it is hypothesized that the dry impinger Method 202 will have less CPM than the wet impinger methods.

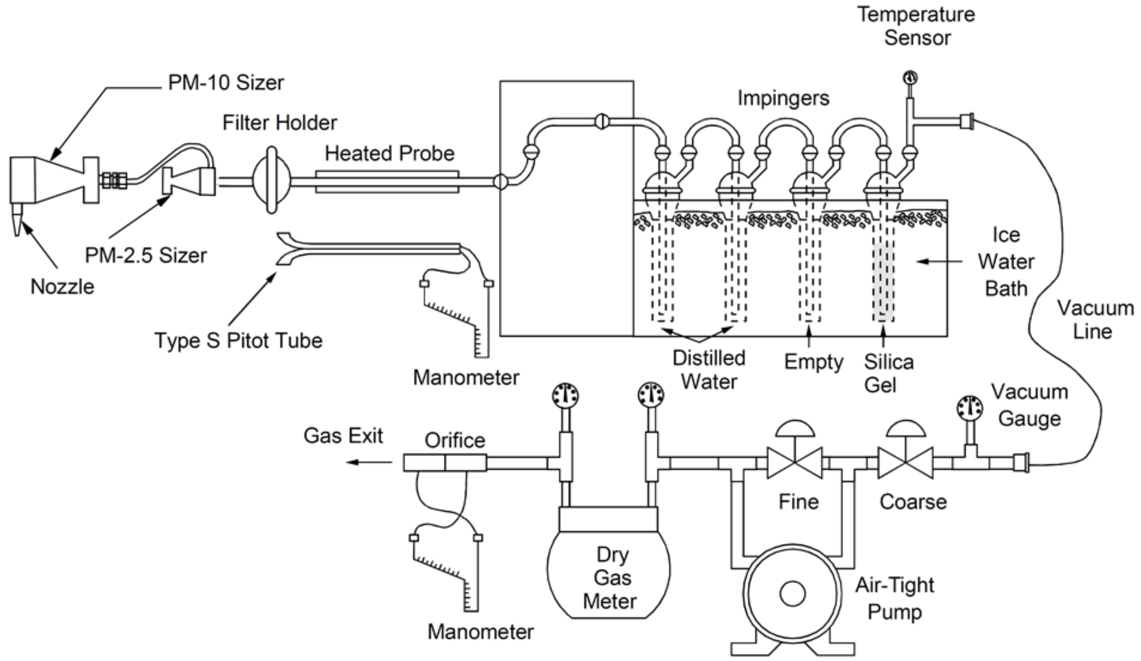


Figure 1-3: EPA Method 201A Sampling Train

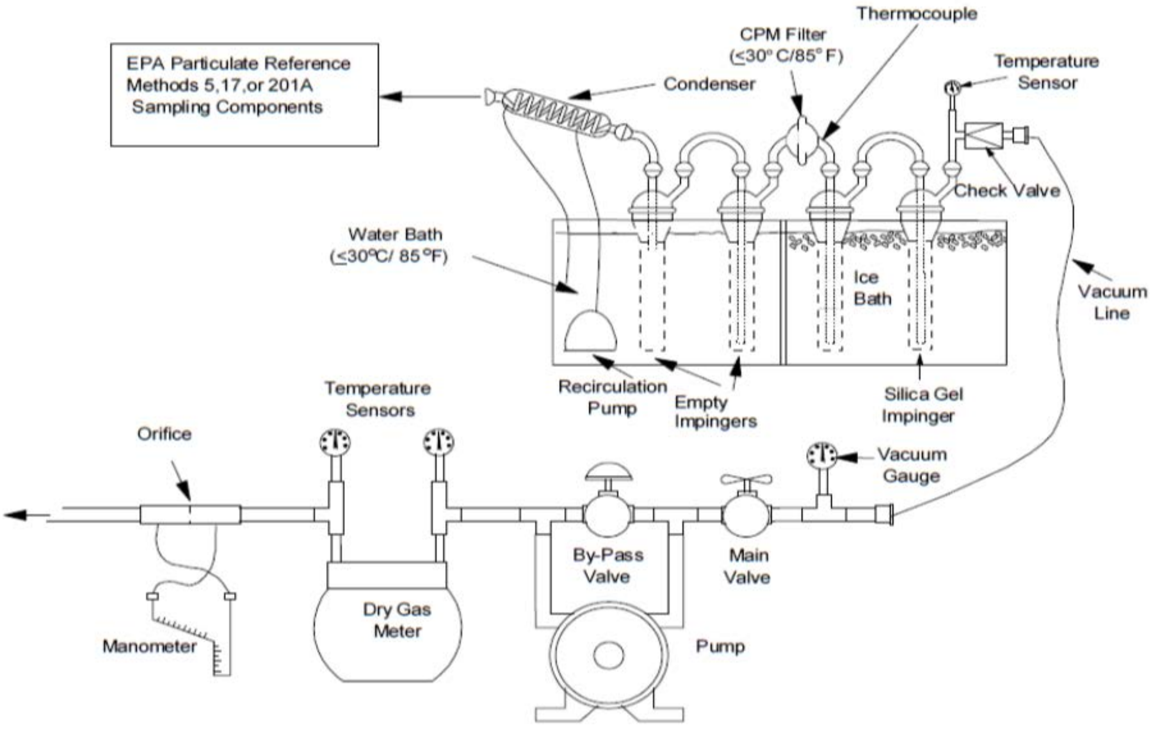


Figure 1-4: EPA Method 202 Sampling Train

1.1.2.3 EPA Method 201A and 202 Test Results

Preliminary laboratory tests were previously conducted with Method 201A in 2006 [15]. Micro Alumina #3 was used with a mass mean diameter of 10 um. Additionally, a starch was used with a mass mean diameter of 19.4 um. Isokinetic sampling was conducted in this previous work. It was determined that Method 201A was 17% below the Micro Alumina #3 concentration and 143% above the starch concentration to which it was exposed. Another set of preliminary tests were conducted with Method 201A with limestone and starch. It was determined that Method 201A sampled high by over 200% in each case beyond the scope of error mentioned by EPA. This necessitates further testing and development for method optimization.

In a review of the wet impinger Method 202, Corio et al [5] stated that the protocol of purging SO_2 by nitrogen was insufficient, as positive bias still resulted from CPM in field evaluations. In a recent comparison study of the old and revised Method 202 by Crosby [6], it was determined that the old or wet method yielded much higher CPM than the revised or dry method for different test sources and concurrent test runs. This indicates that noncondensable gases may oxidize in the impinger solution forming condensable particles resulting in a positive bias of CPM. Another study conducted with a heater and boiler used a dilution method and the wet impinger Method 202. It was determined that Method 202 was significantly biased when compared to the dilution method [16]. It is believed that dilution methods provide a more accurate representation of atmospheric mixing processes and thereby mimick CPM formation better than wet impinger methods. This is one of the reasons why EPA developed the dilution sampling method CTM 039.

In a study conducted by Richards et al. [14], an optimized Method 202 train was used to reduce the inherent biases with the old wet impinger Method 202. The main bias associated with the wet impinger method, as stated earlier, is the aqueous phase oxidation of soluble gasses in the wet impinger measurements. Additionally nitrogen oxides may undergo oxidation in the impingers and be counted towards CPM. Other biases include the penetration of smaller particles through the impingers as well as reactions between ammonia and hydrogen chloride or ammonia and sulfur dioxide in the impingers. The optimized method 202 was composed of a condenser followed by a large knockout impinger, two empty Greenburg-Smith impingers and a CPM filter followed by another empty impinger and silica gel impinger. When testing the SO_2 absorption of both the conventional and optimized Method 202, the optimized method shows that the SO_2 artifact is much smaller than the artifact from the conventional method. With no nitrogen purge, the optimized sample train produced 5.2 mg of sulfate artifact while the conventional method produced 38.0 mg of artifact without a nitrogen purge. It is hypothesized that the optimized sample train will have a much larger impact to bias reduction when used with emission sources rather than laboratory sources.

The Avogadro Group, led by Kevin Crosby piloted a comparison study with the wet (conventional) and dry impinger (OTM 028) methods on a number of sources with varying sulfur fuel content [6]. The sources included steel casting, wood fired boiler and a petroleum coke fired fluidized bed boiler. The steel casting had the least amount of SO_2, followed by the wood fired boiler and pet-coke boiler. The steel casting had no control technology, while the wood fired boiler had a dry electrostatic precipitator for particle removal and ammonia injection selective noncatalytic reduction (SNCR) for NO_x reductions. The pet-coke boiler had SNCR for NO_x control and baghouse for FPM control. What they determined was that OTM 028 had lower PM measurements for each of the source tests. Sources with more SO_2 led to a larger CPM reduction from Method 202 to OTM 028. Additionally, an electrically heated furnace was tested with low SO_2. For each of the four tests, proprietary noncondensable chemicals were applied in increasing concentrations. The results indicate that OTM 028 produced much lower CPM concentrations than the conventional Method 202 even in the presence of other noncondensables. It is hypothesized that OTM 028 reduces the measurement bias associated with the conventional wet impinger method.

1.1.2.4 EPA CTM 039

CTM 039 is a dilution method developed by EPA for $PM_{2.5}$ and PM_{10} measurements shown in Figure 1-5 [17]. This method was created to most closely replicate ambient CPM formation, unlike the current impinger methods. CTM 039 isokinetically withdraws the hot sample gas from the stack through $PM_{2.5}$ and PM_{10} cyclones and the heated sample probe. The sample is then mixed in a mixing cone with filtered, dehumidified (50% or less) ambient air at a fixed dilution ratio and temperature of 85 F or below. After, the mixture is drawn through a residence chamber at a specified residence time for CPM formation. The total PM (FPM and CPM) is then collected on a 142 mm filter for analysis.

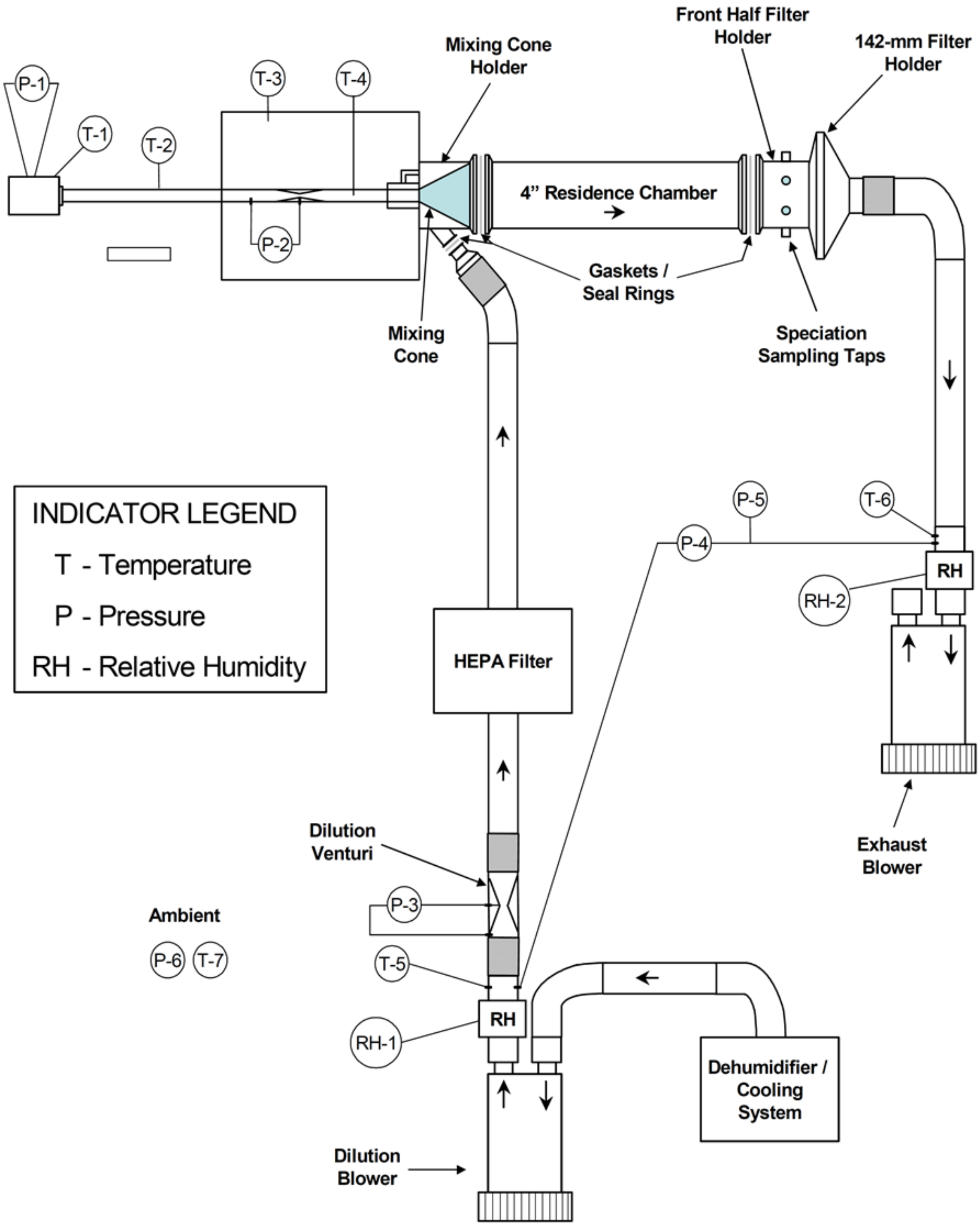


Figure 1-5: EPA CTM 039 Sampling Train

1.1.2.5 EPA CTM 039 Test Results

From a 2006 preliminary field evaluation on a commercial cotton gin, CTM 039 was compared to Method 5 and Method 201A was used for PM_{10} measurements. Sampling was taken from a

No.1 stick machine, feeder dust and the overflow/seed reclaimer. $PM_{2.5}$ and PM_{10} were measured by CTM 039 and compared to the true $PM_{2.5}$ and PM_{10} values measured from PSD analysis of Method 5 filters. It was determined that PM_{10} from CTM 039 was 93-100% of the true PM_{10} while $PM_{2.5}$ from CTM 039 was approximately 11 times higher than the true $PM_{2.5}$ values [15]. This indicates a need for further development and testing.

A pair of revised CTM 039 dilution methods was used by Glenn England at a combined cycle natural gas fueled power plant [18]. The specifications of the power plant were as follows. Two separate units of 170 MWe were equipped with heat recovery steam generators (HRSGs) producing 190 MWe. Additionally, for NOx control, the turbines were fitted with premix combustors while each HRSG was equipped with SCR for NOx reduction. The sulfur content for the turbine was averaged at 7ppmv. For this test, modified CTM 039 systems were used. The modifications from the conventional CTM 039 included two 47 mm ploytetrafluoroethylene (PTFE) filters before the 142 mm filter holder, an ultra-low penetration filter (ULPA) rather than a high efficiency particulate air (HEPA) filter and two filters in the dilution air for blank collection. Additionally, the use of Teflon was minimized and the internal surfaces were electropolished to limit losses due to deposition of electrically charged particle on surfaces within the CTM 039.

The results for the test were as follows. From the 142 mm filter, a negative net weight resulted, indicating that the filter was adhering to the glass ring of the filter holder. From the 47 mm filters, the net weights were positive, but only accounted for 1% of the total PM mass collected when compared to the rinse extractions. This indicates that most of the PM came from the walls inside the system, which is much higher than other tests. Both CTM 039 sampling trains did not compare well indicating that the variability can be at least partially attributed to the low PM emissions. The LOQ and LOD were calculated and it was determined that the plants emission limit of 3.6 mg/dscm lies between the LOD and LOQ indicating that such low concentrations are not accurately measured by this method. It can be concluded that significant variability still exists with the modified CTM 039, and that further modifications are needed for more accurate and precise measurements.

A European Union study was conducted by Giugliano et al [4] on a 150 kW boiler powered by light fuel oil and natural gas and a 100 kW boiler fueled by wood with a cyclone for PM removal. CTM 039 was used to determine the mass concentrations while an ELPI was used for number concentration measurements. CTM 039 was operated with a dilution ratio range of 15:1 to 50:1 with a temperature ranging from 24-33C before the 142 mm filter. The venturi and $PM_{2.5}$ and PM_{10} cyclones were maintained above the stack gas temperature to ensure that the semi-volatiles would not condense before the dilution chamber. The number concentration for the natural gas emissions averaged ~5000 particles cm^{-3} with a mode at 21 nm and 89% of the PM below 100 nm. It was determined that the wood pellet and light fuel oil had the highest mass concentrations. The natural gas, as expected, had the lowest mass concentration. The dilution ratio was increased with no effect on measured natural gas PM. Additionally, for the wood pellet boiler, increasing the dilution ratio over 20:1 had minor effects. Alternatively, at lower temperature loads, higher number concentrations were seen with larger particle modes. For the pellet boiler, the average number concentration was seen at ~4 x 10^7 particles cm^{-3} with a mode diameter at 72 nm for normal load and 204 nm for smaller loads. The fraction of PM under 100 nm was 92% for normal load and only 40% for smaller loads. The shift in PM mode was evident in the mass concentration, which increased from 11 mg m^{-3} to 48 mg m^{-3}. CTM 039 was also operated at hot conditions for the wood fired boiler. The PM number concentration was above the detectable limit of the ELPI under this condition. The dilution ratio did have an effect on the oil boiler. As the dilution ratio was increased from 30 to 50, the number concentration increased from 10^6 particles cm^{-3} to 10^8 particles cm^{-3}. Additionally for the oil fueled boiler, measurements were conducted with CTM 039 under both non-nominal and nominal conditions. Non-nominal conditions meant reducing the oxygen content of the exhaust gas from 3% to 1.5%. This resulted in similar number concentrations, regardless of varying dilution ratio. A shift in the mode from 21 nm to 72 nm did result. This was evident with the mass concentration which increased from 4 mg m^{-3} to 18 mg m^{-3}. Additionally, the PM was measured at hot conditions (undiluted). The particle concentration decreased from $6x10^6$ to $1.3x10^6$ particles cm^{-3} from diluted to non-diluted conditions indicating dependence of CPM results on dilution conditions.

1.1.3 Stationary Source Dilution PM Measurements

A u-shaped dilution method and residence chamber was designed by Hildemann. It measures PM through the following process. The stack gas enters from the nozzle into a 10 um cyclone used to remove particles greater than 10 um. The PM_{10} is then sent to the u-shape dilution tunnel where it mixes with cooled, filtered air (Figure 1-6).

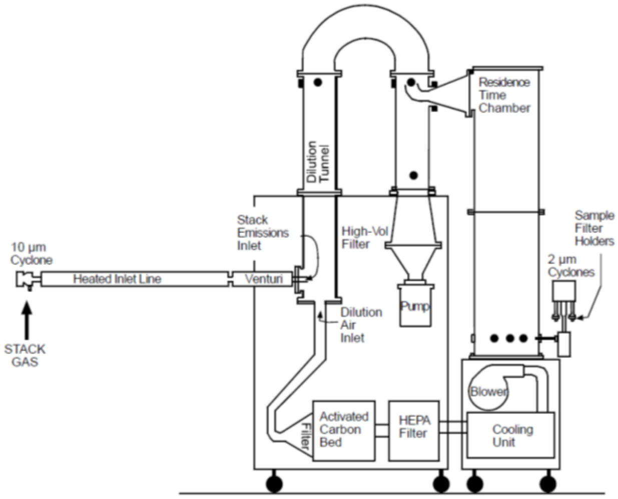


Figure 1-6: Hildemann Dilution Design

Twenty percent of the sample proceeds to the residence chamber for approximately 80 to 90 seconds residence time to allow sufficient time for the organic vapors to condense and form CPM. The sample is then sent through to 2 um cyclones to 12 sample filter ports for subsequent analysis. It has been well documented that the Hildemann design has particle loss before filter collection, both in the venturi and in the dilution tunnel/residence chamber although the characterized dilution tunnel loss is very small compared to the venture losses. Additionally, the venturi loss increases exponentially with the size of the particles being sampled. It was calculated that for $PM_{2.5}$ measurements, a maximum loss of 18% would occur [21]. This indicates that more attention is necessary to particle recovery in the probe and venturi portion of the design.

Another dilution design, developed by the Desert Research Institute, based on the Hildemann dilution sampler, is shown in Figure 1-7 below. A sample between 20 to 30 liters per minute is withdrawn from the stack into the u-shaped dilution tunnel with diluted air entering from the top of the dilution tunnel. The ambient air is filtered with a HEPA for particle removal and then through a carbon bed used to remove organic vapors.

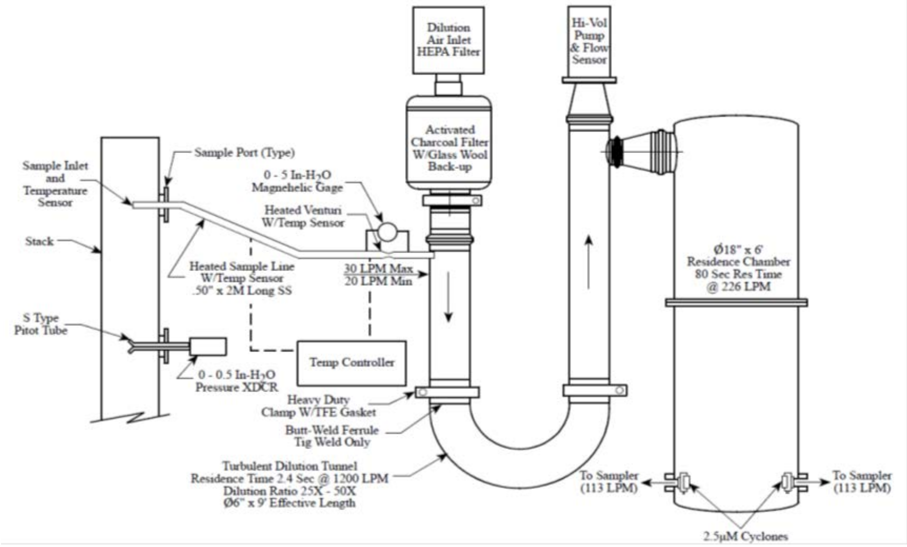


Figure 1-7: Desert Research Institute Dilution Sampler Design

The operational dilution ratio ranges from 25 to 50. The mixed sample is then sent to the aerosol aging chamber for approximately 80 seconds. The sample is then split through two 2.5 um cyclones to different samplers.

Paprican Inc. developed a single point isokinetic dilution sampler (Figure 1-8) based on the DRI dilution sampler below.

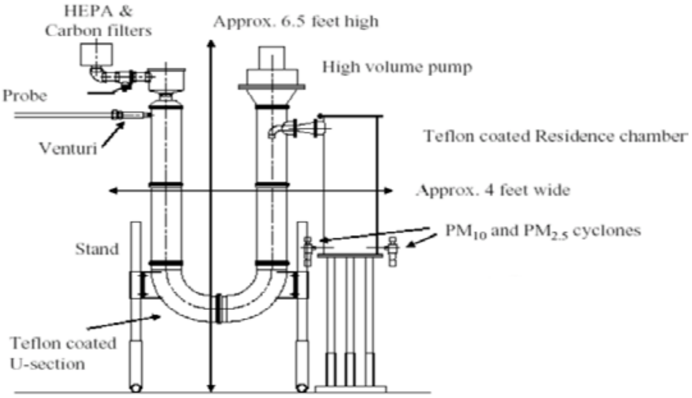


Figure 1-8: Paprican Dilution Design

The sample is extracted from the stack, through the venturi, and to the u-shaped dilution tunnel where the sample is diluted with HEPA and carbon filtered air at a fixed dilution ratio (typically at 30:1). The sample is then sent to the residence chamber and split to two cyclones, one for PM_{10} and the other for $PM_{2.5}$. Although the system has had comparable results with EPA Method 201A, the size of the sampler is much too large for field studies, as the dimensions are 6.5 feet by 4 feet as shown in Figure 6. Ultimately, what is needed is a dilution method which is compact and able to test stationary source PM, which is why the compact dilution sampler was developed by England et al.

England et al. [21] developed a compact dilution sampler shown in Figure 1-9. The sample gas is extracted through a nozzle and 2.5 um cyclone to remove particles greater than 2.5 um. The sample gas is then sent to a mixing chamber where mixing occurs with filtered ambient air. The diluted sample is then run through a residence chamber, where it is aged for approximately 10 seconds. Excess sample is extracted with a bypass while the remaining sample is sent through a 2.5 um cyclone to the sample manifold to the desired sampling method/instrument. The compact sampler was compared to the DRI developed dilution sampler. There are key differences between the two samplers. The compact method has a faster mixing time for more turbulent mixing and to reduce particle loss in the transfer line between the probe and the venturi. Additionally, the size of the sampler is more compact due to the shorter residence time in the aging chamber (reduced from 80 seconds to 10 seconds compared to the DRI sampler). The sampler design was also changed to maintain a linear path for particles to travel to minimize particle losses. It was well characterized from the Hildemann design in Figure 1-6 that particle loss was evident. A pilot study measuring $PM_{2.5}$ mass was conducted with the compact dilution method and the DRI dilution method. The fuel used was No.6 oil [23]. It was determined that the average mass for the compact sampler was 81 mg/dscm while for the DRI sampler was 83 mg/dscm. From the pilot study, the results indicate that both methods have the potential to achieve similar $PM_{2.5}$ mass measurements.

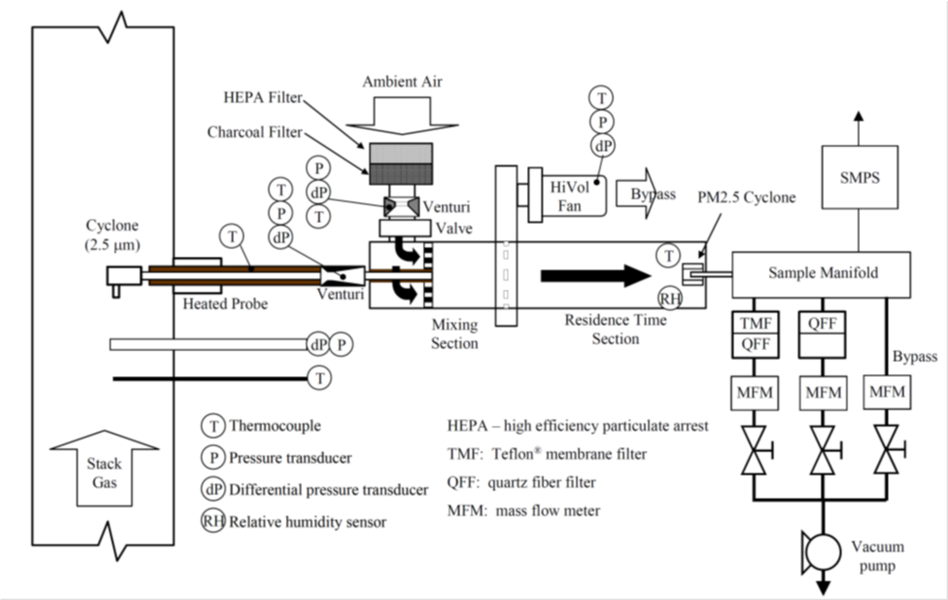


Figure 1-9: Compact Dilution Sampler Design

Tests of Method PRE-004/ Method 202 (Figure 1-10 later) and the compact dilution sampler design were tested on a natural gas run source [21]. The dilution ratio from the dilution sampler was variable from 18 to 22 in order to determine the effect on the $PM_{2.5}$ mass. The FPM measured by Method PRE-004 from the filter is negative and counted as 0 mg/dscm, therefore the measured FPM was controlled by the acetone rinses. This indicates that the FPM may not be very accurate with values close to the lower quantification limit (LQL). For the compact dilution method, as the dilution ratio was lowered, the $PM_{2.5}$ mass was subsequently decreased. The averaged results of the dilution sampler (0.42 mg/dscm) were approximately 55% of the averaged results from the Method PRE-004 (0.77 mg/dscm). Although the dilution sampling method is much lower, the results from Method PRE-004 may be positively biased to the sulfur content and the impingers [5,6,7].

Another comparison study was conducted with the DRI and compact dilution sampler [21]. Two sites were used for testing, the first of which was a diesel fueled back-up generator (BUG) while the second was a natural gas combined cycle power plant. The BUG was tested at 50% and 75% loads, with three runs per load. The compact sampler resulted in higher $PM_{2.5}$ for the majority of the measurements and had greater run to run variability then the DRI sampler. For the natural gas combined cycle power plant, the samplers both showed similar results for the much lower PM emissions than the BUG. The comparisons for the natural gas combined cycle power plant only consisted of the filter measurements as the acetone rinses from the venturi and probe could not be distinguished from the blank. From the field tests, the results indicate that both samplers are comparable at both high and low sources of $PM_{2.5}$ mass

1.1.4 PM Sensitivity to Dilution Parameters

PM number concentrations are sensitive to the dilution ratio, residence time, temperature and relative humidity, thereby making it necessary to identify these sensitivities for optimal PM measurements. Khalek and Kittelson [22] noted that the dilution ratio, residence time and relative humidity will affect the nucleation mode much more than the accumulation mode. These parameters may affect the number concentrations and size of the nucleation mode by over an order of magnitude [1]. PM number emissions from natural gas power plants will have the majority of the particles in the nanoparticle range, with modes typically ranging from 15 nm to 25 nm.

1.1.2.2.1 Dilution Ratio

The effect of dilution ratio on PM changes with the type of fuel. For a pilot scale laboratory study [21] conducted with natural gas, No. 6 fuel oil and coal, the sensitivity of dilution ratio is evident with the change in particle size distributions. For natural gas, a dilution ratio of 20:1 to 50:1 will result in comparable aerosol measurements, but a ratio of 10:1 results in a larger particulate concentration and will shift the peak mode to a larger particle size. This ultimately can be attributed to coagulation and condensational growth [23]. Thus, a dilution ratio of 20:1 or higher should be used to obtain consistent results, which should be used in CTM 039. For No. 6 fuel oil, 50:1 dilution was seen to be constant over different test periods, but 10:1 dilution reduced the number concentration and shifted the peak diameter to larger particle sizes. This can once again be attributed to coagulation and condensation. The particle number concentration decreases as particles begin to grow to the larger sizes. Conversely, for coal it has been determined that a dilution ratio of 50:1 will have twice as high PM concentration than that of 10:1 dilution and consequentially a slight modal shit in the particle size distribution. Studies conducted by Kittelson with diesel exhaust showed a similar sensitivity of the particle size distribution to the dilution ratio. Since natural gas run stationary emission sources emit a small mass concentration, little surface area is available for coagulation and condensation compared to dirtier fuels, such as coal. Therefore, nucleation will become the dominant mechanism, as explained earlier in section 1.1.1.

For the compact and DRI samplers tested by Chung and England [23], there was no correlation between $PM_{2.5}$ and dilution ratio. Additionally it was determined that with a dilution ratio of 20:1 or higher and a residence time greater than 10 seconds, $PM_{2.5}$ was independent of these parameters. As previously discussed in the CTM 039 results section of the report, a study conducted by Giugliano et al.[4] determined that dilution ratio on a 150 kW boiler fired with natural gas did not have much of an effect on the particle size distribution. The number concentration ranged from $4.3\text{x}10^3$ to $6.3\text{x}10^3$ from a dilution ratio of 15:1 to 50:1. For perspective, a light fueled oil boiler was run with dilution ratios ranging from 15:1 to 50:1. The number concentration was highest for the lower dilution ratios and lowest for the higher dilution ratios. Although the number concentrations changed with dilution ratio, the peak mode stayed at 21 nm. Additionally for a 150 kW wood pellet boiler, dilution ratios above 20:1 had minor effects on size and number concentrations. In another study, Mathis et al. [24] showed that nucleation mode PM from diesel engines is sensitive to the dilution ratio, but the accumulation mode particles were largely unaffected. It was determined that the number concentration increased with decreasing dilution ratios (40 to 17) by over two orders of magnitude.

1.1.2.2.2 Residence Time

The particle number concentration is sensitive to residence time. For a CEC pilot study conducted by Glenn England [21] on a natural gas turbine it was determined that for 10 to 80 second residence time, the particle concentration stays relatively constant, but at lower residence times (e.g., ~2 seconds), the particle concentration is much higher. This indicates that a minimum residence time of 10 seconds should be used to achieve representative results. For diesel exhaust, Kittelson et al. showed that the residence time will have an effect on the nucleation mode but not the accumulation mode. With an increase in residence time of 90 to 900 milliseconds, particle concentrations in the nucleation mode were increased by two orders of magnitude [21]. For diesel exhaust, measured by Mathis et al. [24], residence time had an effect on the nucleation mode, but not on the accumulation mode. From 0.6 to 3.1 seconds, the number concentration decreased, with a modal shift to larger sizes due to coagulation. This change in the nucleation mode is due to interactions with volatile and semi-volatile compounds.

1.1.2.2.3 Relative Humidity

Ultrafine particle loadings are sensitive to changes in relative humidity. Generally, as the relative humidity increases, the number concentration will increase while the peak mode will shift to larger sizes due to coagulation and condensational growth. In a diesel vehicle exhaust study conducted by Mathis et al. [24], the particle size distributions increased in number concentration and shifted to larger particle sizes as the relative humidity increased. A rise in relative humidity from 2 to 51 percent led to an increase in number concentration of over 10 times, with a modal shift to larger sizes. The shift in mode size can be attributed to coagulation and interaction with organics.

Alternatively, Glenn England suggests that relative humidity is not a high priority for gas fired sources in his CEC tests, although once the sources of variation are better controlled and understood, the relative humidity could be of some importance. It is known that sulfuric acid is hygroscopic (having the ability to uptake water). The relative humidity is thought to have a limited effect on sulfuric acid up to 80% [21]. Also, because emissions from combustion sources have low hygroscopicity, relative humidity shouldn't have much effect on $PM_{2.5}$ mass.

1.1.2.2.4 Exhaust Temperature/Sample Temperature

Particle concentrations are additionally affected by the exhaust temperature. No. 6 fuel oil was tested at a constant dilution ratio of 50:1 and residence time of 80 seconds and increasing exhaust temperature (450K and 645K) for a laboratory study conducted by Glenn England. In that study the particle mode shifted to a larger size with a higher particle concentration [23]. For coal with constant dilution ratio and residence times, the particle concentration increased while the mode size increased. At higher exhaust gas temperatures, faster quenching occurs where particle growth by condensation and nucleation will become more prevalent due to supersaturation, thereby leading to larger sizes. Also, more condensable species will be available at the higher exhaust temperatures. For the tests conducted in the England CEC program, the $PM_{2.5}$ mass did not have an apparent trend. This could be attributed to the low PM emitted from natural gas sources compared to others such a diesel and oil. The lower emissions will thereby lower the available condensable vapors when compared to other less clean fuels.

1.1.2.2.5 DilutionTemperature

Dilution temperature like the exhaust temperature will play an important role in particle sizing dilution methods for gas fired power plants. England suggests that particle concentration possibly increases with increasing dilution air temperature, at least for the sites tested in the test program. On a test study conducted by Kittelson on diesel particulate emitted from a medium duty diesel engine, he found that the number concentration of the nuclei mode decreased by two orders of magnitude with increasing dilution air temperature from 10 C to 42.5 C [1]. The accumulation mode was nearly unaffected by the 10 C to 42.5 C temperature increase.

1.1.5 CEC Site Comparison Study on PM

1.1.5.1 Site Technologies

In a site comparison study conducted by Glenn England [23], several sites (named "Bravo", "Echo", "Golf") were tested to develop a better understanding for pollution technology and its effect on PM emissions of gas fired power plants. Site Bravo was set at a natural gas combined cycle power plant with a heat recovery steam generator (HRSG) and duct burners to recover steam. The total output of the plant was 240 MW. The turbine had a lean premix combustion system to reduce NOx emissions while the HRSGs were equipped with an oxidation catalyst for CO reduction and SCR for NO_x reduction. Site Echo used two gas turbines with a steam generator turbine, totaling an output of 554 MW. The turbines were fitted with a lean premix combustion system to control NO_x, while the HRSGs had oxidation catalysts for CO reduction and SCR for NO_x control. The final site, Golf was a cogeneration plant with a CO catalyst and SCR with NH3 in the HRSGs. Additionally site Golf used water for cooling the turbine compressor, used to reduce combustion temperatures thereby minimizing NO_x emissions.

1.1.5.2 Measurement Methods and Results

Site Bravo used both a conventional method consisting of Method PRE-004 shown in Figure 1-10 for filterable $PM_{2.5}$ measurements and Method 202 for CPM, as well as a dilution sampler to measure total (FPM and CPM) $PM_{2.5}$ for comparison. The FPM measured from the sampling was variable and measurement limitations were apparent. The filter weights had negative values indicating that the filterable $PM_{2.5}$ mass was low enough that a loss of filter fibers caused a negative filter weight. Additionally, the acetone rinses were negative. From an analysis on the lower quantification limit (LQL) or ten times the standard deviation and the minimum detection limit (MDL), or three times the standard deviation, all the filter samples are below the LQL of this method. Also, the CPM results from Method 202 are all below the calculated LQL of 5 mg/dscm for the method. Since the conventional Method 202 uses wet impingers to cool the sample, the results may have been biased high as it has been shown that aqueous phase oxidation of inorganics, such as sulfur containing compounds will be counted as pseudo particulate and therefore as CPM [5,6,7]. For the dilution sampling system, the results are comparable to ambient conditions.

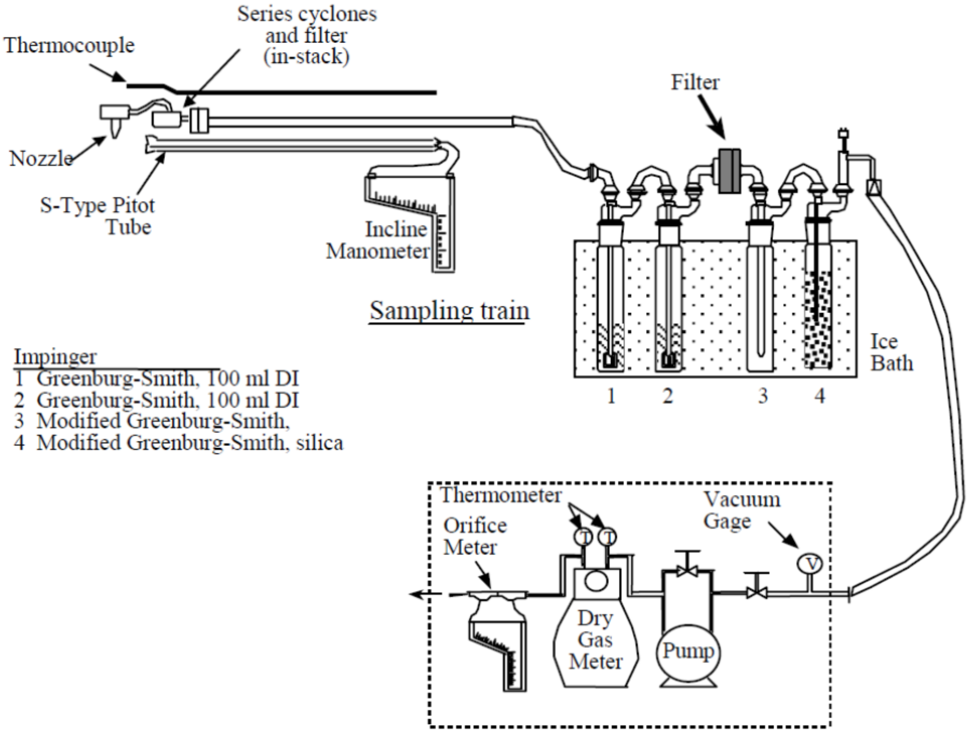


Figure 1-10: EPA PRE-004/202 Sampling train

Site Echo used different dilution methods to measure $PM_{2.5}$. The first of which was a Hildemann type dilution sampler (U-shape) with long residence times for aerosol growth. The second dilution sampler was of a newer design, employing a much shorter residence time (on the order of 10 seconds). Both samplers were compared at both high and low turbine loads. For the high load, the Hildemann style sampler was higher for all runs than the newly developed sampler by about 50 percent, but the gap was reduced at lower testing loads. The $PM_{2.5}$ measurements at site Golf were measured with the newer dilution sampler design (shorter residence time) used at site Echo. The results were very similar for each test run with a standard deviation of 0.04. The $PM_{2.5}$ results from the dilution methods were similar for both sites Bravo and Golf, even though the plants tested were of different power generation with site Golf having 48 MW capacity and site Bravo producing 240 MW. It is hypothesized that the $PM_{2.5}$ results may have been high due to the intercooling stage of the combustion turbine compressor for cooling as well as NO_x control.

1.1.5.3 Measurement Variability

A large variation occurred in the PM measurements when comparing the results of the conventional impinger and dilution methods. The CPM is expected to be biased high due to aqueous phase oxidation of soluble. The plant design and control technologies used within the system also play an important role. The wide range of $PM_{2.5}$ measurements from each site can be at least partially accounted for the control technologies and the different make up of each plant site. The operating conditions such as plant loads as well as the fuel composition will additionally affect the amount of $PM_{2.5}$ emitted from the plants at each site. All of these factors will contribute to the wide range of PM inventory from power plants.

1.1.6 Comparison Study on Dilution and Traditional Stationary Source Measurements

Wein et al. measured boiler, process heater and a steam generator with dilution and traditional PM methods [26]. Although they are not representative of natural gas fired units, they can provide insight into differences between both types of measurement methods. For all three sources, the condensable PM from conventional in-stack methods was much higher than the dilution tunnel method (a similar dilution method to the Hildemann design shown above (Figure 1-6)). The in-stack methods were more than a magnitude higher than the dilution method. The post nitrogen purge is only required for a pH below 4.5. Since the pH was above 4.5 for the boiler and process heater the purge was not conducted on these two sources, but was on the steam generator. The condensable PM from the steam generator resulted in much lower values than the condensable PM from the non-purge test sites. From these results, Wein et al. suggested that the in-stack methods were biased high due to dissolved SO_2. After purging of the SO_2, Wein et al. found that the 6 hour run purge was less efficient than the 1 hour run purge indicating oxidation of SO_2 within this time.

1.1.7 PM Variability from Inventoried Sites

The CEC report conducted by Glenn England and W. Steven Lanvier [27] inventoried PM emissions from turbines in California with different technologies, fuels, power output and control technologies. The units included in the inventory were simple cycle, combined cycle, supplementary firing and several with emission control technologies such as SCR and oxidation catalysts. Ninety two tests were conducted on 36 different units. There was a wide range in both FPM and CPM, which is not surprising considering the different technologies of each plant. The FPM was found to range from approximately 0 to 9 mg/dscm while the condensable ranged from 0 to 7.5 mg/dscm. A probability chart (Figure 1-11) was created with 95% confidence intervals. For FPM shown in Figure 1-11, the first portion of the FPM was increasing rather than following the 95% confidence interval. The remaining data at larger concentrations followed the confidence intervals more closely while low concentrations of PM emitted resulted in far less accuracy and precision. Variables affecting the accuracy of low PM sources include filter weighing and the dry gas measurements. The inaccuracy of the weighing may exceed the mass collected on the filters since the filter weighing only requires accuracy within ± 0.5 mg. Additionally, at small PM mass concentrations, filter fibers that adhering to the filter holders may result in negative net weights. Additionally, the last section of the data for FPM deviates from the confidence intervals indicating some potential biases. For the CPM section of the chart, parts of the data deviate from the confidence intervals also indicating biases, which may be due the oxidation of soluble gasses inside the impingers.

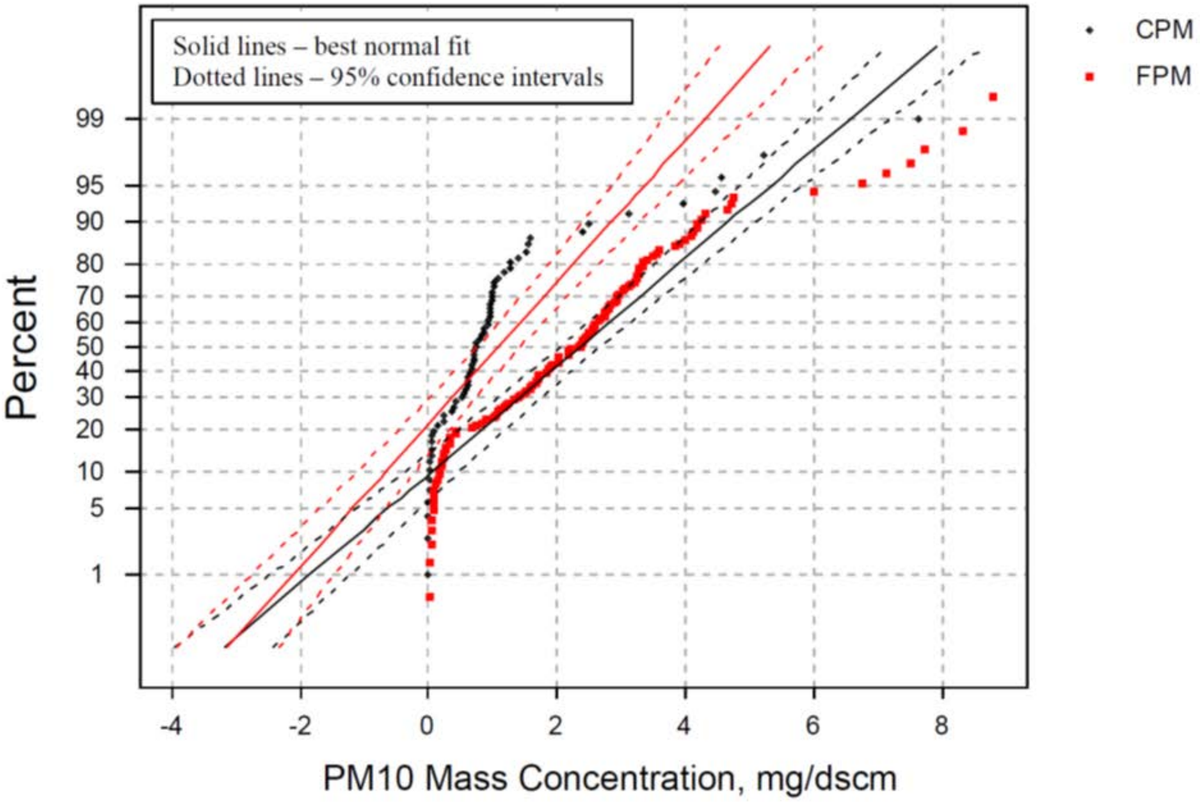


Figure 1-11: FPM and CPM Cumulative Probability Distribution from Gas-Fired NGCC, Cogeneration Plants and Gas Turbines.

1.1.9 Site to Site Sources of PM Variability

PM emissions will vary from site to site. The PM emissions will depend on plant design, more specifically the unit size, operational cycle, combustor design and control technologies [27].

Power Plant Size

The unit ratings will range from kW for smaller units to many MW for combined cycle units. The plant rating will affect the PM emissions, both mass and number concentrations. For larger plants, more fuel is burned which will result in higher PM mass concentrations. It is known that larger units are more efficient than smaller one indicating higher PM number concentrations from smaller turbines.

Operating Cycle

Switching from a simple cycle turbine design to a combined cycle design will increase the efficiency of the plant. Higher efficiency will translate to less fuel burned and therefore less PM mass and number concentrations.

Combustor Design

The general design used to provide optimal fuel/air stoichiometric ratios was the addition of air through the combustor wall of turbines. This was discarded due to the high NO_x formation. To control combustion temperature and therefore NO_x emissions, other methods are used. The first of which is water injection to the combustion chamber, which decreases the flame temperature. Additionally, the second is to premix the inlet fuel and air to raise the stoichiometric ratio, which will subsequently create lean fuel in the inlet of the combustor. The water injection method will form higher condensable PM due to NO_2 formation.

Control Technologies

Selective Catalytic Reduction (SCR) and oxidation catalysts are used for pollutant reduction. SCR is used to reduce NO_x, but will indirectly increase PM number concentrations. Ammonia or urea is used for SCR to convert NO_x into nitrogen and water. It has been well recorded that ammonia may escape from the SCR, known as ammonia slip. Ammonia is soluble in water and will react with sulfur dioxide and hydrogen chloride within conventional sampling methods forming CPM artifact.

Oxidation catalysts are used for the reduction of carbon monoxide and other organic compounds such as hydrocarbons. They have been known to have varying impacts based on their interactions with sulfur and hydrocarbon. At higher temperatures they can oxidize SO_2 to SO_3, which will react with water to form H_2SO_4, therefore increasing PM. The catalyst is also known to decrease the soluble organic fraction (SOF) which will lower PM. Therefore the effect on the particle size distribution is twofold. At lower temperatures the sizes will be smaller due to reductions in organic vapor, while at higher temperatures larger particles will result due to the sulfur oxidation. Vaaraslahti et al. [10] conducted a study on a diesel vehicle with an oxidation catalyst. At 100, 50, and 10 percent loads, the mass concentration composed of soot and SOF was compared with and without the diesel oxidation catalyst (DOC). The mass concentration was reduced at each load with the largest reduction (25%) coming from the 10% load. The SOF fraction of the PM was reduced far more than soot for each load. Diesel particulate filters (DPFs) are used to reduce soot particles, while oxidation catalysts indirectly reduce PM by reducing small amounts of soot and larger amounts of the volatile particulate fraction [9]. Oxidation catalysts are known to cause NO to oxidize to NO_2 [10,27], which can oxidize in impingers to form CPM artifact.

Fuels

The fuel used will have a direct impact on PM. The fuel sulfur and bounded nitrogen content will increase CPM artifacts in impinger methods by increasing SO_x and NO_x emissions. Additionally, hydrogen chloride can react with ammonia to form a positive bias in CPM measurements. Natural gas will have both sulfur and chlorine content. Addition of SCR control technology with ammonia slip can further contribute to CPM biases.

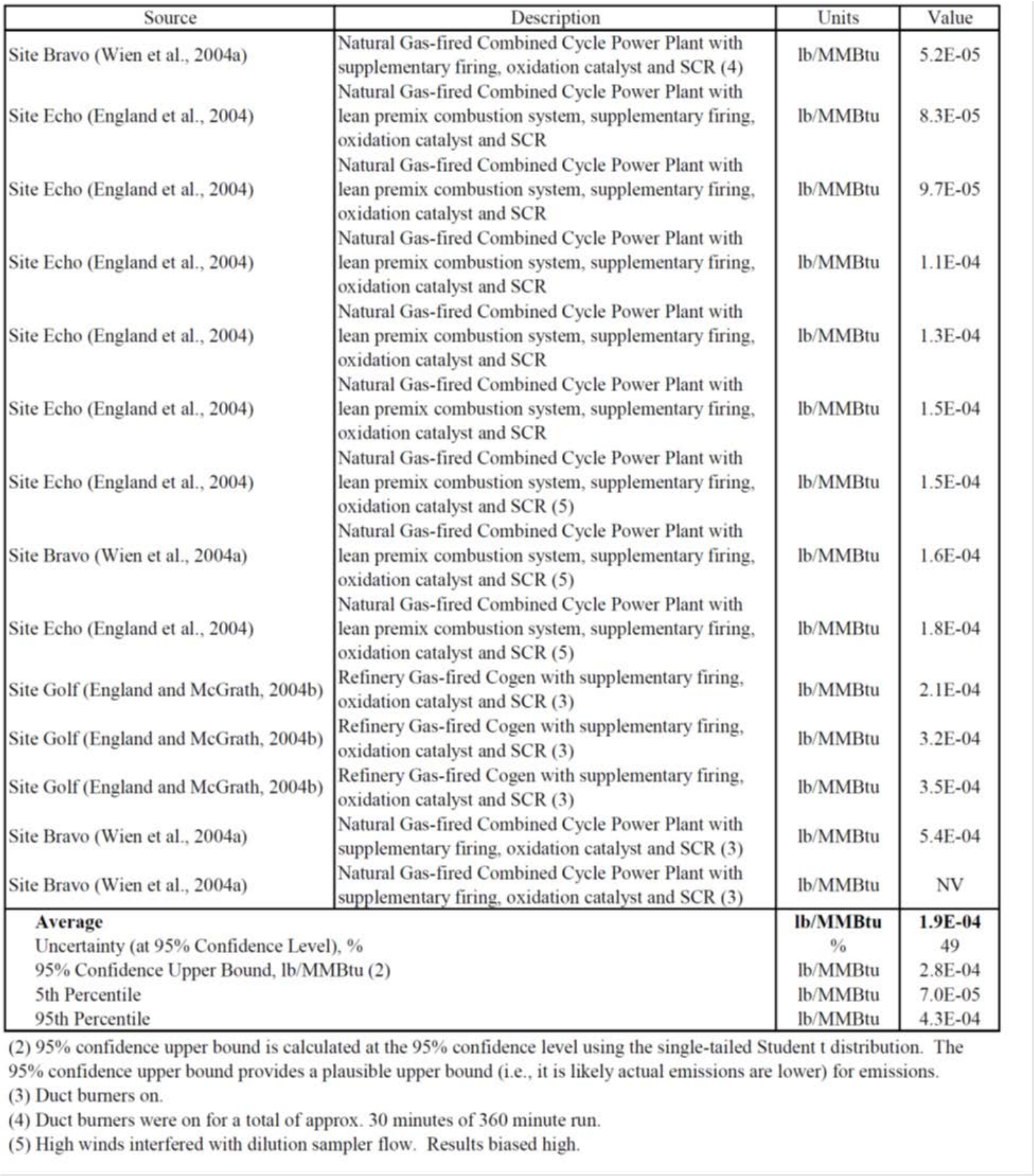
Operational Parameters

The operation of the plant is also important in regards to PM emissions. If for example, the catalyst in SCR has been degraded, more urea will be added to achieve the desired NO_x reduction thereby affecting the PM.

1.1.10 Emission Factor Development from another CEC Project- Glenn England

The technologies for sites Bravo, Echo, and Golf used for the PM2.5 emission factor development were included previously under section 1.1.5. For the gas fired internal combustion, combined cycle and cogeneration plants, the resulting emission factor values have an uncertainty of ± 49% at 95% confidence level. The gas fired boilers and steam generators have an uncertainty of ± 46% at the 95% confidence level, while the oil filed boilers have ± 40% uncertainty. The gas fired heaters have the largest uncertainty of ± 104%. The PM2.5 mass and precursor emission factor tables were included for the units fired with natural gas (Table 1-6 to Table 1-11).

Table 1-6: PM2.5 Emission Factors Developed by Glenn England for Gas Fired Internal Combustion Combined Cycle and Cogeneration Test Sites



Source	Description	Units	Value
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (4)	lb/MMBtu	5.2E-05
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	8.3E-05
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	9.7E-05
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	1.1E-04
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	1.3E-04
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	1.5E-04
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	1.5E-04
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	1.6E-04
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	1.8E-04
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	2.1E-04
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	3.2E-04
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	3.5E-04
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	5.4E-04
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	NV
Average		**lb/MMBtu**	**1.9E-04**
Uncertainty (at 95% Confidence Level), %		%	49
95% Confidence Upper Bound, lb/MMBtu (2)		lb/MMBtu	2.8E-04
5th Percentile		lb/MMBtu	7.0E-05
95th Percentile		lb/MMBtu	4.3E-04

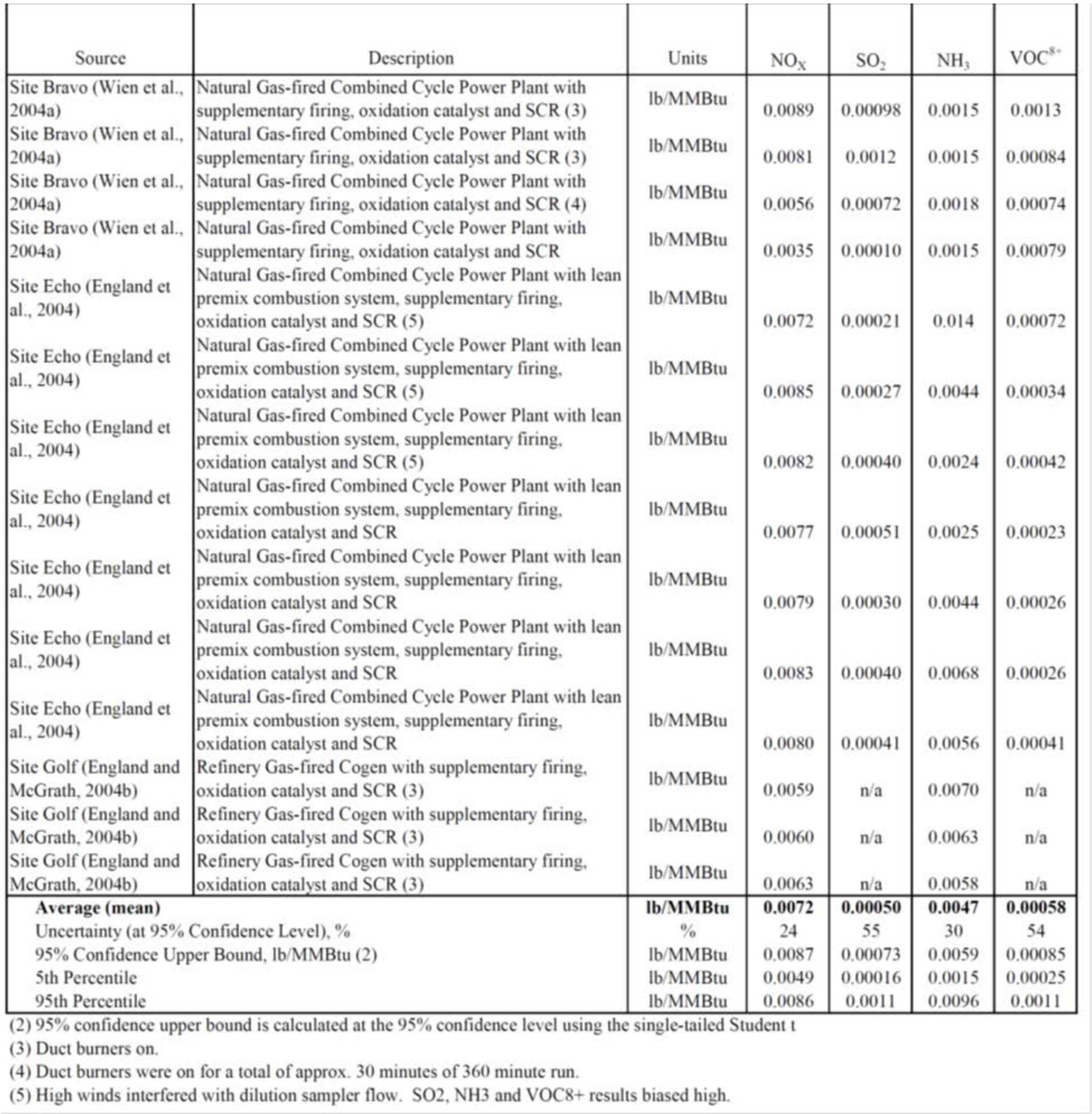
(2) 95% confidence upper bound is calculated at the 95% confidence level using the single-tailed Student t distribution. The 95% confidence upper bound provides a plausible upper bound (i.e., it is likely actual emissions are lower) for emissions.

(3) Duct burners on.

(4) Duct burners were on for a total of approx. 30 minutes of 360 minute run.

(5) High winds interfered with dilution sampler flow. Results biased high.

Table 1-7: PM2.5 Precursor Emission Factors Developed by Glenn England for PM2.5 Emission Factors Developed by Glenn England for Gas Fired Internal Combustion Combined Cycle and Cogeneration Test Sites



Source	Description	Units	NO_X	SO_2	NH_3	VOC^{8+}
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0089	0.00098	0.0015	0.0013
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0081	0.0012	0.0015	0.00084
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR (4)	lb/MMBtu	0.0056	0.00072	0.0018	0.00074
Site Bravo (Wien et al., 2004a)	Natural Gas-fired Combined Cycle Power Plant with supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0035	0.00010	0.0015	0.00079
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	0.0072	0.00021	0.014	0.00072
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	0.0085	0.00027	0.0044	0.00034
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR (5)	lb/MMBtu	0.0082	0.00040	0.0024	0.00042
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0077	0.00051	0.0025	0.00023
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0079	0.00030	0.0044	0.00026
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0083	0.00040	0.0068	0.00026
Site Echo (England et al., 2004)	Natural Gas-fired Combined Cycle Power Plant with lean premix combustion system, supplementary firing, oxidation catalyst and SCR	lb/MMBtu	0.0080	0.00041	0.0056	0.00041
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0059	n/a	0.0070	n/a
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0060	n/a	0.0063	n/a
Site Golf (England and McGrath, 2004b)	Refinery Gas-fired Cogen with supplementary firing, oxidation catalyst and SCR (3)	lb/MMBtu	0.0063	n/a	0.0058	n/a
Average (mean)		**lb/MMBtu**	**0.0072**	**0.00050**	**0.0047**	**0.00058**
Uncertainty (at 95% Confidence Level), %		%	24	55	30	54
95% Confidence Upper Bound, lb/MMBtu (2)		lb/MMBtu	0.0087	0.00073	0.0059	0.00085
5th Percentile		lb/MMBtu	0.0049	0.00016	0.0015	0.00025
95th Percentile		lb/MMBtu	0.0086	0.0011	0.0096	0.0011

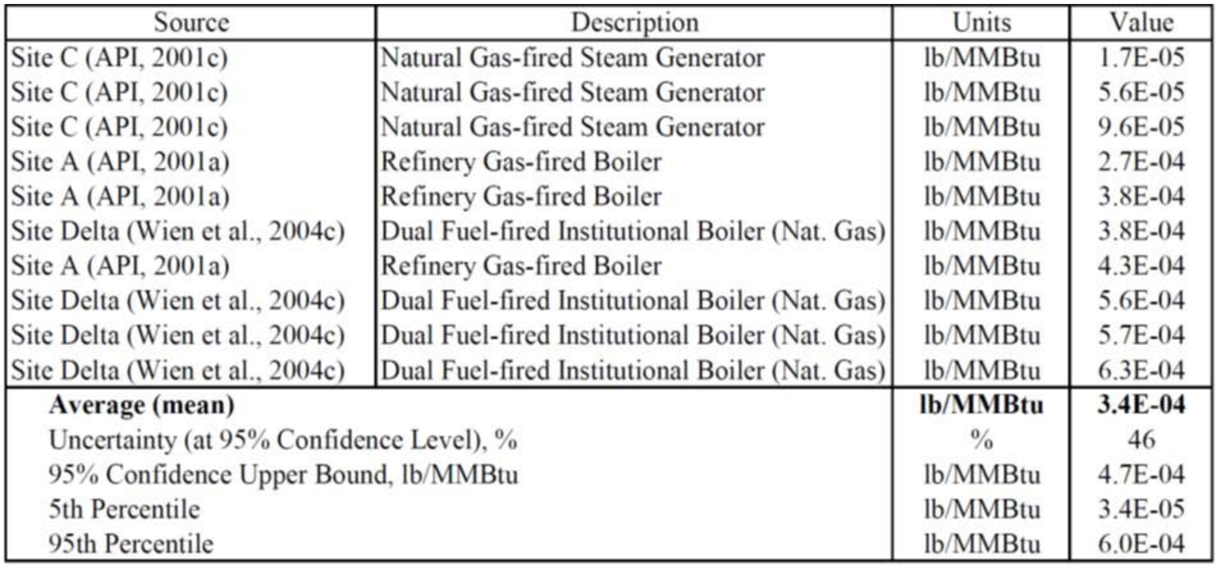
(2) 95% confidence upper bound is calculated at the 95% confidence level using the single-tailed Student t

(3) Duct burners on.

(4) Duct burners were on for a total of approx. 30 minutes of 360 minute run.

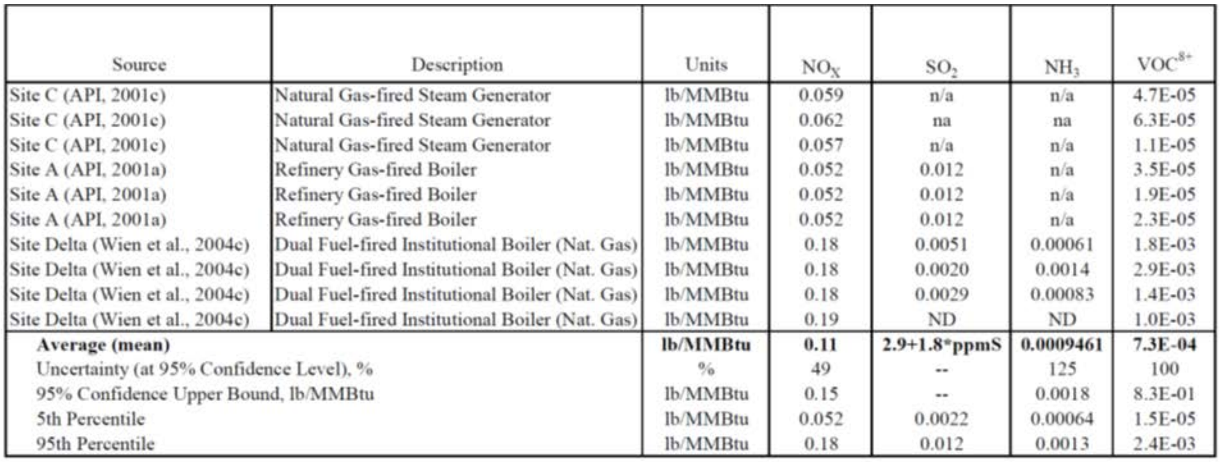
(5) High winds interfered with dilution sampler flow. SO2, NH3 and VOC8+ results biased high.

Table 1-8: PM2.5 Mass Emission Factors Developed by Glenn England for Gas-Fired Boilers and Steam Generators



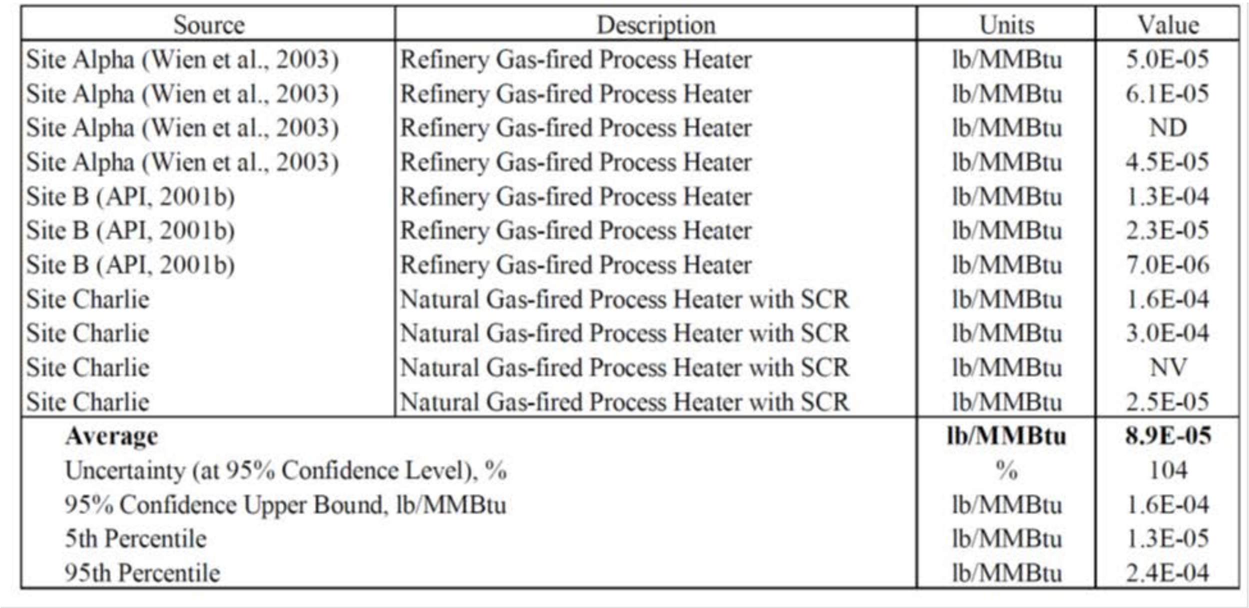
Source	Description	Units	Value
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	1.7E-05
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	5.6E-05
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	9.6E-05
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	2.7E-04
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	3.8E-04
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	3.8E-04
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	4.3E-04
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	5.6E-04
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	5.7E-04
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	6.3E-04
Average (mean)		**lb/MMBtu**	**3.4E-04**
Uncertainty (at 95% Confidence Level), %		%	46
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	4.7E-04
5th Percentile		lb/MMBtu	3.4E-05
95th Percentile		lb/MMBtu	6.0E-04

Table 1-9: PM2.5 Precursor Emission Factors Developed by Glenn England for Gas-Fired Boilers



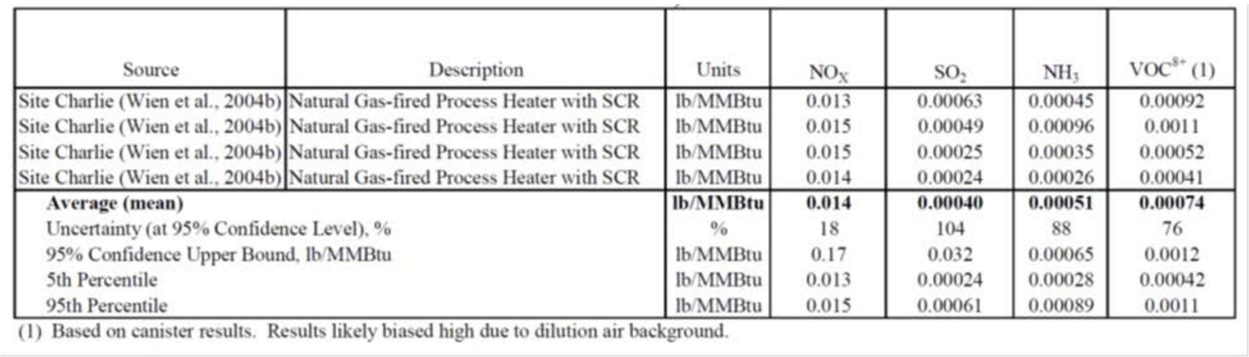
Source	Description	Units	NO_X	SO_2	NH_3	VOC^{8+}
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	0.059	n/a	n/a	4.7E-05
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	0.062	na	na	6.3E-05
Site C (API, 2001c)	Natural Gas-fired Steam Generator	lb/MMBtu	0.057	n/a	n/a	1.1E-05
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	0.052	0.012	n/a	3.5E-05
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	0.052	0.012	n/a	1.9E-05
Site A (API, 2001a)	Refinery Gas-fired Boiler	lb/MMBtu	0.052	0.012	n/a	2.3E-05
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	0.18	0.0051	0.00061	1.8E-03
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	0.18	0.0020	0.0014	2.9E-03
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	0.18	0.0029	0.00083	1.4E-03
Site Delta (Wien et al., 2004c)	Dual Fuel-fired Institutional Boiler (Nat. Gas)	lb/MMBtu	0.19	ND	ND	1.0E-03
Average (mean)		**lb/MMBtu**	**0.11**	**2.9+1.8*ppmS**	**0.0009461**	**7.3E-04**
Uncertainty (at 95% Confidence Level), %		%	49	--	125	100
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	0.15	--	0.0018	8.3E-01
5th Percentile		lb/MMBtu	0.052	0.0022	0.00064	1.5E-05
95th Percentile		lb/MMBtu	0.18	0.012	0.0013	2.4E-03

Table 1-10: PM2.5 Precursor Emission Factors Developed by Glenn England for Gas-fired Heaters



Source	Description	Units	Value
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	5.0E-05
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	6.1E-05
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	ND
Site Alpha (Wien et al., 2003)	Refinery Gas-fired Process Heater	lb/MMBtu	4.5E-05
Site B (API, 2001b)	Refinery Gas-fired Process Heater	lb/MMBtu	1.3E-04
Site B (API, 2001b)	Refinery Gas-fired Process Heater	lb/MMBtu	2.3E-05
Site B (API, 2001b)	Refinery Gas-fired Process Heater	lb/MMBtu	7.0E-06
Site Charlie	Natural Gas-fired Process Heater with SCR	lb/MMBtu	1.6E-04
Site Charlie	Natural Gas-fired Process Heater with SCR	lb/MMBtu	3.0E-04
Site Charlie	Natural Gas-fired Process Heater with SCR	lb/MMBtu	NV
Site Charlie	Natural Gas-fired Process Heater with SCR	lb/MMBtu	2.5E-05
Average		**lb/MMBtu**	**8.9E-05**
Uncertainty (at 95% Confidence Level), %		%	104
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	1.6E-04
5th Percentile		lb/MMBtu	1.3E-05
95th Percentile		lb/MMBtu	2.4E-04

Table 1-11: PM2.5 Precursor Emission Factors developed by Glenn England for Gas-fired Heaters



Source	Description	Units	NO_X	SO_2	NH_3	VOC^{8+} (1)
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	lb/MMBtu	0.013	0.00063	0.00045	0.00092
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	lb/MMBtu	0.015	0.00049	0.00096	0.0011
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	lb/MMBtu	0.015	0.00025	0.00035	0.00052
Site Charlie (Wien et al., 2004b)	Natural Gas-fired Process Heater with SCR	lb/MMBtu	0.014	0.00024	0.00026	0.00041
Average (mean)		**lb/MMBtu**	**0.014**	**0.00040**	**0.00051**	**0.00074**
Uncertainty (at 95% Confidence Level), %		%	18	104	88	76
95% Confidence Upper Bound, lb/MMBtu		lb/MMBtu	0.17	0.032	0.00065	0.0012
5th Percentile		lb/MMBtu	0.013	0.00024	0.00028	0.00042
95th Percentile		lb/MMBtu	0.015	0.00061	0.00089	0.0011

(1) Based on canister results. Results likely biased high due to dilution air background.

CHAPTER 2:
Development of Test Plans & Quality Assurance Project Plans

UCR proposed to carry out the project originally with two different sized units in two phases. However, during conversations with the Advisory team, it was agreed to begin with a pilot test, design the PM system, and then conduct testing. The test plan was designed to test the robustness and sensitivity of the current PM measurement methods using up to four different measurement approaches. The main technical question was to identify the parameters that the accuracy and precision of the flow and concentration measurements so regulators can incorporate that understanding and knowledge into future method improvements.

Following the completion of the trial test, the design of the sampling system and the selection of a proposed PM analysis method, each described below, the project members met with the Energy Commission Manager and the Advisory Committee. During that meeting, the Advisory committee agreed with the planned approach for the sampling system and measuring the PM. They recommended a list of test units as shown in Table 2-1 below. The first unit, a capstone microturbine, would provide additional data for which would be useful to compare with the other units and provide useful feedback for subsequent tests. The third unit would not be a heavy duty frame turbine but instead a Large NG turbine.

Table 1-1: Advisor's Recommended List of Distributed Generators to Test

Test	Distributed Generator
1	Capstone C-65 microturbine (65kW)
2	Solar Titan™ 130 Turbine + SCR (13.5MW) on NG
3	Large NG Turbine (~50MW) + control

2.1 Pilot Test

For the pilot or trial test, we selected a Capstone C-65 microturbine as it was easily accessible and was one of the units in the planned test matrix. The Capstone C-65 microturbine is a simple gas turbine, featuring a radial compressor and turbine rotors and using just one stage of each. These turbines recover exhaust energy to preheat compressed inlet air, thereby increasing electrical efficiency compared with a simple-cycle machine. The air-to-air heat exchanger is termed a "recuperator," and the entire system is typically called a recuperated cycle. The Capstone unit uses maintenance-free air bearing so there are no lubricants. The inlet is air cooled so no coolants are needed.

The unit can run on a variety of fuels, including: natural gas, biogas, flare gas, diesel, propane, and kerosene. According to the manufacturer's brochure, the exhaust gas flows are approximately 1.0 lb/sec of air (nominally 800 scfm) and a typical temperature is 550 to 600°F, versus a specification of 588°F. The exhaust gas exits through a 10-inch diameter stainless steel stack. The unit operates quietly, has a small footprint and high power density as shown in Figure 2-1.

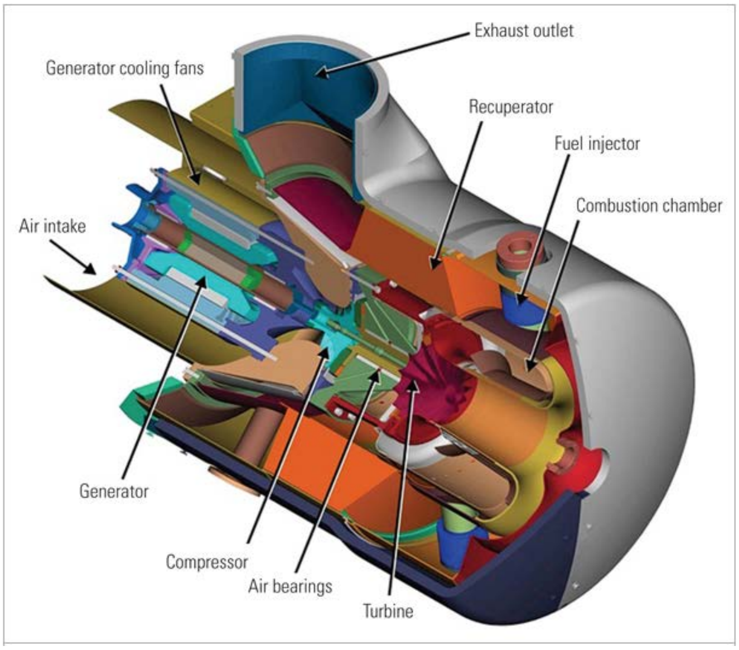


Figure 2-1 Schematic of a Capstone Simple Cycle Turbine[1]

Capstone says one of the benefits of microturbine technology is their design achieves extremely low exhaust emissions levels without the need for exhaust after treatment. Continuous lean premix combustion provides low levels of oxides of nitrogen (NO_x), carbon monoxide, and unburned hydrocarbons. The 65-kW Capstone C65, whose heat rate is about 11,800 Btu/kWh LHV, produces NO_x at a rate of approximately 9 ppmvd, a fraction of rate of a large natural gas–fired reciprocating generator set and about half of the average utility-scale power generation system.

A number of PM test methods were examined during the pilot test that would quickly characterize the PM. All PM instruments were connected to a mini-dilution tunnel (dilution ratio 3 to 4). The dilution air was cleaned of hydrocarbons, moisture, and PM before being sent to the dilution tunnel. Both filter-based mass measurement using protocols outlined in the International Standard Organization (8178-1) and electronic, real-time (non-reference) methods were examined. Some of the electronic methods are being considered for SAE AIR6037, the

---

[1] See http://www.microturbine.com/

measurement of non-volatile PM from jet turbines. Table 2-2 summarizes instruments used while used for this pilot test.

Table 2-2: List of PM Measuring Methods Used in the Trial

Instrument	Model Number Measures
Teflon filter & partial dilution tunnel	PM mass by a reference method, ISO 8178-1
CPC Model: TSI 3781	Water based Condensation Particle Counter (CPC) capable of measuring particles larger than ~6nm
CPC Model: TSI 3776	Butanol based ultra-fine CPC designed to detect particles as small as ~ 2.5nm
Scanning Mobility Particle Sizer (SMPS) Model: TSI 3081	Size Mobility Particle Sizer (SMPS), Range from 7-260 nm, composed of a Differential Mobility Analyzer (DMA) and a CPC

PM filter mass

Even though the turbine was run at 100% power for about 60 minutes to reach steady state before measuring gas concentration and PM mass, there was some concern about the repeatability of the measurements as the unit had not been in use for some time. Accordingly we made triplicate measurements of the PM mass and the results are shown in Table 2-3.

Table 2-3: PM Filter Mass Measured in Triplicate

	PM(g)/CO_2 (kg)	NOx (g)/ CO_2 (kg)	CO (g)/ CO_2 (kg)
Test 1	0.02	0.31	0.45
Test 2	0.01	0.29	0.39
Test 3	0.01	0.29	0.39

As is evident in Table 2-3, the gaseous values were near steady state while the PM mass was being measured so the turbine was operating as a process that was under control. The PM mass for the first reading was higher than the last two values but with only three measurements it is difficult to state whether there is systematic bias. For the first one to be higher might suggest that some of the old soot remained on the wall, but there are too few data to make a statistically significant statement. This study measured ~0.01g PM/kg of CO_2, close to the value of 0.06 gPM/kg CO_2 reported in EPA's AP-42.

PM by electronic measurement

Before the trial test, we were thinking that the CPC would be the best continuous analyzer to select. This thinking was based on: 1) the Europeans are using PM number as criteria for exposure; 2) the SAE specification for measuring solid PM emissions from aircraft was using the CPC and 3) it would be a simple instrument to install and would run unattended after initial setup during the rest of the testing. Data for the SMPS and the 2-CPCs are shown in Table 2-4 below. Analysis of the data revealed a few interesting findings. 1) Ambient concentrations varied widely for the various analyzers; 2) The PM values for the filtered air were greater than the ambient air so the filters were not effective; and 3) for the exhaust air, the butanol CPC measured concentration was about 90-times higher than the CPC value measured with the water-based system. The differences in number oncerntrations measured on the exhaust demonstrate how small the particle sizes were for this unit. The lower cut-size for the CPC-3781 and CPC-3776 are listed by the manufacturer as 2.5 nm and 6 nm, respectively, for DMA classified sucrose particles. However, the cut-size for the water based CPC is can be much higher due to difficulties of the working fluid for combustion aerosol. The cylindrical DMA based SMPS as configured measured particle concentrations down to approximately 7 nm. These results demonstrated how critical measurement of extremely small particles were and that any type of characterization tools would have to be able to handle sub 10 nm particles sizes and that any design for the next stage would have to help mitigate particle losses of such small (highly diffusive) particles.

Table 2-4: PM Data for the SMPS & 2-CPCs

	CPC-SMPS (#/cm³)		CPC-3781 (#/cm³) Water based		CPC-3776 (#/cm³) Butanol based	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Ambient (1)	5623.5	1739.0	3390.0	200.8	9470.0	1940.0
Filtered Air (2)	21479.9	8639.7	32556.6	32573.3	25267.0	6382.3
Exhaust (3)	8452.1	1233.4	652.8	243.2	57128.2	32081.0

2.2 Design of PM Dilution Sampling System

Particles are largely defined by the measurement methodology used to characterize them. The majority of the sensitivities that promote changes in PM occur once the gas phase precursors are emitted from the stack and mix with the cooler ambient air. The formation of new particles via gas to particle precursors and condensational growth is dependent upon a number of important parameters.

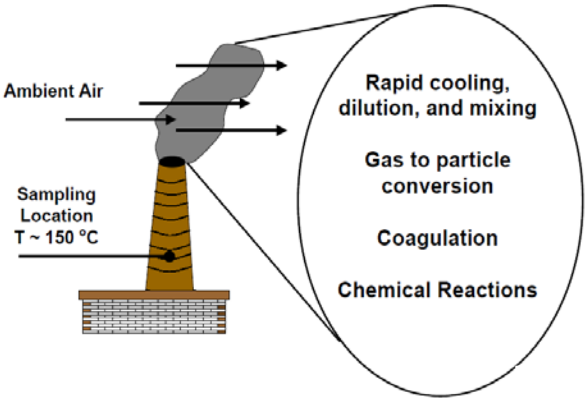


Figure 2-2: Particle Growth and Formation Pathways

Semi-volatiles are sensitive to conditions outside the tailpipe or exhaust stack, the dilution conditions will play a large role in particle formation. Figure 2-2 shows the common mechanisms of PM growth and formation from the exhaust stack of turbines. Dilution can generate new particles through the following pathways. As the temperature cools, the volatile and semi-volatile particles are emitted from the tailpipe or exhaust where rapid dilution will occur and nucleation and particle growth will quickly proceed. Nucleation is dependent upon the number of semi-volatile precursors and the large carbon agglomerates present.

As noted in section 1.1.1, the paricle number and mass condensed will therefore be sensitive to dilution temperature, relative humidy, dilution ratio, and residence time. Therefore, a critical part of this study was to design a dilution system with the capability of varying dilution ratio, residence time, dilution temperature and relative humidity and monitoring changes in real-time with electronic PM instrumentation.

A schematic of the UCR dilution system is shown in Figure 2-3 below. This dilution sampler pulls a fixed flow of emissions at stack temperature. Ambient air is filtered with an ULPA and granulated carbon filters for PM and VOC removal and then mixed with the sample flow at varying dilution ratios, relative humidity and dilution air temperatures. The mixing section is composed of a stainless steel metal frit, where the sample stream will be surrounded by dilution air, mixing with the sample through small pores in the frit. This design minimizes thermophoretic diffusion losses during cooling by convectively transporting the dilution air radially inward and thereby pushing the particles away from the surfaces of the mixing chamber. The mixed sample is then sent through a residence chamber to grow the particles before being collected on Quartz and Teflon filters for $PM_{2.5}$ mass and speciated analysis.

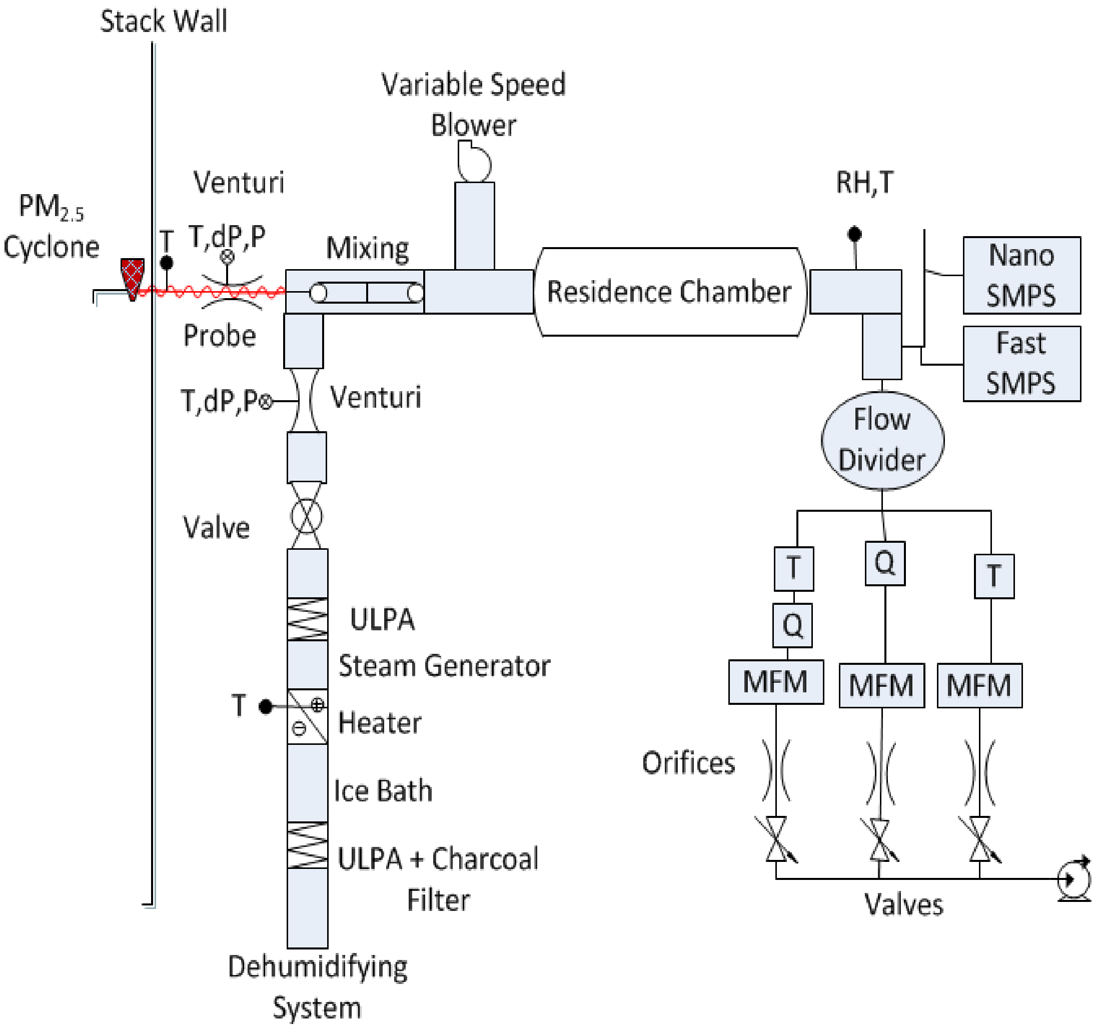


Figure 2-3: UCR Dilution System

2.3 Test Plan Unit 1: Testing of Critical Dilution Parameters Using Capstone Micro-turbine

Test unit 1, the Capstone C-65 microturbine also used for the pilot test (Section 2.1), was used to evaluate the PM dilution system. A parametric study including residence time, dilution ratio, quench rate, sample temperature and relative humidity was designed in coordination with the Advisory committee. The test matrix with the varying dilution parameters and design specifications of the mixing and residence sections are shown in Table 2-5 below.

Table 2-5: Design and Operating Parameters of UCR Dilution System

Residence Chamber			
RT (sec)	10	30	50
Length (inch)	38	38	38
Diameter (inch)	5.834	5.834	5.834
DR	10,30,50	10,30,50	10,30,50
RH (%)	25,50,75	25,50,75	25,50,75
Dilution Temp C	10,30,45	10,30,45	10,30,45
Sample FR (LPM)	15	15	15
Aging FR (LPM)	100	33	20
Bypass FR (LPM)	65,365,665	132,432,732	145,445,745
Re	844	844	844
Mixing Section			
Total Mixing Diameter (inch)	1		
Mixing Length (inch)	10		
Total FR Mixing (LPM)	165	465	765
Reynolds Number	8359	23557	38775

2.4 Test Plan for Unit 2: Testing of Solar Titan™ 130 Turbine with SCR

The second unit selected was a natural gas fired, Solar Titan™ 130 Turbine with SCR for NOx control and the power system included a heat recovery generator. There were several advantages of testing at this site.

1. The unit had controls and low emissions and was on the Advisory group test list
2. The unit had a Continuous Emission Monitor (CEM) for CO, NOx and oxygen providing additional and an independent check on the concentration levels of our measurements.
3. The unit had accurate and continuous monitors for the natural gas flow

2.4.1 General description for a Solar turbine operation

In the Solar turbine operation shown in Figure 2-4, air is drawn into and compressed by a multi-stage, axial-flow engine compressor. Compressed air is directed into the annular combustion chamber at a steady flow where fuel is injected and mixed with the compressed air. The mixture is ignited during the start cycle and combustion is continuous as long as there is an adequate flow of pressurized air and fuel. Hot-pressurized gas from the combustor expands through and drives the turbine, dropping in pressure and temperature as it exits the turbine. The gas turbine only requires approximately one-fourth of the total air it compresses so the excess air is mixed with the combustion products to reduce the gas temperature at the turbine first stage-inlet. The excess air will lower the metal temperatures in the combustor and turbine assembly to prolong service life. The combustion cycle converts the energy in the fuel into kinetic rotating power at the turbine output shaft.

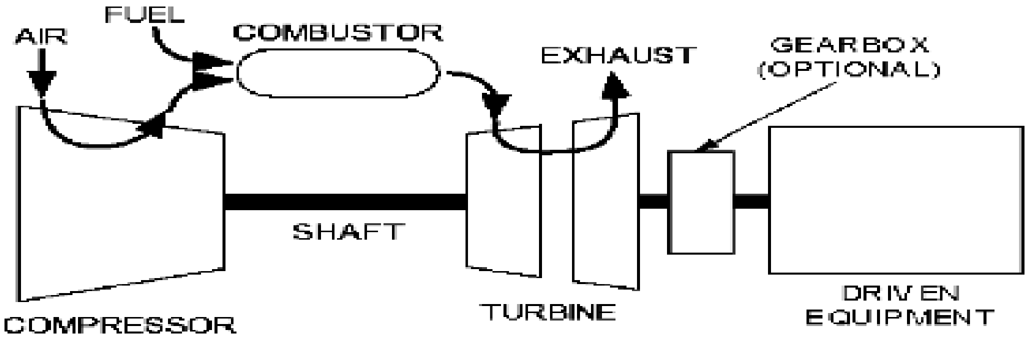
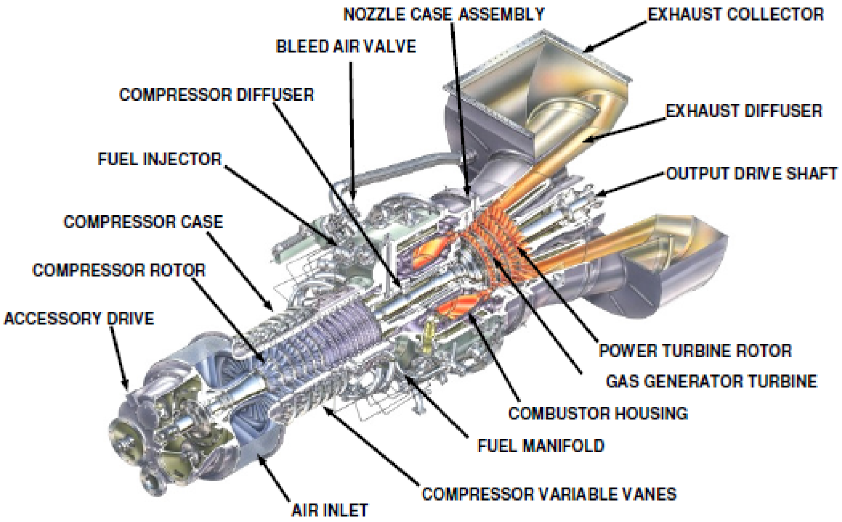


Figure 2-4: Schematic of a Typical Turbine Combustion Unit[2]

2.1.2 General description for Solar Titan 130 Mechanical Drive Package

The second unit tested was a Solar Titan™ 130 Turbine with SCR and followed by an ammonia slip catalyst. The central utility plant at the site used a cogeneration design based on a 13.5MW Solar Titan gas turbine generator and a heat recovery generator that produced about 58,000 lb/hr of steam unfired and 120,000 lb/hr with a duct burner. The produced steam was 230 to 240 psig, slightly superheated and was fed to a condensing steam turbine, which drives a 5MW generator. According to their manual, in typical operation the gas turbine tracks the facility electrical load. The steam chiller would be operated when steam was not needed for space heating and the turbine generator would continuously modulated to maintain the steam header pressure. The tracking would be done manually by the operators with an effort to avoid exporting power to the grid.



---

[2] For information on Solar 130, see http://mysolar.cat.com/cda/layout?m=41108&x=7

Typically, the Solar Model Titan™ 130 gas turbine two-shaft for compressor and mechanical drive applications is designed to deliver a simple-cycle thermal efficiency of 36 percent. The turbine at the test site was a combined cycle gas turbine with a Deltak Heat Recovery Steam Generator (HRSG). The turbine utilizes low-NO_x combustion technology, SoLoNOx Combustion System, capable of achieving NO_x and CO emissions of 10 ppmv and 20 ppmv, respectively. To further reduce NO_x and CO emissions from the turbine, selective catalytic reduction (SCR) technology and CO catalysts are included as exhaust treatment. SCR and CO catalysts are considered BACT, and are reliable, proven technology that reduces NO_x and CO emissions to 2 ppmv and 3 ppmv, respectively. SCR relies upon injection ammonia vapor (NH_3) into the flue gases and subsequent reaction on a downstream catalyst to reduce NO_x to elemental nitrogen and water. Ammonia emissions are limited to 5 ppmv, based upon SCAQMD Permit to Operate.

2.1.3 Test Plan for Unit 2

Two test matrices (Tables 2-6 and 2-7) were designed for test unit 2 with the UCR Dilution system. These included changing the dilution ratio and residence times while keeping the dilution temperature and relative humidity at ambient levels. This test design was based on findings from Test unit 1 (Capstone C-65, the 65 kW microturbine, see Section 3.1). The initial matrix (Table 2-6) was designed to scan through residence times in a stepwise manner to determine changes in particle growth. This stepwise scanning of residence times occurred for each of the dilution ratios chosen. Additionally, protocol methods used to measure PM for stationary sources were used as well. These included SCAQMD Method 5.1 and EPA Method 201A/202. In addition, the ammonia levels were measured by BAAQMD ST-1B method for stationary sources. Two samples were taken for ammonia, one at the beginning and one at the end of the testing. A heated FID was used to monitor total hydrocarbons (THC) as C1 from the turbine.

Table 2-6: Scanning up Residence Times

Dilution Temperature (°C)	Dilution Ratio	Residence Time (s)	Relative Humidity (%)
Uncontrolled	10,25,40	10	Uncontrolled
	10,25,40	20	
	10,25,40	30	
	10,25,40	40	
	10,25,40	50	
	10,25,40	60	
	10,25,40	70	
	10,25,40	80	

	10,25,40	90	

The matrix below in Table 2-7 was then designed to determine changes in PM from different dilution ratio and residence times.

Table 2-7: Initial Matrix

Dilution Temperature (°C)	Dilution Ratio	Residence Time (s)	Relative Humidity (%)
Uncontrolled	10	10,30,50	Uncontrolled
	10	10,30,50	
	10	10,30,50	
Uncontrolled	25	10,30,50	Uncontrolled
	25	10,30,50	
	25	10,30,50	
Uncontrolled	40	10,30,50	Uncontrolled
	40	10,30,50	
	40	10,30,50	

2.5 Test Plan for large, ~50MW, GE LM6000 turbine

In meetings with the permitting staff at AQMD, they identified the GE LM6000 turbine technology with installed SCR control technology as an unit of interest since there were about 30 of these permitted in the District. Meeting with multiple power companies revealed these ‘peaker’ plants only get turned on when ISO requests power; otherwise they are down due to their cost of operation and the limited hours of operation allowed by operating permit. However, we did find one plant that needed its annual Relative Accuracy Test Audits (RATA) and were able to work out an agreement for testing the plant.

2.5.1 Background on GE’s LM6000 gas turbines

According to the literature, the General Electric LM6000 (Figure 2-5) is a turbo-shaft gas turbine derived from the CF6-80C2 aircraft turbofan and is modified depending on application. For example, the turbine section can be expanded to convert thrust into shaft power and the control package reworked for power generation, such as peaking power plants. The LM6000 provides 54,610 shaft horsepower (40,700 kW) from either end of the low-pressure rotor system, which rotates at 3,600 rpm. This twin spool design with the low pressure turbine operating at 60 Hz, a common electrical frequency, eliminates the need for a conventional power turbine.

GE has several option packages for industrial LM6000s, including *SPRINT* (SPRay INTercooling), water injection (widely known as "NOx water"), and Spray Mist Evaporative Cooling (SMEC). The SPRINT and SMEC options are designed to increase efficiency and power of the turbine, and the water injection is for reducing emissions. The SMEC system is a water fogger system that sprays a fine mist of water into the inlet air before the air filters. This system is high maintenance and may be replaced by chillers in newer units. The SPRINT system injects demineralized water into the engine either upstream of the low pressure compressor or between the low pressure and high pressure compressors. The GE LM6000 PC is rated to provide more than 43 MW with a thermal efficiency of around 42% LHV at ISO conditions. Today, with options, this can be increased to above 50MW rated power[3].

Figure 2-5: A 50 MW, Peaker Power Plant Using GE's LM6000 Turbine with SCR

2.5.2 Description of test unit

The peaking plant tested in this project used a LM6000 in simple-cycle mode of operation and was built to exclusively serve a local area. NO_x emissions were restricted to 2.5 ppm dry and attained by using water injection in series with a catalyst system from Express Integrated Technologies. A 3,200t chiller from Turbine Air Systems was part of the installed unit and used

---

[3] See http://www.ge-energy.com/products_and_services/products/gas_turbines_aeroderivative/lm6000_ph.jsp

about 80% of the time that the plant is on-load. The site is sized for additional machines of similar size. Operating parameters are summarized in Table 2-8

Table 2-8: Operating Parameters for the Tested LM6000 Unit

Configuration	2 X 48-MW LM6000 Sprint NxGen gas turbines
Operation	2006
Fuel	Natural gas
T/G supplier	GE

2.5.3 PM Measurement Text Matrix

Unlike the previous 14 MW turbine testing at UC Irvine, a limited amount of time was allocated by the power plant for the testing at the 50 MW Riverside power plant. Therefore a much smaller matrix was designed to collect data as a function of varying dilution ratios and residence times. The test matrix used for this study is shown in Table 2-9 below.

Table 2-9: Test Plan for 50 MW Riverside Power Plant

Matrix	Dilution Temperature (°C)	Dilution Ratio	Residence Time (s)	Relative Humidity (%)
1-Original	Uncontrolled	40 10	20, 250 250, 20	Uncontrolled
2-Repeatability	Uncontrolled	40 10	20, 250 250, 20	Uncontrolled
3-DR Midpoint	Uncontrolled	25	20, 250	Uncontrolled
4-RT Midpoint	Uncontrolled	40 25 10	125 125 125	Uncontrolled
Ambient				

Additionally one sample each of SCAQMD Method 5.1 and EPA Method 201A/202 were collected.

CHAPTER 3: Test Results from Field Testing

3.1 Microturbine Test (Capstone 65kW)

On September, 2013, UCR measured PM from protocol methods, SCAQMD Method 5.1 and EPA Method 201A/202 and the UCR dilution system from the Capstone 65 kW. The goal of this project was to characterize PM emissions from changes in dilution ratio, residence time, dilution temperature and relative humidity. These changes were monitored with real-time instrumentation, a Nano SMPS and a Fast SMPS.

The proposed test matrix for the UCR dilution sampler is outlined in Section 2.1.3 and the dilution system is outlined in Section 2.1.2. It is designed to evaluate the impacts of dilution temperature, dilution ratio, residence time, and relative humidity on the particulate mass emissions from the NG fired turbine. The test matrix was ultimately altered based on the operational load of the turbine. Particles were observed for days with a high load (~14 MW) down to very high dilution and low residence time settings. Much lower PM mass concentrations were observed when the turbine was operated at lower load points (~9MW) dropping in some cases below ambient levels. Therefore, the test matrix was modified to incorporate lower dilution ratio and lower residence time endpoints for lower load point days to obtain higher PM mass concentrations.

Total $PM_{2.5}$ mass from the dilution system was determined by gravimetric analysis of 2μm, 47mm Teflo® (Pall Gelman, Ann Arbor, MI) filters. The filter masses were measured with a Mettler Toledo UMX2 microbalance and were weighing according to the Code of Federal Regulations (CFR). Particle size distributions were collected using a TSI Scanning Mobility Particle Spectrometer (3085 short column, TSI 3776 CPC) for smaller particles and a custom built SMPS (radial DMA, mixing CPC) for larger particle sizes. EPA Method 201A/202 and SCAQMD Method 5.1 were used as the current protocol PM collection methods for stationary sources.

The influence of dilution ratio on the particle size distributions are shown in Figure 3-1 (RH=~25%) and Figure 3-2 (RH=~50%). For each residence time at a fixed dilution temperature and relative humidity there are much higher concentrations with the lower DR compared to the higher DR runs. At lower dilution ratios, there are more volatile species available for nucleation and condensation. This trend is seen to be independent of the residence time.

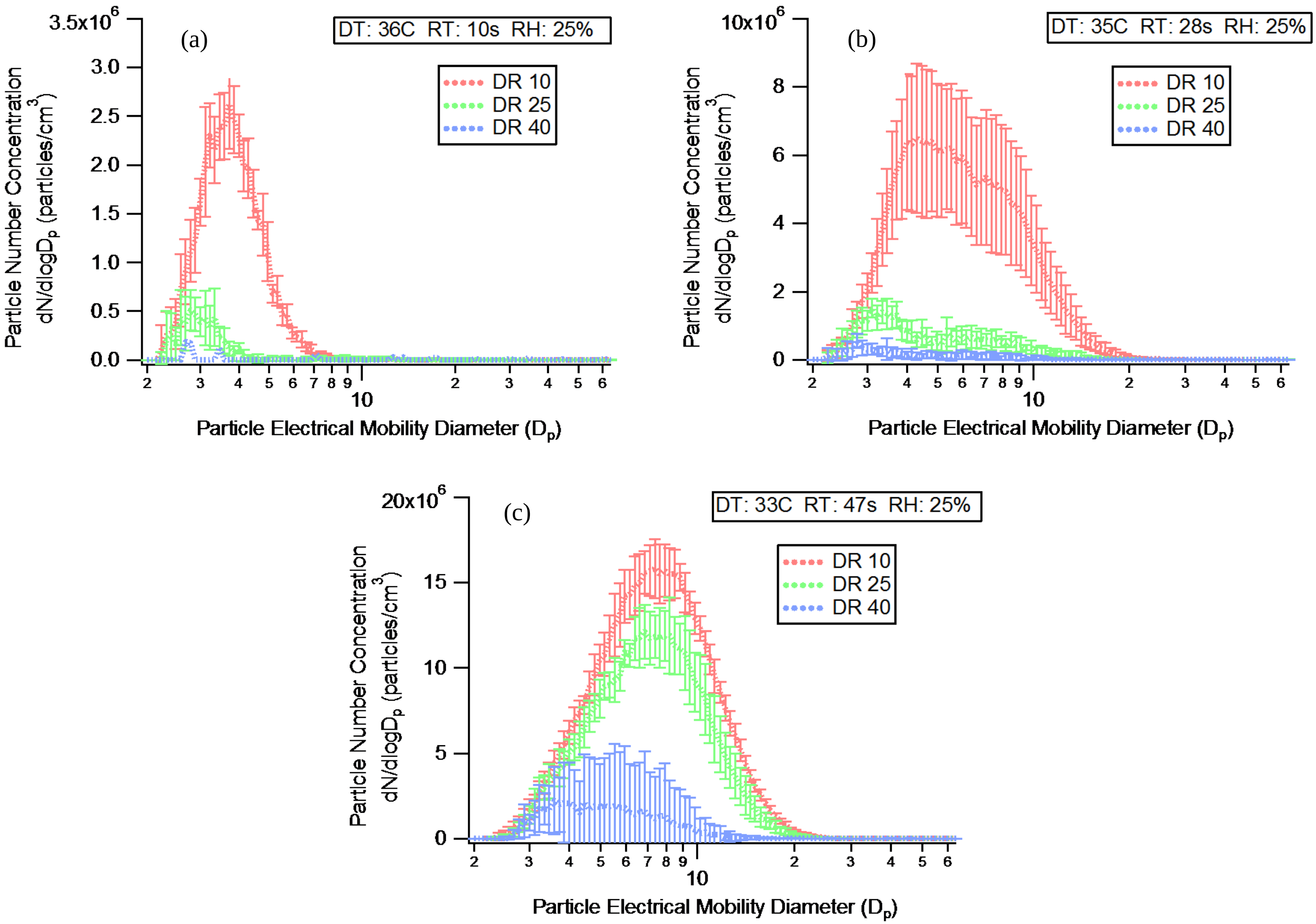


Figure 3-1: Influence of Dilution Ratio (a) RT: 10s (b) RT: 28s (c) RT: 47s

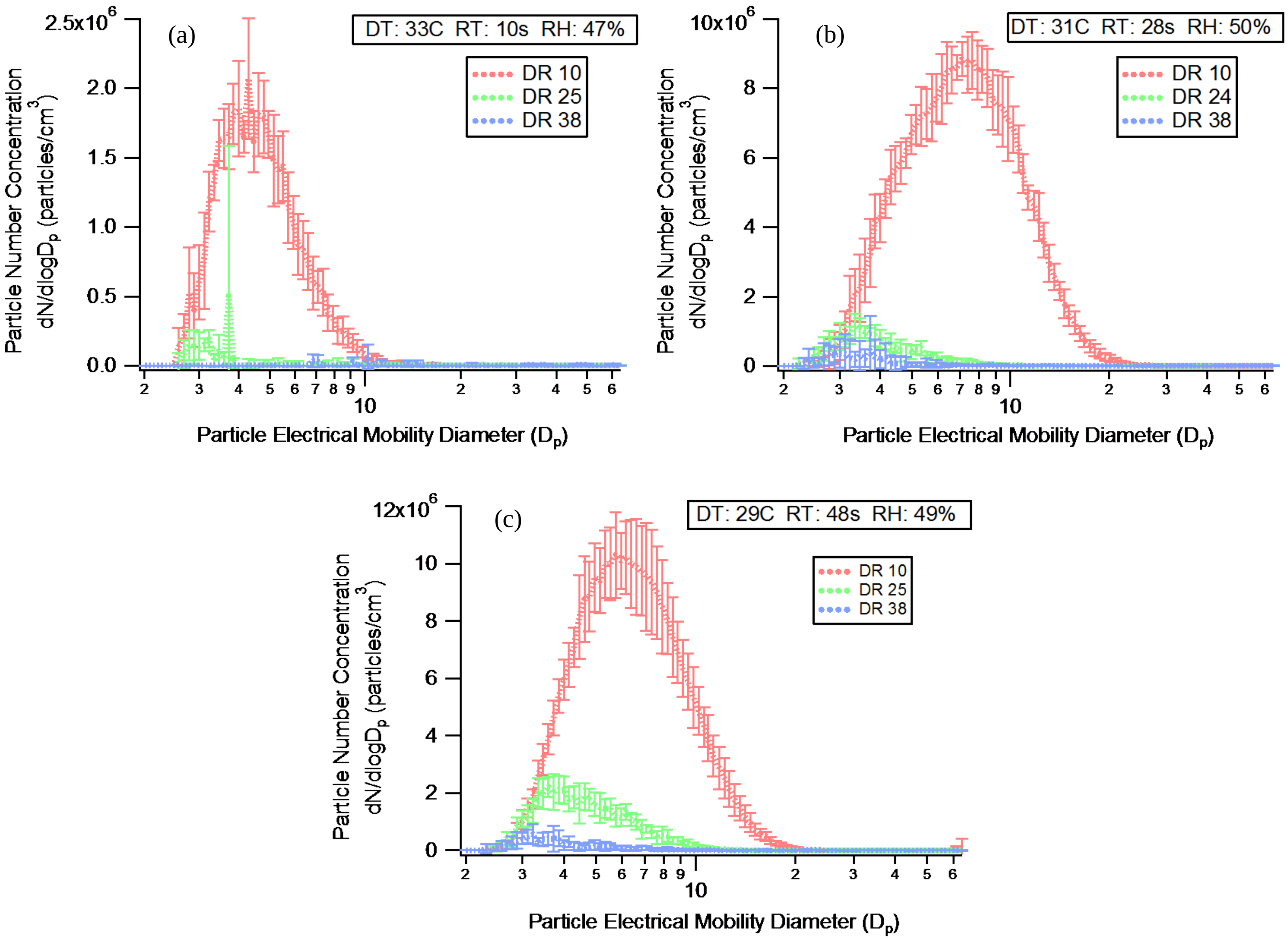


Figure 3-2: Influence of Dilution Ratio (a) RT: 10s (b) RT: 28s (c) RT: 48s

Figure 3-3 below shows both the particle mass distribution as well as the total integrated particle mass. A dilution ratio setting of 10:1 compared to 25:1 and 38:1 results in a much higher particle mass concentration (1.6 ug m^{-3} vs 0.11 ug $m^{-3}$and 0.039 ug m^{-3}, respectively). Overall, the integrated particle mass concentrations are well below the National Ambient Air Quality Standards (NAAQS) annual average for primary $PM_{2.5}$ of 12 ug m^{-3}.

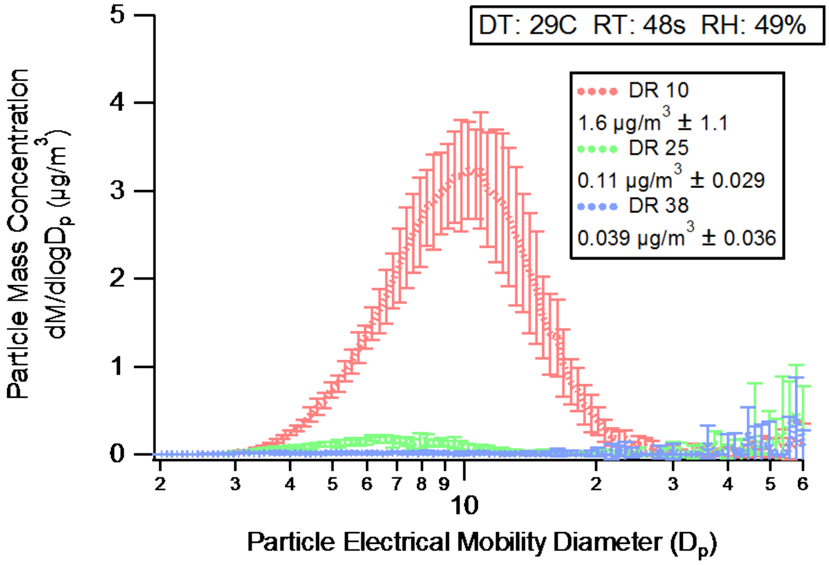


Figure 3-3: Influence of Dilution Ratio on Particle Mass

At fixed dilution ratios of 10:1, 25:1 and 38:1 increasing residence time from 10s to 49s results in higher number concentration and peak diameter (Figure 3-4 (25% RH) and Figure 3-5 (50% RH). Further, assuming a fixed dilution ratio, dilution temperature, and relative humifity, a higher mass concentration is observed for longer residence times compared to shorter residence times (Figure 3-6)) These charts indicates that the growth of the particles are kinetically limited as the particle growth formation continues for all cases as the RT of the system is increased. Therefore, any measurement system requires sufficient residence time to allow for appropriate particle growth after cooling and dilution. The influence of RH on particle number distributions for fixed dilution ratios, temperatures, and residence times is shown in Figure 3-7. RH is seen to have some effect on the particle size distributions although the impact is much smaller than that observed for the other parameters (dilution temperature, dilution ratio, and residence times).

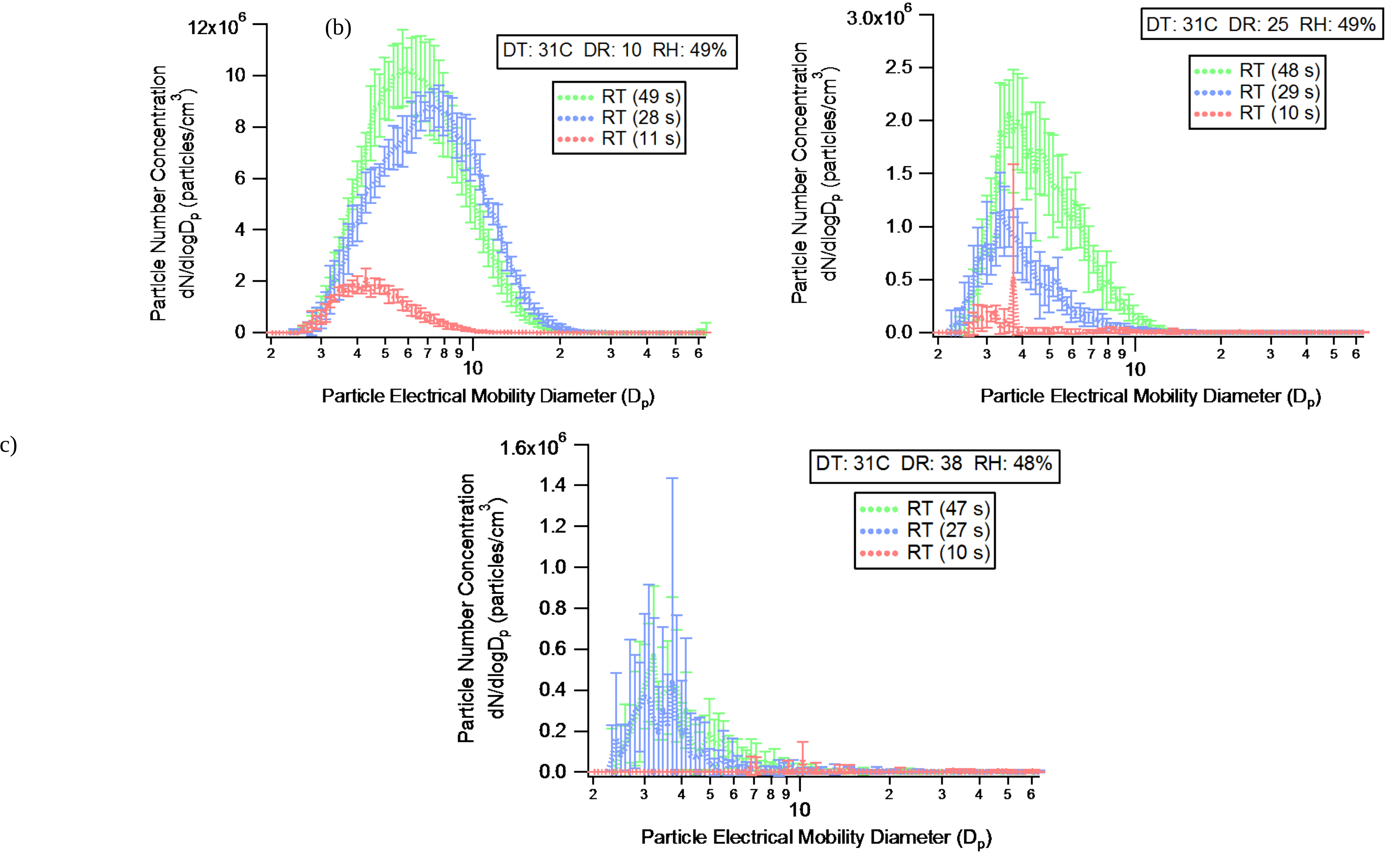


Figure 3-4: Influence of Residence Time at 31C and 49% RH (a) RT: 10s (b) RT: 28s (c) RT: 48s

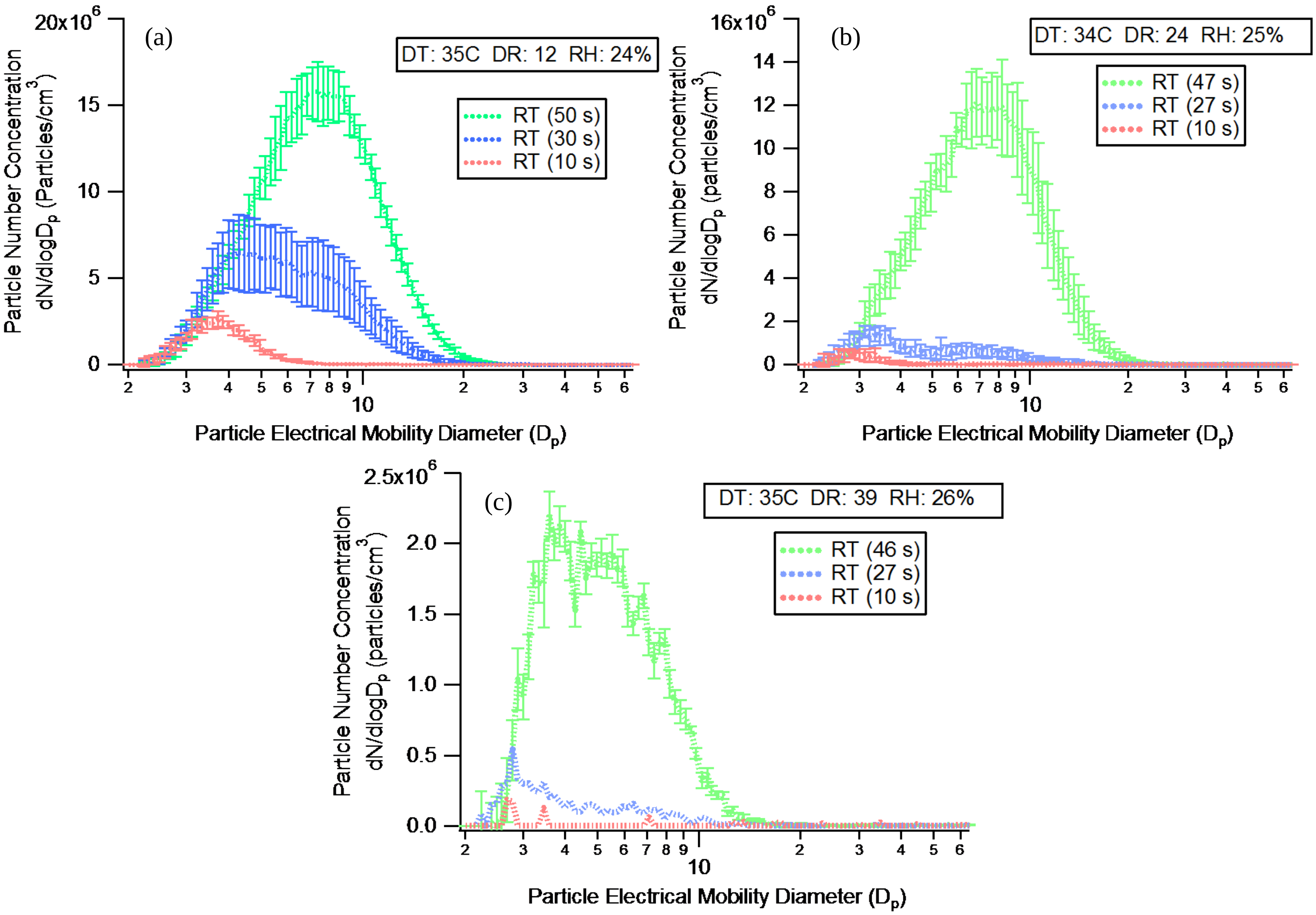


Figure 3-5: Influence of Residence Time at 35C and 25% RH (a) RT: 10s (b) RT: 28s (c) RT: 48s

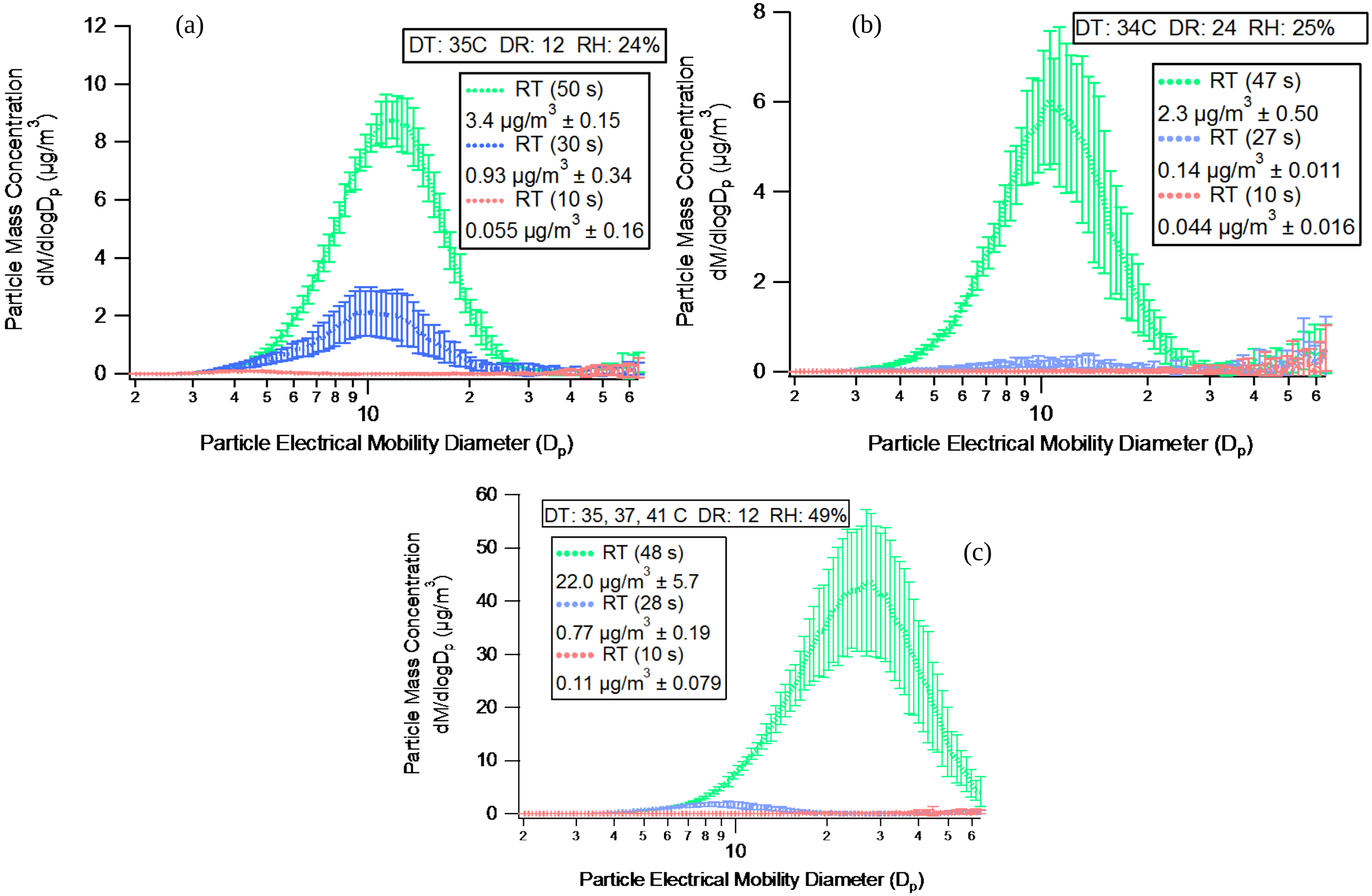
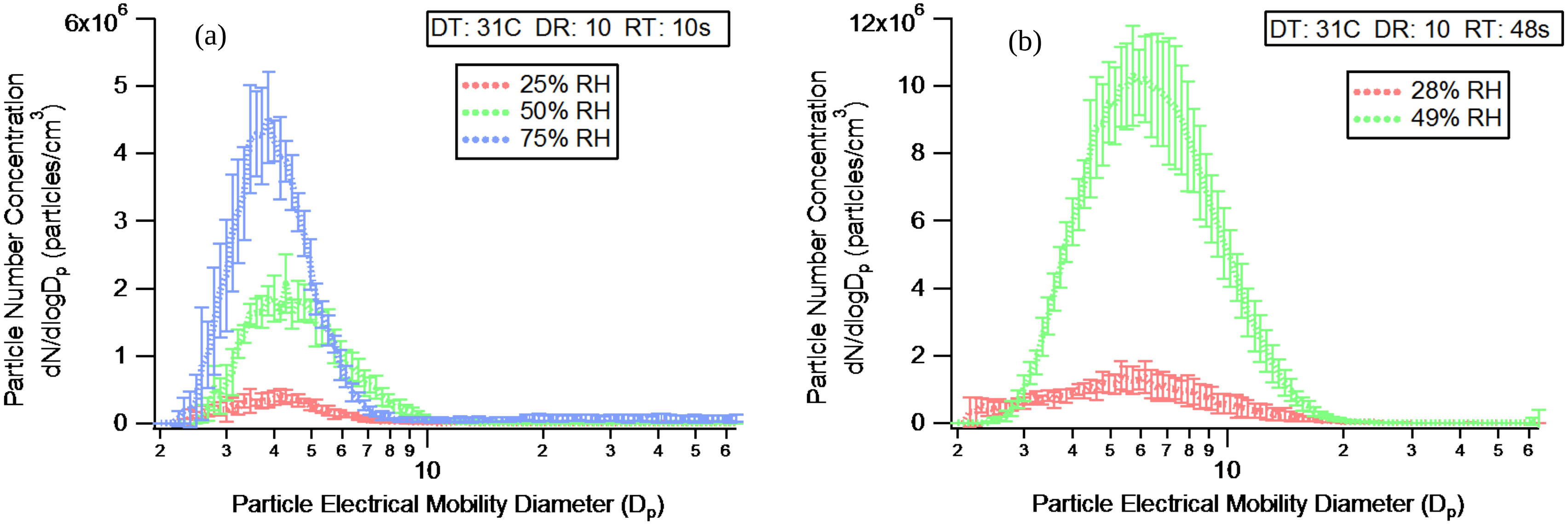


Figure 3-6: Influence of Residence Time on Particle Mass (a) DR: 12, RH: 24% (b) /DR: 24, RH: 25% (c) DR: 12, RH: 49%Figure 10 above shows the influence of residence time on the particle mass.


(a)
DT: 31C DR: 10 RT: 10s
25% RH
50% RH
75% RH
6x10^6
5
4
3
2
1
0
Particle Number Concentration
dN/dlogD_p (particles/cm^3)
2
3
4
5
6
7
8
9
10
2
3
4
5
6
Particle Electrical Mobility Diameter (D_p)
(b)
DT: 31C DR: 10 RT: 48s
28% RH
49% RH
12x10^6
10
8
6
4
2
0
Particle Number Concentration
dN/dlogD_p (particles/cm^3)
2
3
4
5
6
7
8
9
10
2
3
4
5
6
Particle Electrical Mobility Diameter (D_p)

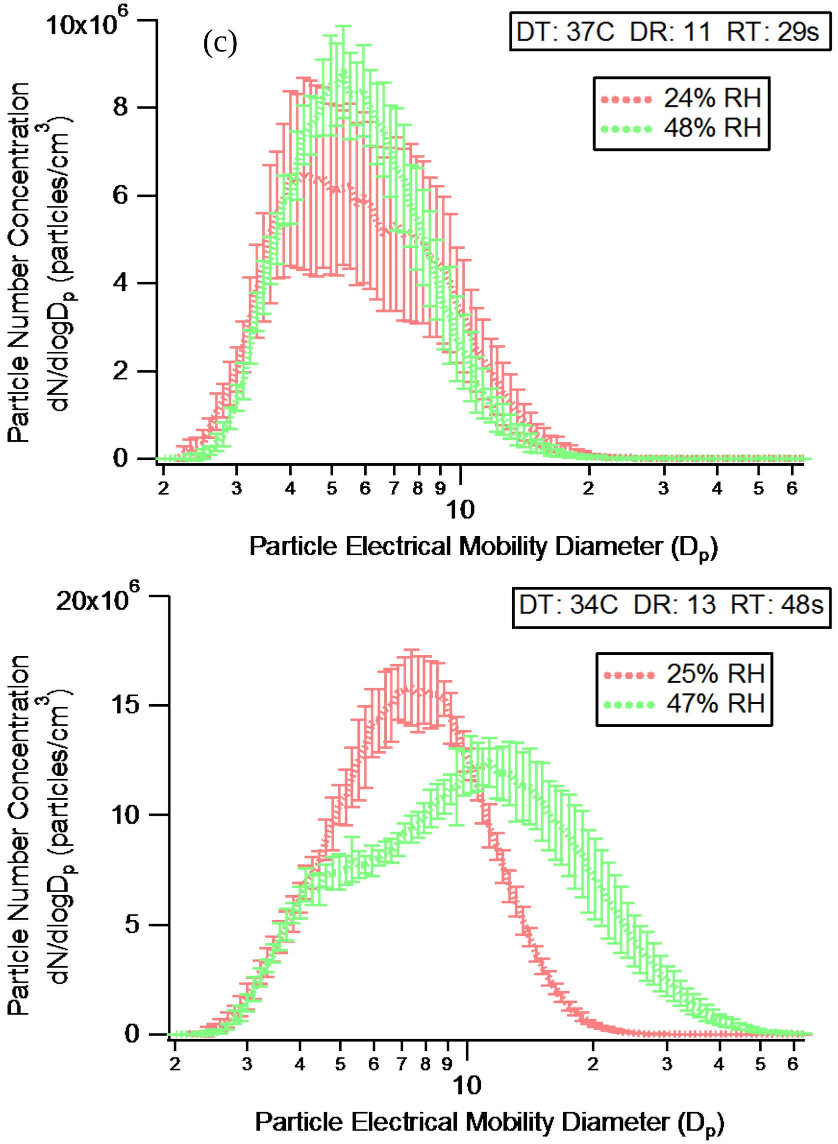


Figure 3-7: Influence of Relative humidity on Particle Number Distribution on Particle Mass (a) DR: 10, DT: 31 C, RT: 10 s (b) DR: 10, DT: 31 C, RT: 48s (c) DR: 11, DT: 37 C, RT: 29 s (d) DR: 13, DT: 34 C, RT: 48 s.

The results for the PM protocol methods are shown in the Figure 3-8 below. A total of one EPA Method 201A/202 and four SCAQMD M5.1 samples were run in the time allocated for this unit.

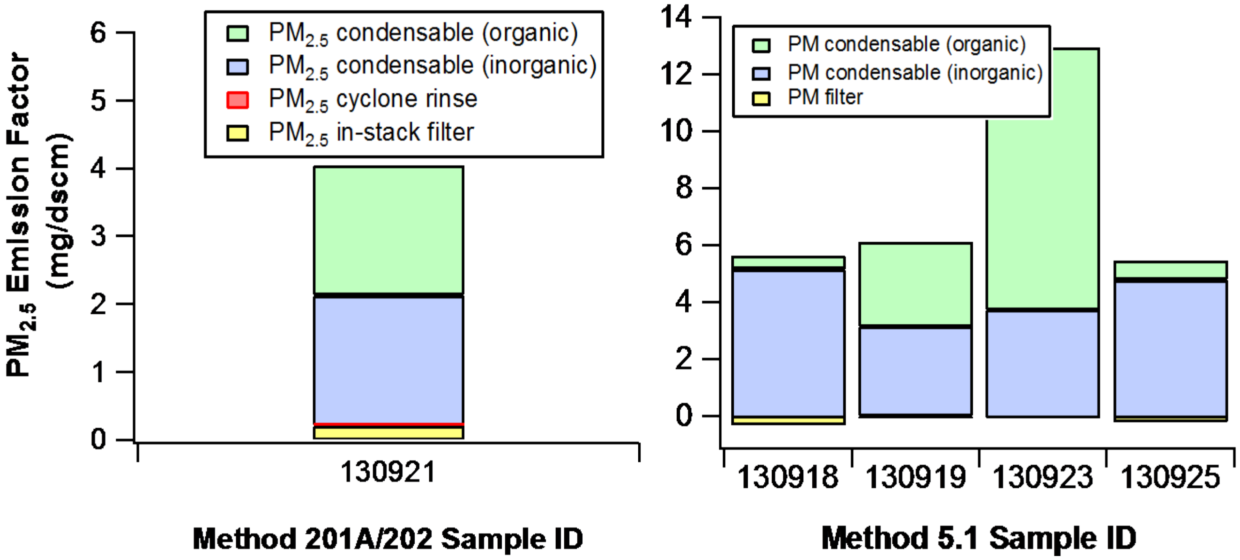


Figure 3-8: Comparison of PM Emissions Measured by Protocol Methods.

For the EPA Method 201A/202 run on 140921, there is a similar organic and inorganic condensable PM fraction. Overall, there is a very small filterable PM fraction as indicated by the cyclone rinse and in-stack filter. Similar to the Method 201A/202 sample, the Method 5.1 samples show very little filterable PM. Sample ID 130918 shows a slightly negative PM mass from the quartz fiber filter. At these very low concentrations, small fibers lost from the filter after collection result in net negative filter weights. Overall, the absolute emission factors for both EPA Method 201A/202 and SCAQMD Method 5.1 are similar except for the sample ID 130923. The high PM emission factor for sample ID 130923 can be attributed to the high level of organics in the condensable PM fraction.

3.2 Test of Solar Titan™ 130 Turbine with SCR (unit 2)

3.2.1 Test Setup for the Solar Turbine with SCR

Setup for this test required a pulley to transfer all equipment to the top of the stack platform. According to the test design (Section 2.4), methods and instrumentation included: EPA Method 201A/202, SCAQMD Method 5.1, BAAQMD ST-1B, FID and the UCR dilution system with the nano SMPS, long column SMPS and Fast SMPS. All parametric data from the UCR dilution system as well as the FID was recorded in real-time via a data logging system. The test matrix was ultimately changed due to the operational load of the turbine. For days with a high load at approximately 14 MW, particles were observed down to very high dilution and low residence time settings. When the turbine was operated at lower load points (~9MW), much lower PM mass concentrations were observed and in some cases were below background as measured with the real-time instruments. For these tests, the test matrix was modified to incorporate lower dilution ratio and lower residence time endpoints to obtain higher PM mass concentrations.

Pictures of the test set-up are shown in the Figures 3-9 and 3-10 on the following two pages.

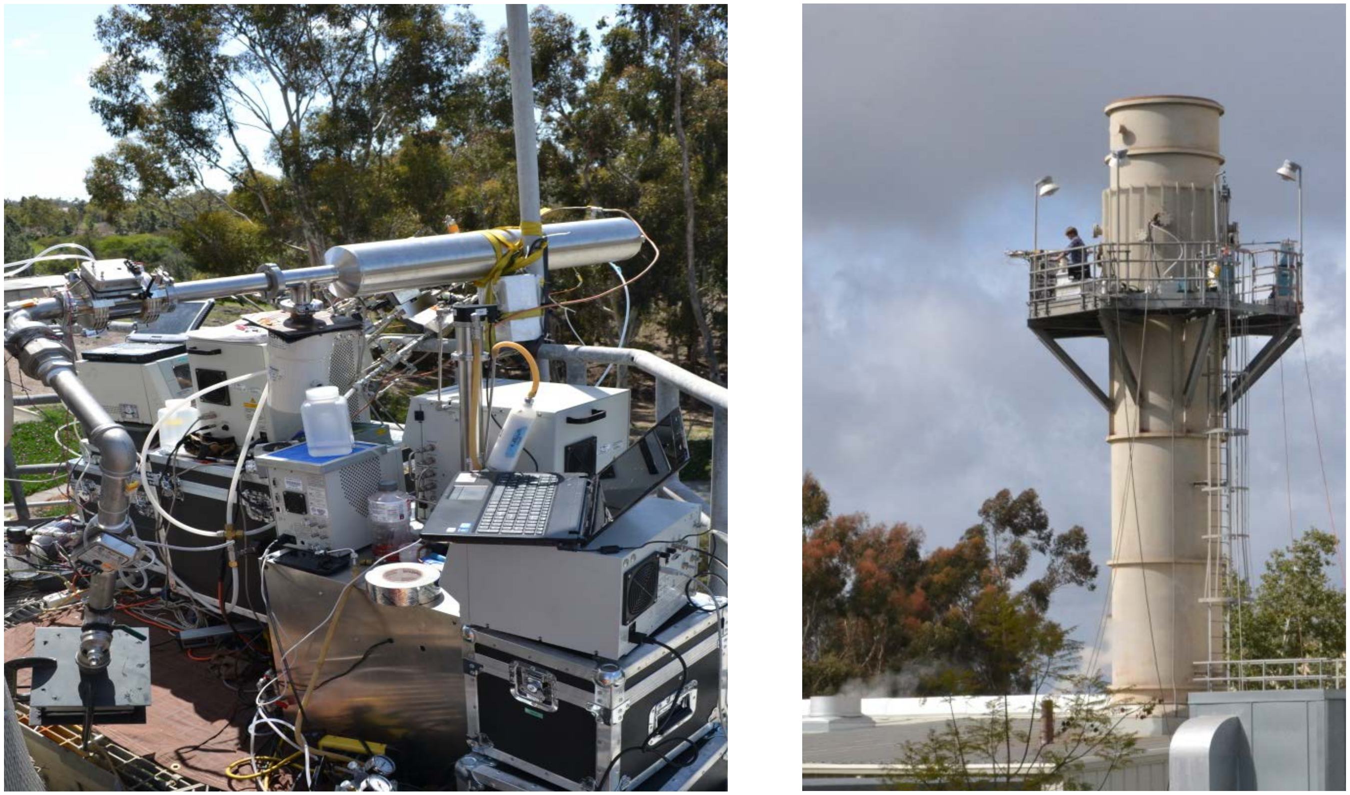


Figure 3-9: Left-Instrumentation set up on Turbine Platform (right)

Figure 3-10: Pictures of the Test Setup Showing the Locations for the Measurement Sites.

Figure 3-11 shows the resulting size distributions from the nano SMPS scanning through residence times in a stepwise manner. At a fixed dilution ratio (Figure 3-11(a-c)), an increase in residence time results in a shift to larger particle diameter particles with an increase in particle number concentration. The corresponding PM mass concentrations are shown in Figure 3-12. At each of the fixed 10, 18 and 25:1 dilution ratio settings, there is an increase in PM mass concentration with increasing residence times. The integrated PM mass values are shown in each Figures corresponding legends. The integrated PM mass concentrations range from 0.07 to 1.6 ug m^{-3} respectively, which are well below the NAAQS annual average hour limit for $PM_{2.5}$ of 12 ug m^{-3}.

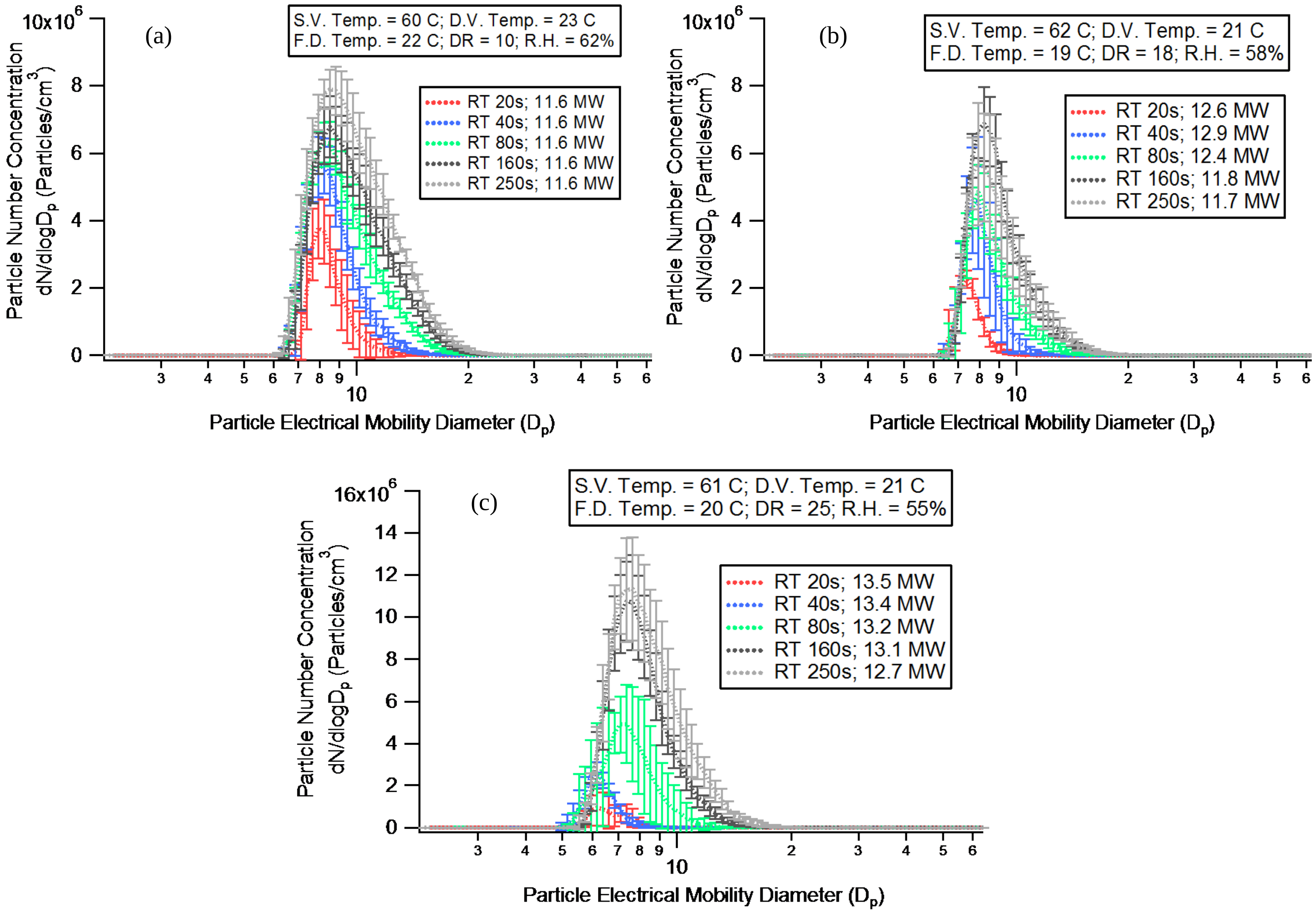


Figure 3-11: PN: Scanning through Residence Times (a) DR = 10 (b) DR = 18 (c) DR = 25

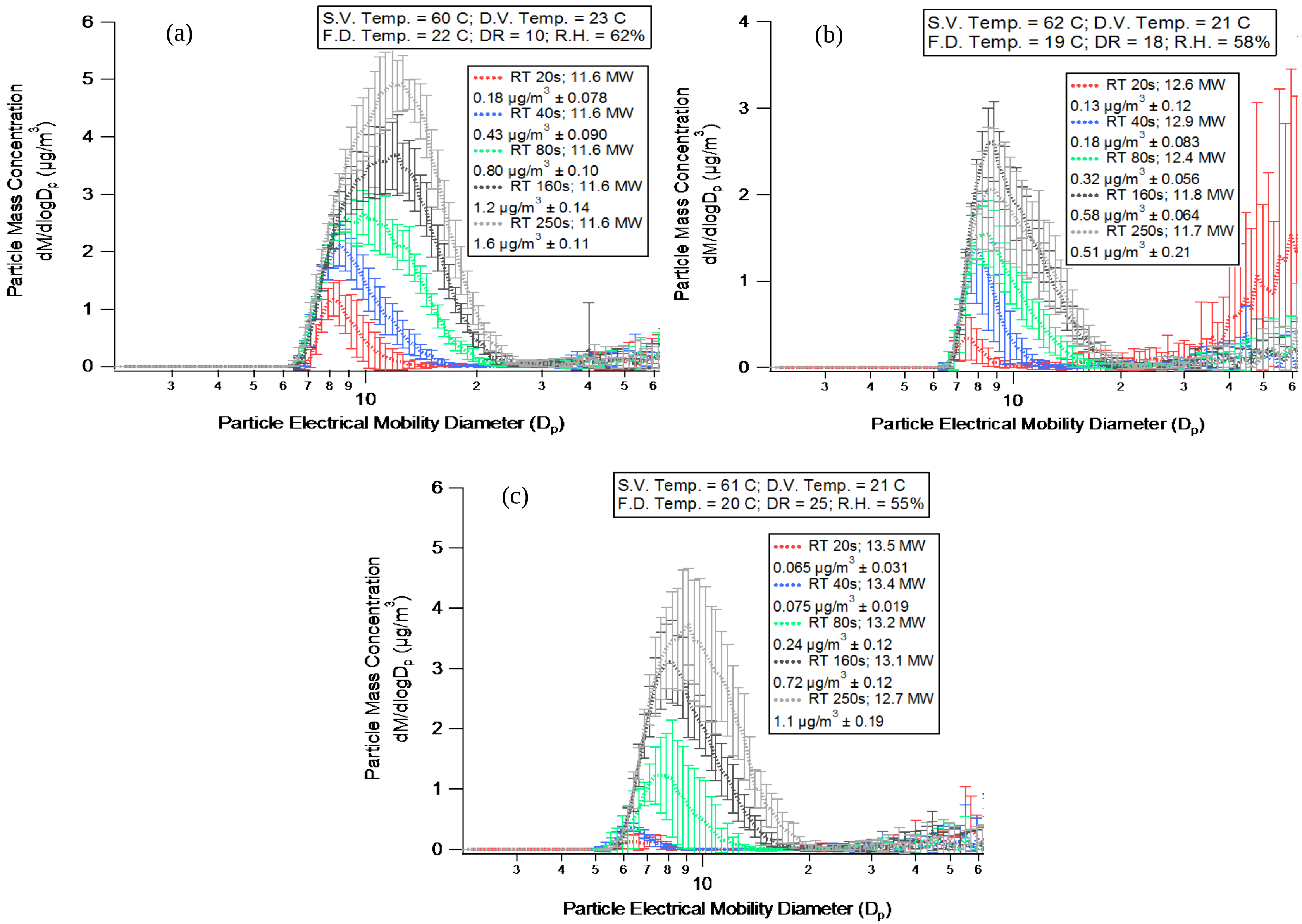


Figure 3-12: PM Mass: Scanning through Residence Times (a) DR = 10 (b) DR = 18 (c) DR = 25

The integrated PM mass concentrations (after correcting for dilution ratio) are displayed as a function of the residence times and dilution ratios shown in Figure 3-13 and 3-14 below. This data is also a function of the turbine operational load as represented by the color scale. Figure 3-13 represents the integrated mass concentration as a function of the residence times for the varying dilution ratios used throughout this study. The trends from the data are difficult to ascertain and therefore are divided into individual graphs based on fixed dilution ratios and residence times. At fixed dilution ratios of 10, 18, 24 and 38, increasing residence times lead to higher PM mass concentrations. After a residence time of approximately 80s, the PM mass begins to plateau. Overall, the majority of the PM mass concentrations are well below 1 μg/m^3.

Figure 3-14 below shows the effect of dilution ratio on particle mass concentration corrected for dilution ratio. Overall, higher PM mass concentrations are observed as dilution ratio is lowered. Figures 10-5 (b-c) are separated from Figure 10-5 (a) based on residence time to more clearly observe the overall trends. The PM mass concentration begins to plateau for the majority of the fixed residence time settings at approximately 25:1. The mass concentrations observed at a dilution ratio setting of 10:1 exceed 10 μg/m$_3$ where at higher dilution ratios, the PM mass concentrations were well below 1 μg/m$_3$. The PM mass concentrations begin to decrease as the dilution ratio increases above 10:1 due to limitations in available condensable hydrocarbon and sulfur containing species.

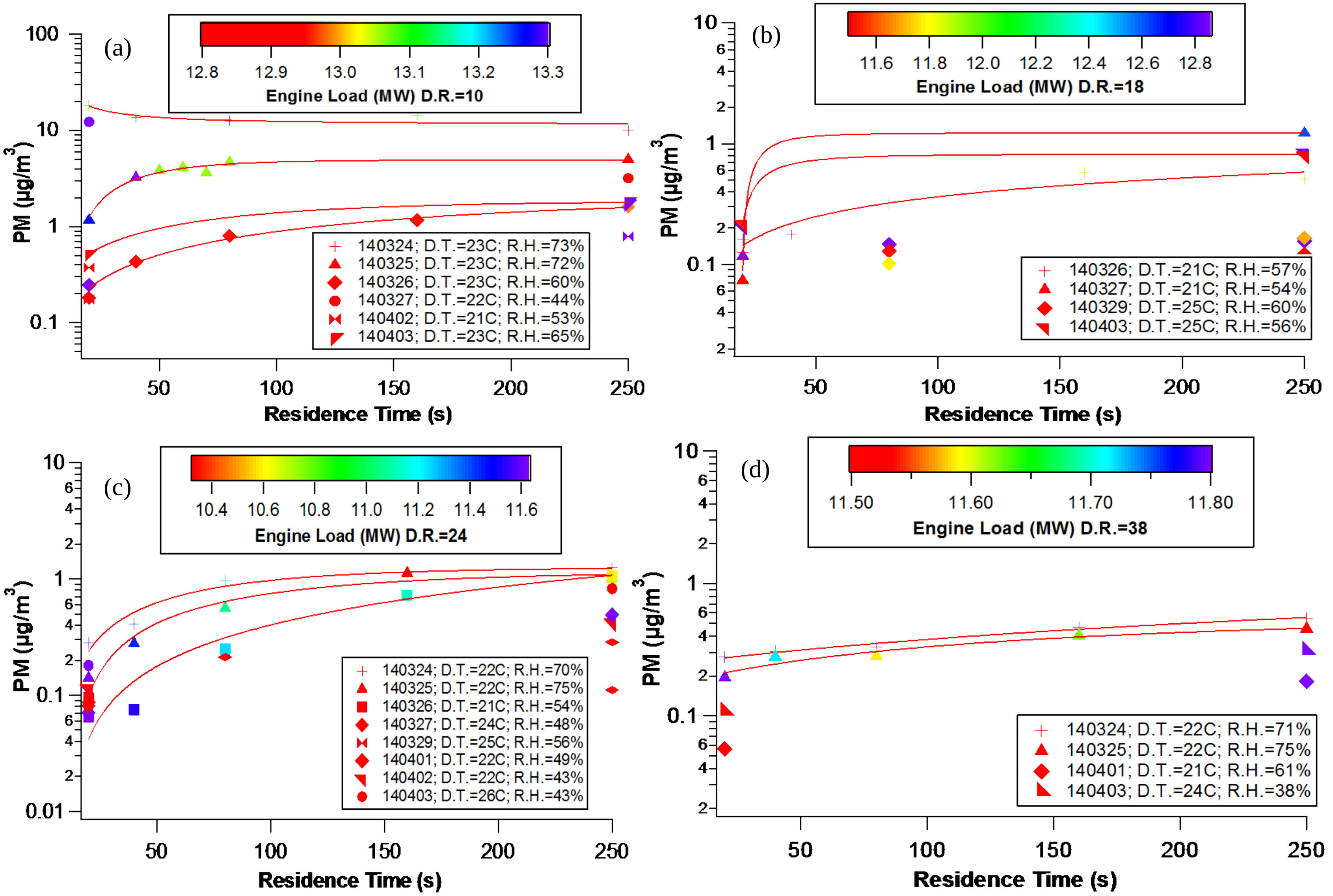
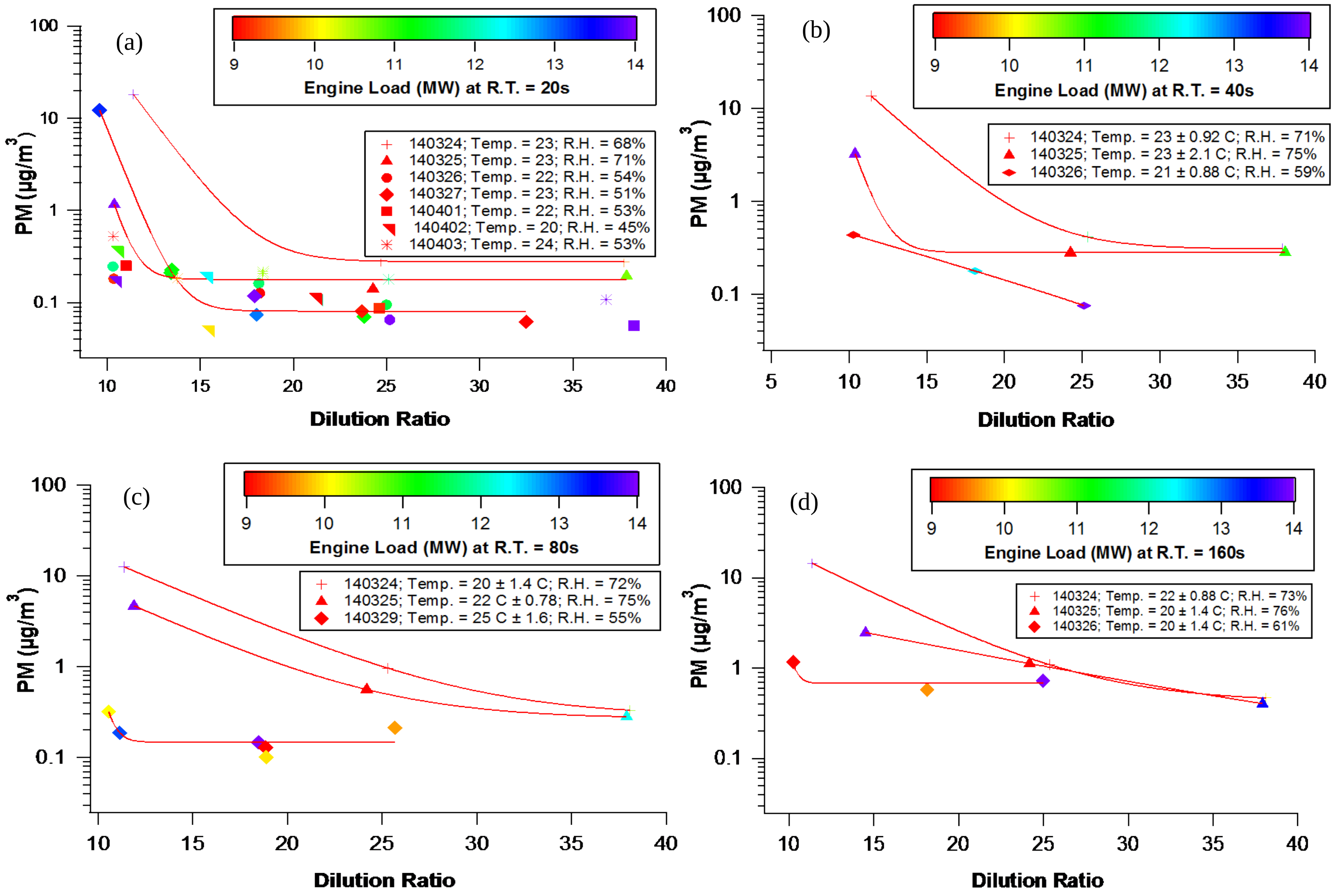


Figure 3-13: PM Mass Concentrations as a Function of Varying Residence Times (a) DR = 10

(b) DR = 18 (c) DR = 24 (d) DR = 24 (e) DR = 38


(a)
Engine Load (MW) at R.T. = 20s
9
10
11
12
13
14
140324; Temp. = 23; R.H. = 68%
140325; Temp. = 23; R.H. = 71%
140326; Temp. = 22; R.H. = 54%
140327; Temp. = 23; R.H. = 51%
140401; Temp. = 22; R.H. = 53%
140402; Temp. = 20; R.H. = 45%
140403; Temp. = 24; R.H. = 53%
PM (μg/m^3)
100
10
1
0.1
10
15
20
25
30
35
40
Dilution Ratio
(b)
Engine Load (MW) at R.T. = 40s
9
10
11
12
13
14
140324; Temp. = 23 ± 0.92 C; R.H. = 71%
140325; Temp. = 23 ± 2.1 C; R.H. = 75%
140326; Temp. = 21 ± 0.88 C; R.H. = 59%
PM (μg/m^3)
100
10
1
0.1
5
10
15
20
25
30
35
40
Dilution Ratio
(c)
Engine Load (MW) at R.T. = 80s
9
10
11
12
13
14
140324; Temp. = 20 ± 1.4 C; R.H. = 72%
140325; Temp. = 22 C ± 0.78; R.H. = 75%
140329; Temp. = 25 C ± 1.6; R.H. = 55%
PM (μg/m^3)
100
10
1
0.1
10
15
20
25
30
35
40
Dilution Ratio
(d)
Engine Load (MW) at R.T. = 160s
9
10
11
12
13
14
140324; Temp. = 22 ± 0.88 C; R.H. = 73%
140325; Temp. = 20 ± 1.4 C; R.H. = 76%
140326; Temp. = 20 ± 1.4 C; R.H. = 61%
PM (μg/m^3)
100
10
1
0.1
10
15
20
25
30
35
40
Dilution Ratio

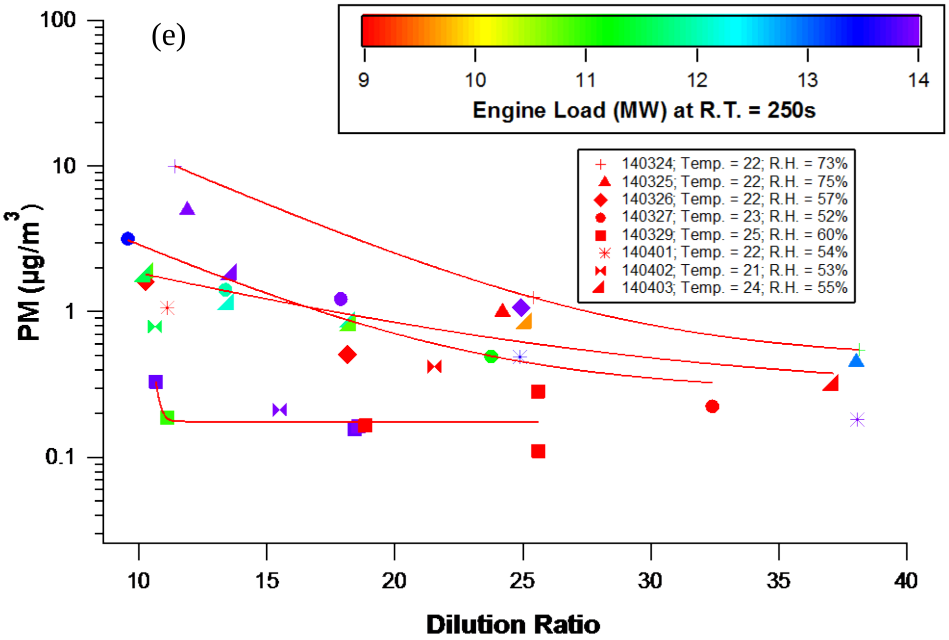


Figure 3-14: PM Mass Concentrations as a Function of Varying Dilution Ratios (a) R.T. = 20s (b) R.T. = 40s (c) R.T. = 80 (d) R.T. = 160s (e) R.T. = 250s

The PM protocol test methods are shown in the Figure 3-15 below. Overall, there were a total of five SCAQMD Method 5.1 samples and four EPA Method 201A/202 samples. EPA Method 201A/202 was equipped with a $PM_{2.5}$ cyclone while SCAQMD Method 5.1 was measuring total suspended PM (TSP). Results from both methods indicated emission factors below 15 mg/dscm. Overall, the filter data for 140324 and 140403 for SCAQMD M5.1 are negative while the filter data for 140321, 140325 and 140402 are negative as well for EPA Method 201A/202. Ultimately, fibers lost from the glass fiber filters resulted in net negative filter weights. The previous size distributions show that the majority of the particles in the nucleation mode and are well below 20nm which contribute very little mass. The majority of the emissions are contributed from the organic and inorganic condensable fraction of PM. EPA Method 201A/202 has overall higher PM emission factors on 3/21/14 compared to SCAQMD M5.1, while SCAQMD M5.1 has higher PM emission factors than EPA Method 201A/202 on 4/2/14. As SCAQMD Method 5.1 does not use an in-stack filter, a Teflon based filter may be used to improve sensitivity.

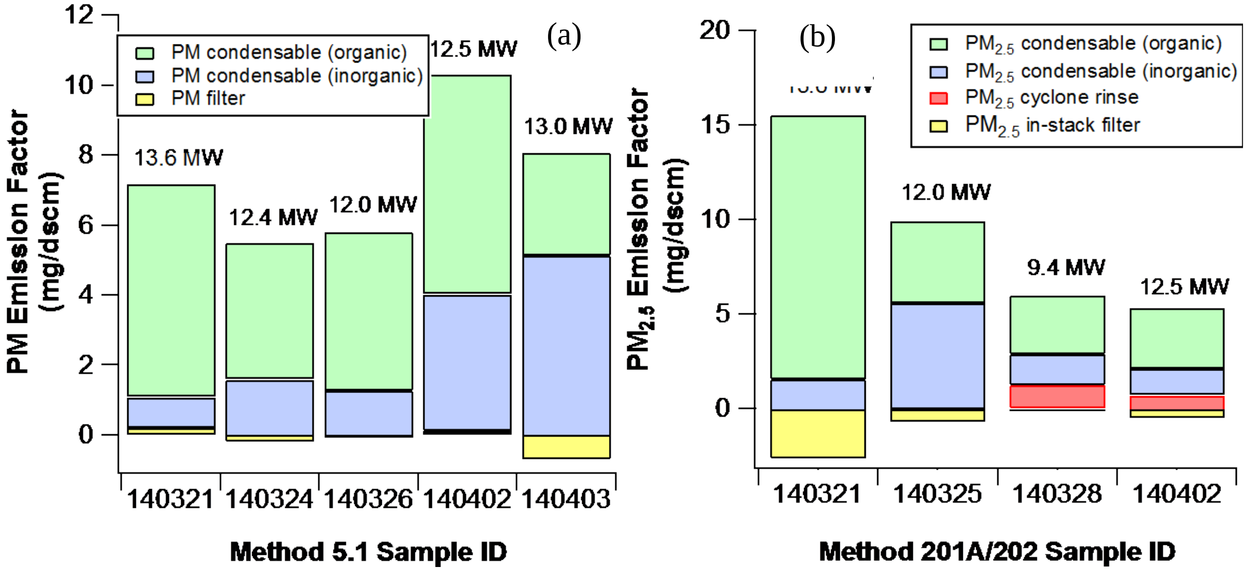


Figure 3-15: PM Protocol Methods (a) SCAQMD Method 5.1 (b) EPA Method 201A/202

The PM mass concentrations are compared between both the protocol methods and the dilution sampler (Figure 10-7). The PM mass concentrations for the dilution sampler as a function of varying dilution ratio and residence time are well below the PM mass concentrations from M5.1 and M201A/202. Highest PM mass concentrations characterized with the UCR dilution sampler extend to ~ 20 μg/m3 compared to ~7-10 mg/m3 measured by the protocol methods. Large differences in PM mass concentrations can be attributed to positive artifact associated with the protocol methods. Figure 3-16 below combines the PM dilution tunnel measurements with the protocol methods.

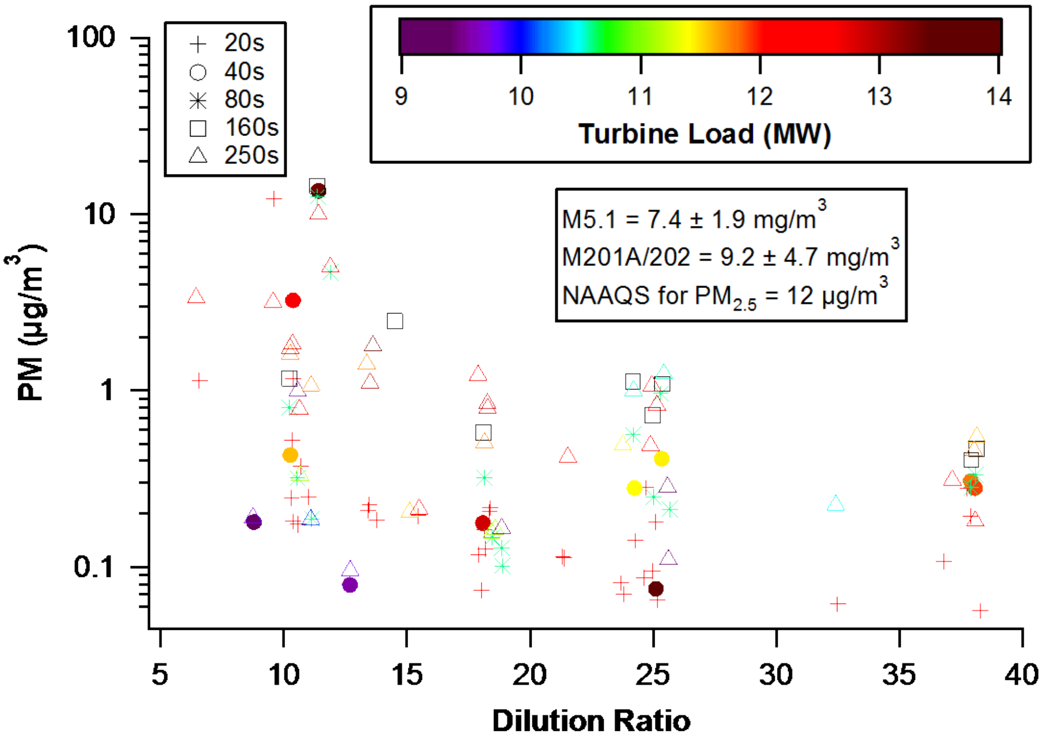


Figure 3-16: Comparison of Different PM Measurement Methods

3.3 Test of Large Turbine

3.3.3 Test Setup for 50 MW Turbine

The setup for this test required a pulley to transfer the equipment to the top of the stack platform at approximately 75 feet above the ground. Methods and instrumentation included: EPA Method 201A/202, SCAQMD Method 5.1, FID and the UCR dilution system with the nano SMPS and Fast SMPS. All parametric data from the UCR dilution system as well as the FID was recorded in real-time via a data logging system. Due to time constraints, the test matrix for the UCR dilution system focused on obtaining low and high endpoints and repeatability of these points (Table 3-1). Time permitting, midpoints were to be obtained. Due to the limited time, dilution ratio and residence time endpoints were chosen as the priority.

Table 3-1: Test points for 50 MW turbine.

Matrix	Dilution Temperature (°C)	Dilution Ratio	Residence Time (s)	Relative Humidity (%)
1-Original	Uncontrolled	40 10	20, 250 250, 20	Uncontrolled
2-Repeatability	Uncontrolled	40 10	20, 250 250, 20	Uncontrolled
3-DR Midpoint	Uncontrolled	25	20, 250	Uncontrolled
4-RT Midpoint	Uncontrolled	40 25 10	125 125 125	Uncontrolled

Figure 3-17: Pictures of the Test Setup Showing the Locations for the Measurement Sites.

Figure 3-18 show the initial size distributions after the turbine was running for approximately one hour. From these figures it is evident that even after one hour of operation, the turbine PM concentrations were not as steady state. Initially, the peak modal diameters range from approximately 35 nm to 5 nm respectively. As this unit was a peaker plant, it is used to supply electricity during modes of high electricity operation. As the distributions were constantly changing and not at steady-state it was therefore difficult to determine changes in PM with varying dilution parameters.

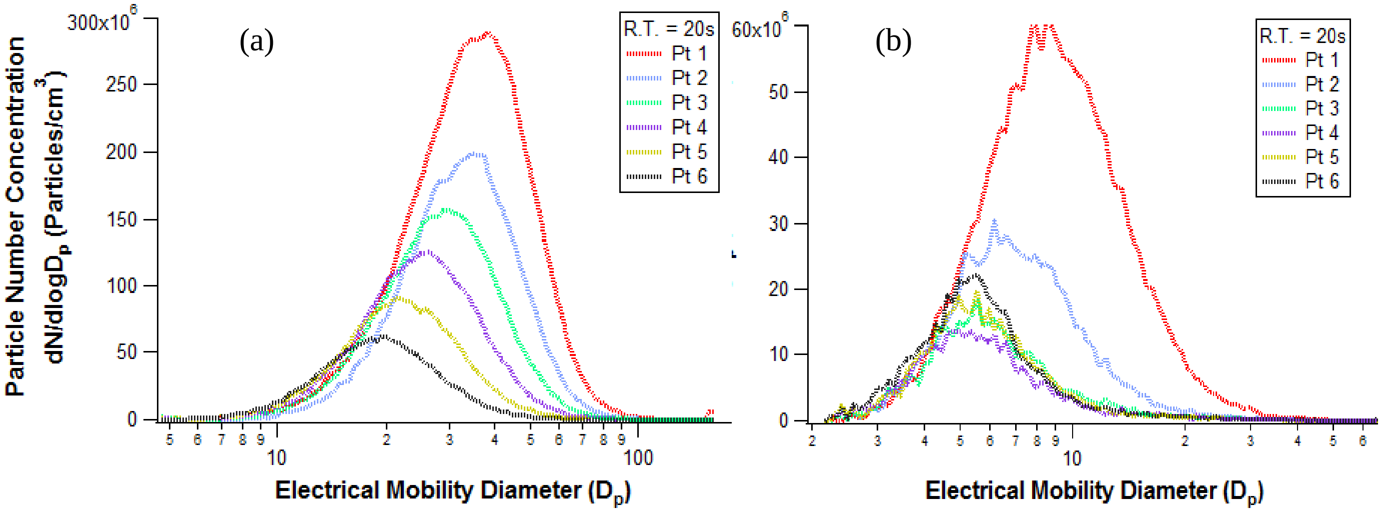


Figure 3-18: Particle Size Distributions during Turbine Start-up (a) Low Flow Mode (b) High Flow Mode

Varying dilution ratio at fixed residence times of 20s and 250s are shown in Figure 3-19 below. At a fixed residence time of 20s, a dilution ratio setting of 25:1 and 40:1 show similar nucleation peak modal diameters and number concentrations which are higher than the 10:1 dilution ratio.

Additionally, the 10:1 dilution ratio has higher concentrations for the accumulation mode particles at 50 nm and above. Repeat runs were conducted as a bookend run after each set of dilution ratios. For example, the 40:1 repeat run occurred after the 40:1, 25:1 and 10:1 dilution ratio test runs. The 40:1 repeat run showed a lower nucleation mode diameter and number concentration the original 40:1 dilution ratio run. For the fixed 250s residence time in Figure 3-19, both repeat runs have higher number concentrations than the original test runs.

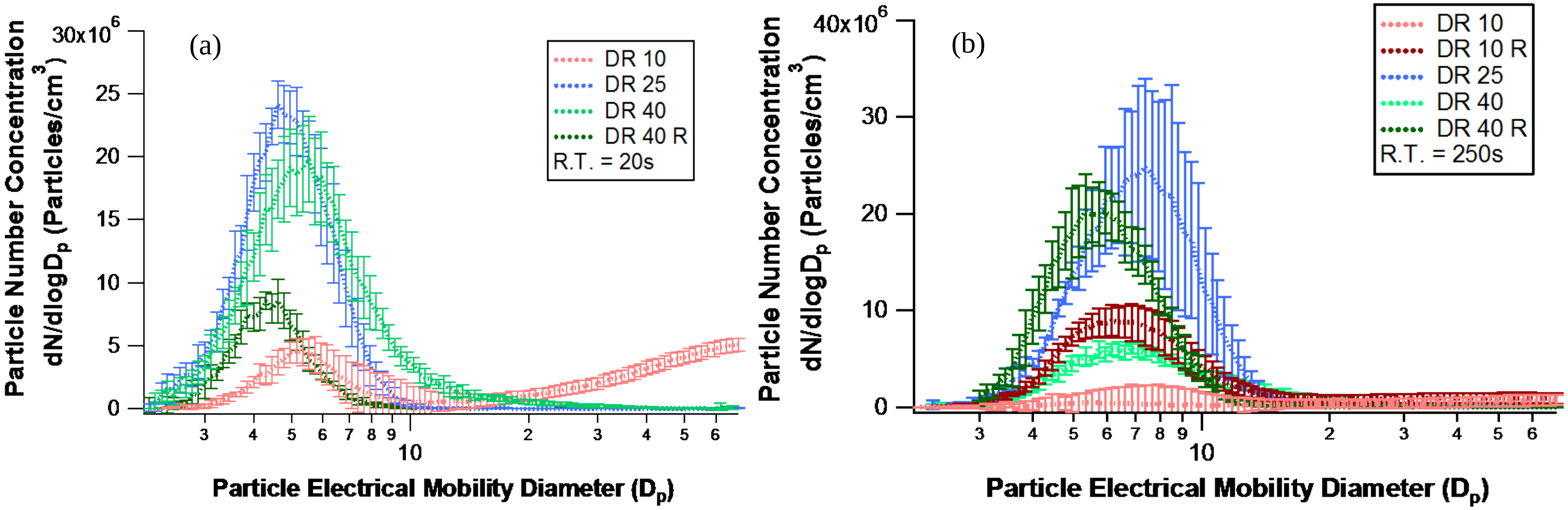


Figure 3-19: Particle Size Distributions at a Fixed Residence Time (a) R.T. = 20s (b) R.T. = 250s

Comparing the effect of residence time on particle size distributions at fixed dilution ratios of 10:1, 25:1 and 40:1 in Figure below, there are contrasting results similar to the dilution ratio trends above. At a dilution ratio of 10:1, the 250s repeatability run shows results in a much higher particle number concentration than the 250s test run. Similarly, the 40:1 repeat run shows a much higher particle number concentration than the original 40:1 test run.

Figure 3-20 below compares the residence time effect on the particle size distributions as a function of fixed dilution ratios. At a dilution ratio setting of 10:1, the RT 250s and RT 250s R runs show a lack of repeatability. Additionally for the 40:1 dilution ratio setting, the 20s and 250s repeatability runs show inconsistencies compared to the original test runs. The 20s repeat run results in a smaller number concentration and modal diameter while the 250s repeat run results in a higher number concentration and smaller modal diameter.

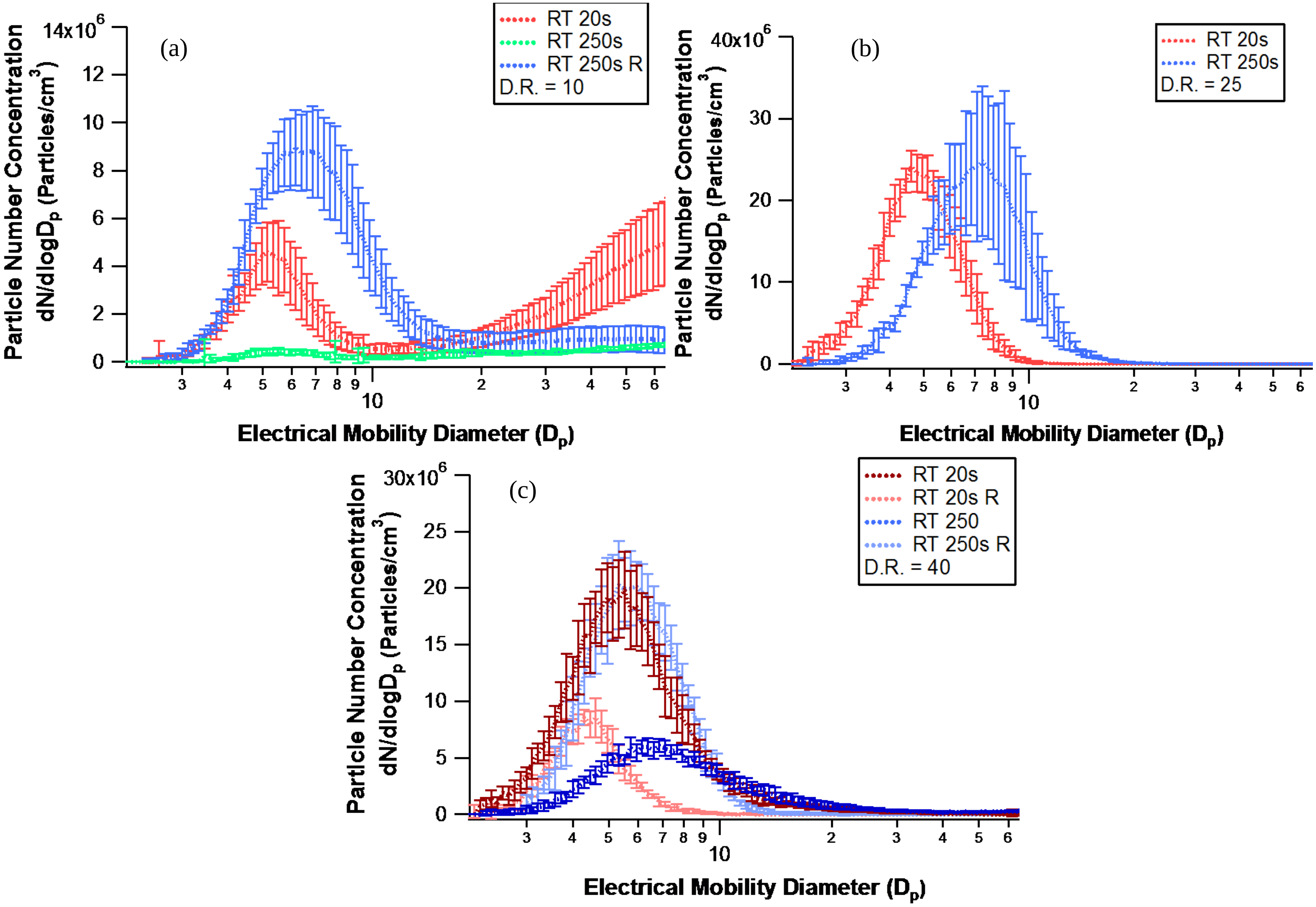


Figure 3-20: Particle Size Distributions as a Function of Varying Residence Time (a) DR = 10 (b) DR = 25 (C) DR = 40

The PM protocol method samples are shown in Figure 3-21 below. Overall, there is a much higher emission factor with the EPA method 201A/202 compared to the SCAQMD Method 5.1.

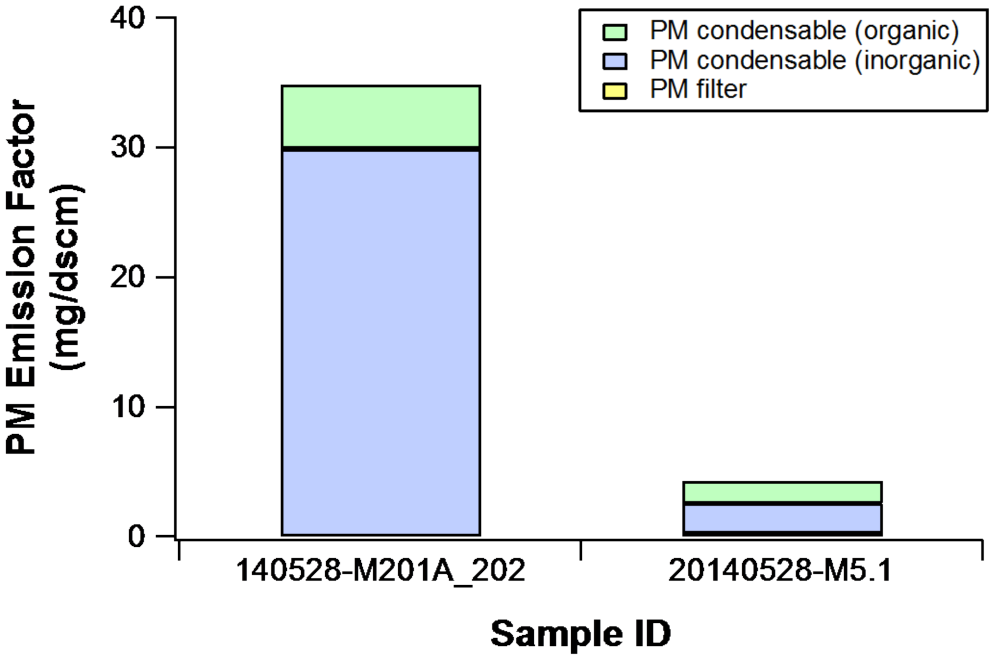


Figure 3-21: PM Protocol Methods

The high emission factor can be attributed to the inorganic fraction of the condensable PM. It is suspected that rust particles and other materials from the stack re-entrained with the exhaust. This theory was suspected as there was a fine rust color on both the in-stack filter and in the impingers for the EPA Method 201A/202 sample.

3.4 Chemical characterization of PM

The test program attempted to utililze an Aeroodyne High Resolution Time-of-Flight Mass Spectromer (AMS) . However, it was determined through the program that the particle sizes in the turbine exhausts were far to small to perform online AMS measurements as the AMS cut-size is around >50 nm.

Therefore, to characterize the PM, the highest loaded filter from the 14 MW (turbine test 2) was extracted (place filter in 10 mL water, sonicate 1 hr, add 2 drops isopropyl alcohol, sonicate 30 minutes, add methanol, sonicate for 30 minutes; leave overnight, remove filter and use clear supernatant liquid) and reaerosolized through a nebulizer. The aerosol was then dried and sent to the AMS to characterize the PM. However, even for the most dirty filter (based on PM loading) the chemical concentrations were too very low and difficult to resolve the chemical composition. Figure 3-22 is the chemical mass spectra and Figure 3-23 shows the relative concentrations of basic components. The concentrations are at or below the minimum detection limits of the AMS.

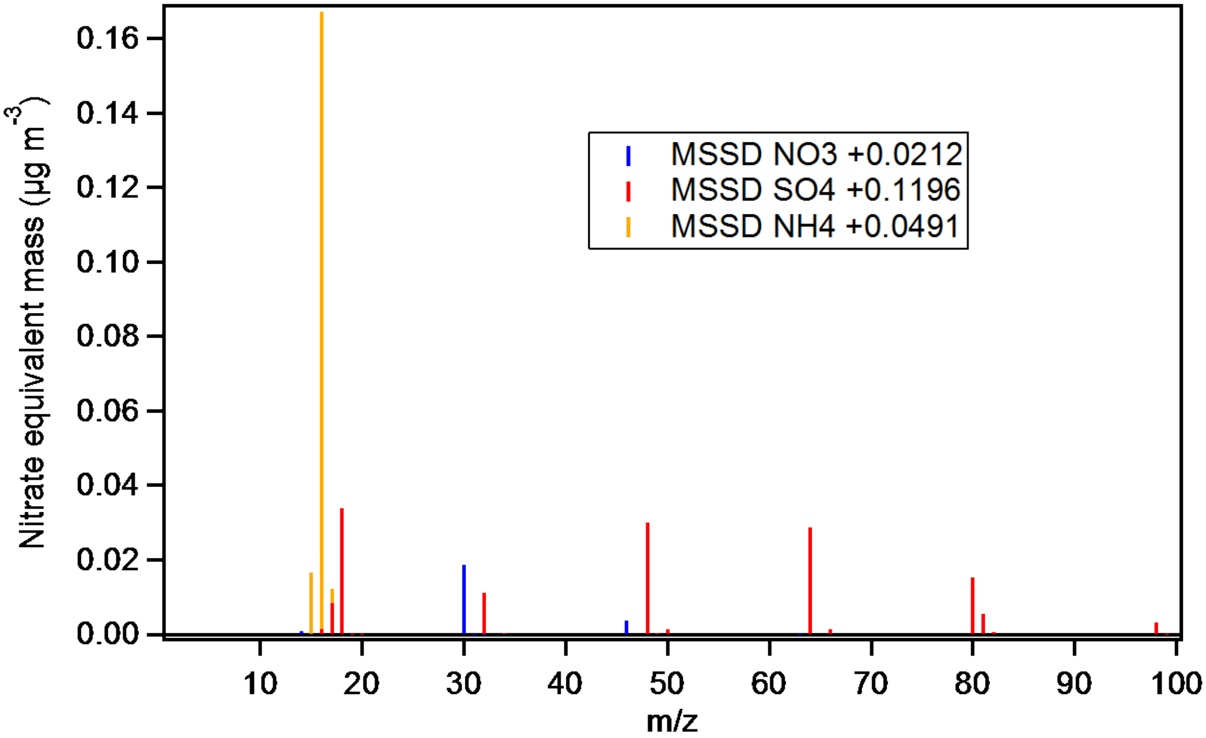


Figure 3-22: AMS Mass Spectra of Reaersolized Filter PM

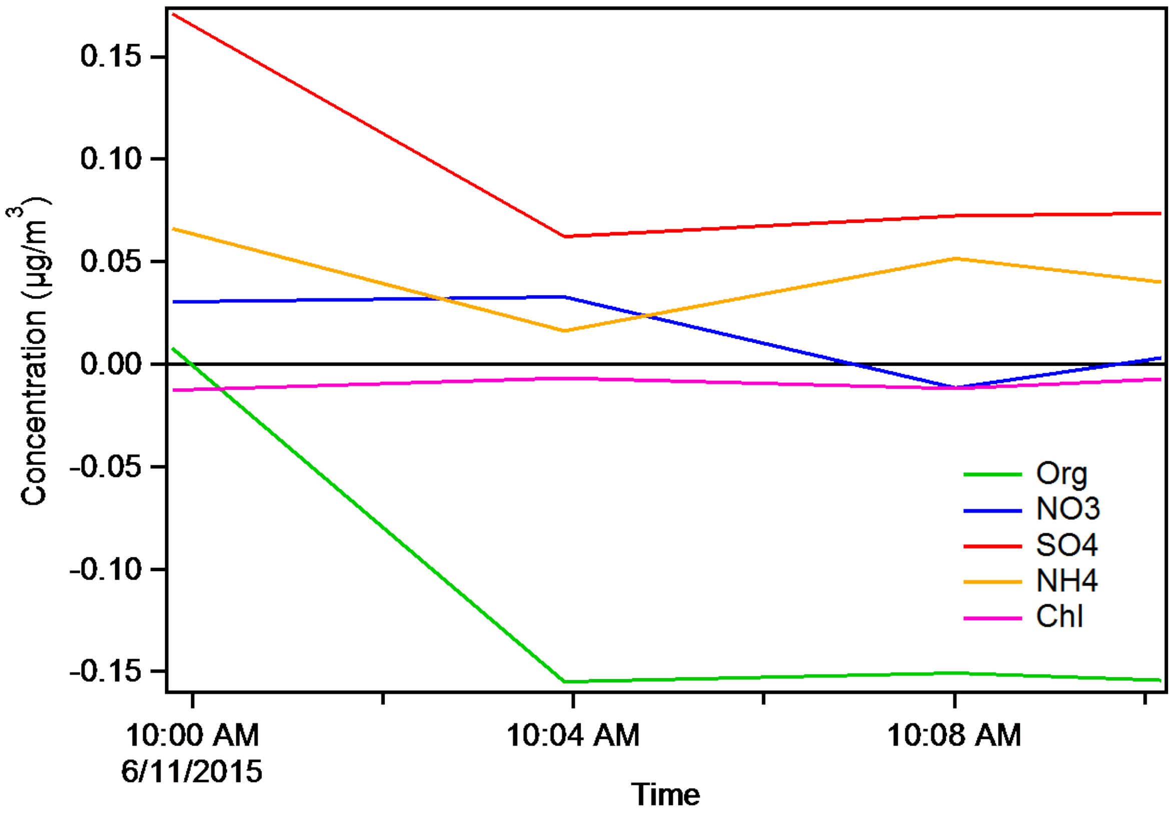


Figure 3-23: AMS Measured Chemical Composition of Reaersolized Filter PM

CHAPTER 4:
Discussion and Conclusions

Extensive testing of three natural gas fired turbines using both existing protocol methods and the dilution methods yielded widely varying results. As documented in the report, PM emissions were well below measurable levels that these protocols were developed for. Further, the method of dilution (temperature, dilution ratio, residence time, and relative humidity) had significant (albeit varied test unit to test unit) impacts on measured particulate matter. While PM mass concentrations measured varied by several order of magnitude, in all cases the PM mass concentrations in the effluent after dilution were below the ambient NAAQS PM standard and were often well below that of the surrounding air ambient concentrations.

Development of an inexpensive electronic monitor or simplified test method requires determination of what the most appropriate dilution conditions to simulate the particle formation near a turbine. This requires additional measurements beyond the scope of this program such as PM mass concentration of the evolving plume near the exit of a turbine. This may be accomplished in future research programs through an ambient field campaign that allows for measurements at the near stack (perhaps weather balloon, drone, or small aircraft).

Clear findings within this work is that NG turbine emissions are far more sensitivie to dilution parameters than has been observed for other emission systems (e.g., diesel exhaust). Decreasing dilution ratio, dilution temperature, dilution ratio and increasing residence time leads to increases in the PM measured, often by orders of magnitude. This is most likely due to the extremely low solid particle formation within the turbines reducing the surface area for condensational growth thereby increasing the impact of nucleation (new particle formation) processes. Due to the incredibly small size of the turbine particles (on the order of 10 – 15 nm), many gas-particle conversion effects are exacerbated as surface tension/energy effects become critical during particle growth.

GLOSSARY

Term	**Definition**
CPC	Condensation particle counter (used to measure particle number concentration)
CPM	Condensable particulate matter
CTM-039	Conditional Test Method 039. Dilution based PM measurement method
DR	Dilution ratio
DT	Dilution temperature
FPM	Filterable particulate matter
H2SO4	Sulfuric acid
ARB Method 5	Stationary test method for PM from California Air Resources Board
Method 201	Stationary filter test method for PM from EPA
Method 202	Stationary impinger test method for condensable PM
NOx	Oxides of nitrogen (nitric oxide plus nitrogen dioxide)
PM2.5	Particulate matter with aerodynamic diameter less than 2.5 um
PM10	Particulate matter with aerodynamic diameter less than 10 um
RH	Relative humidity
RT	Residence time. Time spent allowing gases to condense into particulate matter after dilution.
SCR	Selective Catalytic Reduction: Used to control NOx emissions
SMPS	Scanning Mobility Particle Sizer. Used to measure particle size distribution
SO2	Sulfur dioxide
SO3	Sulfur trioxide (anhydrous sulfuric acid)

REFERENCES

[1] Kittelson, D. B. *Recent Measurements of Nanoparticle Emissions from Engines, Current Research on Diesel Exhaust Particles*; Meeting of Japan Association of Aerosol Science and Technology, Tokyo, Japan, January 2001.

[2] Pope III, C.A., et al., Cardiovascular mortality and long-term exposure to particulate air pollution: epidemiological evidence of general pathophysiological pathways of disease, Circulation 109 (2004) 71–77.

[3] AP-42, Vol. I, CH 3.1: Stationary Gas Turbines, http://www.epa.gov/ttnchie1/ap42/ch03/final/c03s01.pdf

[4] Giugliano, M., et al., Ultrafine particles from combustion sources: sampling and measurement;Chemical Engineering Transactions, Volume 16 (2008) 7-14.

[5] Corio, L.A., Sherwell, J., In-Stack Condensible Particulate Matter Measurements and Issues; Air & Waste Management Association, (2000) 50: 207-218.

[6] Crosby, Kevin. J., Measurement of $PM_{2.5}$ Emissions and the Proposed Method for Condensables; Air & Waste Management Association, (2010) 10-15.

[7] DeWees et al., Laboratory and Field Evaluation of the EPA Method 5 Impinger Catch for Measuring Condensable Matter from Stationary Sources; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1989.

[8] Kittelson, D. B., and Abdul-Khalek, I. (1999). Formation of Nanoparticles During Exhaust Dilution, *EFI Members Conference: Fuels, Lubricants Engines, & Emissions*, 18–20, January.

[9] Ro¨nkko¨, T.; Virtanen, A.; Vaaraslahti, K.; Keskinen, J.; Pirjola, L.; Lappi, M. Effect of dilution conditions and driving parameters on nucleation mode particles in diesel exhaust: Laboratory and on-road study. *Atmos. Environ.* **2006**, *40*, 2893-2901.

[10] Vaaraslahti, K.; Ristimaki, J.; Virtanen, A.; Keskinen, J.; Giechaskiel. B.; Solla, Anu. Effect of Oxidation Catalysts on Diesel Soot Particles. Environ. Sci. Technol. **2006**, 40, 4776-4781.

[11] ARB Method 5, 1997. Determination of Particulate Matter Emissions from Stationary Sources.

[12] US EPA, 2010. Method 201A- Determination of PM10 and PM2.5 Emissions from Stationary Sources (Constant Sampling Rate Procedure).

[13] US EPA, 2010. Method 202 Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources.

[14] Richards, John; Holder, Tom; Goshaw, David, Optimizing Method 202 Sampling Train to Minimize the Biases Associated with Method 202 Measurement of Condensable Particulate Matter Emissions, Air and Waste Water Management Association: Hazardous Waste Combustion Specialty Conference, November 2-3, 2005.

[15] Buser, Michael, D., and Whitelock, Derek, P., 2269 Preliminary Field Evaluation of EPA Method CTM-039 ($PM_{2.5}$ Sampling Stack Method).

[16] England, G.C., et al., Characterizing PM2.5 emission profiles for stationary sources: comparison of traditional and dilution sampling techniques, Fuel Processing (2000) 177–188.

[17] US EPA, 2004. Conditional Test Method (CTM) 039 measurement of $PM_{2.5}$ and PM_{10} emissions by dilution sampling (constant sampling rate procedures). CTM-039 (04_Rev 2) July 2004.

[18] England, Glenn; Matis, Craig; Crosby, Kevin; Tong, Chinghang; Rubenstein, Gary. Comparison of PM10 Measurements Using Dilution and Traditional Methods at a Gas-Fired Combined Cycle Plant. 2010 Manuscript.

[19] Mathis U, Ristimaki J, Mohr M, Keskinen J, Ntziachristos L, Samaras Z, Mikkanen P. (2004) Sampling conditions for the measurement of nucleation mode particles in the exhaust of a diesel vehicle. Aerosol Sci. Technol. 38: 1149-1160. US EPA, 2004. Method 5- Determination of Particulate Matter Emissions From Stationary Sources.

[20] Kittelson, D.B.; Watts, W.F.; Johnson, J.P. On-road and laboratory evaluation of combustion aerosols-Part I: Summary of diesel engine results. Journal of Aerosol Science 37 (2006) 913-930.

[21] England, G.C. 2004. “Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Final Report.

[22] Kittelson, D. B., and Abdul-Khalek, I. (1999). Formation of Nanoparticles During Exhaust Dilution, *EFI Members Conference: Fuels, Lubricants Engines,& Emissions*, 18–20, January.

[23] Chang, M.C. and England, G.C. 2004b. “Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Other Report: Pilot-Scale Dilution Sampler Design And Validation Tests (Laboratory Study),” prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

[24] Mathis U, Ristimaki J, Mohr M, Zenobi, R. (2004) Effect of organic compounds on nanoparticle formation in diluted diesel exhaust; Atmospheric Chemisty and Physics, (2004) 227-265.

[25] England, G.C. 2004. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Impact Of Operating Parameters On Fine Particulate Emissions From Natural Gas-Fired Combined Cycle and Cogeneration Power Plants," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

[26] Wien, S.E.; England, G.C.; Loos, K.R.; Ritter, K. *Investigation of Artifacts in Condensable Particulate Measurements for Stationary Combustion Sources.* Paper No. 536, 2003.

[27] Lanier, W.S. and G.C. England. 2004. "Technical Memorandum: Conceptual Model of Sources of Variability in Combustion Turbine particulate with aerodynamic diameter less than 10 μm (PM10) Emissions Data," prepared for: U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA; Gas Research Institute, Des Plaines, Illinois; and American Petroleum Institute, Washington, D.C.

APPENDIX A: QAPP

QUALITY ASSURANCE PROJECT

PLAN FOR

EVALUATION AND IMPROVEMENT OF PARTICULATE MATTER MEASUREMENT FROM NG POWER PLANTS

Revision: 1

June 4, 2013

Prepared for: Ms. Marla Mueller

Technical Lead, Air Quality Research Program

PIER Environmental Area

Cal Institute of Energy & Environment

901 P Street, Suite 142A

Sacramento, CA 95814

916-551-1870

Authors:

Dr. David Cocker

Dr. Wayne Miller
College of Engineering

Center for Environmental Research and Technology
University of California at Riverside

Riverside, CA 92507

Approvals

Title: Quality Assurance Project Plan for the College of Engineering- Center for Environmental Research and Technology, University of California at Riverside, Evaluation and Improvement of Particulate Matter Measurement from NG Power Plants, Revision 1, June 4, 2013

Signatures indicate that this Quality Assurance Project Plan (QAPP) is approved and will be fully implemented in conducting the research project described in this document.

Dr. David Cocker
Principal Investigator *Signature* *Date*
CE-CERT
University of California at Riverside

Dr. Wayne Miller
Principal Investigator *Signature* *Date*
CE-CERT
University of California at Riverside

Quality Assurance Officer *Signature* *Date*
CE-CERT
University of California at Riverside

(Name) Program
Officer
U.S. Environmental Protection Agency *Signature* *Date*

(Name)
Quality Assurance Officer
U.S. Environmental Protection Agency *Signature* *Date*

Table of Contents

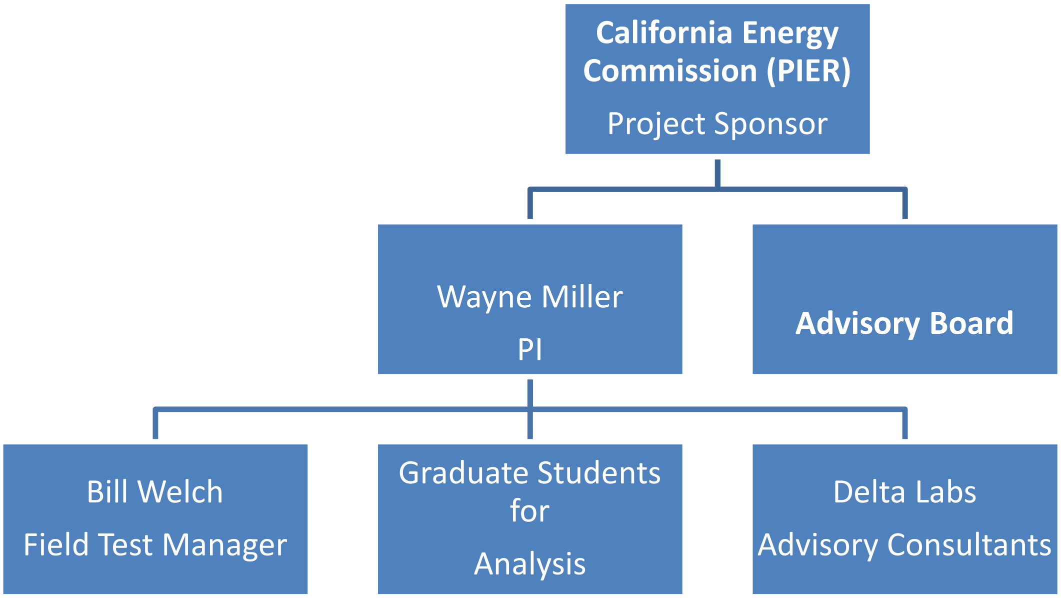
2 PROJECT MANAGEMENT AND OBJECTIVE ELEMENTS

The project management and objectives elements of a QAPP ensure that the project has a defined purpose by documenting the environmental problem, the environmental questions being asked, and the environmental decisions that need to be made. The elements in this part of the QAPP identify the project quality objectives necessary to answer those questions and support those environmental decisions. They also address management considerations, such as roles and responsibilities, for the project.

2.4 Project Organization

The project team should identify the reporting relationships between the organizations, project team members, and other key project personnel and describe their specific roles, responsibilities, and qualifications. In addition, the QAPP text should include an explanation of the lines of authority and paths of communication.

2.4.1 Project Organizational Chart



2.4.2 Communication Pathways

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Regulatory agency interface				
Field progress reports				
Stop work due to safety issues				
QAPP changes prior to field work				
QAPP changes during project execution				
Field corrective actions				
Sample receipt variances				
Laboratory quality control variances				
Analytical corrective actions				
Data verification issues, e.g., incomplete records				
Data validation issues, e.g., non-compliance with procedures				
Data review corrective actions				

2.4.3 Personnel Responsibilities and Qualifications

ORGANIZATION: Prime Contractor

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date

ORGANIZATION: Laboratory

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date

2.4.4 Special Training Requirements and Certification

2.5 Project Planning/Problem Definition

The California Energy Commission has the statutory responsibility for licensing thermal power plants 50 megawatts and larger and the plant's related facilities. The Energy Commission's license/certification includes California Environmental Quality Act (CEQA) and all requirements of state, local, or regional agencies otherwise required before a new plant is constructed. One of the challenging sitting problems is that many populated centers in California are classified as non-attainment areas so emissions from new power sources are required to offset emissions from existing sources. Adding to this challenge are emission levels so low they are often at the lower detection limit of current measurement methods, leading to uncertainty in the actual measured values.

The uncertainty and inaccuracies in measurement of PM can lead to decisions that limit the sitting of plants. For example, in the South Coast AQMD each pound of PM emissions from a new source is very expensive to offset. Emission reduction credits in the South Coast AQMD went as high as $350,000 per pound per day in 2009 and averaged over $140,000. Clearly each excess pound of

PM reported raises significant financial issues for a project. The accuracy of the PM measurement method needs to be improved. The problem of accurate PM measurement needs resolution to ensure timely installation and appropriate costs for new power plants. Understanding analytical methods used to measure the PM emissions are a key element in determining how to apply them to the new NG plants. The path to that understanding will rely on delving into the details and answering a number of questions about the existing test methods with their prescribed protocols. An in-depth analysis is needed to determine whether the current analytical methods provide the required data for measuring PM with an acceptable range, sensitivity, accuracy, and precision. The current test methods were not developed to assess such low emission levels and need to be updated using the many recent advances in PM measurement methods to accurately reflect the low emission levels now being seen from NG power plants. Both the EPA and ARB are aware of the challenge to accurately measure low PM levels. Given this background, new test methods are proposed by the US EPA but they believe that improved tests are needed. Furthermore new real-time instruments are capable of detecting very small concentrations at high exhaust gas velocities that need to be evaluated.

This research will lead to improved emissions estimates from NG plants, lead to a better understanding of the air quality impacts of NG power plants, and help in obtaining permits to site new natural gas power plants.

Development of this project has been closely coordinated with the ARB. This project will include an advisory group with members from regulatory agencies, including ARB, EPA and the air districts, and users and academics.

2.5.1 Project Planning (Scoping)

2.5.2 Problem Definition, Site History, and Background

2.6 Project Quality Objectives and Measurement Performance Criteria - Measurement

2.6.1 Development of Project Quality Performance Criteria Objectives Using the Systematic Table Planning Process

2.6.2 Measurement Performance Criteria

Data Quality Indicator (DQI)	**QC sample or measurement performance activity**	**Measurement Performance Criteria**

Overall Precision	Field Duplicates	RPD ≤ 30% when VOCs are detected in both samples ≥ sample-specific LOQ
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates	RPD ≤ 25%
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Analyte-specific (Attach list)
Analytical Accuracy/Bias (matrix interference)	Matrix Spike Duplicates	Analyte-specific (Attach list)
Overall accuracy/bias (contamination)	Equipment Blanks	No target analyte concentrations ≥ 1/2 LOQ
Sensitivity	LOQ verification sample (spiked at LOQ)	Recovery within ±25% of LOQ
Completeness	See Worksheet #34	See Worksheet #34

2.7 Secondary Data Evaluation

Data type	Source	Data uses relative to current project	Factors affecting the reliability of data and limitations on data use
PM Measurements from Natural Gas Turbines	CEC	Comparison of Dilution and Protocol Methods from NG turbines	None
Impinger Method Comparison	Avogadro Group	Comparison of wet versus dry impinger methods	Not measured on Natural Gas Emission sources
Laboratory and Field EPA Method 5	A&WMA	Determine Biases in wet impinger PM collection	None
Dilution Based PM Measurements	A&WMA	Sampling PM with Dilution methods	Dilution Design differs from UCR and CTM 039
In-stack CPM Measurement Issues	A&WMA	Sampling PM with wet Impingers	None

Dilution vs. Impinger Method	USDA ARS	Sampling with EPA CTM 039, EPA 201A/202 and EPA Method 5	Comparison from Agricultural Equipment

2.8 Project Overview and Schedule

The project overview and schedule including specific activities and details are provided below.

2.8.1 Project Overview

Through project planning, the project team should agree on the purpose of the project, the environmental questions that are being asked, and the environmental decisions that must be made. The project team should establish the PQOs (i.e., specify the type, quantity, and quality of data needed to ensure that project data can be used for the intended purpose) to answer specific environmental questions, support environmental decisions, and determine technical activities that will be conducted. Figure 20 (QAPP Worksheet #14) provides an example of the Summary of Project Tasks table.

Activity	**Responsible party**	**Planned start date**	**Planned completion date**	**Deliverable(s)**	**Deliverable due date**
Sample collection: Micro-Turbine	UC Riverside	2 October 2010	4 October 2010	Field notes	1 November 2010
Sample collection: Heavy-Duty Turbines	UC Riverside	5 October 2010	10 October 2010	Field notes	1 November 2010

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
Analysis	UC Riverside	October 2010	November 2010	Report of Analyses/Data package	NLT 5 November 2010
Validation	UC Riverside	November 2010	December 2010	Validation Summary report	NLT 1 December 2010
Summarize data	UC Riverside	December 2010	15 February 2011	Draft RI Report	15 February 2011
Final Report	UC Riverside	March 2011	March 2011	Meeting minutes/Usability assessment summary report	March 2011

2.8.2 Project Schedule

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
Task 1: Quarterly Reports	UCR	Beginning of every quarter	End of every quarter	Final Progress Report	End of every quarter
Task 1: Draft Final Report	UCR	December 1, 2013	February 1, 2013	Draft Report	February 1, 2013
Task 1: Final Report	UCR	February 1, 2013	March 15, 2014	Final Report	March 15, 2014
Task 2: Review Existing Data/Literature Review	UCR	Completed	Completed	Data/Literature Review Report	Completed
Task 2:Establish Advisory Committee Members	UCR	Completed	Completed	Finalize Advisory Committee	Completed
Task 2: Develop Test Plan	UCR			Draft Test Plan	
Task 2: Preliminary Approval of Test Plan and QAPP discussion	UCR				
Task 2:					

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
Finalize Test Plan and QAPP					

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
Task 3: Acquire CTM 039	UCR				
Task 3: Build Dilution System	UCR				
Task 3: Test Systems at UCI	UCR				
Task 3: Report Recommendations to committee	UCR				
Task 4: Test Unit 1	UCR				
Task 4: Test Unit 2	UCR				
Task 4: Test Unit 3	UCR				
Task 4: Test Unit 4	UCR				

Activity	Responsible party	Planned start date	Planned completion date	Deliverable(s)	Deliverable due date
Task 5: Analyze Data and Finalize PM Test Method	UCR				2/1/14

3.0 MEASUREMENT AND DATA ACQUISITION TASKS

3.1 Sampling Tasks

3.1.1 Sampling Process Design and Rationale

The data collection processes for this project will include a multitude of samples per method and test site as shown below.

	Description	SCAQMD M5.2	EPA 201A/202	EPA CTM 39	UCR dilution	SMPS
Unit 1 (UCI)	14M	10	10	10	10	10
Unit 2 (LMS 100)	100M	6	6	6	6	6
Unit 3 (Bay Area)	100M	6	6	6	6	6
Unit 4 (Romoland?)	400M	6	6	6	6	6

The number of samples is designed to study the accuracy and precision of each separate methodology per test site.

3.1.2 Sampling Procedures and Requirements

Sampling procedures will follow the guidelines as specified by EPA. For SCAQMD

Method 5.2, the guidelines specified in the DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES USING HEATED PROBE AND FILTER protocol method will be followed while EPA Method 201A/202 and EPA CTM 039 will follow the EPA methodology while the UCR dilution sampler will follow the same protocol as EPA CTM 039.

3.1.2.3 Equipment/Sample Containers Cleaning and Documentation Procedures

All methods must use glass with screw cap liners or polyethylene storage containers for the in field rinses.

3.1.2.4 Field Equipment Calibration, Maintenance, Testing and Inspection Procedures

Field Equipment	Activity	SOP Reference	Title or position of responsible person	Frequency	Acceptance Criteria	Corrective Action
Nano SMPS	Calibration	Tech 001	Grad Student			
Nano SMPS	Maintenance	Operators Manual	Grad Student			
Nano SMPS	Testing	Tech 001	Grad Student			
Nano SMPS	Inspection	Tech 001	Grad Student			
Fast SMPS	Calibration	Tech 001	Grad Student			
Fast SMPS	Maintenance	Operators Manual	Grad Student			
Fast SMPS	Testing	Tech 001	Grad Student			
Fast SMPS	Inspection	Tech 001	Grad Student			
AMS	Calibration					
AMS	Maintenance					
AMS	Testing					
AMS	Inspection					
CTM 039	Calibration					
CTM 039	Maintenance					

Field Equipment	Activity	SOP Reference	Title or position of responsible person	Frequency	Acceptance Criteria	Corrective Action
CTM 039	Testing					
CTM 039	Inspection					
EPA 201A/202	Calibration					
EPA 201A/202	Maintenance					
EPA 201A/202	Testing					
EPA 201A/202	Inspection					
SCAQMD M5.2	Calibration					
SCAQMD M5.2	Maintenance					
SCAQMD M5.2	Testing					
SCAQMD M5.2	Inspection					
UCR VPDS	Calibration					
UCR VPDS	Maintenance					
UCR VPDS	Testing					
UCR VPDS	Inspection					

3.1.2.5 Supply Inspection and Acceptance Procedures

All sampling techniques will follow the protocol specified by the methods used in this program.

3.1.2.6 Field Documentation Procedures

3.2 Analytical Tasks

3.2.1 Analytical SOPs

Analytical SOPs for this project are shown in the table below.

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	‡Modified for Project? Y/N
R-1	*EPA Method 201A/202 In-Field Rinse Procedure*	Definitive	EPA Method 201A/202	Sampling Train	N
R-2	*EPA CTM 039 In-Field Rinse Procedure*	Definitive	EPA CTM 039	Dilution Tunnel	N
R-3	*SCAQMD M5.2 In-Field Rinse Procedure*	Definitive	SCAQMD M5.2	Sampling Train	N
R-4	*UCR VPDS In-Field Rinse Procedure*	Definitive	UCR VPDS	Dilution Tunnel	N

3.2.2 Analytical Instrument Calibration Procedures

Instrument	Calibration Procedure	Calibration Range	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
TSI Nano SMPS	90nm Polystyrene Latex Spheres Solution	92±3.7 nm	Before each field study	92±3.7 nm			
UCR Fast SMPS	90nm Polystyrene Latex Spheres Solution	92±3.7 nm	Before each field study	92±3.7 nm			

Instrument	**Calibration Procedure**	**Calibration Range**	**Frequency**	**Acceptance Criteria**	**Corrective Action (CA)**	**Title/position responsible for Corrective Action**	**SOP Reference**
AMS							
EC/OC Analyzer							

The instrument calibration procedures are listed in the table above.

3.2.3 Analytical Instrument and Equipment Calibration Table Maintenance, Testing, and Inspection Procedures

Instrument / Equipment	**Maintenance Activity**	**Testing Activity**	**Inspection Activity**	**Frequency**	**Acceptance Criteria**	**Corrective Action**	**Title/position responsible for corrective action**	**Reference**
TSI Nano Classifier 3085								
TSI CPC 3776								
UCR Fast SMPS								
AMS								

3.2.4 Analytical Supply Inspection and Testing, and Inspection Acceptance Procedures

3.3 Sample Collection Documentation Handling, Tracking, and Custody Procedures

3.3.1 Sample Collection Documentation

Field sampling documentation of the samples will include a field logbook used to record the necessary data parameters as well as to record the correct labeling of each sample. The samples themselves will be labeled according to that specified in the method books provided by the EPA and the SCAQMD. Multiple pre made labels will be placed on each corresponding sample and then subsequently taped with clear type tape to ensure the sample ID will not be compromised.

3.3.2 Sample Handling and System

The samples will be labeled according to the field site, sample date and time stamp that the sample was taken at. This will also correspond with the sampling label specified by the methods protocol. Pre-test the samples will be stored in an environment at a temperature of 26.7 ºC or 80ºF according to the sampling protocol of the methods used in this program.

3.3.2.1 Sampling Handling

Activity	**Organization and title or position of person responsible for the activity**	**SOP reference**
Sample labeling		
Chain-of-custody form completion		
Packaging		
Shipping coordination		
Sample receipt, inspection, & log-in		
Sample custody and storage		
Sample disposal		

3.3.2.2 Sample Delivery

The samples will be transported to the UCR CE-CERT Analytical laboratory via delivery from the sampling team after testing is completed. The samples will be kept at a controlled environment and delivered with completed chain of custody forms.

3.3.3 Sample Custody

Chain of custody forms will be used to submit filter samples for EC/OC analysis and PM mass weighting collected from the sampling methods used in this program. Separate chain of custody forms will be used to record the in-field containers as part of the method rinses which include the sample train rinses and the dilution tunnel rinses.

3.4 Quality Control Samples

Table 4. Recommended Types and Frequency of Sampling QC Samples for Chemical Data Collection

Sampling QC[1]	**Data Quality Indicator[2]**	**Recommended Frequency**
Field Blank (including VOA Trip Blank)[3]	Contamination (Accuracy/Bias)	Minimum 1 per shipment cooler per analytical group per concentration level
Equipment Blank (rinsate blank)[3]	Contamination (Accuracy/Bias)	Minimum 5% per analytical group per matrix per sampling procedure per sampling team
Proficiency Testing Sample[3, 4]	Accuracy/Bias	Minimum 1 per SDG per analytical group per matrix per concentration level
Field Duplicates – Co-located Samples[3]	Precision	Minimum 5% per analytical group per matrix per sampling procedure per
– Split Samples	Interlaboratory Comparability	As specified by method and based on PQOs

[1] Co-located and analyzed to measure errors introduced during sampling and other field activities.

[2] See Table 6 for additional DQI information.

[3] Minimum QC activity from Part 2B of the UFP-QAPP.

[4] Proficiency testing samples have been included under field sampling QC samples since they may be introduced during that stage. They primarily measure analytical error, since their composition is unknown to the laboratory and they originate outside of the laboratory.

Table 5. Recommended Types and Frequency of Analytical QC Samples for Chemical Data Collection

Analytical QC	**Data Quality Indicators[1]**	**Recommended Frequency**

Method Blank	Accuracy/Bias (Contamination)	Minimum 1 per SDG per analytical group per matrix per concentration level
Instrument (System) Blank	Accuracy/Bias (Contamination)	As specified by method and based on
Laboratory Duplicates[2]	Precision	Minimum 1 per inorganic SDG per analytical group per matrix per concentration level
Internal Standards	Precision and Accuracy/Bias	As specified by method and based on PQOs
Matrix Spike (inorganics only)[2]	Bias	Minimum 1 per inorganic SDG per analytical group per matrix per concentration level
PT Sample – Single Blind and Double Blind[2]	Bias	Minimum 1 per SDG per analytical group per matrix per concentration level
Surrogate Spikes	Bias	As specified by method and based on PQOs
Laboratory Control Sample (LCS)	Bias	As specified by method and based on PQOs

3.5 Data Management Tasks

3.5.1 Project Documentation and Records

The following table provides the sample collection and records that will be used to identify the samples in the field as well as for transportation to the laboratory for analysis.

Sample Collection and Field Records			
Record	Generation	Verification	Storage location/archival
Field logbook or data collection sheets	Field Task Leader (name)	Project Director (name)	Project File
Chain-of-Custody Forms			
Air Bills			
Contractor Daily QC Reports			

Sample Collection and Field Records			
Deviations			
Corrective Action Reports			
Correspondence			

Project Assessments			
Record	Generation	Verification	Storage location/archival
Field audit checklists			
Data verification checklists			
Data validation report			
Data usability assessment report			

Laboratory Records			
Record	Generation	Verification	Storage location/archival

Record	Quartz Filters	Teflon Filters	CPM Filters	Rinses	Other
Narrative	X	X	X	X	

COC	X	X	X	X	
Summary Results	X	X	X	X	
QC Results	X	X	X	X	

3.5.2 Data Package Deliverables

DATA DELIVERABLE ELEMENTS	VOA	SVOC	PEST/PCB	METALS	CN	OTHER
• INVENTORY SHEET (Org. and Inorg. DC-2 Form)	X	X	X	X	X	X
• NARRATIVE (Org. Narrative, Inorg. Cover Page)	X	X	X	X	X	X
• EPA SHIPPING/RECEIVING DOCUMENTS AND INTERNAL LABORATORY CHAIN-OF-CUSTODY RECORDS:	X	X	X	X	X	X
- Chain-of-Custody Records/Forms (Traffic Report)	X	X	X	X	X	X
- Sample Tags	X	X	X	X	X	X
- Sample Log-In Sheet (Org. and Inorg. DC-1 Form)	X	X	X	X	X	X
- Miscellaneous Shipping/Receiving Records	X	X	X	X	X	X
			X	X	X	X
• SAMPLE DATA: - Tabulated Summary Form for Field Sample and PT Sample Results (Org. and Inorg. Form I)	X	X	X	X	X	X
- Tentatively Identified Compounds Tabulated	X	X				
- Reconstructed total ion chromatogram (RIC) for each	X	X				
- Raw spectra of target compound and background-	X	X				
- Mass spectra of all reported TICs/three best library	X	X				
- Chromatograms from both columns for each sample			X			
- GC integration report or data system printouts and			X			
- PEST/PCB Identification Tabulated Summary Form			X			
- For PEST/PCBs confirmed by GC/MS, copies of raw			X			
- Gel permeation chromatography sample		X	X			
- UFP-QAPP Manual worksheets	X	X	X	X	X	X
- Sample preparation/extraction/digestion log (Inorg.	X	X	X	X	X	X

3.5.3 Data Reporting Formats

3.5.4 Data Handling and Management

3.5.4.1 *Data Recording*

Data entry for pretest, during test and posttest calculations will be conducted in

sampling excel spreadsheets containing formulas and other necessary notes used to obtain accurate and precise measurements from the different PM methods used in this program.

For the UCR VPDS, a labview program will be used to record the temperature, RH as well as other necessary parameters.

3.5.4.2 *Data Transformations and Data Reduction*

Formulas for data conversion are located in the calculation spreadsheets for EPA Method 201A/202, SCAQMD M5.2, EPA CTM 039 and the UCR VPDS.

3.5.4.3 Data Transfer and Transmittal

Internal QC checks will be performed by a document to assess the validity of the calculations made from the excel files per each method.

3.5.4.4 *Data Analysis*

Excel files with the necessary formulas for calculations of total PM concentrations, including the filterable and condensable programs will be used. The laboratory results will be inputted into the program that will then be used to calculate the PM concentrations.

3.5.4.5 Data Review

Statistical programs used for this study will include ANOVA. The computer programs used to review the collected data will include, Microsoft Excel, IGOR and Labview.

3.5.5 Data Tracking and Control

The procedures for data tracking, storage, archiving, retrieval, and security, including both hard-copy and electronic data and information, and identifying the personnel responsible are displayed in the section below.

3.5.5.1 Data Tracking

Each test per each method will have its own corresponding calculation file labeled to the test number and test date. Once the in-field procedures are complete a chain of custody will be filled out for the separate filters for filter weighing and the analysis of the rinses and impinger contents will have their separate chain of custody's as well. The results of the filter weighing, rinse and impinger analysis will be updated in the calculation files to provide the total concentrations of PM.

3.5.5.2 Data Storage, Archiving, and Retrieval

All data will be stored on the CE-CERT server and hard copies including the chain of custody's will be stored in a project binder.

C Identify specific project data, documents, records, reports, etc. that will be stored and/or archived. Differentiate between hard-copy and electronic data and information, and between documentation stored at a subcontracted laboratory and documentation archived by the lead organization. If data package deliverables do not include all project data documentation, describe what data (for on-site screening, on-site definitive, and off-site laboratory) will be kept by which laboratory or other organization and the exact physical location for each (i.e., complete laboratory or organization name, address, and specific location in the building).

C Identify the organizations and personnel responsible for storing, archiving, and retrieving specific project documents. Identify responsible document control personnel, including organizational affiliation, telephone, e-mail address, and fax number (see Sections 2.4.1 and 2.4.3).

Describe where the documents will be stored during the project and where the documents will be archived. Provide exact locations (organization name, complete address, and specific location in building) and timeframes in which documents will be moved from one location to another.

C Indicate when documents will be archived at a final location.

3.5.5.3 Data Security

All files used for calculations and analysis will be locked for editing for others besides the individual conducting the calculations and analyzing the data. The files will be saved on the personal computer as well as on the University server, open to those individuals involved in the project.

Computer security will compose of locked user accounts for data safety.

4.0 ASSESSMENT AND OVERSIGHT ELEMENTS

4.1 Assessments and Response Actions

4.1.1 Planned Assessments

4.1.2 Assessment Findings and Corrective Action Responses

Records Reviewed	Requirement Documents	Process Description	Responsible Person, Organization
Field logbook	QAPP, SOP Field 02	Verify that records are present and complete for each day of field activities. Verify that all planned samples including field QC samples were collected and that sample collection locations are documented. Verify that meteorological data were provided for each day of field activities. Verify that changes/exceptions are documented and were reported in accordance with requirements. Verify that any required field monitoring was performed and results are documented.	Daily - Project Manager At conclusion of field activities - Project QA Manager
Chain-of-custody forms	QAPP, SOP Field 02	Verify the completeness of chain-of-custody records. Examine entries for consistency with the field logbook. Check that appropriate methods and sample preservation have been recorded. Verify that the required volume of sample has been collected and that sufficient sample volume is available for QC samples (e.g., MS/MSD). Verify that all required signatures and dates are present. Check for transcription errors.	Daily - Field Crew Chief At conclusion of field activities - Project Chemist

4.2 QA Management Reports

4.2.1 Planned Assessments

Assessment Type	Responsible Party & Organization	Number/Frequency	Estimated Dates	Assessment Deliverable	Deliverable due date
Readiness Review	ABC Task Manager and QAM, ABC Engineering	One assessment one week prior to mobilization	[fill in planned dates]	Readiness Review Memorandum and Checklist	24 hours following assessment
Field Sampling TSA	ABC QAM & Florida DEP	One each on first day of soil, biota, and groundwater sampling episodes		TSA Memorandum and Checklist	24 hours following assessment
On-site analytical TSA	Project Chemist ABC Engineering	Prior to start of on-site analytical work and every 2 weeks thereafter		On-site Analytical TSA Memorandum and Checklist	48 hours following assessment
Project-specific PT samples	Project Chemist ABC Engineering	One sample per medium sampled for SVOCs and metals	Three weeks prior to start of field sampling	PT Deficiency Report	48 hours following receipt of PT results
Management Review	ABC Project Manager & ABC QAM	Interim Management Review following site mobilization. Final management review upon completion of field work.	[fill in anticipated dates]	QA Management Report	48 hours following Management Review

4.2.2 Assessment Findings and Corrective Action Responses

4.3 QA Management Reports

4.4 Final Project Report

5.0 Data Review Elements

5.1 Overview

5.2 Data Review

5.2.1 Step I: Verification

	Item	Step I Verification	Step IIa Compliance	Step IIb Comparison	Step III Usability
Planning Documents					
1	Evidence of required approval of plan (QAPP)	**X**			Uses outputs from previous steps
2	Identification of personnel (those involved in the project and those conducting verification steps)	**X**			
3	Laboratory name	**X**			
4	Methods (sampling and analysis)	**X**	**X**		
5	Performance requirements (including QC criteria) for all inputs	**X**	**X**	**X**	
6	Project quality objectives	**X**		**X**	
7	Reporting forms	**X**	**X**		
8	Sampling plans, location, maps, grids, and sample ID numbers	**X**	**X**		
9	Site identification	**X**			
10	SOPs (sampling and analytical)	**X**	**X**		
11	Staff training and certification	**X**			
12	List of project-specific analytes	**X**	**X**		
Analytical Data Package					
13	Case narrative	**X**	**X**	**X**	Uses outputs from previous steps
14	Internal laboratory chain of custody	**X**	**X**		
15	Sample condition upon receipt, and storage records	**X**	**X**		
16	Sample chronology (time of receipt, extraction, and analysis)	**X**	**X**		
17	Identification of QC samples (sampling or lab, temporal, and spatial)	**X**	**X**		
18	Associated (batch or periodic) PT sample results	**X**	**X**	**X**	
19	Communication logs	**X**	**X**		
20	Copies of laboratory notebook, records, prep sheets	**X**	**X**		
21	Corrective action reports	**X**	**X**		
22	Definitions of laboratory qualifiers	**X**	**X**	**X**	
23	Documentation of corrective action results	**X**	**X**	**X**	
24	Documentation of individual QC results (e.g., spike, duplicate, LCS)	**X**	**X**	**X**	
25	Documentation of laboratory method deviations	**X**	**X**	**X**	
26	Electronic data deliverables	**X**	**X**		
27	Instrument calibration reports	**X**	**X**	**X**	
28	Laboratory name	**X**	**X**		
29	Laboratory sample identification numbers	**X**	**X**		
30	QC sample raw data	**X**	**X**	**X**	
31	QC summary report	**X**	**X**	**X**	

32	Raw data	**X**	**X**	**X**	
33	Reporting forms, completed with actual results	**X**	**X**	**X**	
34	Signatures for laboratory sign-off (e.g., laboratory QA manager)	**X**	**X**		
	Item	**St e**	**St e**	Step IIb	
35	Standards traceability records (to trace standard source from NIST, for example)	**X**	**X**	X	
Sampling Documents					
36	Chain of custody	**X**	**X**		
37	Communication logs	**X**	**X**		
38	Corrective action reports	**X**	**X**	**X**	
39	Documentation of corrective action results	**X**	**X**	**X**	
40	Documentation of deviation from methods	**X**	**X**	**X**	
41	Documentation of internal QA review	**X**	**X**	**X**	
42	Electronic data deliverables	**X**	**X**		
43	Identification of QC samples	**X**	**X**	**X**	
44	Meteorological data from field (e.g., wind, temperature)	**X**	**X**	**X**	
45	Sampling instrument decontamination records	**X**	**X**		
46	Sampling instrument calibration logs	**X**	**X**		
47	Sampling location and plan	**X**	**X**	**X**	
48	Sampling notes and drilling logs	**X**	**X**	**X**	
49	Sampling report (from field team leader to project manager describing sampling activities)	**X**	**X**	**X**	
External Reports					
50	External audit report	**X**	**X**	**X**	Uses outputs from previous steps
51	External PT sample results	**X**	**X**		
52	Laboratory assessment	**X**	**X**		
53	Laboratory QA plan	**X**	**X**		
54	MDL study information	**X**	**X**	**X**	
55	NELAP accreditation	**X**	**X**		

5.2.2 Step II: Validation

5.2.2.1 Step IIa: Validation Activities

5.2.2.2 Step IIb: Validation Activities

Records Reviewed	**Requirement Documents**	**Process Description**	**Responsible Person, Organization**
Field logbook	QAPP, SOP Field 02	Verify that records are present and complete for each day of field activities. Verify that all planned samples including field QC samples were collected and that sample collection locations are documented. Verify that meteorological data were provided for each day of field activities. Verify that	Daily - Project Manager At conclusion of field activities -

		changes/exceptions are documented and were reported in accordance with requirements. Verify that any required field monitoring was performed and results are documented.	Project QA Manager
Chain-of-custody forms	QAPP, SOP Field 02	Verify the completeness of chain-of-custody records. Examine entries for consistency with the field logbook. Check that appropriate methods and sample preservation have been recorded. Verify that the required volume of sample has been collected and that sufficient sample volume is available for QC samples (e.g., MS/MSD). Verify that all required signatures and dates are present. Check for transcription errors.	Daily - Field Crew Chief At conclusion of field activities - Project Chemist
Laboratory Deliverable	QAPP	Verify that the laboratory deliverable contains all records specified in the QAPP. Check sample receipt records to ensure sample condition upon receipt was noted, and any missing/broken sample containers were noted and reported according to plan. Compare the data package with the CoCs to verify that results were provided for all collected samples. Review the narrative to ensure all QC exceptions are described. Check for evidence that any required notifications were provided to project personnel as specified in the QAPP. Verify that necessary signatures and dates are present.	Before release – Laboratory QAM Upon receipt - Project Chemist
Audit Reports, Corrective Action Reports	QAPP	Verify that all planned audits were conducted. Examine audit reports. For any deficiencies noted, verify that corrective action was implemented according to plan.	Project QAM

5.2.3 Step III: Usability Assessment

5.2.3.1 Data Limitations and Actions from Usability Assessment

5.2.3.2 Activities

5.3 Streamlining Data Review

C The types and amounts of data reviewed should be sufficient to develop a clear understanding of the quality of the data.

C The practice of reviewing a subset of data (or a data indicator such as a successful PT sample) as a substitute for reviewing all data should be reevaluated if problems are detected that call into question the quality of the data set.

Streamlining data review occurs when efficiencies are created in the data review process by the following actions:

C Looking at a subset of data that is representative of a larger universe.

C Examining the data in an alternative manner (e.g., through the use of batch-specific PT samples).

Different EPA Regions, DoD components, and DOE facilities have negotiated a variety of streamlining options with different projects. The decision as to the nature and type of streamlining to be conducted is determined by the project team on a site-by-site or facility-by-facility basis and must be documented in the QAPP. The QAPP should also contain decision criteria that allow for revision of the initial streamlining plan. For example, decision criteria contained in the QAPP could specify that if problems are identified in the investigation, then streamlining cannot occur. Other factors may also lead to a revision of the initial streamlining decision, such as intense political interest and concern on the part of the community. The QAPP should contain a statement that prohibits streamlining when conditions are not optimal.

Applicability of streamlining options is addressed in three ways: data review steps for which streamlining may be applicable, criteria for considering the streamlining of data review, and level and type of streamlining to be applied. Each of these is addressed below.

5.3.1 Data Review Steps To Be Streamlined

Verification:

5.3.2 Criteria for Streamlining Data Review
5.3.3 Amounts and Types of Data Appropriate for Streamlining