Source Sampling Fine Particulate Matter: A Kraft Process Recovery Boiler at a Pulp and Paper Facility: Volume 1, Report

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by

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Abstract

Fine particulate matter of aerodynamic diameter 2.5 µm or less ($PM_{2.5}$) has been implicated in adverse health effects, and a National Ambient Air Quality Standard for $PM_{2.5}$ was promulgated in July 1977 by the U.S. Environmental Protection Agency. A national network of ambient monitoring stations has been established to assist states in determining areas which do not meet the ambient standard for $PM_{2.5}$. For such areas, it is important to determine the major sources of the $PM_{2.5}$ so states can devise and institute a control strategy to attain the ambient concentrations set by the standard.

One of the tools often used by states in apportioning ambient $PM_{2.5}$ to the sources is a source-receptor model. Such a model requires a knowledge of the $PM_{2.5}$ chemical composition emitted from each of the major sources contributing to the ambient $PM_{2.5}$ as well as the chemical composition of the $PM_{2.5}$ collected at the receptor (ambient monitoring) sites. This report provides such a profile for a Recovery Boiler at a pulp and paper facility. Along with the $PM_{2.5}$ emission profile, data are also provided for gas-phase emissions of several organic compounds. Data are provided in a format suitable for inclusion in the EPA source profile database, SPECIATE.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Lawrence W. Reiter, Acting Director.
National Risk Management Research Laboratory

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Nomenclature

Term	Definition
CMB	chemical mass balance
DNPH	2,4-dinitrophenylhydrazine
EC/OC	elemental carbon and organic carbon
ELPI	electrical low pressure impactor
EPA	U.S. Environmental Protection Agency
ERG	Eastern Research Group
FID	flame ionization detector
GC	gas chromatography analytical technique
GRAV	gravimetric analytical technique
HEPA	high efficiency particulate arresting
HPLC	high performance liquid chromatography analytical technique
IC	ion chromatography analytical technique
MDLs	method detection limits
MOPs	method operating procedures
MS	mass spectrometry analytical technique
MSD	mass selective detector
NH_3	ammonia
NMOCs	nonmethane organic compounds
NO_X	nitrogen oxides
PM	particulate matter
$PM_{2.5}$	particulate matter of aerodynamic diameter 2.5 µm or less
PM_{10}	particulate matter of aerodynamic diameter 10 µm or less
PUF	polyurethane foam
QAPPs	quality assurance project plans
SIPs	State Implementation Plans
SNMOCs	speciated nonmethane organic compounds
SOPs	standard operating procedures
SO_X	sulfur oxides
TMS	trimethylsilyl
TOE	thermal-optical evolution
VOCs	volatile organic compounds
XRF	X-ray fluorescence analytical technique

Acknowledgments

Introduction

In July 1997, the U.S. Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards for ambient particulate matter of aerodynamic diameter 2.5 µm or less ($PM_{2.5}$) and revised the existing standard for ambient particles of aerodynamic diameter 10 µm or less (PM_{10}). In 1999, a national network of ambient monitoring stations was started under the overall guidance of the EPA's Office of Air Quality Planning and Standards to assist the States in determining regulatory non-attainment areas and to develop State Implementation Plans (SIPs) to bring those areas into compliance with the law for $PM_{2.5}$ and revised PM_{10} regulations. One component of the monitoring network is a number of regional airsheds in which intensive coordinated PM-related research will be carried out to better understand the linkages between source emissions and actual human dosages of fine PM.

The mission of the Emissions Characterization and Prevention Branch of the Air Pollution Prevention and Control Division is to characterize source emissions and to develop and evaluate ways to prevent those emissions. Source characterization as defined here includes the measurement of PM mass emission factors, source PM profiles (PM chemical composition and associated chemical mass emission factors), and emission factors for ambient aerosol precursors such as sulfur oxides (SO_X), nitrogen oxides (NO_X), and ammonia (NH_3).

PM mass emission factors are used in emission inventories and as inputs to atmospheric dispersion models that yield estimates of ambient PM concentrations from considerations of atmospheric transport and transformation of emitted particles. Emissions composition data are used in receptor models to enable apportionment of ambient concentrations of PM to the various sources that emitted the particles. EPA has interest and investments in source apportionment, ambient monitoring, and regulatory matters related to fine PM. For example, states rely on source-receptor and dispersion models to target major sources of $PM_{2.5}$ and to devise cost-effective strategies for achieving compliance with the standard. EPA has a longstanding effort to produce the models for use by the States and EPA. An example of a source-receptor model is the Chemical Mass Balance (CMB) model, which requires as input chemical composition data from both ambient and source samples. The field test reported here focused on the collection of fine particles emitted by a recovery boiler at a pulp and

paper facility. Data were collected to evaluate new measurement techniques and to update and improve source emission profiles and emission factors for $PM_{2.5}$.

Characterization of a Recovery Boiler at a Pulp and Paper Facility

During the last quarter of 2001, a sampling campaign was conducted at a large pulp and paper mill to measure emissions from three of the mill's sources of emissions to the atmosphere; i.e., a recovery boiler fired with concentrated liquid wastes from the wood digestion and pulp washing processes, an auxiliary boiler combusting a mixture of wood bark (hogged wood waste) and coal, and a vent from the smelt tank. The primary aim of these tests was to measure the mass emission factors and chemical compositions of the fine particulate matter emitted. This test report presents results from the emissions testing of the recovery boiler.

Previous work to determine PM emissions for this type of source focused on the filterable and condensible fractions of total PM emitted as measured by EPA Method 5 or Method 202.[1] A number of potential biases have been identified with the use of these EPA methods including a negative mass bias when filterable PM is collected in a hot exhaust stream without first cooling and diluting the exhaust, and a positive mass artifact of condensible PM when the hot exhaust is quenched by passing it through a series of cold impinger solutions without first diluting the exhaust stream. To minimize these sampling artifacts, the present test campaign employed a state-of-the-art dilution sampling system designed to dilute and cool the hot exhaust gas to near ambient conditions prior to collecting the PM. Also, sufficient time was provided prior to collection of the PM to enable any semivolatile organic compounds to distribute between the gas and particle phases as they would do in the ambient air downstream from the stack. Sampling in this way should yield more accurate, artifact-free, PM mass emission factors and particles whose composition is the same as that in the ambient air downstream of the source.

Recovery boilers, common to nearly all pulp and paper mills, are usually one of the major contributors to atmospheric emissions from the mill. Processing wood chips in a pulp mill utilizing the Kraft process involves digesting the wood in a solution of sodium sulfide and sodium hydroxide. The spent digestion liquor combined with water used to wash the resulting pulp is called "black liquor." After undergoing concentration by evaporation to about 65% solids, the black liquor is fed to the recovery boiler as fuel. Dissolved organics in the concentrated black liquor are combusted in the recovery boiler to yield heat to generate process steam and to convert sodium sulfate formed in the process back to sodium sulfide

which can be recycled to the digestion step as a reactant. The recovery boiler tested here was equipped with two parallel electrostatic precipitators with 169,194 linear feet of plate area per precipitator, installed in the flue gas exhaust ducting.

Although fine PM was the focus of this particular test campaign, gas-phase organic emissions were also collected concurrently and analyzed. Reduced sulfur gas emissions, such as hydrogen sulfide, methyl mercaptan, and dimethyl sulfide, were not tested. This report presents the results of these tests which were conducted over a 3-day period in late October to early November of 2001. Prior to the sampling runs, EPA Methods 1, 2, and 4[2,3,4] were performed to establish the stack gas velocity, temperature, pressure, and exhaust gas moisture content. The exhaust gas flow rate was calculated from these measurements and was assumed to remain constant throughout the following three-day test series.

This report describes the nature of the source, the method of sampling, analysis methods used to determine the composition of the PM and gas phase emissions, and the analysis results—both in the form of mass emission factors (mass of emitted species per mass of fuel consumed) and as mass fraction compositions. Results presented as mass emission factors are expected to be useful in emission inventories. The composition of PM and gas-phase emissions expressed as mass fractions can be used as source profiles for input to source-receptor models such as the CMB model employed by environmental regulatory agencies for apportioning ambient PM to the various sources contributing to the ambient PM.

Report Organization

This report is organized into five additional sections plus references and appendices. Section 2 provides a summary of results and conclusions derived from the study results and Section 3 describes the process operation and the test site. Section 4 outlines the experimental procedures used in the research and Section 5 presents and discusses the study results. Section 6 presents the quality control/quality assurance procedures used in the project to ensure generation of high quality data.

Conclusions

Combustion of organic components in the black liquor fuel was essentially complete in the recovery boiler as evidenced by the non-detectable amount of organic carbon in the fine PM emissions and by the very low quantities of volatile organic compounds in the gas-phase emissions from the boiler. Total measured non-methane organic compounds in the gas-phase emissions amounted to 43.6 µg/m^3 on average, which was lower than the concentration of these compounds found in the ambient air at the facility (74.0 µg/m^3). The lower concentration of organic compounds in the boiler emissions may be attributed to the fact that the ambient air used to dilute the stack gas prior to sample collection was purged of contaminants before mixing with the stack gas.

On the first test day (10/30/01) of the three-day test series, the boiler was fired with a mixture of black liquor and #2 distillate oil (8.8 wt% oil, 91.2 wt% black liquor). Firing on this day was occasioned by repair of one of the two fuel inlet nozzles, which normally inject black liquor into the boiler. On the second and third days of testing, only black liquor was used as the fuel. On the single test day when distillate oil was used together with black liquor as the boiler fuel, the PM mass emissions, the elemental carbon content of the fine PM, and the mass emissions of gaseous nonmethane organic compounds were significantly higher than on the other two test days. For this reason, uncertainties associated with the reported emission factors are higher when results of all three test days are considered than when only the results of the second and third test days are considered. The higher emission factors for Day 1 should be viewed as anomalous and reflective of an upset condition in the boiler operation.

Even when the relatively higher emissions measured on Test Day 1 are included, the measured emission factors for fine PM are lower than estimated in the EPA's emission inventory (AP-42) for pulp and paper recovery boilers equipped with electrostatic precipitators. EPA's current estimates for this source category are 1000 mg of total PM/kg of fuel and 600 mg of PM$_{2.5}$ per kg of fuel. These estimates are based on previous measurements of the filterable portion of PM emitted as defined by EPA Method 5, "Determination of Particulate Matter Emissions from Stationary Sources." Mass emission factors of PM$_{2.5}$ determined by this study range from 45.4 to 10.6 mg per kg of fuel with an average over all three tests of 23.3 mg per kg of fuel. In this connection, it should also be

noted that this particular recovery boiler had just completed two months of line-out operation (i.e., checkout and optimization) following a major reconditioning and overhaul of the system, including replacement of the burners.

Results of the three replicate test runs conducted during three consecutive days may be summarized as follows. Essentially no organic compounds were detected in either the fine PM or the gas-phase emissions from the recovery boiler stack, indicating that the organic components of the black liquor fuel were essentially completely combusted in the boiler. Organic carbon in the collected fine PM (a measure of the organic composition of the PM) was non-detectable, and the total volatile organic compounds (total VOCs) in the collected gas-phase emissions amounted to only 33.6 mg/m^3 on average. In fact, the total VOC concentration in the boiler emissions averaged slightly less than that found in the ambient air at the plant site (40.4 mg/m^3). This observation may be attributed to the fact that the ambient air used to cool and dilute the sampled exhaust gas had been rigorously purged of organics prior to mixing with the exhaust gas.

PM$_{2.5}$ mass emissions ranged from 10.6 to 45.4 mg per kg of fuel with an average of 23.3 mg per kg fuel over the three test days. The highest emission factor (45.4 mg per kg fuel) was found on the one day #2 distillate oil was added to the black liquor fuel (8.8 wt% oil, 91.2 wt% black liquor). Reasons for a higher mass emission factor for fine PM when co-firing the boiler with oil are not clear.

Approximately 83% of the PM$_{2.5}$ mass was identified and quantified and was found to consist largely of sodium and/or potassium sulfate with a smaller amount of sodium and/or potassium chloride. The mean aerodynamic particle diameter of the PM$_{2.5}$ was found to be 1.31 μm.

Methods and Materials

A field test was conducted (October 30–November 1, 2001) on a recovery boiler at a pulp and paper facility to obtain source emissions measurements of high and known quality. The objectives of the testing activities were to evaluate the sampling equipment and to characterize the fine particulate and volatile organic emissions from a Kraft Process recovery boiler. To simulate the behavior of fine particles as they enter the ambient atmosphere from an emissions source, dilution sampling was performed to cool, dilute, and collect gaseous and fine particulate emissions from the recovery boiler exhaust. Gaseous and fine particulate samples collected were chemically characterized. Eastern Research Group (ERG) coordinated all field test activities; laboratory testing activities were divided between EPA and ERG according to the breakdown shown in Table 1.

Table 1. Sampling Medium Used for Collection of Samples, Analysis Performed, Analytical Method, and Responsible Laboratory

Sampling Medium	Analysis	Method	Laboratory
Teflon Filter	$PM_{2.5}$ Mass	Gravimetric (GRAV)	EPA
Teflon Filter	Elemental Analysis	X-Ray Fluorescence (XRF)	EPA
Teflon Filter	Inorganic Ions	Ion Chromatography (IC)	EPA
Quartz Filter	Elemental Carbon/ Organic Carbon	Thermal-Optical Evolution (TOE)	EPA
Quartz Filter, XAD-4 Denuder, and PUF	Semivolatile Organic Species	Gas Chromatography/ Mass Spectrometry (GC/MS)	EPA
DNPH-Impregnated Silica Gel Tubes	Carbonyl Compounds	High Performance Liquid Chromatography (HPLC)	ERG
SUMMA Canisters	Air Toxics Speciated Nonmethane Organic Compounds	Method TO-15 (GC/MS) ERG Concurrent Analysis	ERG
Particle Size Analyzer	Particle sizes	Electrical Low Pressure Impactor (ELPI)	ERG

ERG performed source sampling to collect artifact-free, size-resolved particulate matter in a quantity and form sufficient to identify and quantify trace elements and organic

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compounds and to distinguish gas-phase and particle-phase organic compounds. Total particulate matter mass in the diluted and cooled emissions gas was size resolved at the PM_{10} and $PM_{2.5}$ cut points with the $PM_{2.5}$ fraction further continuously resolved down to 30 nm diameter using an electrical low pressure impactor (ELPI). Fine particle emission profiles can be used in molecular marker-based source apportionment models, which have been shown to be powerful tools to study the source contributions to atmospheric fine particulate matter.

To assist in the characterization of the recovery boiler stationary source emissions and to obtain chemical composition data representative of particle emissions after cooling and mixing with the atmosphere, ERG performed the following activities at the test site:
- Performed preliminary measurements using EPA Methods 1, 2, and 4[2–4] to evaluate source operating conditions and parameters;
- Installed the precleaned dilution sampling system, sample collection trains, and ancillary equipment at the field site without introduction of contaminants;
- Calibrated flow meters before and after sampling, monitoring, and adjusting gas flows (as necessary) throughout the tests;
- Acquired process data for the test periods, including temperatures, pressures, flows, fuel consumption, and such;
- Determined the type of combustion fuel and the rate of consumption during the source testing;
- Collected three sets of stationary source samples as prescribed in the Site-Specific Test Plan, including one set of field blanks; and
- Recovered the dilution sampling unit and sample collection arrays for analysis for specific parameters and returned the dilution sampling unit to EPA.

ERG transported the dilution sampling system to the test site to collect integrated samples, performed whole air analysis of volatile organic compounds collected in SUMMA-polished stainless steel canisters and gas-phase carbonyl compounds collected on silica gel cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH), and evaluated particle size distribution data. EPA was responsible for pretest cleaning of the dilution sampling system, for analysis of semivolatile organic compounds from XAD-4 denuders and polyurethane foam (PUF) sampling modules resulting from the test efforts, and for characterization of the particle phase emissions and mass loading on quartz and Teflon filters.

Description of Test Equipment
The test equipment consisted of a dilution sampling system and its instrumentation.

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Dilution Sampling System

The dilution sampling system used in the source test was based on an original design by L. M. Hildemann[5] and modified to incorporate more secure closure fittings and electronic controls. Automatic flow control and data acquisition capabilities were added to the dilution sampler to improve the ease of operation of the unit. A touch screen interface connected to the main controller was used to monitor current conditions and allow set points to be entered into the system readily. A laptop computer was used for continuous monitoring of operating parameters and logging of the sampler operation.

The dilution sampling system dilutes hot exhaust emissions with clean air to simulate atmospheric mixing and particle formation. Control of residence time, temperature, and pressure allows condensible organic compounds to adsorb onto fine particles as they might in ambient air. The sampler is also designed and fabricated to minimize any contamination of samples, especially organic compound contamination, and to minimize particle losses to the sampler walls.

Figure 1 shows a schematic diagram of the dilution sampling system and dilution air cleaning and conditioning system. As shown, the dilution air cleaning system provides high efficiency particulate arresting (HEPA) and activated carbon-filtered air. Acid gases (if present) will not be removed completely by the dilution air cleaning system, but the presence of acid gases can be monitored in the dilution tunnel immediately downstream of the dilution air inlet. The dilution air cleaning system can be modified to add a heater, cooler, and dehumidifier as needed. Cleaned dilution air enters the main body of the sampling system prior to the dilution sample arrays.

The key zones of the dilution sampling system and their function are described below.

Sample Inlet Zone—

> *Stack Emissions Inlet:* designed to allow stationary source exhaust gas to be sampled through an inlet cyclone separator to remove particles with nominal aerodynamic diameters greater than 10 μm. The PM_{10} cyclone prevents large particles from entering the sampler to plug or damage the equipment. Three ports are dedicated to sampling the dilution air before it mixes with the source gas.

Turbulent Mixing Chamber

$Re \cong 10,000$

RESIDENCE TIME CHAMBER

DILUTION TUNNEL

ACCESS PORTS

STACK EMISSIONS

10 μm CYCLONE

2.1 μm CYCLONES

HEATED INLET LINE

VENTURI

HIGH-VOL FILTER

STACK EMISSIONS INLET

SAMPLE ARRAYS

D1
D2
D3

SAMPLE ARRAYS

Blower

FILTER

BLOWER

COOLING UNIT

HEPA FILTER

ACTIVATED CARBON BED

DILUTION AIR

R2   R3   R5   R6
     R4

DILUTION AIR INLET

VACUUM PUMPS

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Figure 1. Diagram of the Dilution Sampler and Dilution Air Conditioning System.

Heated Inlet Line: 3/4 in. heated stainless steel sampling probe draws source gas through a venturi meter into the main body of the sampler. Sample flow rate can be adjusted from 15 to 50 L/min (typically 30 L/min).

Venturi Meter—

Constructed of low carbon, very highly corrosion-resistant stainless steel; equipped for temperature and pressure measurement. Wrapped with heating coils and insulated to maintain the same isothermal temperature as the inlet cyclone and inlet line.

Turbulent Mixing Chamber—

The mixing chamber incorporates an entrance zone, U-bend, and exit zone. The inside diameter is 6 in., which yields a Reynolds number of approximately 10,000 at a flow rate of 1000 L/min. Dilution air enters the mixing chamber in a direction parallel to the flow of source gas. Hot source emission gas enters the chamber perpendicular to the dilution air flow, 4.5 in. downstream of the dilution air inlet. The combined gas flow travels 38 in. before entering the U-bend. After the residence chamber transfer line, the mixing chamber continues for 18 in. then expands to an in-line, high-volume sampler filter holder. Collected particulate material has not experienced time to equilibrate with the gas phase in the diluted condition. Sampling and instrumentation ports are installed on the turbulent mixing chamber at various locations, as shown in Figure 1.

Residence Time Chamber—

The inlet line to the residence time chamber expands from a 2-in. line (sized to provide a quasi-isokinetic transfer of sample gas from the turbulent mixing chamber to the residence time chamber at a flow rate of approximately 100 L/min) within the mixing chamber to a 7-in. line at the wall of the residence chamber. The flow rate is controlled by the total sample withdrawal from the bottom of the residence time chamber and provides a 60-sec residence time in the chamber. Twelve ports are installed at the base of the residence time chamber, nine ports for sample withdrawal and three ports for instrumentation.

Sample Collection Zone—

Samples collected from the sampling ports at the base of the residence time chamber have experienced adequate residence time for the semivolatile organic compounds to repartition between the gas phase and the particle phase.

Because it is very difficult to maintain both isokinetic sampling and a fixed cyclone size cut during most stack sampling operations, the inlet cyclone may be operated to provide a rough PM_{10} cut while maintaining near-isokinetic sampling. The rough inlet size cut has

minimal impact on sampling operations since the dilution sampling system is used mainly to collect fine particulate matter from combustion sources, and the critical fine particle size cut is made at the end of the residence time chamber. For the test conducted on October 30–November 1, 2001, the calculated total time the sample spent in the dilution sampling system was 73 sec with 2.4 sec for the turbulent mixing chamber and 70.6 sec for the residence chamber.

Dilution Sampling System Control Instrumentation

Instrumentation for control and analysis of the dilution sampling system is shown in Figure 2. Differential pressure measurements made across the venturi and orifice meters are used to determine the dilution air flow rate, the sample gas flow rate, and the exhaust gas flow rate. Since flow equations used for determination of the flow across venturi and orifice meters correct for flowing temperature and pressure, the flowing temperature and pressure of the venturi and orifice meters must be recorded during sampling operations. Thermocouples for monitoring temperature are placed at each flow meter as well as at the inlet PM_{10} cyclone, at various points on the sample inlet line, at the inlet to the mixing chamber U-bend, and at the outlet of the residence time chamber. An electronic relative humidity probe is used to determine the relative humidity of the sample gas. The dilution sampling system is equipped with automated data logging capabilities to better monitor source gas testing operations and to minimize manpower requirements during sampling operations. Dilution sampling system flows and temperatures are monitored and controlled automatically at set points established by the operator using a QSI Corporation QTERM-K56 electronic touch screen interface. The dilution sampling system was operated by three testing staff members during the test at the Kraft Process recovery boiler.

In operation, the source sample flow, the dilution airflow, and the total air flow (not including the sample collection arrays) were each measured by separate flow meters and pressure transducers. A venturi meter measured the source sample flow and orifices were used for the dilution and total flows. A ring compressor was used to push the dilution air through a HEPA filter, a carbon adsorber, and a final filter into the turbulent mixing chamber. The compressor motor was modulated by a variable frequency drive to match the desired dilution flow based on a set point entry. A separate blower (connected to a speed controller adjusted to achieve the desired sample flow based on a set point entry) at the end of the dilution sampling system pulled the source sample flow through the venturi. Flow through this blower consisted of the dilution airflow plus the source sample flow, not including the flow exiting through the sample collection arrays.

Key:
TE = Temperature Indicator
PT = Pressure Indicator
RH = Relative Humidity Indicator

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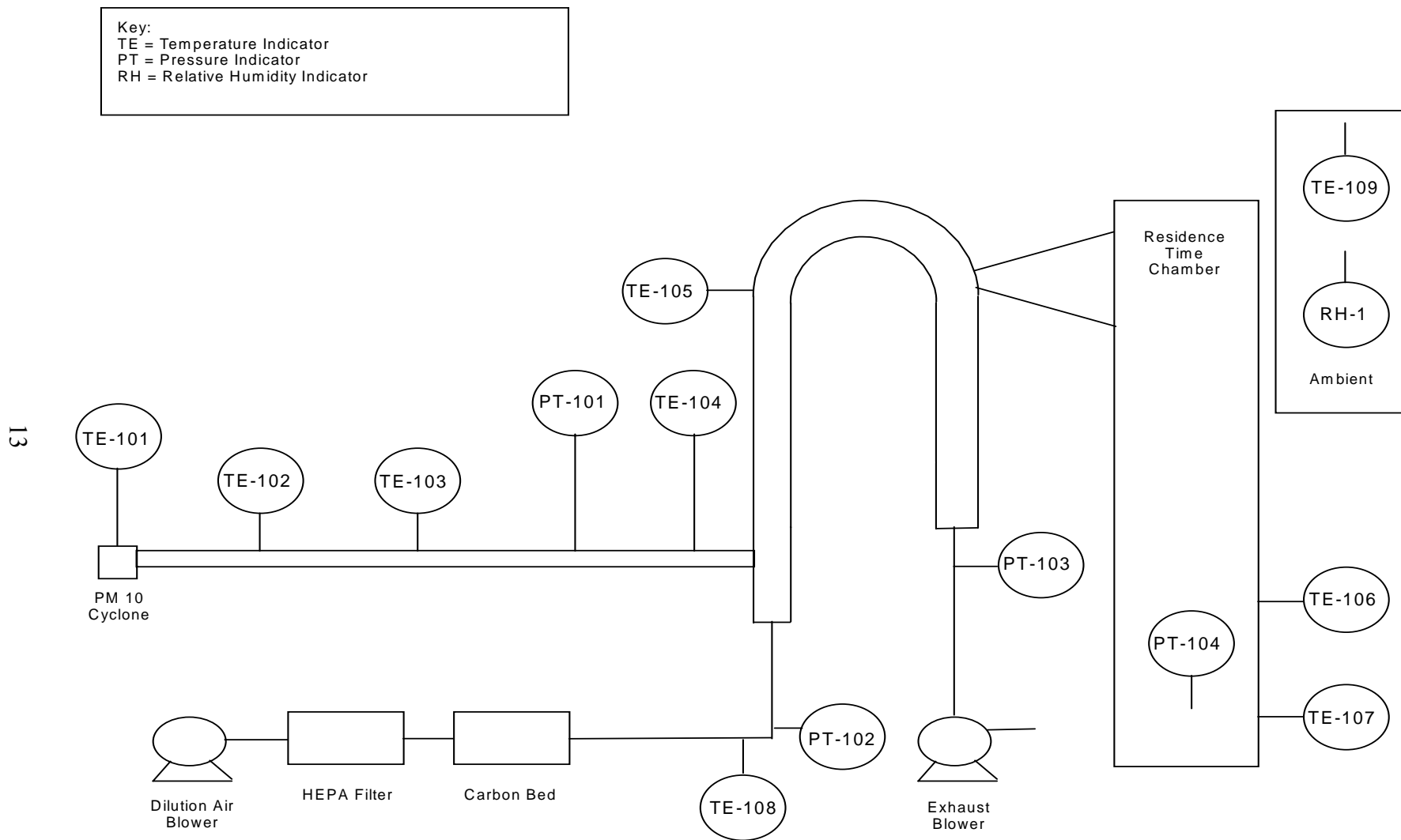
Figure 2. Instrumentation for Control and Analysis of the Dilution Sampler.

The main controller modulated the power used to heat the sample probe (32 in. long, one heated zone). The controller switched solid-state relays on and off as needed to maintain the probe temperature, which had been entered by the operator.

Sample Collection Arrays

Virtually any ambient sampling equipment—including filters of various types (quartz, Teflon, Nylon), denuders, PUF modules, DNPH-impregnated silica gel sampling cartridges, SUMMA-polished canisters, cyclones, particle size distribution measurement instrumentation—can be employed with the dilution sampling system. The exact number and type of sample collection array is uniquely configured for each testing episode.

Process Description/Site Operation

The recovery boiler tested (referred to as "Recovery Boiler No. 5") burns as much as 130 tons per hour of black liquor solids. Recovery Boiler No. 5 is equipped with two electrostatic precipitators (169,194 feet of plate area per precipitator) installed on the flue gas exit system from the boiler. The Recovery Boiler No. 5 sampling site is located on the vertical wall of a boiler duct, with a sampling port at a point that meets EPA Method 1 requirements for length of straight run and for orientation of the port with respect to the plane of bends in the ductwork. The sampling location is elevated approximately 50 feet above ground level. A schematic diagram of the layout of the sampling site is shown in Figure 3. The area around the sampling port is 16 to 17 feet long and approximately 36 in. wide.

Access to this location required use of a catwalk-type platform. The whole site is in a "welled" area, enclosed on three sides, with limited access from above because of pipes and duct work. Large pieces of sampling equipment (i.e., the dilution sampling system and the control unit) were lifted up to the sampling location using a crane available at the site. The dilution sampling system was lifted to the location shown in Figure 3 then rolled into position at the sampling port (Figure 4) on an elevated secondary platform constructed to facilitate rolling the dilution sampling system along a corridor with railings on one side. With the agreement of the facility staff, some of these railings were removed to allow passage of the dilution sampling unit along the corridor.

The elevated walkway shown in Figure 3 allowed minimal space around the dilution sampling system. The control unit for the dilution sampling system was therefore located on the opposite side of the elevated walkway (Figure 3) and connected to the dilution sampling unit by approximately 10 feet of flexible tubing.
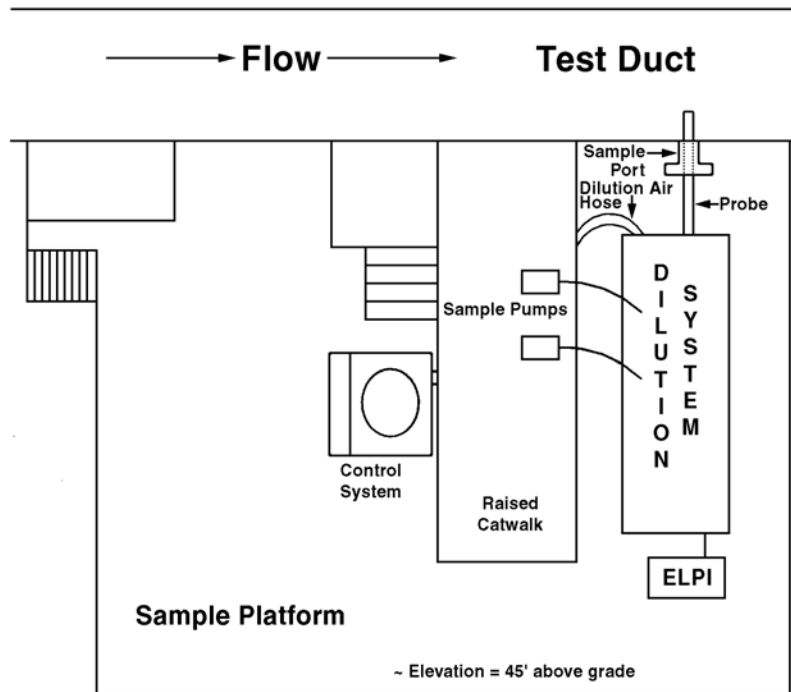
Figure 3. Schematic Diagram of Layout of Recovery Boiler No. 5 Sampling Site.
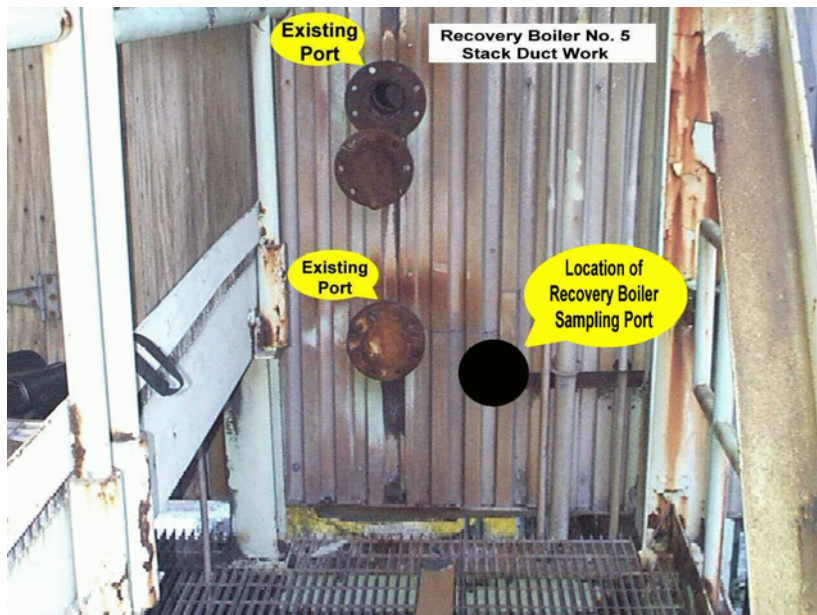
Figure 4. Recovery Boiler Sampling Port Location.

Supplemental equipment such as the ELPI was transported up stairs to reach the sampling site. There was no space in the vicinity of the sampling port for location of an appropriate enclosed area for preparation of sampling components or for recovery of the sample collection arrays. An appropriate area at ground level was therefore identified for preparation of sampling components and for recovery of the sample collection arrays and preparation for transport to the laboratories.

Recovery Boiler No. 5 burns the high concentration of heavy black liquor solids generated in the concentrator. The combustion process in the boiler oxidizes the organic compounds to produce heat and allows the inorganic solids (smelt) to be recovered at the base of the boiler. Recovery Boiler No. 5 (one of several recovery boilers that function independently) is a noncontact, low-odor boiler with a rated capacity of 520 gal/min of black liquor (density 11.4 lb/gal) or a mass flow rate of 121 tons per hour black liquor solids (BLS). In addition, Recovery Boiler No. 5 is equipped to fire fuel oil during startup, shutdown, and malfunction. The heat recovered is used to produce 35% of the steam and electricity required by the facility. Smelt recovered at the base of the boiler is dropped into both of the two smelt dissolving tanks. At the request of ERG, a sample of the black liquor was collected for analysis by facility environmental staff. The black liquor sample was collected at the inlet to the fuel injector during the first test day; analytical results are shown in Table 2.

Table 2. Analysis of Black Liquor

Parameter	Value
Sulfur	2.73%
Btu per pound	4208
Ash	23.18%
Carbon	23.86%
Hydrogen	6.93%
Nitrogen	0.07%
Oxygen	43.23%
Chlorine	870.6 ppm

Exhaust gases from Recovery Boiler No. 5 are routed through two parallel electrostatic precipitators (ESPs) for particulate control prior to release to the atmosphere through the No. 1 Hogged Fuel Boiler stack. The ash generated in the ESPs contains large amounts of sodium in the form of sodium sulfate (Na_2SO_4) and is known as the "salt cake." This salt cake is recovered by pumping heavy liquor from a tank called "the precipitator mix tank" to a ribbon mixer in the base of the ESPs. This heavy liquor/salt cake combination is then

discharged to a salt cake mix tank where it is heated and mixed with direct steam injection prior to being fed to the recovery boiler. However, the volume of recovered salt cake injected is negligible compared to the volume of black liquor injected. A significant amount of vapor is generated in the salt cake mix tank, which is captured and controlled by the Noncondensible Gases System. The precipitator mix tank vents to the atmosphere.

One of the purposes of the recovery boiler is to chemically convert the inorganics in the black liquor into a form that can later be recovered and converted to white liquor, mostly sodium hydroxide (NaOH), to recycle to the digesters. This conversion is accomplished by control of the combustion process to the extent that the Na_2SO_4 present in the black liquor or generated in the oxidizing section of the furnace is predominantly converted into sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3), which comprise the smelt. This is the principal reason for recycling the ash (salt cake, Na_2SO_4) from the ESPs. The sulfates are produced in the oxidizing section of the boiler, where odor-producing sulfides and mercaptans are minimized by conversion to sulfur dioxide (SO_2).

The fuel use for Recovery Boiler No. 5 during the testing period is summarized in Table 3. A more detailed description of the fuel fired for each specific test is provided in Table 4.

Table 3. Recovery Boiler No. 5 Fuel Use During the Test Period (Average Stack Gas Velocity Based on Traverse = 2745.8 ft/min)

Test #	Fuel Type	Feed Rate (gal/min)	Test Duration (min)	Total Volume Used (gal)	Combined Overall Total Volume Used (gal)
1	Black Liquor[a]	265.43	482	127937.3	
1	#2 Oil	41.31	482	19911.4	
1					147848.7
2	Black Liquor	471.43	480	226483.2	
2	#2 Oil	None	480	0	
2					226483.2
3	Black Liquor	506.33	479	242532.1	
3	#2 Oil	None	479	0	
3					242532.1

[a] Black Liquor Nominal Density = 11.4 lb/gal

Table 4. Process Data for Testing Days: Black Liquor, Black Liquor Solids, and #2 Oil

Test #	Test Date 2001	Start Time	End Time	Black Liquor[a] Firing Rate (gpm)	Black Liquor Solids (%)	Tons Black Liquor Solids/Hour	Total Tons Black Liquor Solids Fired	#2 Oil Firing Rate (gal/min)
1	10/30	0850	1650	265.43	67.72	61.47	491.79	41.31
2	10/31	0800	1600	471.84	67.74	109.31	874.49	0
3	11/1	0730	1530	506.33	67.75	117.32	938.55	0

[a]Black Liquor nominal density, 11.4 lb/gal

Pre-Test Survey

A thorough survey of the test site was conducted to determine that the test equipment could gain access to the test location and that the dilution sampling system and the control module would fit in the test location, to identify and gain access to the utilities needed to operate the dilution sampling system and its ancillary equipment, to arrange for the installation of a sample collection port (Figure 4) at the outlet of the electrostatic precipitators, and to determine and evaluate the means of positioning the dilution sampling system at the desired location. The pre-test survey considered access to utilities and personnel, legal, and safety requirements. Limited source data—such as exhaust gas flow rate and velocity, exhaust gas temperature and water vapor content, and approximate particulate matter concentration—were obtained for estimating appropriate dilution ratios and duration of sample collection. Arrangements were made to position the dilution sampling system on a catwalk platform at the test location (Figure 3). A second pre-test survey was made to verify that the sampling port had been installed correctly, that all necessary utilities had been installed, and that arrangements for lifting the dilution sampling system to the sampling platform were complete. The dilution sampling system, the control module, and all ancillary equipment were then transported to the test site, and the dilution air supply/control module and the sampler module were positioned at the sampling location using a crane supplied and operated by the facility. Electrical power (250V, single phase, 40 A) was provided and installed by the facility.

Experimental Procedures

The EPA/ECPB dilution sampling system (schematic diagram in Figure 1), sample collection arrays, sample substrates, and dilution air cleaning system were used for sampling undiluted hot exhaust gas streams. To minimize introduction of contaminants, EPA precleaned and preassembled the dilution sampling system and sample collection arrays in a clean environment prior to transport to the test site. The dilution sampling system and dilution air cleaning system were assembled on separate portable aluminum frames equipped with wheels and tie-down and hoisting lugs for transport to and from the test site. A crane provided by the facility was used to position the dilution sampling system at the test site. ERG maintained the dilution sampling system and sample collection arrays in a contaminant-free condition prior to collection of recovery boiler samples and field blanks.

A sampling system blank test was performed prior to transporting the dilution sampling system to the test site to ensure that the system had been cleaned properly and was leak free. The blank test was performed in the laboratory by completely assembling the dilution sampling system, including the sample collection arrays connected to the residence time chamber, and all instrumentation. The blank test was conducted for a time period consistent with the expected duration of the source tests (approximately eight hours). Following the blank test, the dilution sampling system was shut down in reverse order from start-up, and all substrates were unloaded, preserved as appropriate, and analyzed to verify the absence of contamination in the dilution sampling system.

Preparation for Test Setup

Prior to the deployment of the dilution sampling system at the test site and initiation of sampling with the dilution sampling system and associated sample collection arrays, EPA Methods 1, 2, and 4 were conducted to establish key experimental parameters for test conditions.

Traverse Point Determination Using EPA Method 1

EPA Method 1, "Sample and Velocity Traverses for Stationary Sources" (40 CFR Part 60, Appendix A, pp. 181-206),[2] was used to establish the number and location of sampling traverse points necessary for isokinetic and flow sampling. These parameters are based on

how much duct distance separates the sampling ports from the closest downstream and upstream flow disturbances. The Recovery Boiler No. 5 sampling site is located on the vertical wall of a boiler duct, with the sampling port at a location that meets EPA Method 1 requirements for length of straight run and for orientation of the port with respect to the plane of bends in the duct work. Sampling at the test site was performed at the point determined by Method 1 to represent the average velocity of the exhaust duct from the two electrostatic precipitators used on Recovery Boiler No. 5 (Figure 3).

The following duct dimensions were measured:
- Inside of far wall to outside of nipple (Distance A): 150 in.
- Inside of near wall to outside of nipple (Distance B): 4 in.
- Inside stack dimensions: 146 in.

Traverse point locations for a the rectangular recovery boiler duct are listed in Table 5. A table of metric unit conversions is shown in Appendix A.

Table 5. EPA Method 1 Traverse Point Locations for Recovery Boiler No. 5 Exhaust (a Rectangular Duct)

Traverse Point Number	Fraction of Inside Stack Dimension[a] (%)	Distance from Stack Wall (in.)	Traverse Point Location (in.)
1	5.0	7 ¼	11 ¼
2	15.0	21 ⅞	25 ⅞
3	25.0	36 ½	40 ½
4	35.0	51 ⅛	55 ⅛
5	45.0	65 ¾	69 ¾
6	55.0	80 ⅜	84 ⅜
7	65.0	94 ⅞	98 ⅞
8	75.0	109 ½	113 ½
9	85.0	124 ⅛	128 ⅛
10	95.0	138 ¾	142 ¾

[a] Inside stack depth: 146 in. Distance from lip of flange to inside stack wall: 4 in.

The absolute pressure of the flue gas (in inches of mercury) was calculated according to the equation

$$PS = P_{bar} + \frac{P_g}{13.6} \qquad \text{(4-1)}$$

where:

    PS = absolute gas pressure, inches of mercury

    P_{bar} = barometric pressure, inches of mercury (30.24 in.)

    P_g = gauge pressure, inches of water (static pressure) (0.11 in.).

The value 13.6 represents the specific gravity of mercury (1 inch of mercury = 13.6 inches of water). For the stack tested, the absolute gas pressure under the test conditions was 30.248 inches of mercury.

Volumetric Flow Rate Determination Using EPA Method 2

Volumetric flow rate was measured according to EPA Method 2, "Velocity–S-Type Pitot" (40 CFR Part 60, Appendix A, pp. 214-153).[3] A K-type thermocouple and S-type pitot tube were used to measure flue gas temperature and velocity, respectively. All of the isokinetically sampled methods that were used incorporated EPA Method 2.

Pitot Tube Calibration

The EPA has specified guidelines concerning the construction and geometry of an acceptable S-type pitot tube. If the specified design and construction guidelines are met, a pitot tube coefficient of 0.84 is used. Information pertaining to the design and construction of the S-type pitot tube is presented in detail in Section 3.1.1 of report EPA 600/4-77-027b. Only S-type pitot tubes meeting the required EPA specifications were used. Pitot tubes were inspected and documented as meeting EPA specifications prior to field testing.

Calculation of Average Flue Gas Velocity

The average flue gas velocity for each traverse point is calculated using the equation

$$V_s = K_p \times C_p \times \sqrt{\frac{\Delta P_{avg} \times (460 + T_s)}{P_s \times M_s}} \qquad (4\text{-}2)$$

where:

    V_s = average flue gas velocity, ft/sec

    K_p = pitot constant (85.49)

    C_p = pitot coefficient (dimensionless), typically 0.84 for S type

    ΔP_{avg} = average flue gas velocity head, inches of water (0.28 in.)

    460 = 0 °F, expressed as degrees Rankin

    T_s = flue gas temperature, °F (367.7 °F)

    P_s = absolute stack pressure (barometric pressure at measurement site plus stack static pressure), inches of mercury (30.248 in.)

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M_s = wet molecular weight, pounds per pound-mole (27.67 pounds/pound-mole).

The flue gas velocity calculated for each traverse point and the average velocity are shown in Table 6.

Table 6. Average Flue Gas Velocity for Each Traverse Point (Average Flue Gas Velocity)

Traverse Point (Calculated in Table 5)	Velocity (ft/min)
1	2276.5
2	2641.2
3	2743.7
4	2809.6
5	2776.7
6	2461.4
7	2874.4
8	2937.4
9	2968.5
10	2968.5
Average Velocity	**2745.8**

The point of average velocity has the closest relationship to Traverse Point #3.

Nozzle Size Determination

It is desirable to sample at or near isokinetic velocities at the probe inlet nozzle. The nozzle size is based on the required sample flow rate. Prior to using an Excel macro to perform nozzle size calculations according to the procedures of EPA Method 5 (40 CFR part 60, Appendix A, pp. 371-443), the velocity in the stack (feet per minute) must be determined from the pitot traverses prior to the start of the test run. The additional input required by the macro is sampling rate (liters/minute). The nozzle selected for use at Recovery Boiler No. 5 was 0.267 in. id.

Measurement of O_2, CO_2, and CO Concentrations for Calculating Stack Parameters

The O_2 and CO_2 concentrations were determined using a Fyrite bulb during the traverse. The CO concentration was determined using the facility's installed CO continuous emissions monitor (certified).

Stationary Gas Distribution (as Percent Volume)

The following concentrations were measured:

$O_2 = 6.5\%V$

$CO_2 = 13.0\%V$

$CO = 0.03\%V$

The percentage of nitrogen (N_2) was calculated by

$$N_2\%V = 100 - (O_2\%V + CO_2\%V + CO\%V) = 80.47\%V \tag{4-3}$$

Dry Molecular Weight of Flue Gas

The dry molecular weight of the flue gas (M_d) was calculated by

$$M_d = (0.44 \times CO_2\%V) + (0.32 \times O_2\%V) + [0.28 \times (CO\%V + N_2\%V)]$$
$$= 30.36 \text{ lb/lb} \cdot \text{mole} \tag{4-4}$$

where:

M_d = molecular weight of flue gas, dry basis (lb/lb-mole)

$CO_2\%V$ = percent CO_2 by volume, dry basis (13.0)

$O_2\%V$ = percent O_2 by volume, dry basis (6.5)

$CO\%V$ = percent CO by volume, dry basis (0.03)

$N_2\%V$ = percent N_2 by volume, dry basis (80.47)

0.44 = molecular weight of CO_2, divided by 100

0.32 = molecular weight of O_2, divided by 100

0.28 = molecular weight of N_2 or CO, divided by 100.

Wet Molecular Weight of Flue Gas

The wet molecular weight of the flue gas (M_s) was calculated by

$$M_s = (M_d \times M_{fd}) + (0.18 \times H_2O\%V)$$
$$= 27.67 \text{ wet lb/lb} \cdot \text{mole} \tag{4-5}$$

where:

M_s = wet molecular weight of flue gas, wet lb/lb-mole

M_d = molecular weight of flue gas, dry basis (30.36 lb/lb-mole)

M_{fd} = dry mole fraction of effluent gas, calculated as [1 - $H_2O\%V$/100] (0.7826)

0.18 = molecular weight of H_2O, divided by 100

$H_2O\%V$ = percent H_2O, by volume (21.739).

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Determination of Average Moisture Using EPA Method 4

EPA Method 4, "Moisture Content," (40 CFR Part 60, Appendix A, pp. 347-371),[4] was used to determine the average moisture content of the duct gas. A gas sample was extracted from the boiler, moisture was removed from the sample stream, and the moisture content was determined gravimetrically. Before sampling, the initial weight of the impingers was recorded. When sampling was completed, the final weights of the impingers were recorded, and the weight gain was calculated. The weight gain and the volume of gas sampled were used to calculate the average moisture content (percent) of the duct gas by computer. Method 4 was incorporated into the techniques used for all of the manual sampling methods that were used during the test. The measurements shown in Table 7 were made on October 29, 2001.

Table 7. Moisture Recovery for Method 4 (Measured on 10/29/01)

Impinger Number	Impinger Solution	Weight of Impinger Contents (g)	Impinger Tip Configuration	Impinger Weight		Weight Gain (g)
				Final (g)	Initial (g)	
1	Water	100	Standard	792.8	569.3	223.8
2	Water	100	Standard	626.6	584.8	41.8
3	Empty	--	Standard	513.6	507.8	5.8
4	Silica Gel	300	Standard	771.0	761.3	9.7
			Total Weight Gain (g)			**281.1**

Volume of Dry Flue Gas Sampled at Standard Conditions (dscf)

The volume of dry flue gas sampled under standard conditions was calculated by

$$V_{m(std)} = 17.64 \times y \times V_m \times \left[\frac{P_{bar} + \dfrac{\Delta H}{13.6}}{460 + T_m} \right] = 47.632 \; dscf \qquad (4\text{-}6)$$

where:

$V_{m(std)}$ = volume of dry gas sampled at standard conditions, dry standard cubic feet (dscf)

V_m = volume of gas metered, cubic feet, dry (49.418 ft³)

y = dry gas meter calibration factor (0.980)

P_{bar} = barometric pressure at measurement site, inches of mercury (30.24 in.)

ΔH = sampling rate, measured as differential pressure at the meter orifice, inches of water (1.82 in.)

T_m = dry gas meter temperature, °F (84.7 °F).

The constant 17.64 was used for conversion to standard conditions; 460 is 0 °F in degrees Rankin. Using measured values from the field data sheet, the volume of dry flue gas sampled at standard conditions is calculated to be 47.632 dscf.

Volume of Water Vapor at Standard Conditions (dscf)
The volume of water vapor under standard conditions was calculated by

$$V_{w(std)} = 0.04707 \times V_{lc} = 13.231 \text{ dscf} \tag{4-7}$$

where:
$V_{w(std)}$ = volume of water vapor at standard conditions, dry standard cubic feet (dscf)
V_{lc} = volume of liquid catch (281.1 mL).

The constant 0.04707 is the standard cubic feet per gram (or milliliter) of water at standard conditions. Using the total weight gain for water determined using Method 4 (Table 7, above), the volume of water vapor at standard conditions is calculated to be 13.231 dscf.

Calculation of Moisture/Water Content (as percent volume)
The moisture content of the gaseous stack emissions is calculated by

$$H_2O\%V = 100 \times \frac{V_{w(std)}}{V_{w(std)} + V_{m(std)}} = 21.7\%V \tag{4-8}$$

Using values measured using EPA Method 4 and values calculated previously, the moisture content was calculated to be 21.7%V.

Calculation of Dry Mole Fraction of Flue Gas
The dry mole fraction of flue gas is calculated by

$$M_{fd} = 1 - \frac{H_2O\%V}{100} = 0.783 \tag{4-9}$$

where:
M_{fd} = dry mole fraction of flue gas.

Using the percent moisture determined above, the dry mole fraction of flue gas is calculated as 0.783.

Setup of the Dilution Sampling System

The Recovery Boiler No. 5 sampling location was the vertical wall of a boiler duct, with the sampling port elevated approximately 50 feet above ground level (schematic diagram of test site in Figure 3). The area around the sampling port was 16 to 17 feet long and approximately 36 inches wide. Access to this location was by a catwalk-type platform. The whole site was in a "welled" area and enclosed on three sides with limited access from above because of pipes and duct work. The large pieces of the dilution sampling system (i.e., the dilution sampling system itself and the control unit) were lifted up to the sampling location using a crane provided and operated by the facility, then rolled into position at the sampling port (Figure 4) on an elevated secondary platform constructed to facilitate rolling the sampling unit along a corridor, which had railings on one side.

Since the elevated walkway shown in Figure 3 allowed minimal space around the dilution sampling unit, the control unit for the dilution sampling system was located on the opposite side of the elevated walkway and connected to the dilution sampling unit by approximately 10 feet of flexible tubing. The dilution sampling system positioned at the sampling location is shown during operation in Figure 5.

Figure 6 shows the sampling probe installed in the 6 in. flanged port used for sampling.

The control module (Figure 7) was located on the opposite side of the elevated walkway, connected to the dilution sampling unit using the flexible tubing visible at the left side of the control unit.

An ELPI, manufactured by Dekati (Figure 8), with associated laptop computer, was also connected to the sampling module together with other sample collection arrays; one sample collection array is visible in the background.

The dilution system sampling module with all sample collection arrays and instruments attached is shown in Figure 9. Note the ELPI in the foreground and the various sample collection arrays (the white filter holders are readily visible) attached to the various ports of the dilution system sampling module.

Figure 5. Dilution Sampling System Positioned at the Sampling Location During Operation.

Figure 6. Dilution Sampling Probe Installed in 6-in. id Flanged Port.

Figure 7. Dilution System Control Module Positioned at the Sampling Location.

Figure 8. Dilution System with Sample Collection Arrays and Instruments Attached.
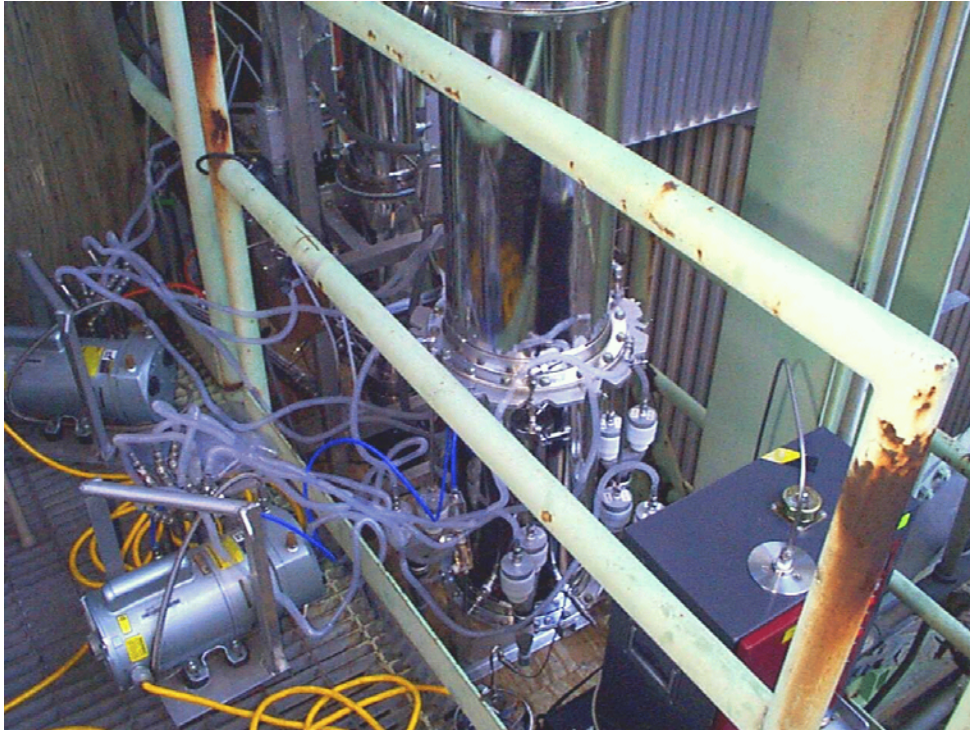
Figure 9. Dilution System Sampling Module with All Sample Collection Arrays and Instruments Attached. White Filter Holders Are Readily Visible.

Sample collection arrays were transported intact to the recovery area in the mobile laboratory (note two assembled collection arrays on the table in front of the analyst) and disassembled. Samples were then labeled, packaged for transport, and placed in a chest-style freezer. Chain of custody forms for the samples are shown in Appendix B.

Pre-Test Leak Check

To perform a pre-test leak check on the assembled dilution sampling system in the field, the end of the probe was plugged with a Swagelok fitting. Solvent-cleaned blank-off plates were inserted in place of the orifice plates at the orifice meter run flanges using gaskets on each side. A new, tared, 8- × 10-in. quartz filter was inserted into the filter holder, and the fittings were carefully sealed. A vacuum pump was attached to the residence chamber, and a Magnehelic gauge was attached to an available port. The valve between the pump and the chamber was opened, and the vacuum was read as the pump was turned on. As the reading passed 27 in., a stopwatch was started and the valve between the pump and the chamber was closed. The leak rate was timed between 25 to 20 in. and again from 20 to 15 in., and the two times were averaged. Using the recorded data, the leakage rate in cubic feet/minute was calculated according to Equation 4-10.

Figure 10. Recovery Area for Dilution Sampling System Sample Collection Arrays.

$$\text{leakage rate} = \frac{\Delta P}{\Delta T} \times V \times CF < 0.1 \text{ ft/min} \qquad (4\text{-}10)$$

where:

leakage rate = rate of leakage (ft³/min)

ΔP = change in pressure (in. water)

ΔT = time increment (sec)

V = volume of the evacuated dilution sampler (15.3 ft³)

CF = unit conversion factors (60 sec/min; 1 atm/406.8 in. water)

The criteria for an acceptable leak are less than or equal to 0.1 ft³/ min, or more than 1 min 53 sec for a pressure change of 5 in. water. For this test, an average time of 1 min 51 sec was required for a 5-in. pressure change to occur. The resulting leak rate was 0.1 ft³/min, satisfying the criteria for acceptability.

Orifice Flow Check

Critical orifice flows on the sampling pumps were checked without sample collection arrays in place by using a rotameter to verify that the channels on sampling array pumps were

the specified flow rate of 16.7 L/min. Rotameters were calibrated with a National Institute of Standards and Technology (NIST) traceable electronic bubble flow meter, and the readings were converted to flow (liters per min) using a spreadsheet.

Determination of Test Duration

To ensure the best possible collection of PM, the sampling tests were conducted for the maximum amount of time permitted by the facility (eight hours).

Canister/Veriflow Blanks

Prior to deployment in the field, SUMMA-polished canisters and Veriflow canister filling units were cleaned, and blank analysis was performed in the laboratory. All units met the cleanliness criterion of less than 10 ppbC (parts per billion carbon, Table 8).

Table 8. Blank Values for Veriflows and Canisters

Unit	Blank Value (ppbC)
Veriflows	
EPA Unit #418 (Source Veriflow)	0.3
ERG-1 Ambient Veriflow	1.2
EPA Unit #315 (Dilution Veriflow)	6.3
Canisters	
4030	2.4
1439	1.4
1435	3.7
4010	1.1
1480	1.4
3970	0.0
1892	0.1
4039	0.2

Determination of Flow Rates

A Visual Basic macro was written to process raw data files of flow rate information and convert this information to actual flow based on temperature, pressure, and calibration data. For venturi flows, the macro converted differential pressure into a reported flow rate. The square root of the differential pressure was then multiplied by a previously determined

calibration factor based on the flowing temperature, and the resulting value was converted to standard liters per minute (sL/min) using Ideal Gas Law relationships (1 atm, 70 °F).

Calibration data for the venturi were generated by placing a dry gas meter at the inlet to the sample probe. The flows reported by the data acquisition system were corrected to actual liters per minute (aL/min) and compared to those produced by the dry gas meter corrected to the venturi conditions. An Excel macro automatically selected a correct calibration value to be applied based on the flowing temperature.

Since the actual venturi flow was dependent upon the operating conditions, the set point value displayed and entered on the viewing screens needed to be adjusted to achieve the desired flow. Information to be entered included the desired flow, flow temperature, flow pressure, and barometric pressure; the Excel macro automatically selected the correct value to be applied based on the flow temperature.

Sample Collection Arrays

Prior to actual testing (Test Run #1, 10/30/01; Test Run #2, 10/31/01; Test Run #3, 11/01/01), sample collection arrays were attached to various ports on the dilution sampling system, as shown in Figure 11. Ten sampling ports were available and were attached to either the dilution chamber or the residence chamber (available sampling ports are shown in Figure 1.). The following sample collection arrays were used for Tests #1, #2, and #3:

Dilution Chamber Sample Collection Arrays

Samples of the dilution air were collected to evaluate the analyte background in the dilution air.

- *Dilution Chamber Collection Array D1, Port #D1*
  Sample Collection Array D1 collected gas-phase semivolatile organic compounds, particle-bound organic materials, and metals. The array consisted of a cyclone separator to remove particulate matter with an aerodynamic diameter greater than 2.5 μm. One leg contained a quartz filter followed by two PUF sampling modules in series. The other leg of Array D1 consisted of a Teflon filter.
- *Dilution Chamber Collection Array D2, Port #D2*
  Sample Collection Array D2 collected fine particulate matter and gas-phase organic compounds. This array consisted of a single filter unit followed by a SUMMA polished stainless steel canister.

Figure 11. Sample Collection Arrays Used with Recovery Boiler No. 5.

- *Dilution Chamber Collection Array D3, Port #D3*
  Sample Collection Array D3 collected carbonyl compounds using three DNPH impregnated silica gel sampling cartridges in series and a pump.

Residence Chamber Sample Collection Arrays

Samples of the air were collected from the residence chamber to evaluate the analyte presence in diluted stationary source air.

- *Residence Chamber Sample Collection Array R2, Port #R2*
  Sample Collection Array R2 collected fine particulate matter. The array consisted of a 2.5 μm cyclone followed by two identical legs containing Teflon filters.
- *Residence Chamber Sample Collection Array R3, Port #R3*
  Sample Collection Array R3 collected fine particulate matter and carbonyl compounds. This array consisted of a pair of carbonyl collection cartridges in series, with a pump.
- *Residence Chamber Sample Collection Array R4, Port #R4*
  Sample Collection Array R4 collected fine particulate matter on paired quartz filters for total carbon and elemental analysis, as well as semivolatile organic compounds using two PUF sampling modules in series. This sampling array consisted of a 2.5 μm cyclone with two quartz filters in parallel; one of these quartz filters was followed by two PUF sampling modules in series.
- *Residence Chamber Sample Collection Array R5, Port #R5*
  Sample Collection Array R5 collected fine particulate matter and gas-phase organic compounds. This array consisted of a single Teflon filter unit followed by a SUMMA polished stainless steel canister.
- *Residence Chamber Sample Collection Array R6, Port #R6*
  Sample Collection Array R6 collected fine particulate matter. This array consisted of a 2.5 μm cyclone followed by two identical legs containing Teflon filters.
- *Residence Chamber Sample Collection Array R8, Port #R8*
  Sample Collection Array R8 collected fine particulate matter on paired quartz filters for total carbon and elemental carbon analysis and collected semivolatile organic compounds using two PUF sampling modules in series. This sample collection array consisted of a 2.5 μm cyclone with two quartz filters in parallel; one of these quartz filters was followed by two PUF sampling modules in series.
- *Residence Chamber Sample Collection Array R10, Port #R10*
  Sample Collection Array R10 collected fine particulate matter on two quartz filters in parallel and collected semivolatile organic compounds on two XAD-4-coated

denuders in series and on two PUF sampling modules in series. This sample collection array consisted of a 2.5 µm cyclone immediately prior to two XAD-4-coated annular denuders in series, followed by two identical legs each containing a quartz filter; one of these quartz filters is followed by two PUF sampling modules in series.

Use of the ELPI Particle Size Distribution Analyzer

In addition to the sample collection arrays, an ELPI continuous particle size analyzer was used on the residence chamber to collect data on particle size distribution in the diluted source sample. The ELPI measures airborne particle size distribution in the size range 30 to 1000 nm (0.03 to 10 µm) with 12 channels. The principle of operation is based on charging, inertial classification, and electrical detection of the aerosol particles. The instrument consists primarily of a corona charger, low pressure cascade impactor, and multichannel electrometer.

In operation, the sample first passed through a unipolar positive polarity charger in which particles in the sample were electrically charged by small ions produced in a corona discharge. After the charger, the charged particles were size classified on a low pressure impactor. The impactor is an inertial device classifying the particles according to their aerodynamic diameter, not their charge. The stages of the impactor are insulated electrically, and each stage is connected individually to an electrometer current amplifier. The charged particles collected in a specific impactor stage produce an electrical current, which is recorded by the respective electrometer channel. A larger charge correlates to a higher particle population. The current value of each channel is proportional to the number of particles collected and thus to the particle concentration in the particular size range. The current values are converted to an aerodynamic size distribution using particle size-dependent relationships describing the properties of the charger and the impactor stages.

The precalibrated instrument was transported to the field and placed in the vicinity of the sample collection arrays on a sturdy table. Twenty minutes prior to the start of the test run, the ELPI was turned on to warm up and equilibrate. The computer was turned on, and the sample acquisition program was initiated in the flush mode. On the ELPI, the sample flow was manually adjusted to the manufacturer's specifications (vacuum setting to 100 ± 1 mbar). The ELPI was set to monitor the range of 0.03 to 10 µm (30 to 1000 nm) midpoint particle diameter to provide an indication of particle size distribution in the range below 10 µm, as well as the concentration distribution of the particles within this size range. The data system was initially set up to collect data for particles ranging from 0.03 to 10 µm; the particles were collected over the duration of each test.

Shortly before the initiation of the test run, the data system was programmed to collect particulate data that encompassed the expected duration of the test run. The ELPI was the last piece of equipment connected to the residence chamber. When the test run was started, the inlet line was attached to the port, and flushing of the inlet line was terminated by the data system. Data were continually saved on the computer hard drive, and a real-time display on the computer screen showed the particle distribution. Graphical presentations of the data were prepared off-line.

For each run, impactor stages were covered with tared aluminum foils. After test runs, the foils were recovered and individually weighed for additional mass data.

Measurement of O_2 and CO_2 Process Concentrations

Measurements taken using Fyrite bulbs every 30 minutes across the duration of the test each day (17 points) were used to determine O_2 and CO_2 concentrations during test conditions.

Operation of the Dilution Sampling System with Sample Collection Arrays

After completion of the pre-test run on 10/29/01to establish experimental parameters for the test, the dilution sampling system was prepared for a full test run. Sampling probe temperature set points were set equal to or slightly above the measured stack temperature. The system was equilibrated at temperature. Sample collection arrays were loaded with appropriate collection media, and flow/leak checks were performed with each array to ensure that the entire system would be leak free in operation. Sampler flows were set just before initiation of the test to prevent heat loss from the heated probe. The blower and the ring compressor were started to achieve a slightly positive pressure; then the blower flow was adjusted to cause the stack gas to flow into the dilution sampling system after the probe was inserted into the duct. Sample collection array pumps were started, and valves for the SUMMA canisters were opened to initiate canister air sample collection. The sampling process was carefully monitored by the sampling team based on the pressure change in the canister to ensure that the filters were not overloaded in the course of sampling. Start time and other pertinent data were recorded.

At the end of the eight-hour sampling interval, the sampling process was stopped by stopping the pumps for the sample collection arrays and closing the valves on the SUMMA canisters. The probe was withdrawn from the stack, the blower and ring compressor were

turned off, and heaters were turned off and allowed to cool. Each sample collection array was leak checked at the end of the sampling period and ending flow rates were documented. Experimental parameters for Tests 1, 2, and 3 are shown in Tables 9 to 11; blower flow, dilution flow, and venturi flow for Tests 1, 2, and 3 are shown graphically in Figures 12 through 20. The dilution ratio is defined as the sum of the dilution airflow rate plus the sample gas flow rate divided by the sample gas flow rate. For the three replicate test runs conducted on the recovery boiler, the dilution ratio averaged 45.5.

Table 9. Run Time Summary Information, Test Run #1 (10/30/01)

Run Parameter	Value
Start Time	8:46:55 A.M.
End Time	4:49:20 P.M.
Run Time	482.42 min
Barometric Pressure	29.93 in. Hg
Nozzle Size	#8 (186.5 °C, 2745.8 ft/min)
Canister Flow	dilution canister, 8.125 cm^3/min
	residence chamber canister 8.125 cm^3/min
	ambient canister, 8.125 cm^3/min

Measurement Parameter	Value
Venturi Flow	29.31 aL/min[a] (20.25 sL/min[b])
PT-101[c]	-1.21 in. WC[d]
TE-104[e]	151.71 °C
Dilution Flow	863.23 aL/min (861.48 sL/min)
PT-102	-1.52 in. WC
TE-108	19.32 °C
Blower Flow	861.19 aL/min (819.92 sL/min)
PT-103	-16.74 in. WC
TE-105	22.15 °C
Dilution Ratio	43.61
TE-101	101.28 °C
TE-102	149.88 °C
TE-103	149.89 °C

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Table 9. (concluded)

Sample Flow Rates

Sample	Location	Port	Start/ End	Flow (sL/min)	Flow (aL/min)	Average Flow (sL/min)
$PM_{2.5}$	Dilution Air	—	start	17.08	17.10	17.08
$PM_{2.5}$	Dilution Air	—	end	17.08	17.10	
$PM_{2.5}$	Residence Chamber	10	start	15.59	15.61	15.01
$PM_{2.5}$	Residence Chamber	10	end	14.43	14.45	
$PM_{2.5}$	Residence Chamber	8	start	17.38	17.40	17.38
$PM_{2.5}$	Residence Chamber	8	end	17.38	17.40	
$PM_{2.5}$	Residence Chamber	6	start	17.69	17.71	17.69
$PM_{2.5}$	Residence Chamber	6	end	17.69	17.71	
$PM_{2.5}$	Residence Chamber	4	start	17.53	17.55	17.46
$PM_{2.5}$	Residence Chamber	4	end	17.38	17.40	
$PM_{2.5}$	Residence Chamber	2	start	17.69	17.71	17.69
$PM_{2.5}$	Residence Chamber	2	end	17.69	17.71	
DNPH	Residence Chamber	3	start	1.51	1.51	1.49
DNPH	Residence Chamber	3	end	1.46	1.46	
DNPH	Dilution Chamber	3	start	1.26	1.27	1.25
DNPH	Dilution Chamber	3	end	1.24	1.24	

[a] aL/min = actual liters per minute
[b] sL/min = standard liters per minute
[c] PT = pressure transducer
[d] WC = water column
[e] TE = thermocouple

Table 10. Run Time Summary Information, Test Run #2 (10/31/01)

Run Parameter	Value
Start Time	7:59:03 A.M.
End Time	3:59:05 P.M.
Run Time	480.03 min
Barometric Pressure	29.91 in. Hg
Nozzle Size	#8 (186.5 °C, 2745.8 ft/min)
Canister Flow	dilution canister, 8.958 cm^3/min
	residence chamber canister 8.125 cm^3/min

Table 10. (concluded)

Measurement Parameter	Value
Venturi Flow	30.57 aL/min[a] (18.88 sL/min[b])
PT-101[c]	-1.13 in. WC[d]
TE-104[e]	201.95 °C
Dilution Flow	865.21 aL/min (859.33 sL/min)
PT-102	-1.27 in. WC
TE-108	20.77 °C
Blower Flow	858.83 aL/min (813.40 sL/min)
PT-103	-15.82 in. WC
TE-105	24.23 °C
Dilution Ratio	46.59
TE-101	182.43 °C
TE-102	196.83 °C
TE-103	197.05 °C

Sample Flow Rates

Sample	Location	Port	Start/ End	Flow (sL/min)	Flow (aL/min)	Average Flow (sL/min)
PM$_{2.5}$	Dilution Air	—	start	17.65	17.44	17.65
PM$_{2.5}$	Dilution Air	—	end	17.65	17.44	
PM$_{2.5}$	Residence Chamber	10	start	17.65	17.44	17.65
PM$_{2.5}$	Residence Chamber	10	end	17.65	17.44	
PM$_{2.5}$	Residence Chamber	8	start	17.80	17.59	17.65
PM$_{2.5}$	Residence Chamber	8	end	17.50	17.29	
PM$_{2.5}$	Residence Chamber	6	start	17.65	17.44	17.65
PM$_{2.5}$	Residence Chamber	6	end	17.65	17.44	
PM$_{2.5}$	Residence Chamber	4	start	17.80	17.59	17.73
PM$_{2.5}$	Residence Chamber	4	end	17.65	17.44	
PM$_{2.5}$	Residence Chamber	2	start	17.80	17.59	17.80
PM$_{2.5}$	Residence Chamber	2	end	17.80	17.59	
DNPH	Residence Chamber	3	start	1.23	1.21	1.18
DNPH	Residence Chamber	3	end	1.14	1.12	
DNPH	Dilution Chamber	3	start	1.18	1.17	1.16
DNPH	Dilution Chamber	3	end	1.14	1.12	

[a] aL/min = actual liters per minute
[b] sL/min = standard liters per minute
[c] PT = pressure transducer
[d] WC = water column
[e] TE = thermocouple

Table 11. Run Time Summary Information, Test Run #3 (11/01/01)

Run Parameter	Value
Start Time	7:30:05 A.M.
End Time	3:29:07 P.M.
Run Time	479.03 min
Barometric Pressure	29.85 in. Hg
Nozzle Size	#8 (186.5 °C, 2745.8 ft/min)
Canister Flow	dilution canister, 8.958 cm^3/min
	residence chamber canister 8.125 cm^3/min

Measurement Parameter	Value
Venturi Flow	30.57 aL/min[a] (18.87 sL/min[b])
PT-101[c]	-1.01 in. WC[d]
TE-104[e]	201.32 °C
Dilution Flow	870.16 aL/min (854.46 sL/min)
PT-102	-1.20 in. WC
TE-108	23.54 °C
Blower Flow	865.45 aL/min (810.83 sL/min)
PT-103	-15.93 in. WC
TE-105	26.80 °C
Dilution Ratio	46.34
TE-101	186.96 °C
TE-102	196.85 °C
TE-103	196.85 °C

Sample Flow Rates

Sample	Location	Port	Start/ End	Flow (sL/min)	Flow (aL/min)	Average Flow (sL/min)
PM$_{2.5}$	Dilution Air	—	start	17.63	17.46	17.63
PM$_{2.5}$	Dilution Air	—	end	17.63	17.46	
PM$_{2.5}$	Residence Chamber	10	start	17.32	17.16	17.24
PM$_{2.5}$	Residence Chamber	10	end	17.17	17.01	
PM$_{2.5}$	Residence Chamber	8	start	17.78	17.61	17.71
PM$_{2.5}$	Residence Chamber	8	end	17.63	17.46	
PM$_{2.5}$	Residence Chamber	6	start	17.63	17.46	17.71
PM$_{2.5}$	Residence Chamber	6	end	17.78	17.61	
PM$_{2.5}$	Residence Chamber	4	start	17.78	17.61	17.78
PM$_{2.5}$	Residence Chamber	4	end	17.78	17.61	

Table 11. (concluded)

Sample Flow Rates

Sample	Location	Port	Start/ End	Flow (sL/min)	(aL/min)	Average Flow (sL/min)
PM$_{2.5}$	Residence Chamber	2	start	17.78	17.61	17.78
PM$_{2.5}$	Residence Chamber	2	end	17.78	17.61	
DNPH	Residence Chamber	3	start	1.32	1.31	1.31
DNPH	Residence Chamber	3	end	1.29	1.28	
DNPH	Dilution Chamber	3	start	1.13	1.12	1.13
DNPH	Dilution Chamber	3	end	1.13	1.12	

[a]   aL/min = actual liters per minute
[b]   sL/min = standard liters per minute
[c]   PT = pressure transducer
[d]   WC = water column
[e]   TE = thermocouple
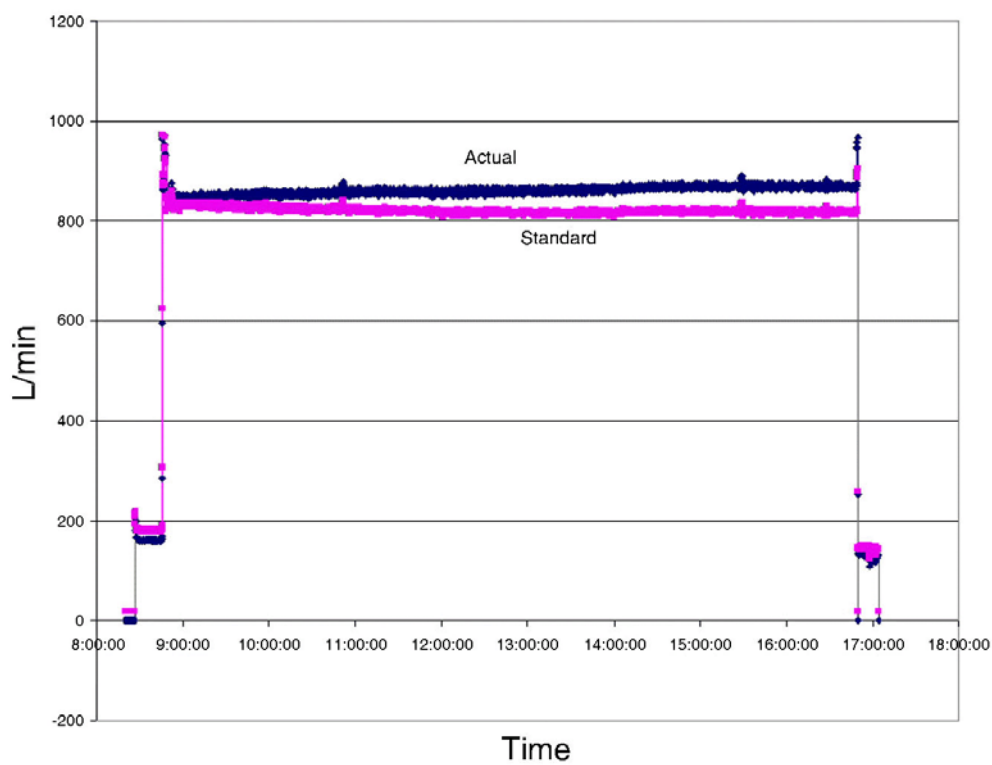
Figure 12. Blower Flow, Day 1 (10/30/01).
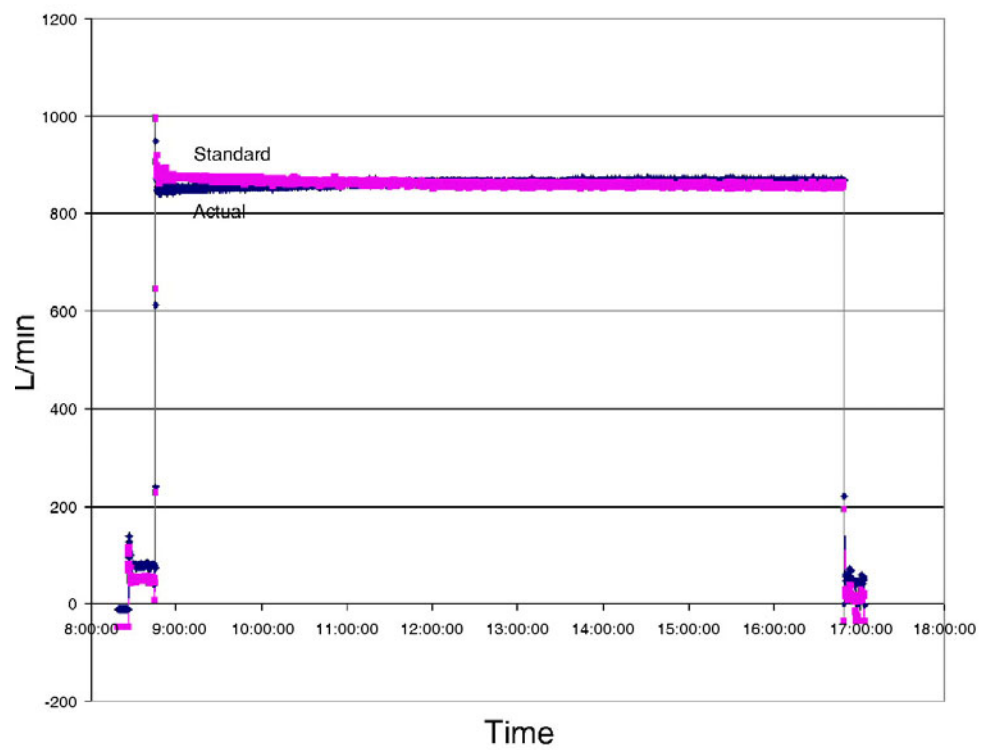
Figure 13. Dilution Flow, Day 1 (10/30/01).
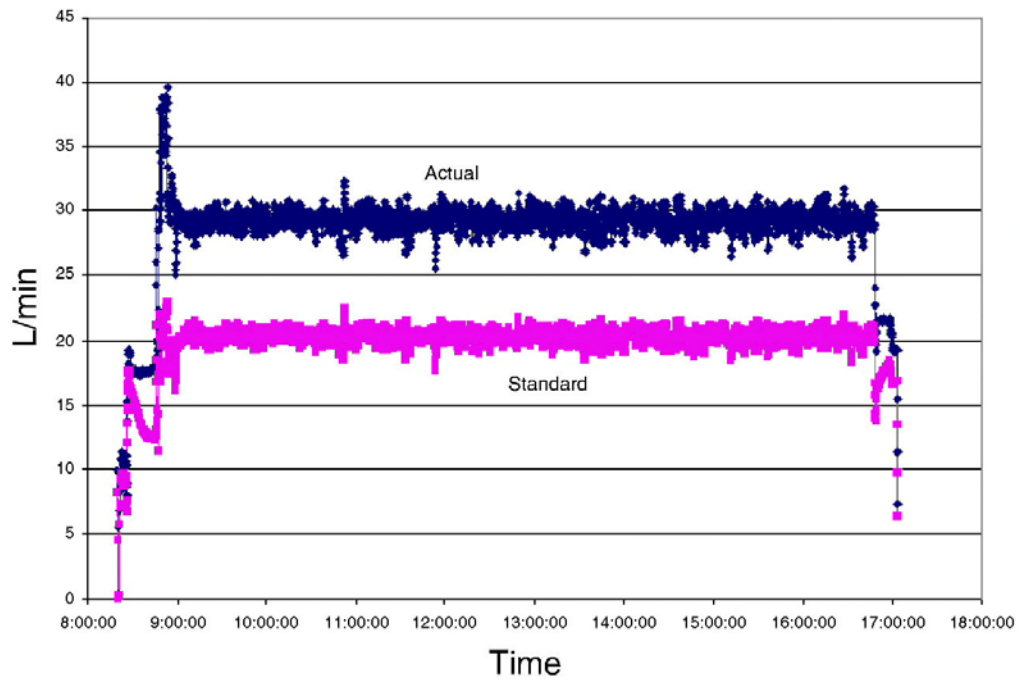
Figure 14. Venturi Flow, Day 1 (10/30/01).

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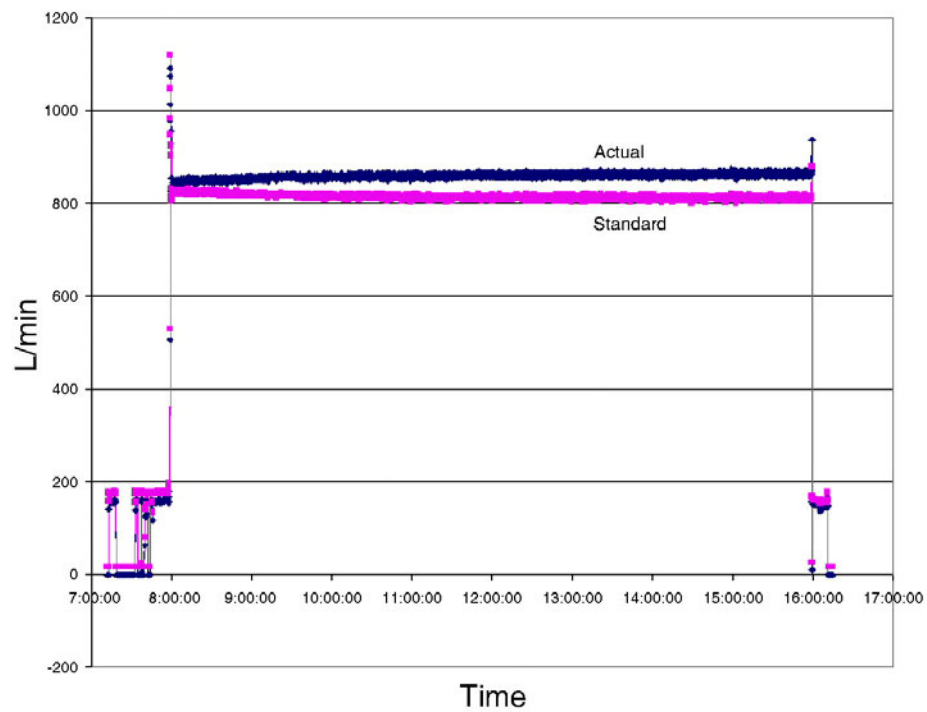
Figure 15. Blower Flow, Day 2 (10/31/01).
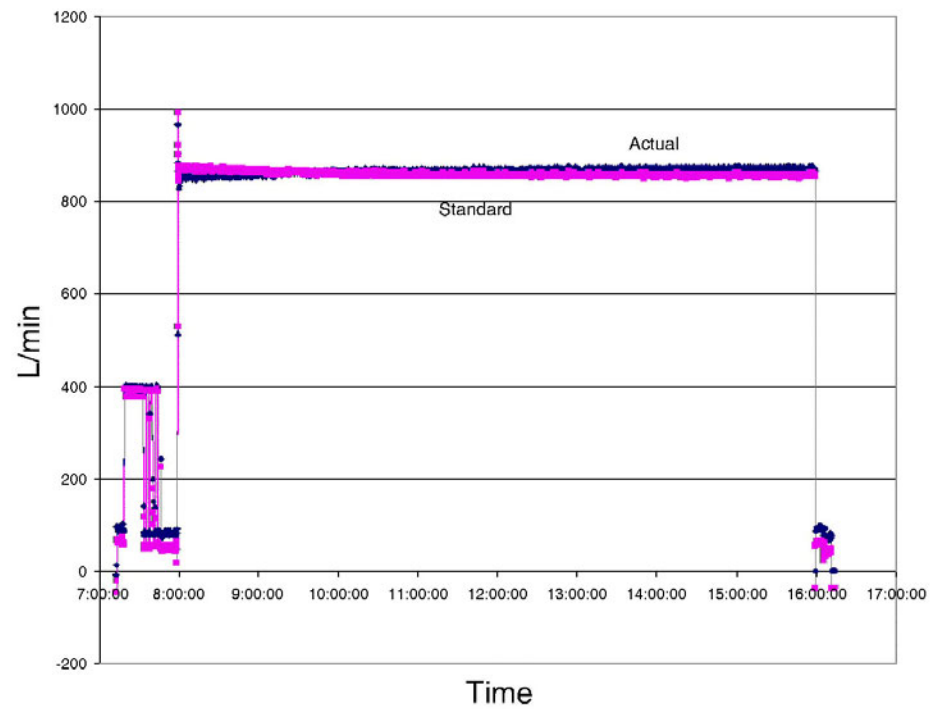
Figure 16. Dilution Flow, Day 2 (10/31/01).
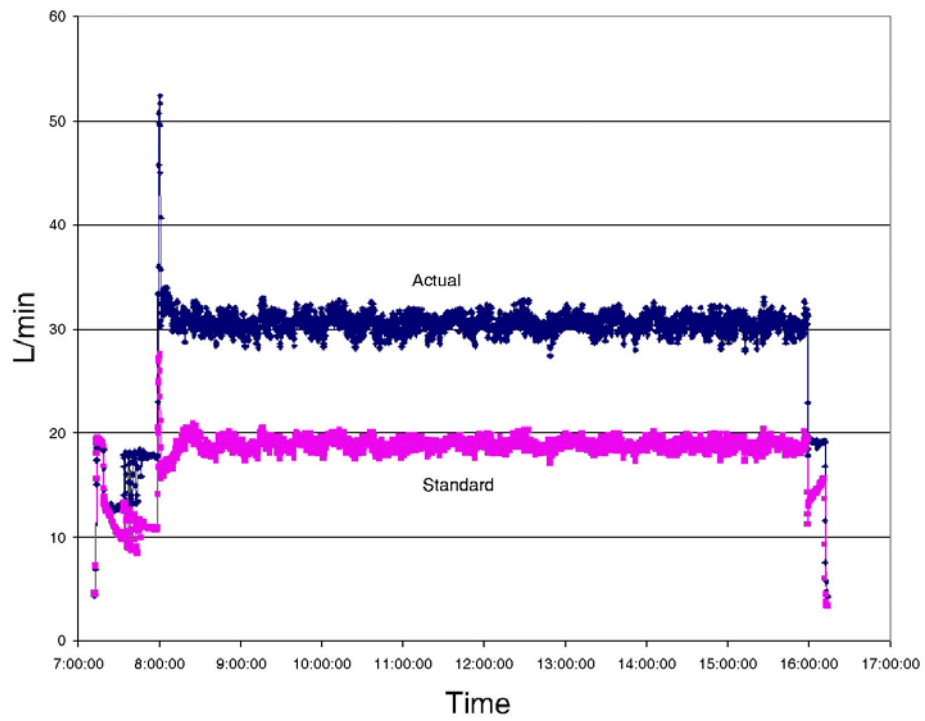
Figure 17. Venturi Flow, Day 2 (10/31/01).
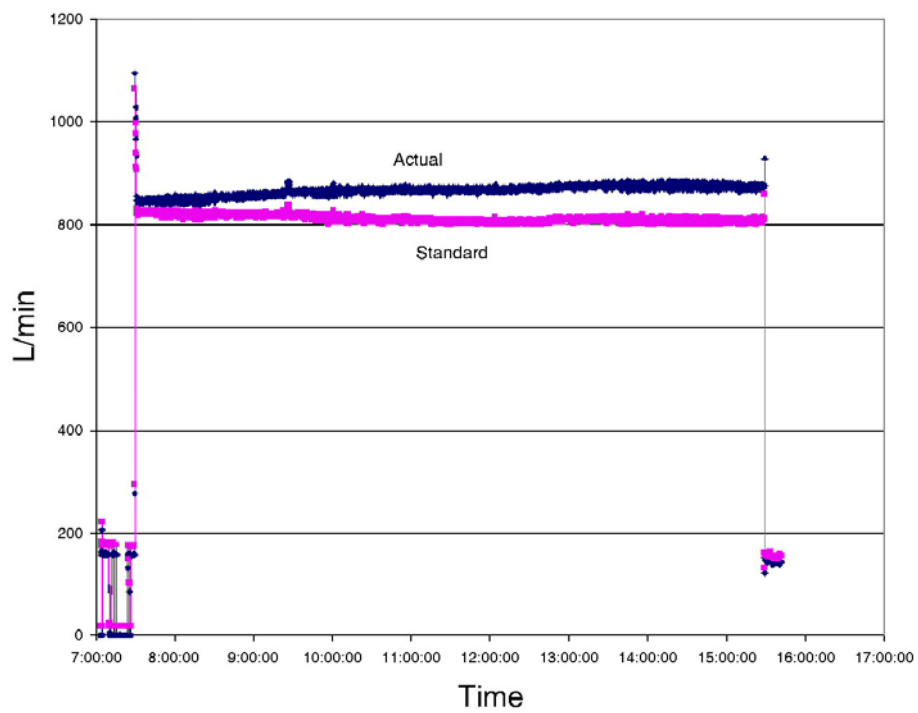
Figure 18. Blower Flow, Day 3 (11/01/01).

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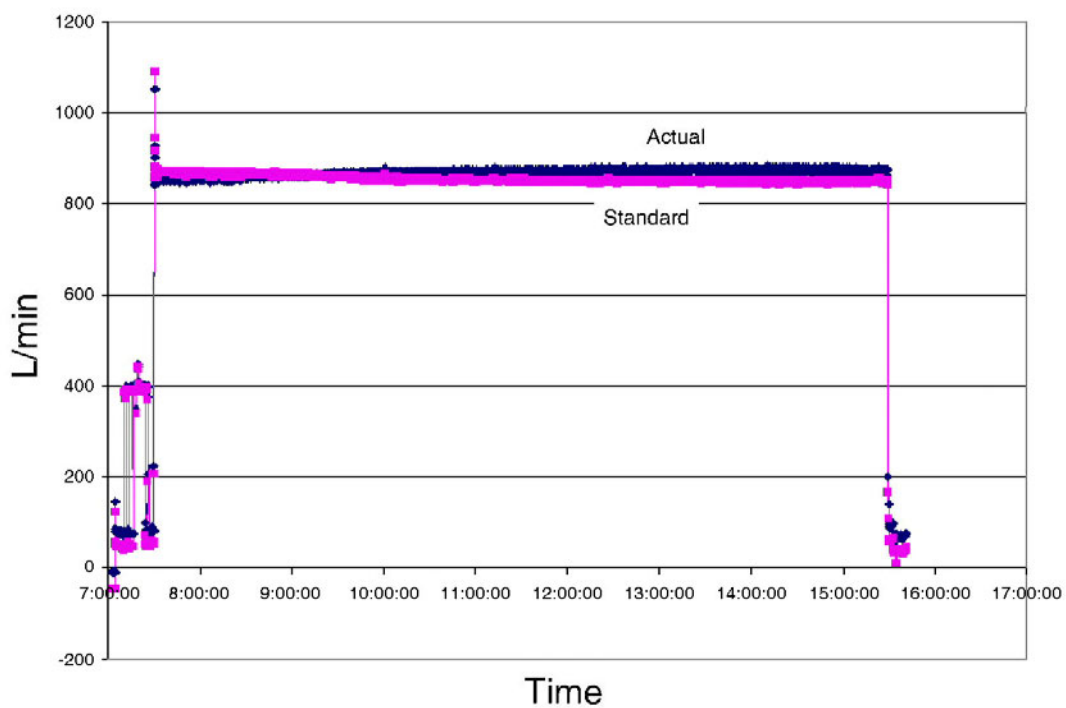
Figure 19. Dilution Flow, Day 3 (11/01/01).
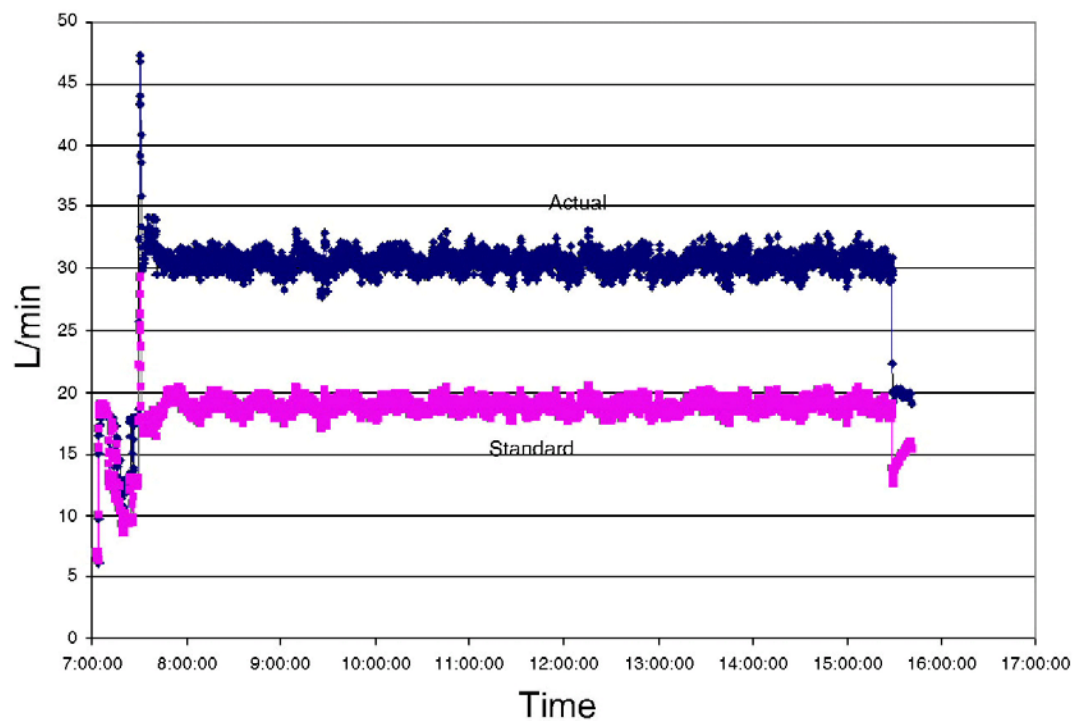
Figure 20. Venturi Flow, Day 3 (11/01/01).

Dilution System Sample Collection Arrays: Sample Recovery

At the end of the sampling period, the pumps on the dilution system were turned off, and recovery of the dilution sampling system consisted of removing the sample collection arrays and turning off the particle size analyzer. Sample collection arrays were then carried to the recovery area and disassembled, the parts were carefully labeled, and the components of the sample collection arrays were carefully packaged for transport back to the laboratories.

The sample collection arrays were removed sequentially at the cyclone connection. Each individual collection array was removed, and the ends of the assembly were covered with aluminum foil. As each sample collection array was removed from the dilution sampling system, the sampling aperture was covered to avoid introduction of any contaminants into the dilution sampling system. The ends of the sample collection array were capped and the array placed in a secure container for transport to the sample recovery area.

In the sample recovery area, the sample collection arrays were disassembled into the following components:

- PUF modules were disassembled from the sample collection array as a module. Both ends of the PUF sampling module were capped, the module placed in a sealable plastic bag, the bag appropriately labeled, and chain of custody documentation initiated.
- Filters were positioned in specific filter holder assemblies as part of several of the sample collection arrays. In the sample recovery area, the filter holder assemblies were disassembled, and the filter was removed with Teflon-tipped tweezers and placed in a prenumbered custom filter container with a locking lid. The appropriate label was affixed to the filter container, and chain of custody documentation was initiated. The filter holder assembly was reassembled without the filter, placed in a sealable plastic bag, and labeled.
- Denuders were disassembled, the ends of the sorbent tube closed with Teflon caps and sealed with Teflon tape, the sealed denuder tubes placed in a sealable plastic bag, labeled, and chain of custody documentation initiated.
- Carbonyl sampling tube assemblies (two carbonyl sampling tubes in series) were disassembled. The ends of the individual tubes were sealed with plastic caps and the sealed tubes placed in an aluminum foil packet, labeled to preserve the front/back order from the sample collection array, placed in a plastic bag, labeled, and chain of custody documentation initiated.

- Canister sampling was terminated by closing the valve on the canister at the end of the sampling period. The canister with closed valve was disconnected from the dilution sampling system and capped; chain of custody documentation was initiated.

At a later time, extraction was performed on-site for the denuders. The denuders were rinsed with a mixture of methylene chloride:acetone:hexane in a volume ratio of 2:3:5. The solvent mixture was added to the denuder, and the denuder tube was capped and shaken four times. An internal standard was added to the first extraction. The rinses were combined in a precleaned glass jar for paired denuders; the jar was labeled and sealed with Teflon tape; chain of custody documentation was initiated for the extract, and the jar was stored over ice. After extraction, the denuders and caps were dried using high purity nitrogen and capped until ready for reuse.

Denuders, PUF modules, and filters were all bagged and stored over ice. Canisters and carbonyl tubes were transported to the ERG laboratory for analysis; and the filters, PUF modules, and denuder extracts were transported to the EPA laboratory for analysis. Chain of custody documentation is supplied in Appendix B. The field sample log with sample identification is provided in Appendix C.

Laboratory Experimental Methodology

Components of the sample collection arrays, filters, DNPH-impregnated silica gel tubes used to sample carbonyl compounds, and canisters used to sample volatile organic compounds were returned for analysis to EPA and ERG laboratories (see Table 1 for responsible laboratory). The analyses described in the following sections were performed with the analytical methodology used by the respective laboratories summarized in Table 1; standard operating procedures (SOPs) (ERG) and method operating procedures (MOPs) (EPA) supporting the analyses are listed in Appendix D.

$PM_{2.5}$ Mass

Teflon membrane (Gelman Teflon) filters of 2 μm pore diameter were used to collect fine PM samples for mass determinations. Filters before and after sample collection were maintained at 20–23 °C and a relative humidity of 30%–40% for a minimum of 24 hours prior to weighing on a microbalance. Sample mass was determined by gravimetric analysis before and after sample collection.

Elemental Analysis

Individual elements above atomic number 9 (fluorine) were measured using a Philips Model 2404, wavelength-dispersive, X-ray fluorescence (XRF) spectrometer running the UniQuant program. This program gives qualitative and quantitative information on the elements present on a Teflon membrane filter. The filter to be analyzed was covered with a 0.4-µm thick Prolene film, which was attached using glue. The glue was only on the outer rim of the filter and did not interfere with the analysis. Only elements that gave amounts greater than one standard error above the detection limit were reported.

Water-Soluble Inorganic Ions

Teflon filter samples were analyzed for major inorganic anions and cations using a Dionex DX-120 ion chromatograph equipped with a 25-µL sample loop and a conductivity detector. Major ions determined were chloride, nitrate, sulfate, calcium, magnesium, potassium, and ammonium. Prior to extraction, the filters were wetted with 350 to 500 µL of ethanol. Two sequential extractions with HPLC-grade water were performed using mild sonication of the filters followed by filtration of the extracts. The two extracts were combined for analysis.

Anions were separated using an Ion Pac AS14 (4 × 250 mm) column with an alkyl quaternary ammonium stationary phase and a carbonate-bicarbonate mobile phase. Cations were separated using an Ion Pac CS12 (4 × 250 mm) column with an 8-µm poly(ethylvinylbenzene-divinylbenzene) macroporous substrate resin functionalized with a relatively weak carboxylic acid stationary phase and a sulfuric acid mobile phase. Ion concentrations were determined from four-point calibration curves using an external standard method. All samples were extracted and analyzed in duplicate or triplicate.

Elemental Carbon/Organic Carbon

Elemental carbon and organic carbon (EC/OC) content of PM samples collected on pre-fired quartz filters was determined by National Institute for Occupational Safety and Health (NIOSH) Method 5040 (NIOSH, 1994)[6] using a Sunset Laboratory thermal evolution instrument. In this method, a 1.0×1.5 cm punch of the quartz filter sample is placed in the instrument, and organic and carbonate carbon are evolved in a helium atmosphere as the temperature is raised to 850 °C. Evolved carbon is catalytically oxidized to CO_2 in a bed of granular MnO_2 then reduced to methane in a methanator. Methane is subsequently quantified by a flame ionization detector (FID). In a second stage, the sample oven temperature is reduced, an oxygen-helium mixture is introduced, and the temperature is increased to 940 °C.

With the introduction of oxygen, pyrolytically generated carbon is oxidized, and the transmittance of a laser light beam through the filter increases. The point at which the filter transmittance reaches its initial value is defined as the split between OC and EC. Carbon evolved prior to the split is considered OC (including carbonate), and carbon volatilized after the split is considered EC. Elemental carbon evolved is similarly oxidized to CO_2 and subsequently reduced to methane to be measured by the FID.

Organic Compounds

Individual organic compounds present in the fine PM collected on pre-fired quartz filters were determined by extracting the filters with hexane (two extractions) followed by a 2:1 mixture by volume of benzene and isopropanol (three extractions). Prior to extraction, the filters were composited as necessary to achieve a total of approximately 0.5 mg of OC and spiked with a mixture of 16 deuterated internal recovery standards. These standards were selected to represent the range of expected solubilities, stabilities, chromatographic retention times, and volatilities of organic compounds present in the samples. All extracts from the five extraction steps were combined and concentrated using an automated nitrogen blow-down apparatus.

An aliquot of the combined extract was derivatized with diazomethane to yield methyl esters of any fatty acids which might be present. After the methylation reaction was complete, the methylated extract aliquot was reconcentrated by nitrogen blow-down. A separate portion of the methylated extract was derivatized a second time using bis(trimethylsilyl)-trifluoroacetamide-N,O-bis(trimethylsilyl) acetamide (Sylon BFT) reagent to convert compounds such as levoglucosan and cholesterol to their trimethylsilyl (TMS) derivatives. Both derivatization reactions were performed in order to allow the compounds to be separated and eluted from a gas chromatograph column. Since the TMS derivatives are somewhat unstable over time, the silylation was carried out just prior to analysis.

Gas chromatography coupled with a mass spectrometer detector (GC/MS) was used to identify and quantify the individual organic compounds present in the extracts. A Hewlett-Packard 6890 GC equipped with an HP 5973 mass spectrometer detector was used. A 5-MS column (30 m, 0.25 mm diameter, 0.25 μm film thickness) was employed along with an injector temperature of 65 °C and a GC/MS interface temperature of 300 °C. The initial GC oven temperature was set at 65 °C with an initial hold time of 10 minutes. The oven temperature was then ramped upward at 10 °C/min to 300 °C and held at the upper temperature for an additional 41.5 minutes. Helium was used as the carrier gas (1 mL/min), and the GC was operated in the split/splitless mode.

Positive identification of target compounds was obtained by comparing mass spectra of the analytes with those obtained from 132 authentic compound standards. Iso- and anteiso-alkanes were identified using secondary standards derived from paraffin candle wax. Additional compounds were identified as "probable" based on a comparison of the GC retention times and mass spectra with commercially available spectral libraries. Quantification of the individual compounds involved referencing each compound against one or more of the deuterated internal standards spiked into the sample to correct for losses of the analytes that may have occurred in the compositing, extracting, concentrating, and derivatizing steps. An extensive set of standards of target compounds at known concentrations, which also included the deuterated internal standard compounds, was used to establish three-point or five-point calibration curves from which the concentrations of the analytes were determined.

Carbonyl Compounds

Sep-Pak chromatographic-grade silica gel cartridges impregnated with DNPH were used in series for carbonyl sample collection. The tubes were used in series to check for compound breakthrough. Following sample collection in the field, the cartridges and accompanying chain of custody documentation were transported to the ERG laboratory, where they were logged into the laboratory sample tracking system. The cartridges were extracted and analyzed for the carbonyl compounds using an adaptation of EPA Compendium Method TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)".[7] The analytical instrument was a Varian 5000 HPLC with a multiwavelength detector operated at 360 nm. The HPLC was configured with a 25-cm, 4.6-mm id, C18 silica analytical column with a 5-μm particle size. An automatic sample injector was used to inject 25-μL aliquots into the HPLC. MDLs[8] for the carbonyl analysis are shown in Appendix E.

The chromatography data acquisition system was used to retrieve data from the HPLC. The data were processed and peak identifications were made using retention times and relative retention times determined by analysis of analytical standards. After peak identifications were made, the concentration of each target analyte was determined using individual response factors for the carbonyl compounds.

Per Table 19, daily calibration checks were performed to ensure that the analytical procedures were in control. Daily quality control checks were performed after every 10 samples on the days that samples were analyzed, with compound responses within ±15% of the current calibration curve. Compound retention time drifts were also measured from the

analysis of the quality control check sample and tracked to ensure that the HPLC was operating within acceptable parameters.

As part of the daily quality control check, if the analysis of the daily quality control sample was not acceptable, a second quality control standard was injected. If the second quality control check also did not meet acceptance criteria or if more than one daily quality control check did not meet acceptance criteria, a new calibration curve (at five concentration levels) was established. All samples analyzed with the unacceptable quality control checks would be reanalyzed.

An acetonitrile system blank was analyzed after the daily calibration check and before sample analysis. The system was considered in control if target analyte concentrations were less than the current method detection limits.

Canister Analyses: Air Toxics and Speciated Nonmethane Organic Compounds

The combined analysis for gas-phase air toxics and speciated NMOCs was performed on a GC/FID/mass selective detector (MSD). A Hewlett-Packard 5971 MSD and a Hewlett-Packard 5890 Series II GC with a 60-m by 0.32-mm id and a 1-μm film thickness J&W DB-1 capillary column followed by a 2:1 splitter was used to send the larger portion of the column effluent to the MSD and the smaller fraction to the FID. The chromatograph oven containing the DB-1 capillary column was cooled to -50 °C with liquid nitrogen at the beginning of the sample injection. This temperature was held for five minutes and then increased at the rate of 15 °C per minute to 0 °C. The oven temperature was then ramped at 6 °C/minute to 150 °C, then ramped at 20 °C/minute to 225 °C and held for eight minutes. The gas eluting from the DB-1 capillary column passed through the 2:1 fixed splitter to divide the flow between the MSD and the FID.

The air toxics analysis was performed according to the procedures of EPA Compendium Method TO-15, "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canister and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)".[9] The analysis of speciated nonmethane organic compounds was performed according to the procedures of "Technical Assistance Document for Sampling and Analysis of Ozone Precursors".[7] Detection limits[8] for air toxics and for the speciated nonmethane organic compounds are shown in Appendix E.

Particle Size Distribution Data

The ELPI was operated and collected data during all three test days. Data were reduced using the Dekati software package.

Results and Discussion

Analyses were performed in either EPA or ERG laboratories according to the responsibilities delineated in Table 1 and with the analytical procedures described in the previous section. Results of these analyses are discussed in this section.

Calculated Emission Factors for PM Mass, Carbonyls, and Nonmethane Organic Compounds

Emission factors reported in Table 12 show the following:

- Uncertainties are the standard deviations of the values for each of the three tests; Uncertainties in reported emission factors reflect the fact that the recovery boiler was operated differently on Day 1 than on Days 2 and 3. Reported uncertainties are smaller if the results of only Days 2 and 3 are considered;
- Values for the Tests 2 and 3 $PM_{2.5}$ mass emissions decrease by a factor of approximately three compared to the value for Test 1. Test 1 (10/30/01) was conducted on the only day #2 oil was burned in addition to black liquor;
- The highest value for the NMOC emission factor (both speciated and total) is observed on 10/30/01, the day #2 oil was burned; and
- Carbonyl compounds show their lowest value on the day #2 oil was burned.

Table 12. Fine Particle, Carbonyl, and Nonmethane Organic Compound Emission Factors from a Recovery Boiler at a Pulp and Paper Facility

Emission Factor	10/30/01[a]	10/31/01	11/01/01	Mean	Standard Deviation
$PM_{2.5}$ Mass Emission Factor (mg/kg fuel burned)	45.41	10.57	13.92	23.30	19.22
Speciated Carbonyl Compounds Mass Emission Factor (mg/kg fuel burned)	0.0741	1.1209	0.4788	0.5579	0.7402
Total (speciated + unspeciated) Carbonyl Compounds Mass Emission Factor (mg/kg fuel burned)	0.5548	1.7382	1.0783	1.1238	0.5930
Speciated NMOC Mass Emission Factor (mg/kg fuel burned)	4.4157	2.0432	1.9267	2.7952	1.4046
Total (speciated + unspeciated) NMOC Mass Emission Factor (mg/kg fuel burned)	9.0266	4.3971	4.3294	5.9177	2.6926

[a] Fuel on this day was a mixture of black liquor and #2 distillate oil.

Gas-Phase Carbonyl Compounds

Analytical results for the carbonyl field samples for each of the three test days are shown in Table 13. Results of the analysis are reported for the difference between the summed paired DNPH-impregnated silica gel tubes for the residence chamber (RC) and the summed paired DNPH-impregnated silica gel tubes for the dilution air (DA). At the bottom of the table, the entry reported as "Total Unspeciated" is the total mass (front plus back tube) of the compounds characterized as carbonyl compounds but not identified as a specific compound because no analytical standard was available. The entry reported as "Total Speciated plus Unspeciated" includes the total mass (front and back tube) of both specifically identified carbonyl compounds and unspeciated carbonyl compounds.

A significant portion of the reported results for carbonyl compounds are the unspeciated compounds. Masses for these unspeciated carbonyl compounds are based on the calibration factor for formaldehyde. Mass fractions shown in Table 13 were calculated by dividing the mass of each species by the total (speciated plus unspeciated) mass of the carbonyl compounds found. Reported uncertainties for each species are the standard deviations of results from the three source sampling tests. For Test Days 1 and 3, more unspeciated carbonyl compounds are reported than speciated compounds. The field blank is included in Table 13 as a reference. On Test Day 1, when both #2 oil and black liquor were burned, only unspeciated carbonyl compounds show an analytical value above the field blank. On Test Days 2 and 3, when only black liquor was burned, the overall level of carbonyl compounds (both speciated and unspeciated) was significantly higher than on Day 1. Supporting data showing results for each individual carbonyl sampling tube (front and back) are included in Appendix I. Additional quality control checks for the carbonyl analysis are presented in Table 19.

Gas-Phase Air Toxic Compounds

Analytical results for the air toxics canister samples are shown in Table 14. The ERG concurrent analysis produces analytical results for both air toxics and speciated/nonspeciated nonmethane organic compounds; these results are presented separately.

Method detection limits (MDLs) for air toxic compounds are shown in Appendix E, with values typically 1.65 $\mu g/m^3$ or less. The values for the small number of air toxic compounds

Table 13. Carbonyl Compounds, Recovery Boiler: Carbonyl Compounds Collected in Dilution Air Subtracted from Carbonyl Compounds Collected in Residence Chamber, with Mass Fraction of Each Analyte, Mean, and Uncertainty

Compound	CAS No.	Field Blank (µg)	Carbonyls RC-DA 10/30/01 (µg)	Mass Fraction 10/30/01	Carbonyls RC-DA 10/31/01 (µg)	Mass Fraction 10/31/01	Carbonyls RC-DA 11/01/01 (µg)	Mass Fraction 11/01/01	Mean Mass Fraction	Uncertainty
formaldehyde	50-00-0	0.0235	0.8200	0.2447	1.2550	0.1476	1.7495	0.2953	0.2292	0.0751
acetaldehyde	75-07-0	0.0760	0.4590	0.1370	3.4015	0.4001	0.3250	0.0549	0.1973	0.1803
acetone	67-64-1	0.1965	ND[a]	ND	0.4060	0.0478	0.3090	0.0522	0.0333	0.0289
propionaldehyde	123-38-6	ND	ND	ND	0.0195	0.0023	0.0255	0.0043	0.0022	0.0022
crotonaldehyde	4170-30-0	ND	ND	ND	ND	ND	ND	ND	ND	ND
butyr/isobutyraldehyde	123-72-8	0.0460	0.0290	0.0087	0.0195	0.0023	0.0360	0.0061	0.0057	0.0032
benzaldehyde	100-52-7	ND	0.0140	0.0042	0.0100	0.0012	0.0145	0.0024	0.0026	0.0015
isovaleraldehyde	590-86-3	ND	ND	ND	ND	ND	ND	ND	ND	ND
valeraldehyde	110-62-3	0.0065	ND	ND	0.1095	0.0129	ND	ND	0.0043	0.0074
o-tolualdehyde	529-20-4	ND	0.0155	0.0046	ND	ND	ND	ND	0.0015	0.0027
m-tolualdehyde	620-23-5	ND	ND	ND	ND	ND	ND	ND	ND	ND
p-tolualdehyde	104-87-0	0.0365	0.0235	0.0070	ND	ND	ND	ND	0.0023	0.0040
hexaldehyde	66-25-1	0.0170	0.0085	0.0025	0.0205	0.0024	0.0070	0.0012	0.0020	0.0007
2,5-dimethylbenzaldehyde	5779-94-2	ND	ND	ND	ND	ND	ND	ND	ND	ND
diacetyl	431-03-8	ND	ND	ND	ND	ND	ND	ND	ND	ND
methacrolein	78-85-3	ND	ND	ND	0.0210	0.0025	ND	ND	0.0008	0.0014
2-butanone	78-93-3	0.0230	ND	ND	0.1620	0.0191	0.1850	0.0312	0.0168	0.0157
glyoxal	107-22-2	0.0900	0.0830	0.0248	0.0720	0.0085	0.0870	0.0147	0.0160	0.0082
acetophenone	98-86-2	ND	ND	ND	0.0040	0.0005	ND	ND	0.0002	0.0003
methylglyoxal	78-98-8	0.0420	0.0470	0.0140	0.0320	0.0038	ND	ND	0.0059	0.0073
octanal	124-13-0	ND	0.0270	0.0081	0.0320	0.0038	ND	ND	0.0039	0.0040
nonanal	124-19-6	0.0990	ND	ND	0.0220	0.0026	ND	ND	0.0009	0.0015

Table 13. (Concluded)

Compound	CAS No.	Field Blank (µg)	Carbonyls RC-DA 10/30/01 (µg)	Mass Fraction 10/30/01	Carbonyls RC-DA 10/31/01 (µg)	Mass Fraction 10/31/01	Carbonyls RC-DA 11/01/01 (µg)	Mass Fraction 11/01/01	Mean Mass Fraction	Uncertainty
Sum, Speciated		0.6560	1.5265	0.4555	5.5865	0.6570	2.7385	0.4622		
Sum, Unspeciated		0.7885	1.8245	0.5445	3.0195	0.3551	3.2935	0.5559		
Total (speciated + unspeciated)		1.4445	3.3510		8.5025		5.9245			
Emission Factor, mg/kg fuel	(Speciated)		0.0741		1.1209		0.4788		0.5579	0.7402
Emission Factor, mg/kg fuel	(Total)		0.5548		1.7382		1.0783		1.1238	0.5930

[a] ND = not detected.

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Table 14. Summarized Analytical Results for Air Toxics Compounds Observed on Each of the Three Test Days (10/30/01 through 11/1/01)

Compounds Detected	CAS No.	Ambient (µg/m³)	RC-DA 10/30/01 (µg/m³)	RC-DA 10/31/01 (µg/m³)	RC-DA 11/1/01 (µg/m³)
acetylene	74-86-2	0.71	1.95	0.37	0.30
propylene	115-07-1	0.26	0.38	0.29	0.27
dichlorodifluoromethane	75-71-8	2.85	0.09	ND[a]	ND
chloromethane	74-87-3	1.11	0.02	ND	ND
trichlorofluoromethane	75-69-4	1.41	ND	ND	ND
methylene chloride	75-09-2	0.15	ND	ND	ND
trichlorotrifluoroethane	26253-64-8	0.65	ND	ND	ND
1,1,1-trichloroethane	71-55-6	0.16	ND	ND	ND
benzene	71-43-2	0.74	0.60	0.76	1.08
carbon tetrachloride	56-23-5	0.65	ND	ND	ND
toluene	108-88-3	1.11	0.71	0.69	0.69
ethylbenzene	100-41-4	0.30	0.28	0.25	0.22
m-, *p*-xylene	108-38-3/106-42-3	1.40	0.69	1.00	1.11
o-xylene	95-47-6	0.35	0.37	0.25	0.23
1,3,5-trimethylbenzene	108-67-8	0.08	ND	ND	ND
1,2,4-trimethylbenzene	95-63-6	0.31	0.29	0.25	0.30

[a] ND = not detected.

actually observed occur at the lower end of the calibration curve for this analysis; analytical results are shown in Table 14. Analytical results for an ambient canister taken at the test location are included for reference. For nearly all of the air toxic compounds, the values observed in the ambient air are higher than the values observed in the stack emissions. Supporting data for the air toxics are shown in Appendix J, with analytical results for each individual canister.

Gas-Phase Speciated Nonmethane Organic Compounds

Analysis of whole air samples of dilution air and residence chamber air generated analytical data for speciated nonmethane organic compounds (SNMOC), as well as unspeciated NMOC. Analytical results are presented as mass fractions of total NMOC (speciated plus unspeciated). Mass emission factors of total SNMOC and total (speciated plus unspeciated) NMOC are also provided. Mass fractions in Table 15 represent the mass of each species divided by the total mass (speciated plus unspeciated) of the NMOCs found. Uncertainties are the standard deviations of results from the three replicate sampling runs. Results (Table 15) are reported as the difference between residence chamber samples and dilution air. The dilution air is used to dilute the stationary source matrix; samples of the

Table 15. Speciated and (Speciated + Unspeciated) NMOC Data for All Three Test Days, with Mass Fraction, Mean, and Uncertainty

Compound	CAS No.	RC-DA 10/30/01 (µg)	Mass Fraction 10/30/01	RC-DA 10/31/01 (µg)	Mass Fraction 10/31/01	RC-DA 11/01/01 (µg)	Mass Fraction 11/01/01 (µg)	Mean Mass Fraction	Uncertainty
ethylene	74-85-1	375.04	0.0162	359.87	0.0184	347.4519	0.0170	0.0172	0.0011
acetylene	74-86-2	852.09	0.0369	82.50	0.0042	30.22804	0.0015	0.0142	0.0197
ethane	74-84-0	273.60	0.0118	143.04	0.0073	181.7271	0.0089	0.0093	0.0023
propylene	115-07-1	192.04	0.0083	137.03	0.0070	106.5256	0.0052	0.0068	0.0016
propane	74-98-6	287.07	0.0124	254.38	0.0130	306.2917	0.0150	0.0135	0.0013
propyne	74-99-7	ND[a]	ND	ND	ND	ND	ND	ND	ND
isobutane	75-28-5	133.72	0.0058	115.91	0.0059	89.84241	0.0044	0.0054	0.0009
isobutene/1-butene	115-11-7/106-98-0	112.94	0.0049	204.62	0.0105	161.4141	0.0079	0.0077	0.0028
1,3-butadiene	106-99-0	ND	ND	ND	ND	ND	ND	ND	ND
n-butane	106-97-8	266.85	0.0116	235.12	0.0120	204.4243	0.0100	0.0112	0.0011
trans-2-butene	624-64-6	149.95	0.0065	144.51	0.0074	160.1486	0.0078	0.0072	0.0007
cis-2-butene	590-18-1	205.74	0.0089	178.78	0.0091	172.9703	0.0085	0.0088	0.0004
3-methyl-1-butene	563-45-1	ND	ND	ND	ND	ND	ND	ND	ND
isopentane	78-78-4	253.50	0.0110	246.68	0.0126	220.0737	0.0108	0.0115	0.0010
1-pentene	109-67-1	154.40	0.0067	127.65	0.0065	130.5928	0.0064	0.0065	0.0002
2-methyl-1-butene	563-46-2	ND	ND	ND	ND	ND	ND	ND	ND
n-pentane	109-66-0	175.96	0.0076	128.01	0.0065	168.8772	0.0083	0.0075	0.0009
isoprene	78-79-4	137.19	0.0059	98.05	0.0050	109.856	0.0054	0.0054	0.0005
trans-2-pentene	646-04-8	ND	ND	ND	ND	ND	ND	ND	ND
cis-2-pentene	627-20-3	184.67	0.0080	174.29	0.0089	223.1725	0.0109	0.0093	0.0015
2-methyl-2-butene	513-35-9	ND	ND	ND	ND	ND	ND	ND	ND
2,2-dimethylbutane	75-83-2	245.10	0.0106	343.28	0.0176	311.659	0.0152	0.0145	0.0035
cyclopentene	142-29-0	ND	ND	ND	ND	ND	ND	ND	ND
4-methyl-1-pentene	691-37-2	ND	ND	ND	ND	ND	ND	ND	ND
cyclopentane	287-92-3	172.10	0.0075	165.41	0.0085	201.9837	0.0099	0.0086	0.0012

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Table 15. (continued)

Compound	CAS No.	RC-DA 10/30/01 (µg)	Mass Fraction 10/30/01	RC-DA 10/31/01 (µg)	Mass Fraction 10/31/01	RC-DA 11/01/01 (µg)	Mass Fraction 11/01/01 (µg)	Mean Mass Fraction	Uncertainty
2,3-dimethylbutane	79-29-8	304.65	0.0132	284.72	0.0146	282.4648	0.0138	0.0139	0.0007
2-methylpentane	107-83-5	521.00	0.0226	506.97	0.0259	40.00183	0.0020	0.0168	0.0130
3-methylpentane	96-14-0	253.21	0.0110	237.98	0.0122	298.9277	0.0146	0.0126	0.0019
2-methyl-1-pentene	763-29-1	ND	ND	ND	ND	ND	ND	ND	ND
1-hexene	592-41-6	334.32	0.0145	305.61	0.0156	307.5659	0.0150	0.0150	0.0006
2-ethyl-1-butene	760-21-4	ND	ND	ND	ND	ND	ND	ND	ND
n-hexane	110-54-3	231.55	0.0100	182.81	0.0094	150.0387	0.0073	0.0089	0.0014
trans-2-hexene	4050-45-7	ND	ND	ND	ND	ND	ND	ND	ND
cis-2-hexene	7688-21-3	ND	ND	ND	ND	ND	ND	ND	ND
methylcyclopentane	96-37-7	201.48	0.0087	165.59	0.0085	181.6989	0.0089	0.0087	0.0002
2,4-dimethylpentane	108-08-7	218.50	0.0095	187.03	0.0096	214.8958	0.0105	0.0098	0.0006
benzene	71-43-2	222.75	0.0096	389.29	0.0199	448.9918	0.0219	0.0172	0.0066
cyclohexane	110-82-7	172.29	0.0075	229.37	0.0117	235.723	0.0115	0.0102	0.0024
2-methylhexane	591-76-4	128.88	0.0056	123.25	0.0063	134.9571	0.0066	0.0062	0.0005
2,3-dimethylpentane	565-59-3	385.66	0.0167	331.00	0.0169	354.2172	0.0173	0.0170	0.0003
3-methylhexane	589-34-4	285.78	0.0124	120.21	0.0062	206.5288	0.0101	0.0095	0.0031
1-heptene	592-76-7	ND	ND	172.84	0.0088	255.1943	0.0125	0.0071	0.0064
2,2,4-trimethylpentane	540-84-1	278.05	0.0120	229.19	0.0117	156.1459	0.0076	0.0105	0.0025
n-heptane	142-82-5	167.06	0.0072	152.85	0.0078	164.2417	0.0080	0.0077	0.0004
methylcyclohexane	108-87-2	239.77	0.0104	165.77	0.0085	185.5208	0.0091	0.0093	0.0010
2,2,3-trimethylpentane	564-02-3	ND	ND	ND	ND	ND	ND	ND	ND
2,3,4-trimethylpentane	565-75-3	162.91	0.0071	152.76	0.0078	131.4064	0.0064	0.0071	0.0007
toluene	108-88-3	253.41	0.0110	241.11	0.0123	256.731	0.0125	0.0120	0.0009
2-methylheptane	592-27-8	132.94	0.0058	131.50	0.0067	138.8695	0.0068	0.0064	0.0006
3-methylheptane	589-81-1	150.05	0.0065	148.36	0.0076	143.2338	0.0070	0.0070	0.0005
1-octene	111-66-0	ND	ND	ND	ND	ND	ND	ND	ND

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Table 15. (continued)

Compound	CAS No.	RC-DA 10/30/01 (μg)	Mass Fraction 10/30/01	RC-DA 10/31/01 (μg)	Mass Fraction 10/31/01	RC-DA 11/01/01 (μg)	Mass Fraction 11/01/01 (μg)	Mean Mass Fraction	Uncertainty
n-octane	111-65-9	192.49	0.0083	123.52	0.0063	160.239	0.0078	0.0075	0.0010
ethylbenzene	100-41-4	128.49	0.0056	114.55	0.0059	117.9519	0.0058	0.0057	0.0002
m-xylene/*p*-xylene	108-38-3/106-42-3	175.96	0.0076	ND	ND	205.9864	0.0101	0.0059	0.0052
styrene	100-42-5	ND	ND	ND	ND	ND	ND	ND	ND
o-xylene	95-47-6	128.78	0.0056	156.70	0.0080	210.0796	0.0103	0.0080	0.0023
1-nonene	124-11-8	ND	ND	ND	ND	ND	ND	ND	ND
n-nonane	111-84-2	103.16	0.0045	127.38	0.0065	113.8588	0.0056	0.0055	0.0010
isopropylbenzene	98-82-8	188.23	0.0082	165.77	0.0085	197.4386	0.0096	0.0088	0.0008
alpha-pinene	80-56-8	ND	ND	ND	ND	ND	ND	ND	ND
n-propylbenzene	103-65-1	107.22	0.0046	122.98	0.0063	146.4229	0.0072	0.0060	0.0013
m-ethyltoluene	620-14-4	94.56	0.0041	101.81	0.0052	88.57691	0.0043	0.0045	0.0006
p-ethyltoluene	622-96-8	188.43	0.0082	215.91	0.0110	139.0502	0.0068	0.0087	0.0022
1,3,5-trimethylbenzene	108-67-8	111.28	0.0048	80.91	0.0041	76.20716	0.0037	0.0042	0.0006
o-ethyltoluene	611-14-3	137.00	0.0059	139.93	0.0072	134.5052	0.0066	0.0066	0.0006
beta-pinene	127-91-3	129.17	0.0056	0.00	ND	ND	ND	0.0019	0.0032
1,2,4-trimethylbenzene	95-63-6	129.07	0.0056	102.26	0.0052	143.3241	0.0070	0.0059	0.0009
1-decene	872-05-9	ND	ND	ND	ND	ND	ND	ND	ND
n-decane	124-18-5	120.67	0.0052	106.66	0.0055	89.66163	0.0044	0.0050	0.0006
1,2,3-trimethylbenzene	526-73-8	ND	ND	ND	ND	ND	ND	ND	ND
m-diethylbenzene	141-93-5	124.04	0.0054	ND	ND	130.5928	0.0064	0.0039	0.0034
p-diethylbenzene	105-05-5	ND	ND	ND	ND	ND	ND	ND	ND
1-undecene	821-95-4	ND	ND	ND	ND	ND	ND	ND	ND
n-undecane	1120-21-4	130.44	0.0056	81.64	0.0042	ND	ND	0.0033	0.0029
1-dodecene	112-41-4	ND	ND	ND	ND	ND	ND	ND	ND
n-dodecane	112-40-3	ND	ND	ND	ND	ND	ND	ND	ND
1-tridecene	2437-56-1	ND	ND	ND	ND	ND	ND	ND	ND

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Table 15. (concluded)

Compound	CAS No.	RC-DA 10/30/01 (µg)	Mass Fraction 10/30/01	RC-DA 10/31/01 (µg)	Mass Fraction 10/31/01	RC-DA 11/01/01 (µg)	Mass Fraction 11/01/01 (µg)	Mean Mass Fraction	Uncertainty
n-tridecane	629-50-5	ND	ND	ND	ND	ND	ND	ND	ND
Total Speciated		**11005.22**	**0.476618**	**9237.38**	**0.4726**	**9368.49**	**0.457679**	**5922.41**	**5450.64**
Total Unspeciated		**12085.01**	**0.523382**	**10308.06**	**0.52739**	**11101.07**	**0.542321**	**6699.04**	**6147.19**
Total (speciated + unspeciated)[b]		**23090.23**		**19545.44**		**20469.56**		**21035.08**	**1838.81**
Speciated NMOC Mass Emission Factor (mg/kg fuel burned)		**4.4157**		**2.0432**		**1.9267**		**2.7952**	**1.4046**
Total (speciated + unspeciated) NMOC Mass Emission Factor (mg/kg fuel burned)		**9.0266**		**4.3971**		**4.3294**		**5.9177**	**2.6926**

[a] ND = not detected.
[b] Total NMOC with unknowns is an estimate based on propane only.

dilution air have not been exposed to the stationary source matrix. The residence chamber air represents the sample of the diluted stationary source matrix collected at the end of the residence chamber. Supporting data for the NMOC/SNMOC analyses are shown in Appendix K; mass emission factor calculations are shown in Appendix F.

EC/OC, Major Inorganic Ions, and Major Elements

Emissions of EC/OC, major inorganic ions, and major elements are reported in Table 16 as mass fraction of measured $PM_{2.5}$ mass. Results reported in Table 16 show the following:

- Organic carbon (as defined by NIOSH Method 5040) in the $PM_{2.5}$ was below detectable limits;
- Potassium is found in significant amounts in the recovery boiler emissions and is indicative of the biomass fuel contribution;
- Nearly all of the potassium in the particulate matter from the recovery boiler is water-soluble; and
- By far, the major components of the particulate matter from the recovery boiler were elemental sodium and potassium and the ions sulfate and chloride. Organics constituted a small, nonquantifiable fraction of the particulate matter recovered from the recovery boiler emissions.

Supporting data are presented in Appendices L, M, and N.

Table 16. Fine Particle Chemical Composition of Emissions from a Recovery Boiler at a Pulp and Paper Facility

	10/30/01	10/31/01	11/01/01	Mean	Uncertainty
PM-2.5 Composition (mass fraction)					
Organic Carbon	ND[a]	ND	ND	ND	—
Elemental Carbon	0.0043	0.0003	0.0010	0.0019	0.0021
Elements (mass fraction)					
Sodium	0.2952	0.2934	0.2964	0.2950	0.0088
Sulfur	0.1556	0.1742	0.1758	0.1685	0.0112
Potassium	0.0279	0.0262	0.0282	0.0274	0.0011
Chlorine	0.0207	0.0202	0.0216	0.0208	0.0007
Magnesium	0.0005	0.0029	0.0022	0.0003	0.0002
Major Water-Soluble Ions (mass fraction)					
Sulfate	0.4528	0.5056	0.5062	0.4882	0.0307
Potassium	0.0239	0.0269	0.0256	0.0255	0.0015
Chloride	0.0196	0.0201	0.0193	0.0197	0.0004

[a] ND = Not Detected

Particle Size Distribution Data

The ELPI system was operated in a "charged" mode on all three test days and collected data on particle size distribution in the range from approximately 30 to 10,000 nm. The ELPI was run in continuous mode throughout all three of the analytical runs. When the dilution sampling system was started and flow was initiated, the ELPI operational mode was changed from "flush" mode to sampling mode. Stack emissions were collected for the entire run of slightly more than eight hours.

Results of the individual runs are summarized in the following tables, diagrams, and figures. Table 17 lists the collected mass in each of twelve stages for each test day. The mean particle diameter (Di) of each stage is listed in increasing size order from 42.78 to 8328.12 nm. Also shown are the particle counts versus size expressed as log plots dN/dlog(Dp) and particle mass versus size expressed as log plots dM/dlog(Dp). A bar plot of particle mass by channel is also shown.

Foils from each impactor stage were recovered in the field for individual gravimetric mass determinations. Foils were tared before shipment to the field, used for collection with each sampling run, and individually recovered for determination of mass using a sensitive electronic balance. Plots of particle counts versus size, particle mass versus size, and particle mass versus stage are shown for each test day (Figures 21, 22, and 23). The mass of particles collected appears to be a maximum at Stage 8 (1276.71 nm) for the first two test days and at Stage 9 (2010.57 nm) on the third test day.

Semivolatile Organic Compounds

Thermal evolution analysis of fine PM samples collected on quartz filters indicated there were no detectable quantities of organic carbon in the PM emitted from the recovery boiler. Nevertheless, the presence or absence of particle-phase or gas-phase semivolatile organic compounds in the recovery boiler emissions was checked by GC/MS analysis of solvent extracts from the quartz filters and PUF plug samples collected during the tests. Results of these analyses confirmed the absence of quantifiable organic species as shown in Appendix G in which standard deviations reported for the mass emission factors of individual organic compounds equal or exceed the average values in every case.

Table 17. Particle Size Distribution Data

October 30, 2001

Stage[a]	1	2	3	4	5	6	7	8	9	10	11	12
D_i,[b] nm	42.78	80.03	132.82	208.19	320.04	506.03	803.12	1276.71	2010.57	3157.47	5212.98	8328.12
dN/dlog(Dp),[c] 1/cm^3	1.02×10^4	0.00	0.00	0.00	6.02×10^2	2.28×10^3	2.85×10^3	1.17×10^3	1.74×10^2	6.94	8.04×10^{-1}	1.76×10^{-1}
M,[d] mg/m^3	0.0001	ND[e]	ND	ND	0.0019	0.0327	0.1473	0.2703	0.1352	0.0240	0.0135	0.0096
dM/dlog(Dp), mg/m^3	4.16×10^{-4}	0.00	0.00	0.00	1.03×10^{-2}	1.55×10^{-1}	7.73×10^{-1}	1.27	7.42×10^{-1}	1.14×10^{-1}	5.96×10^{-2}	5.32×10^{-2}

October 31, 2001

Stage	1	2	3	4	5	6	7	8	9	10	11	12
D_i, nm	42.78	80.03	132.82	208.19	320.04	506.03	803.12	1276.71	2010.57	3157.47	5212.98	8328.12
dN/dlog(Dp), 1/cm^3	0.00	0.00	105.	0.00	26.3	756.	1.09×10^3	480.	64.1	1.72	4.63×10^{-1}	0.00
M, mg/m^3	ND	ND	ND	ND	0.0001	0.0108	0.0563	0.1109	0.0497	0.0060	0.0078	ND
dM/dlog(Dp), mg/m^3	0.00	0.00	1.29×10^{-4}	0.00	4.52×10^{-4}	5.13×10^{-2}	2.95×10^{-1}	5.23×10^{-1}	2.73×10^{-1}	2.84×10^{-2}	3.43×10^{-2}	0.00

November 1, 2001

Stage	1	2	3	4	5	6	7	8	9	10	11	12
D_i, nm	42.78	80.03	132.82	208.19	320.04	506.03	803.12	1276.71	2010.57	3157.47	5212.98	8328.12
dN/dlog(Dp), 1/cm^3	0.00	0.00	0.00	0.00	0.00	723.	1.15×10^3	698.	256.	26.8	8.75	0.00
M, mg/m^3	ND	ND	ND	ND	ND	0.0103	0.0596	0.1614	0.1988	0.0927	0.1466	ND
dM/dlog(Dp), mg/m^3	0.00	0.00	0.00	0.00	0.00	4.91×10^{-2}	3.13×10^{-1}	7.61×10^{-1}	1.09	4.42×10^{-1}	6.49×10^{-1}	0.00

[a] Stage shows the individual stages of the 12-stage ELPI.
[b] D_i is the midpoint value used in the distribution calculations; D_i is the geometric mean of the boundaries of each stage.
[c] Particle counts are expressed as log dN/dlogDp, 1/cm^3, or as log dM/dlogDp, mg/cm^3, and plotted vs. particle diameter (Dp).
[d] M is the mass distribution, which gives the total mass of all particles in each size range. Mass distribution is calculated by multiplying the current distribution by the conversion vector and by a vector formed from the masses of spheres having diameter equal to midpoint values (D_i) of each stage.
[e] ND = not detected.

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Figure 21. Plots of Particle Counts vs. Size, Particle Mass vs. Size, and Particle Mass per Stage for Test Day 1 (10/30/01).
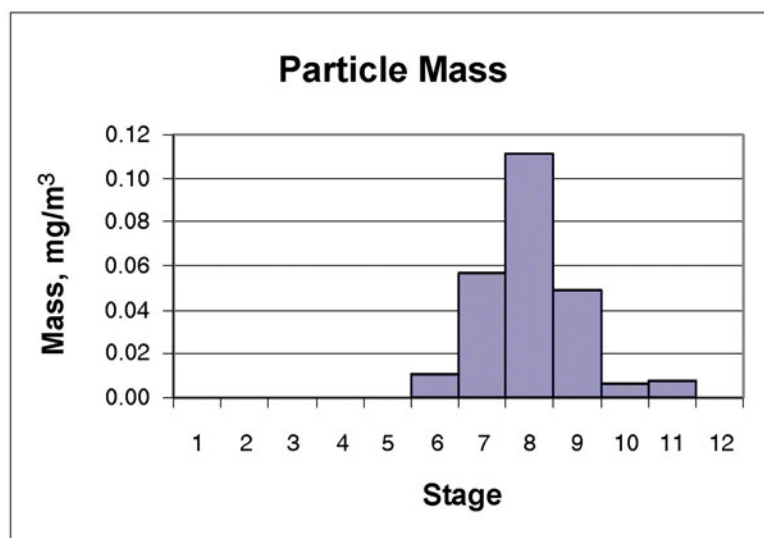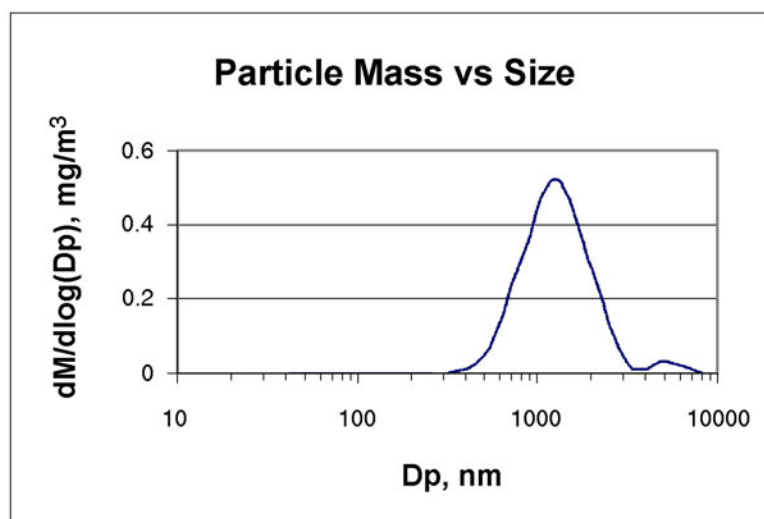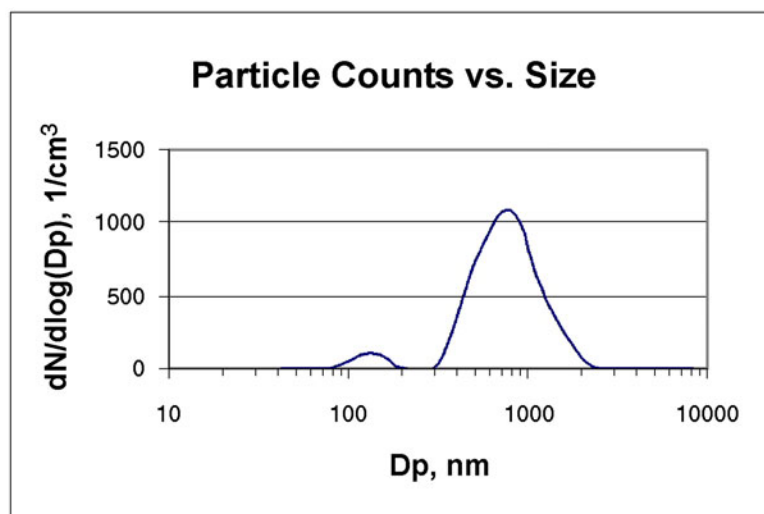
Figure 22. Plots of Particle Counts vs. Size, Particle Mass vs. Size, and Particle Mass per Stage for Test Day 2 (10/31/01).
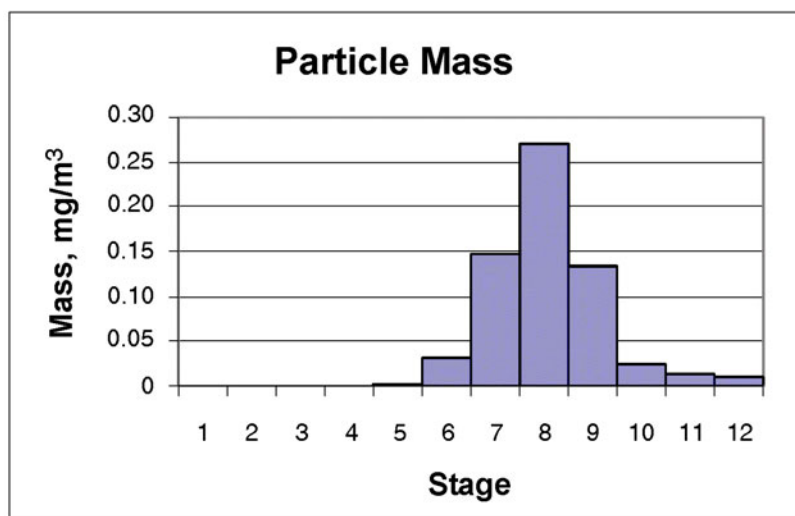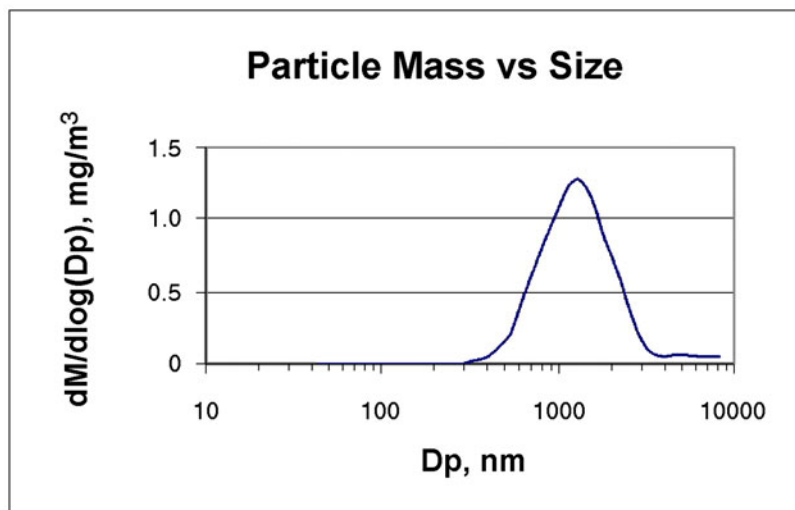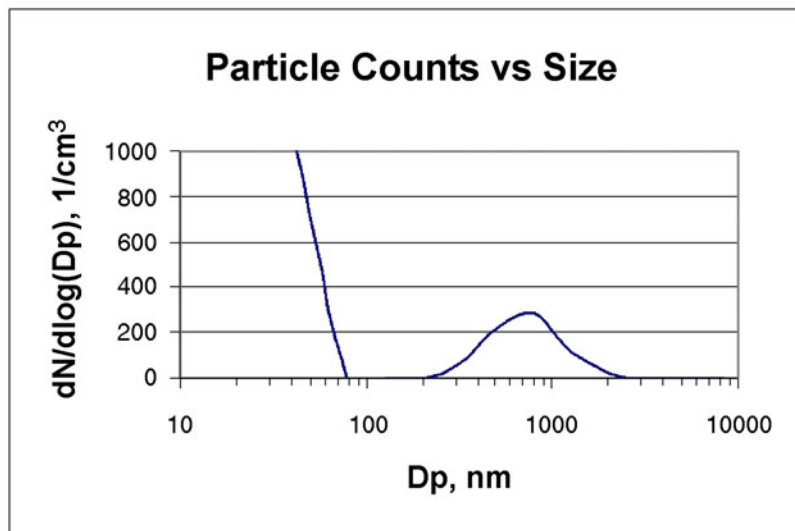
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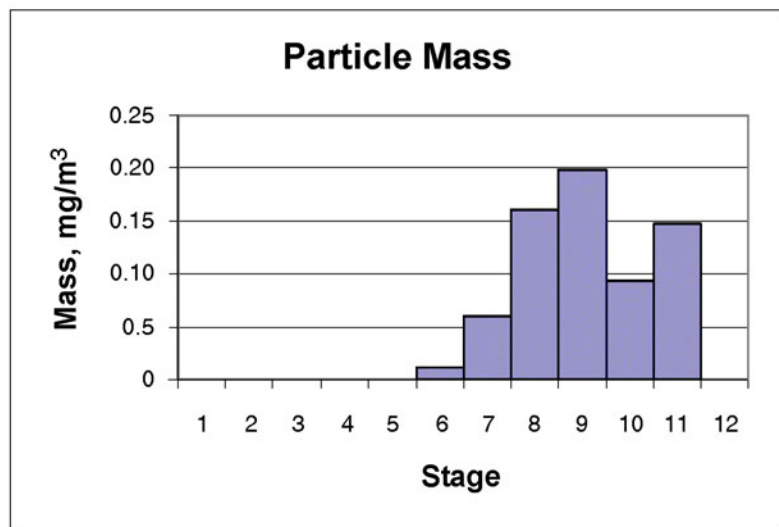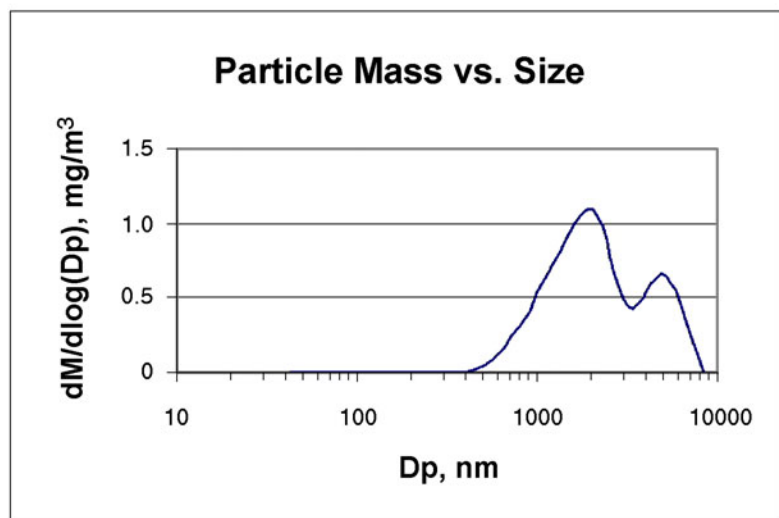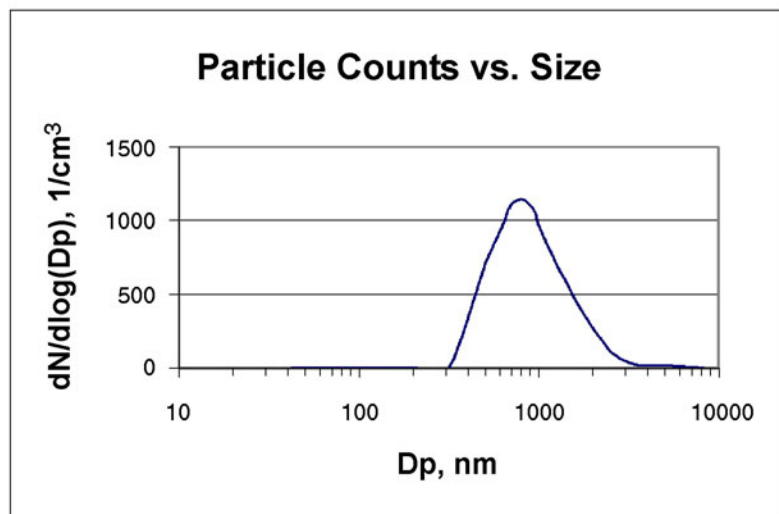
Figure 23. Plots of Particle Counts vs. Size, Particle Mass vs. Size, and Particle Mass per Stage for Test Day 3 (11/01/01).

Process O_2 and CO_2 Concentrations

Observed values for each test day are shown in Figures 24 through 26. Average concentrations of O_2 and CO_2 for each test day are shown below:

- 10/30/01: $O_2 = 7.4\%V$; $CO_2 = 11.3\%V$;
- 10/31/01: $O_2 = 6.8\%V$; $CO_2 = 11.9\%V$; and
- 11/01/01: $O_2 = 5.9\%V$; $CO_2 = 13.6\%V$.
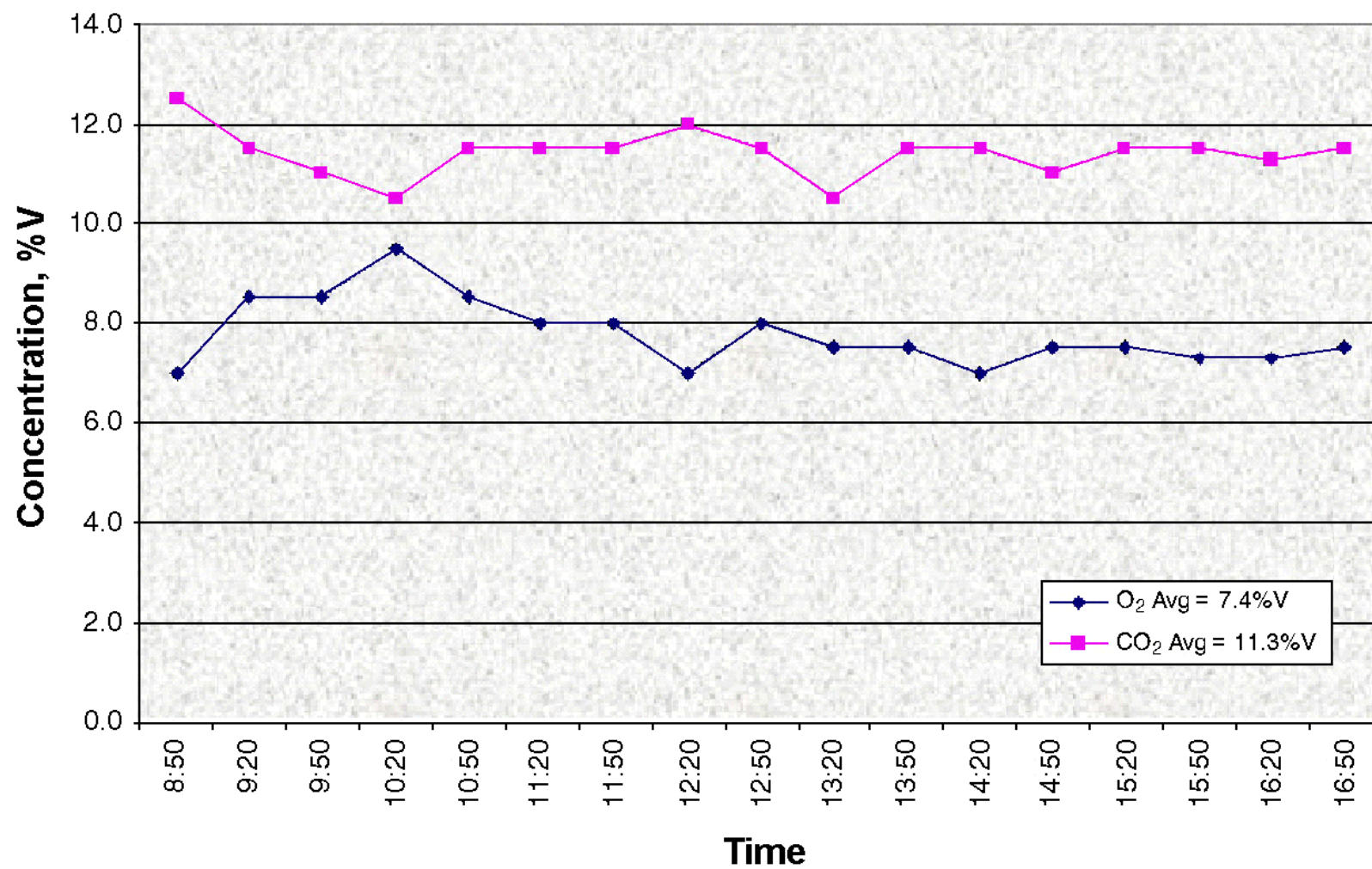
Figure 24. O_2 and CO_2 Concentrations for Recovery Boiler No. 5 on Test Day 1 (10/30/01).
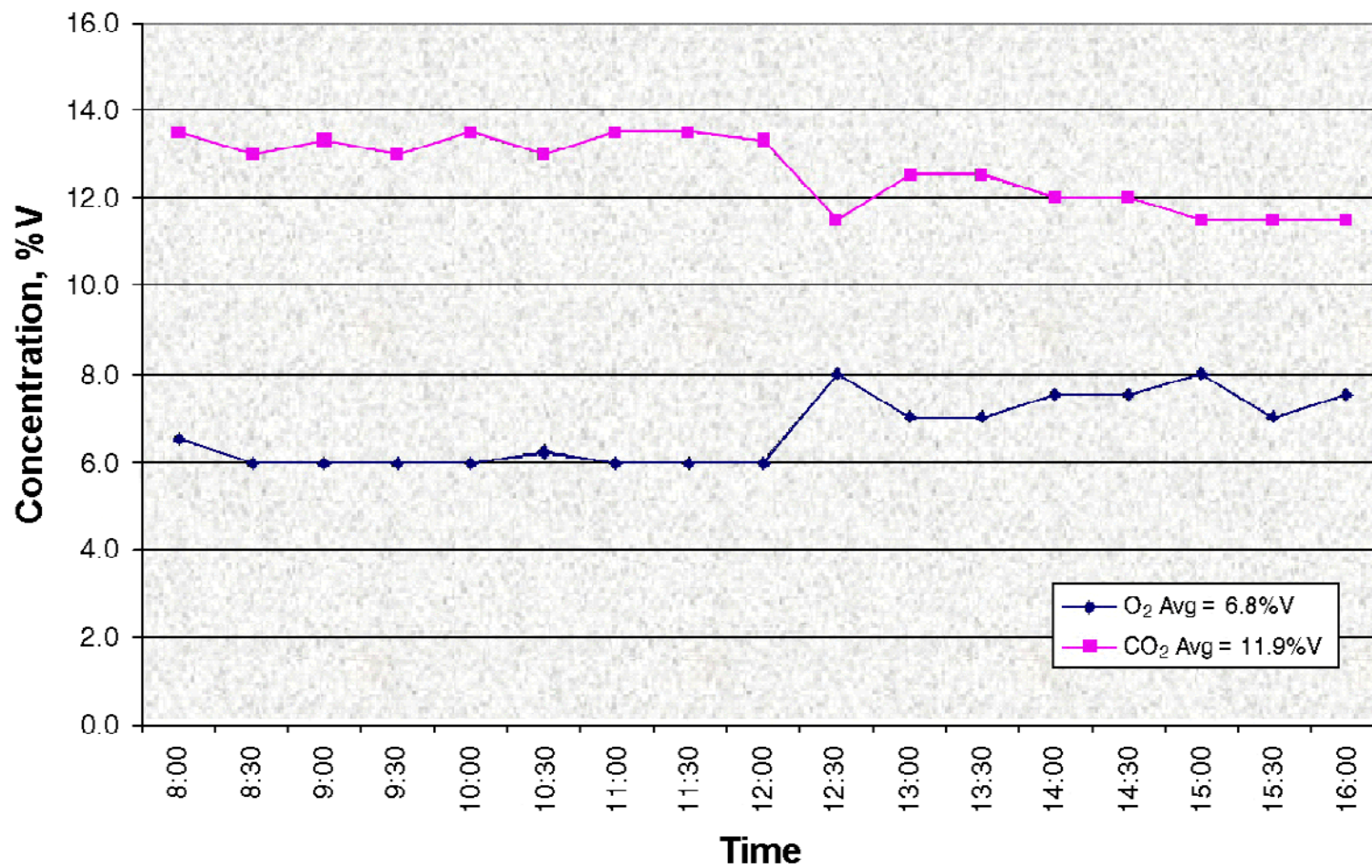
Figure 25. O_2 and CO_2 Concentrations for Recovery Boiler No. 5 on Test Day 2 (10/31/01).
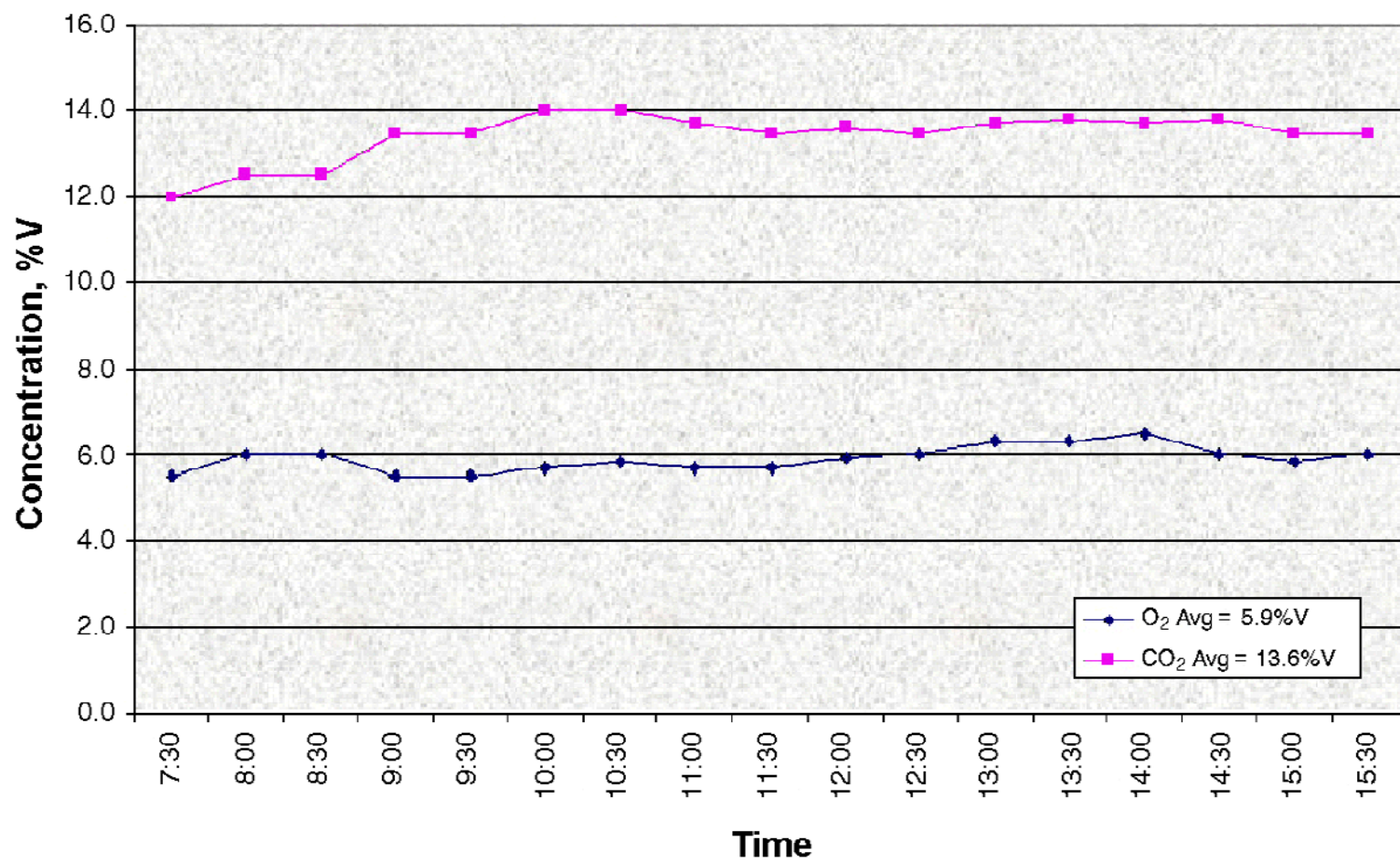
Figure 26. O_2 and CO_2 Concentrations for Recovery Boiler No. 5 on Test Day 3 (11/01/01).

Quality Assurance/Quality Control

The sampling and analysis procedures performed for this study adhered to approved EPA Quality Assurance Project Plans (QAPPs) QTRAK No. 99051[10] and QTRAK No. 99002[11], respectively. MOPs, which describe the quality control (QC) checks performed for each procedure, are listed in Appendix D. QAPPs, MOPs, and files of raw data and QC supporting data for the project were archived for future reference. Summaries of the QC measures implemented for the field sampling activities and for the various analytical methods are presented in Tables 18 through 25.

Field Sampling

In field sampling with the dilution sampling system, the following QC procedures were implemented:

- A leak check of the dilution sampling system with all sample collection arrays was performed before field testing was initiated;
- Pitot tubes and meter boxes were calibrated;
- Analytical balance(s) were calibrated;
- Flow control collection devices for the canisters were calibrated using a primary flow standard;
- Multipart forms recording field conditions and observations were used for canisters and carbonyl samples; and
- Strict chain of custody documentation for all field samples was maintained.

Field sampling equipment QC requirements that were met in the course of preparing for the field test and execution of testing activities are summarized in Table 18.

Table 18. Field Sampling Equipment Quality Control Measures[10]

Equipment	Effect	Acceptance Criteria	Criteria Achieved?
Orifice meters (volumetric gas flow calibration)	Ensures the accuracy of flow measurements for sample collection	±1%	Yes
Venturi meters (volumetric gas flow calibration)	Ensures the accuracy of flow measurements for sample collection	±1% of reading	Yes
Flow transmitter (Heise gauge with differential pressure)	Ensures the accuracy of flow measurements for sample collection	±0.5% of range	Yes
Analytical balances	Ensures control of bias for all project weighing	Calibrated with Class S weights	Yes
Thermocouples	Ensures sampler temperature control	±1.5 °C	Yes
Relative humidity probes	Ensures the accuracy of moisture measurements in the residence chamber	±2% relative humidity	Yes
Sampling equipment leak check and calibration (before each sampling run)	Ensures accurate measurement of sample volume	1%	Yes
Sampling equipment field blanks	Ensures absence of contamination in sampling system	<5.0% of sample values	Yes

Strict chain of custody procedures were followed in collecting and transporting samples and in sampling media to and from the field sampling location. Sample substrates (filters, denuders, PUF modules, DNPH cartridges) were prepared in advance in accordance with the numbers and types of samples designated in the sampling matrix of the approved field test plan. Clean SUMMA-polished collection canisters and the DNPH-coated sampling cartridges used to collect carbonyl compounds were prepared and supplied by ERG. The PUF, XAD-4-coated denuders and $PM_{2.5}$ sampling substrates were prepared and supplied by EPA. Chain of custody forms were initiated when the sampling media were prepared. Each sample substrate was assigned a unique identification number by the laboratory supplying the substrates. Copies of the chain of custody forms are included in Appendix B.

Sample identification numbers include a code to track:
- Source type;

- Test date(s);
- Sampler type;
- Substrate type;
- Sampler chamber (i.e., dilution chamber or residence chamber);
- Sampler port;
- Lane/leg;
- Position; and
- Holder number.

For samples to be analyzed in the EPA laboratories, whole sample collection arrays were assembled by EPA, assigned a unique tracking number, and used for sample collection. Sample collection arrays were recovered in the field as a complete unit and transferred to the EPA laboratory for disassembly and analysis.

After collection, samples were transported to the analysis laboratories by ERG with careful documentation of sample collection and chain of custody records for the samples being transported. Samples were stored in a secure area until they were transported to the laboratories performing the analysis.

Carbonyl Compound Analysis

QC criteria for the carbonyl analysis performed by ERG are shown in Table 19. Supporting calibration and QC data are a part of the project file at ERG.

Table 19. Carbonyl Analysis: Quality Control Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
HPLC Column Efficiency	Analyze second source QC sample (SSQC)	At setup and 1 per sample batch	Resolution between acetone and propionaldehyde ≥1.0 Column efficiency >500 plates	Eliminate dead volume, backflush, or replace column; repeat analysis	Yes
Linearity Check	Analyze 5-point calibration curve and SSQC in triplicate	At setup or when calibration check does not meet acceptance criteria	Correlation coefficient ≥0.999, relative error for each level against calibration curve ±20% or less Relative Error	Check integration, reintegrate or recalibrate	Yes

(continued)

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Table 19. (continued)

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Linearity Check (continued)			Intercept acceptance should be ≤10,000 area counts/ compound; correlates to 0.06 mg/mL	Check integration, reintegrate or recalibrate	Yes
Retention Time	Analyze calibration midpoint	Once per 10 samples	Acetaldehyde, benzaldehyde, hexaldehyde within retention time window established by determining 3 σ or ±2% of the mean calibration and midpoint standards, whichever is greater	Check system for plug, regulate column temperature, check gradient and solvents	Yes
Multipoint Calibration: 0.01 μg/mL 0.02 μg/mL 0.05 μg/mL 0.10 μg/mL 0.30 μg/mL 0.50 μg/mL per compo-nent	Analyze each point of trace-able standards	Minimum of every 6 months or when the analytical column is replaced or when detector lamp is replaced	r ≤0.9999	Check instru-ment for malfunction; reinspect standards. If calibration still fails, reprepare standards and recalibrate.	Yes
Calibration Check	Analyze standard at 0.15 μg/mL from a second source	Once per 12 hours	85−115% recovery	Check integration, recalibrate or reprepare standard, reanalyze samples not bracketed by acceptable standard	Yes
Calibration Accuracy	SSQC	Once after calibration in triplicate	85−115% recovery	Check integration; recalibrate or reprepare standard, reanalyze samples not bracketed by acceptable standard	Yes

(continued)

Table 19. (concluded)

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
System Blank	Analyze acetonitrile	Bracket sample batch, 1 at beginning and 1 at end	Measured concentration $\leq 5 \times$ MDL	Locate contamination and document levels of contamination in file	Yes
Duplicate Analyses	Duplicate samples	As collected	$\pm 20\%$ difference	Check integration; check instrument function; re-analyze duplicate samples	Yes
Replicate Analyses	Replicate injections	Duplicate samples only	$\leq 10\%$ relative percent difference for concentrations greater than 1.0 µg/mL	Check integration, check instrument function, re-analyze duplicate samples	Yes
Method Spike/Method Spike Duplicate (MS/MSD)	Analyze MS/MSD	One MS/MSD per 20 samples	80–120% recovery for all compounds	Check calibration, check extraction procedures	Yes

Concurrent Air Toxics/Speciated Nonmethane Organic Compound (SNMOC) Analysis

The analytical system performing the concurrent analysis is calibrated monthly and blanked daily prior to sample analysis. A QC standard is analyzed daily prior to sample analysis to ensure the validity of the current monthly response factor. Following the daily QC standard analysis and prior to the sample analysis, cleaned, dried air from the canister cleaning system is humidified and then analyzed to determine the level of organic compounds present in the analytical system. Upon achieving acceptable system blank results—less than or equal to 20 ppbC—sample analysis begins. Ten percent of the total number of samples received are analyzed in replicate to determine the precision of analysis for the program. After the chromatography has been reviewed, the sample canister is returned to the canister-cleaning laboratory to be prepared for subsequent sample collection

episodes or sent to another laboratory for further analysis. QC procedures for the Air Toxics and SNMOC analyses are summarized in Table 20.

Table 20. Quality Control Procedures for the Concurrent Analysis for Air Toxics and SNMOCs

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
Air Toxics Analysis				
Bromofluorobenzene Instrument Tune Check	Daily prior to calibration check	Evaluation criteria in data system software; consistent with Method TO-15	Retune mass spectrometer; clean ion source and quadrupoles	Yes
Five-point Calibration Bracketing the Expected Sample Concentration (0.25−15 ppbv)	Following any major change, repair, or maintenance if daily QC check is not acceptable. Calibration is valid for six weeks if calibration check criteria are met.	RSD of response factors ≤30% relative retention times (RRTs) for target peaks ±0.06 units from mean RRT	Repeat individual sample analysis; repeat linearity check; prepare new calibration standards and repeat analysis	Yes
Calibration Check Using Midpoint of Calibration Range	Daily	Response factor ≤30% bias from calibration curve average response factor	Repeat calibration check; repeat calibration curve	Yes
System Blank	Daily following tune check and calibration check	0.2 ppbv/analyte or MDL, whichever is greater Internal Standard (IS) area response ±40% and retention time ±0.33 min of most recent calibration check	Repeat analysis with new blank; check system for leaks, contamination; reanalyze blank.	Yes
Laboratory Control Standard (LCS)	Daily	Recovery limits 70-130% Internal Standard Retention Time ±0.33 min of most recent calibration	Repeat analysis; repeat calibration curve.	Yes

continued

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Table 20. (concluded)

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Replicate Analysis	All duplicate field samples	<30% RPD for compounds >5 × MDL	Repeat sample analysis	Yes
Samples	All samples	IS RT ±0.33 min of most recent calibration	Repeat analysis	Yes
SNMOC Analysis				
System Blank Analysis	Daily, following calibration check	20 ppbC total	Repeat analysis; check system for leaks; clean system with wet air	Yes
Multiple Point Calibration (Minimum 5); Propane Bracketing the Expected Sample Concentration Range (4–100 ppbC)	Prior to analysis and monthly	Correlation coefficient $(r^2) \geq 0.995$	Repeat individual sample analysis; repeat linearity check; prepare new calibration standards and repeat	Yes
Calibration Check: Midpoint of Calibration Curve Spanning the Carbon Range (C_2–C_{10})	Daily	Response for selected hydrocarbons spanning the carbon range within ±30% difference of calibration curve slope	Repeat calibration check; repeat calibration curve.	Yes
Replicate analysis	All duplicate field samples	Total NMOC within ±30% RSD	Repeat sample analysis	Yes

PM Mass Measurements, Elemental Analysis, Water-Soluble Ion Analysis, Organic/Elemental Carbon, and GC/MS Analysis

QC criteria for analyses of $PM_{2.5}$ mass and $PM_{2.5}$ elements, ions, and speciated organics are summarized in Tables 21 through 25.

.

Table 21. PM Mass Measurements: Quality Control Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Acheived?
Deposition on Filter during Conditioning	Analyze laboratory filter blank	Bracket sample batch, 1 at beginning and 1 at end	Mass within ±15 mg of previous weight	Adjust mass for deposition	Yes
Laboratory Stability	Analyze laboratory control filter	Bracket sample batch, 1 at beginning and 1 at end	Mass within ±15 mg of previous weight	Adjust mass to account for laboratory difference	Yes
Balance Stability	Analyze standard weights	Bracket sample batch, 1 at beginning and 1 at end	Mass within ±3 mg of previous weight	Perform internal calibration of balance; perform external calibration of balance	Yes

Table 22. Elemental Analysis: Quality Control Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Performance Evaluation Check	Analyze monitor sample	Once per month	≤2% change in each element from previous measurement	Recalibrate	Yes

Table 23. Water-Soluble Ion Analysis: Quality Control Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Linearity Check	Analyze 4-point calibration curve	At setup or when calibration check does not meet acceptance criteria	Correlation coefficient $r^2 \geq 0.999$	Recalibrate	Yes
System Dead Volume	Analyze water	Bracket sample batch, 1 at beginning and 1 at end	Within 5% of previous analysis	Check system temperature, eluent, and columns	Yes
Retention Time	Analyze standard	At setup	Each ion within ±5% of standard retention time	Check system temperature and eluent	Yes
Calibration Check	Analyze 1 standard	Once every 4−10 samples	85−15% recovery	Recalibrate or reprepare standard, re-analyze sample not bracketed by acceptable standard	Yes
System Blank	Analyze HPLC grade water	Bracket sample batch, 1 at beginning and 1 at end	No quantifiable ions	Reanalyze	Yes
Replicate Analyses	Replicate injections	Each sample	$\leq 10\%$ RPD for concentrations greater than 1.0 mg/L	Check instrument function, re-analyze samples	Yes

Table 24. Quality Control Procedures for Organic/Elemental Carbon Analysis of PM$_{2.5}$

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Instrument Gas Flows	Once at start of each new batch of source samples every six months	Obtain best polynomial fit to 6 data points for each gas	Re-enter data into instrument operation software	Yes
Amount of Internal Standard (CH$_4$/He) in Calibration Gas Loop	Whenever methane tank is changed	Determine volume of calibration gas loop	Re-enter new calibration gas loop volume in instrument operation software	Yes
Instrument Blank	Start of each run	<0.2 µg C/cm^2	Repeat oven bake-out	Yes
3-Point Calibration with Standard Sucrose Solutions Bracketing Concentration Range	Start of new set of samples	Within 5% of previous calibration	Repeat calibration	Yes
1-Point Calibration with Standard Sucrose Solution	Start of each analysis	Within 5% of previous calibration	Repeat calibration	Yes

Table 25. Quality Control Procedures for Gas Chromatography-Mass Spectrometry Analysis of Semivolatile Organic Compounds

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Mass Spectrometer Instrument Tune Check	Daily prior to calibration check	Mass assignments m/z = 69, 219, 502 (± 0.2) Peak widths = 0.59–0.65 Relative mass abundances = 100% (69); ≥30% (219); ≥1% (502).	Retune mass spectrometer; clean ion source	Yes
Five-Point Calibration Bracketing the Expected Concentration Range	Following maintenance or repair of either gas chromatograph or mass spectrometer or when daily quality control check is not acceptable	Correlation coefficient of either quadratic or linear regression ≥0.999	Check integration, reintegrate or recalibrate	Yes
Calibration Check Using Midpoint of Calibration Range	Daily	Compounds in a representative organic compound suite >80% are ±15% of individually certified values. Values ≥20% are not accepted.	Repeat analysis; repeat calibration curve	Yes
System Blank	As needed after system maintenance or repair	Potential analytes less than or equal to detection limit values	Repeat analysis; check system integrity. Reanalyze blank	Yes
Retention Time Check	Daily	Verify that select compounds are within ±2% of established retention time window	Check inlet and column flows and the various GC/MS temperature zones	Yes

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16. ABSTRACT

The report provides a profile of the chemical composition of particulate matter (PM) with aerodynamic diameter 2.5 µm or less ($PM_{2.5}$) emitted from a recovery boiler at a pulp and paper facility using the Kraft pulping process. Recovery boilers, common to nearly all pulp and paper mills, are usually one of the major contributors to atmospheric emissions from the mill. Processing wood chips in a pulp mill utilizing the Kraft process involves digesting the wood in a solution of sodium sulfide and sodium hydroxide. The spent digestion liquor combined with water used to wash the resulting pulp is called "black liquor." After undergoing concentration by evaporation to about 65% solids, the black liquor is fed to the recovery boiler as fuel. Dissolved organics in the concentrated black liquor are combusted in the recovery boiler to yield heat to generate process steam and to convert sodium sulfate formed in the process back to sodium sulfide which can be recycled to the digestion step as a reactant. The recovery boiler tested here was equipped with two parallel electrostatic precipitators with 169,194 linear feet of plate area per precipitator, installed in the flue gas exhaust ducting. The data obtained during this research will assist States in determining the major sources of $PM_{2.5}$ so they can devise and institute a control strategy to attain the ambient concentrations set by the National Ambient Air Quality Standard for $PM_{2.5}$ that was promulgated in July 1977 by the U.S. EPA. Along with the $PM_{2.5}$ emission profile, data are also provided for gas-phase emissions of several organic compounds. Data are provided in a format suitable to be included in the EPA source profile database, SPECIATE.

17.	KEY WORDS AND DOCUMENT ANALYSIS	
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Paper Industry Wood Pulp Fine Particulate Matter Chemical Composition Organic Compounds Volatility	Pollution Control Stationary Sources	13B 11L 14G 07D 07C 20M
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