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



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

by

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Abstract

Fine particulate matter of aerodynamic diameter 2.5 μ m 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 a chemical composition profile for the PM_{2.5} emitted from an auxiliary boiler fired with a mixture of wood bark (hogged wood waste) and bituminous coal at a pulp and paper mill utilizing the Kraft process. The boiler was rated to generate a maximum of 889 Mbtu/hour and was equipped with a control system which included a multicyclone-electroscrubber system installed on the flue gas duct and bag filters installed on the vents of the coal bins, scrubber ash silo, and boiler ash silo. Along with the PM_{2.5} emission profile, data are also provided for gas-phase emissions of several organic compounds. Gaseous reduced sulfur compound emissions, however, were not included in this study. Data are presented both as mass emission factors (mass of emitted species per unit mass of fuel consumed) and as mass fraction compositions (e.g., mass fraction of individual components comprising the $PM_{2.5}$). Data are provided in a format suitable for inclusion in the EPA source profile database, SPECIATE.

Foreword

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

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Nomenclature

Definition		
chemical mass balance		
2,4-dinitrophenylhydrazine		
elemental carbon and organic carbon		
electrical low pressure impactor		
U.S. Environmental Protection Agency		
Eastern Research Group		
flame ionization detector		
gas chromatography analytical technique		
gravimetric analytical technique		
high efficiency particulate arresting		
high performance liquid chromatography analytical technique		
high volume, low concentration		
ion chromatography analytical technique		
method detection limits		
method operating procedures		
mass spectrometry analytical technique		
mass selective detector		
ammonia		
nonmethane organic compounds		
nitrogen oxides		
particulate matter		
particulate matter of aerodynamic diameter 2.5 µm or less		
particulate matter of aerodynamic diameter 10 µm or less		
polyurethane foam		
quality assurance project plans		
State Implementation Plans		
speciated nonmethane organic compounds		
standard operating procedures		
sulfur oxides		
trimethylsilyl		
thermal-optical evolution		
volatile organic compounds		
X-ray fluorescence analytical technique		

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Introduction

In July 1997, the U.S. Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards for ambient particulate matter (PM) of aerodynamic diameter 2.5 μ m or less (PM_{2.5}) and revised the existing standard for ambient particles of aerodynamic diameter 10 μ m or less (PM₁₀). 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 PM₁₀ 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 (NH₃).

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 hogged fuel 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 $PM_{2.5}$. For this particular model, more and better source data are needed to allow:

- The characterization of secondary organic aerosols formed by condensation of semivolatile organic compounds and/or reaction of volatile organic compounds to form higher molecular weight aerosols;
- Increased differentiation of specific sources within source types; and
- The major sources of ammonia emissions, which result in ammonium sulfate and ammonium nitrate fine PM.

These data needs exist because:

- Relatively few data exist on the organic composition of PM, particularly of carbonaceous PM_{2.5}, and the data that do exist represent only 5 wt% or less of the total organic fraction of the PM;
- Current PM_{2.5} organic speciation profiles are derived from tests of only a few sources within a relatively few air sheds across the United States;
- Certain organic components of PM_{2.5} may be responsible for observed adverse human health effects associated with ambient fine PM;
- Organic aerosols typically represent approximately 30% to 40% of the mass of ambient PM_{2.5} in urban areas; and
- Unlike SO_x and NO_x, ammonia emissions are poorly characterized since ammonia is not considered a "criteria pollutant." However ammonia, in combination with atmospheric sulfate and nitrate, forms secondary PM, which represents a substantial portion of the total fine PM in ambient air.

Characterization of a Hogged Fuel Boiler at a Pulp and Paper Facility

A sampling campaign was conducted during the last quarter of 2001 at a large pulp and paper mill using the Kraft process to measure emissions from three of the mill's major sources of atmospheric emissions; i.e., a recovery boiler fired with concentrated liquid wastes (black liquor) from the wood digestion and pulp washing processes, an auxiliary boiler combusting a mixture of wood bark (hogged wood waste) and bituminous coal, and a vent from the smelt dissolving tank. This test report presents results from the emissions testing of the auxiliary (hogged fuel) boiler. The primary aim of these tests was to determine the amount and nature of the fine PM ($PM_{2.5}$) emitted.

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 5¹ or Method 202.² 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.

In pulp and paper mills, process steam is largely supplied by combustion of concentrated black liquor in the recovery boiler. Organic compounds present in the concentrated black liquor constitute the combustible fuel for the recovery boiler. However, in most cases, the recovery boiler alone cannot supply all of the heat to generate the process steam needed. Conventional boilers burning coal, oil, natural gas, wood bark, or some combination of these fuels are used to make up the deficiency. The boiler tested in this research was used to provide auxiliary process steam and utilized as fuel a mixture of 72.6 wt% wood bark (hogged wood waste), 27.4 wt% low-sulfur bituminous coal, and an insignificant amount of high volume, low concentration (HVLC) gases from the black liquor evaporation process. The HVLC gases typically make up less than 1% of the total fuel consumed during normal operation.

The hogged fuel boiler tested was rated to generate a maximum of 889 MBtu/hour and was equipped with a multistage control system, composed of the following components:

- One multicyclone/electroscrubber system (one electrified granular filter bed);
- Three bag filters installed on the de-entrainment vessel for the granular media used in the electroscrubber;
- Two filters installed on vents on the two coal bins;
- Two bag filters installed on the vents of the boiler ash silo;
- Two bag filters installed on vents on the scrubber ash silo; and
- One bag filter installed on the storage vessel which holds the gravel media used in the electroscrubber.

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 1³, 2⁴, and 4⁵ were performed to establish the stack gas velocity, temperature, pressure, and exhaust gas moisture content.

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 used to apportion ambient atmospheric pollutants to the various sources contributing to the ambient air pollution.

Report Organization

This report is organized into five additional sections plus references and appendices, which are in a separate volume. 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

During three replicate test runs conducted during three consecutive days (11/27-29/01), the fine PM (PM_{2.5}) emission factor averaged 50.0 mg/kg of fuel and was fairly consistent (48.2–52.0 mg/kg fuel). This value is roughly twice the PM_{2.5} mass emission factor found for the recovery boiler at the same facility. The size distribution of fine PM emitted from the hogged fuel boiler was bimodal with a minor peak at 0.13 μ m and a major peak at 1.7 μ m particle aerodynamic diameter. The overall mean diameter of the PM_{2.5} particles was 1.16 μ m.

Approximately 68.5% of the PM composition by mass was identified and quantified. Sulfate and chloride ions constituted 10% of the PM mass. Aluminum and silicon were the dominant elements and together comprised 32.8%. Silicon, aluminum, and iron are the three elements typically found in coal in the largest amounts. This fact, along with the possibility of minor amounts of crustal material (alumino-silicate minerals) admixed with the wood and coal fuels probably accounts for the predominance of these elements in the fine PM emitted. Potassium was found to constitute 6.8% of the PM mass on average. Potassium is frequently considered a marker for combustion of biomass (hogged wood waste in this case).

Elemental and organic carbon together averaged 7.9% of the fine PM mass. Organic carbon alone (a measure of the organic compound content of the PM) was determined to be 6.2 wt% of the PM mass emitted. Although a number of organic compounds, principally alkanes, were positively identified in the organic carbon fraction, the amounts of these individual organic species were generally below the analytical limits for accurate quantitation. Consequently, mass emission factors and composition mass fractions for the individual organic compounds in the fine PM could not be accurately determined.

Significant concentrations of *n*-hexane, methylene chloride, and acetone were also observed in the gas samples collected from the dilution sampler during all three test days with unusually high concentrations of these compounds observed on the second test day. However, the presence of these compounds may be artifactual. Different sets of the XAD-coated annular denuders were extracted near the sampling location using these same three solvents, and the denuders were placed into service on an alternating schedule to avoid exceeding the capacity of a single set of denuders during a test run. Therefore, the presence

of these three compounds in the stack gas samples collected by the dilution sampler and in the ambient air sample collected on the stack are considered suspect and are likely due to contamination arising from on-site extraction of the organic denuders. Values for nonmethane organic compounds (both speciated and total), carbonyl compounds (both speciated and total), and air toxics compounds have been recalculated deleting these compounds on the second test day (11/28/01).

Gas-phase nonmethane organic compound emissions on the first and third test days were about twice the level found in the recovery boiler emissions at the facility (11.30 mg/kg of fuel for the hogged fuel boiler versus 5.92 mg/kg of fuel for the recovery boiler). On only the second test day (11/28/01), the gas-phase nonmethane organic compound (NMOC) emissions were much higher (246.96 mg/kg fuel) largely due to the presence of a single compound, *n*-hexane. The *n*-hexane is a contaminant arising from the solvents used to extract the denuders on-site. When the values are recalculated for 11/28/01 deleting *n*hexane, a value of 34.07 mg/kg fuel is obtained, much more consistent with the other test days. When values for Test Day 2 were recalculated with the omission of acetone, a value of 2.74 mg/kg fuel was obtained.

Gas-phase carbonyl compound emissions on the first and third test days were about three times the emission levels found in the Recovery Boiler emissions at the same facility (3.46 mg/kg fuel vs. 1.12 mg/kg fuel, respectively). Similarly to the NMOCs, the total gas-phase carbonyl emissions were much higher on Test Day 2 (79.12 mg/kg fuel) largely due to the presence of high levels of acetone observed in the emissions on that day.

Ambient air at the plant site was sampled on Test Day 1 (11/27/01) and was found to contain 1147.86 μ g/m³ of gas-phase NMOCs with *n*-hexane, 3-methyl-pentane, methylcyclopentane, and α -pinene being the dominant species. *n*-Hexane alone accounted for approximately 35% of the NMOCs in the ambient air on that day. Methylene chloride was the only air toxic compound found in the ambient air in significant quantities. Sampling of the ambient air was done to ensure the dilution air cleanup system associated with the dilution sampler was removing any pollutants present in the ambient air prior to being mixed with the stack gas. Samples of the cleaned dilution air confirmed that ambient background gases resulting from the on-site handling of the denuders and PM were indeed removed.

Methods and Materials

A field test was conducted (November 27 to 29, 2001) on hogged fuel boiler No. 2 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 hogged fuel 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 hogged fuel 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.

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

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

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 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 PM.

To assist in the characterization of the hogged fuel 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 1³, 2⁴, and 4⁵ 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, 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.

Dilution Sampling System

The dilution sampling system used in the source test was based on an original design by L. M. Hildemann⁶ which was 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. A preliminary investigation into particle losses within the sampler was conducted as part of another source sampling campaign at a different site. Results of that study indicate that particle losses in the sampler (including wall losses in the probe, dilution tunnel, and residence chamber) amounted to approximately 21.2% of the total PM that entered the sampler from the stack. However, those losses include all of the nominally PM₁₀ material that passed through the in-stack PM₁₀ cyclone, not just PM_{2.5} material alone. Therefore, losses of PM_{2.5} particles would be expected to be less than 21.2%. Hildemann reported losses of approximately 7% in a dilution sampler of the same design and dimensions, but his value did not include probe losses.

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.

Turbulent Mixing Chamber



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

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 μ m. The PM₁₀ 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.

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 inline, 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. Typically, the calculated total time the sample spends in the dilution sampling system ranges from 58 to 75 sec with 2 to 3 sec for the turbulent mixing chamber and 56 to 72 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 PM₁₀ 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 hogged fuel boiler.

In operation, the source sample flow, the dilution air flow, 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



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



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

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.

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, polyurethane foam (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 test.

Process Description/Site Operation

The hogged fuel boiler can fire hogged fuel, No. 6 fuel oil, coal, waste oil, sludge, and HVLC gases, singly or in combination, generating up to 889 MBtu/hour maximum heat input from the combined fuels; only hogged wood and coal were used as fuel during the testing. The hogged fuel boiler is equipped with a multistage control system composed of the following components:

- One multicyclone/electroscrubber system (one electrified granular filter bed);
- Three bag filters installed on the de-entrainment vessel for the granular media used in the electroscrubber;
- Two filters installed on vents of the north and south coal bins;
- Two bag filters installed on the vents of the boiler ash silo;
- Two bag filters installed on vents on the scrubber ash silo; and
- One bag filter installed on the storage vessel which holds the gravel media used in the electroscrubbers.

The hogged fuel boiler No. 2 sampling location was in the vertical exit stack downstream of the multistage control system, with the sampling port installed 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 port, elevated approximately 90 feet above ground level, is shown in Figure 3; a schematic diagram of the layout of the sampling site is shown in Figure 4. The area around the sampling port is an enclosed space (called the dough-nut) approximately eight feet wide from the stack wall to the outside wall of the doughnut.



Figure 3. Hogged Fuel Boiler No. 2 Sampling Port Location.

Access to this location required use of elevator and stairs to a catwalk-type platform. The sampling equipment was lifted by crane to the location shown in Figure 3, and the dilution unit was then rolled into position in the doughnut. The control unit was located just inside the door of the enclosed space and was connected to the dilution unit using electrical wiring and approximately 10 feet of flexible hose.

Supplemental equipment was brought to the sampling location by elevator and stairs. There was no space in the vicinity of the sampling port to place an enclosure for preparation of sampling components or for recovery of the sample collection arrays. Therefore, an appropriate area at ground level was identified for sampling component preparation and for sample collection array recovery and preparation for transport to the laboratories.

The hogged fuel (coal and wood chips) was stored outdoors in large piles near the hogged fuel boiler (Figures 5 and 6, respectively). Samples of the coal and wood chips were collected during Test Day 2; analytical results for these fuel samples are shown in Table 2. Fuel use for Hogged Fuel Boiler No. 2 during the testing period is summarized in Table 3.



Figure 4. Hogged Fuel Boiler Sampling Location Layout—Top View.



Figure 5. Hogged Fuel Outdoor Coal Storage Area.



Figure 6. Hogged Fuel Outdoor Wood Storage Area

Table 2. Analysis of Coal and Wood Chip Hogged Fuel

	Coal Content		Wood Chij	o Content
Constituent	As Received	Dry	As Received	Dry
Moisture	4.10%		46.60%	
Volatile Matter	35.29%	36.80%	42.41%	79.41%
Fixed Carbon	53.21%	55.49%	8.95%	16.77%
Ash	7.40%	7.71%	2.04%	3.82%
Sulfur	0.68%	0.71%	0.04%	0.07%
Carbon	74.55%	77.74%	26.54%	49.70%
Hydrogen	4.51%	4.70%	3.07%	5.76%
Nitrogen	1.53%	1.60%	0.07%	0.13%
Oxygen	7.23%	7.54%	21.64%	40.52%
Chlorine	0.11%		0.12%	0.23%
Btu per pound	13335	13906	4392	8224

Test No.	Fuel Type	Feed Rate (lbs/min)	Test Duration (min)	Total Weight Used (lbs)	Combined Overall Total Weight Used (lbs)	Combined Overall Total Weight Used (kg)
1	Coal	506.7	479	242,709.3		
1	Wood	1,236.7	479	592,379.3		
1					835,088.6	378,789.8
2	Coal	504.7	480	242,240.0		
2	Wood	1,357.7	480	651,360.0		
2					893,600.0	405,330.1
3	Coal	470.0	481	226,070.0		
3	Wood	1,333.3	481	641,317.3		
3					867,387.3	393,440.2

Table 3. Hogged Fuel Boiler No. 2 Fuel Use During the Test Period

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 3) in the boiler exhaust stack, 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 inside the enclosed housing attached to the boiler exhaust stack (Figure 3) approximately 90 ft above ground level. A second pretest 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 1³, 2⁴, and 4⁵ were conducted to establish key experimental parameters for test conditions.

Traverse Point Determination Using EPA Method 1

EPA Method 1² 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 hogged fuel boiler No. 2 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 used on hogged fuel boiler No. 2 (Figure 3). Although the overall duct diameter was 12 ft, only 6 ft (or approximately one-half of the diameter) were traversed to determine stack velocity because the longest probe available for the dilution system was 6 ft long.

The following duct dimensions were measured:

- Center of stack to outside of nipple (Distance A): 89 in.
- Inside of near wall to outside of nipple (Distance B): 17 in.
- Inside stack dimension from center of stack to inside of near wall: 72 in.

Traverse point locations for a the circular hogged fuel boiler duct are listed in Table 4. A table of metric unit conversions is provided in Appendix A.

Traverse	Fraction of Inside Stack		Traverse Point	
Point	Dimension ^a	Distance from Stack Wall	Location	
Number	(%)	(in.)	(in.)	
1	2.6	1 7⁄8	18 1⁄8	
2	8.2	5 7/8	22 7/8	
3	14.6	10 ½	27 1/2	
4	22.6	16 ¼	33 1/4	
5	34.2	24 5/8	41 5⁄8	
6	65.8	47 3 ⁄8	64 3 ⁄8	
7	77.4	55 ³ / ₄	72 3⁄4	
8	85.4	61 ½	78 1/2	
9	91.8	66 ¹ /8	83 1⁄8	
10	97.4	70 1⁄8	87 1/8	

Table 4. EPA Method 1 Traverse Point Locations for the Circular Hogged Fuel BoilerNo. 2 Exhaust Duct

^a Inside stack depth from center of stack to inside of near wall:72 in. Distance from lip of flange to inside stack wall: 17 in.

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

$$PS = P_{bar} + \frac{P_g}{13.6} \tag{4-1}$$

where:

PS = absolute gas pressure, inches of mercury

 P_{bar} = barometric pressure, inches of mercury (29.91 in.)

 P_g = gauge pressure, inches of water (static pressure) (-0.95 in.).

The value 13.6 represents the specific gravity of mercury (1 in. of mercury = 13.6 in. of water). For the stack tested, the absolute gas pressure under the test conditions was 29.84 in. of mercury.

Volumetric Flow Rate Determination Using EPA Method 2

Volumetric flow rate was measured according to EPA Method 2³. 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

$$V_{s} = K_{p} \times C_{p} \times \sqrt{\frac{\Delta P_{avg} \times (460 + T_{s})}{P_{s} \times M_{s}}}$$
(4-2)

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

460 = 0 °F, expressed as degrees Rankin

 T_s = flue gas temperature, °F (320 °F)

 P_s = absolute stack pressure (barometric pressure at measurement site plus stack static pressure), inches of mercury (29.84 in.)

 M_s = wet molecular weight, pounds per pound-mole (28.26 lb/lb-mole).

The flue gas velocity calculated for each traverse point and the average velocity are shown in Table 5. The velocity at traverse points 9 and 10 are closest to the average velocity. However, sampling at traverse point 9 or 10 was not possible because neither of the two probes available with the Dilution Sampling System were long enough to reach traverse point 9 or 10. Only traverse points 1 to 6 could be reached using the available dilution system probes. Consequently, Traverse Point No. 3 was selected for sampling because it represented the accessible point closest to the calculated average velocity.

Traverse Point (Calculated in Table 4)	Velocity (ft/min)	
1	1797.2	_
2	2007.1	
3	2173.5	
4	2329.6	
5	2260.0	
6	2309.2	
7	2232.2	
8	2114.8	
9	2155.1	
10	2155.1	
Average Velocity	2153.4	

Table 5. Average Flue Gas Velocity for Each Traverse Point

The average flue gas velocity of 2153.4 ft/min was assumed constant for all three test days. However, there was a range of approximately 7% in the fuel feed rate among the three test days, and the coal content ranged from 27% to 35% of the fuel. The exact nature of the effect of the variation in these parameters on the emission factors is uncertain. Since the term "kg of fuel" appears in the denominator of the emission factor, an increase or decrease in the fuel feed will have a direct effect on the value of the emission factor. The change in composition of the fuel will also have an effect on the amount and size of the particulate matter as well as the amount and composition of the gas phase emissions, but the exact nature and value of this effect and the interaction with an increase or decrease in the fuel feed rate are unknown.
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 5¹, 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 hogged fuel boiler No. 2 was 0.299 in. inside diameter (id).

Measurement of O₂, CO₂, 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:

 $O_2 = 13.0\%V$ $CO_2 = 8.0\%V$ CO = 0.03%V

The percentage of nitrogen (N_2) was calculated by

$$N_2\%V = 100 - (O_2\%V + CO_2\%V + CO\%V) = 78.97\%V$$
(4-3)

Dry Molecular Weight of Flue Gas

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

$$M_d = (0.44 \times \text{CO}_2\%\text{V}) + (0.32 \times \text{O}_2\%\text{V}) + [0.28 \times (\text{CO}\%\text{V} + \text{N}_2\%\text{V})]$$

= 29.80 lb/lb • mole (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 (8.0) $O_2\%V$ = percent O_2 by volume, dry basis (13.0) CO%V = percent CO by volume, dry basis (0.03) $N_2\%V$ = percent N_2 by volume, dry basis (78.97) 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

$$M_{s} = (M_{d} \times M_{fd}) + (0.18 \times H_{2}O\%V)$$

= 28.26 wet lb/lb • mole (4-5)

where:

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

 M_d = molecular weight of flue gas, dry basis (29.80 lb/lb • mole)

 M_{fd} = dry mole fraction of effluent gas, calculated as [1 - H₂O%V/100] (0.869)

0.18 =molecular weight of H₂O, divided by 100

 $H_2O\%V = percent H_2O$, by volume (13.11).

Determination of Average Moisture Using EPA Method 4

EPA Method 4⁵ 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. The initial weight of the impingers was recorded before sampling. 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. 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 6 were made prior to the actual test dates, using Method 4 to determine moisture recovery.

		Weight of		Impinger Weight		
Impinger Number	Impinger Solution	Impinger Contents (g)	Impinger Tip Configuration	Final (g)	Initial (g)	Weight Gain (g)
1	Water	100	Standard	672.4	608.6	63.8
2	Water	100	Standard	621.0	573.6	47.4
3	Empty		Standard	496.9	483.6	13.3
4	Silica Gel	300	Standard	776.9	759.2	17.7
			Total	Weight Ga	ain (g)	142.2

Table 6. Moisture Recovery for Method 4

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

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

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

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 (44.607 ft³) y = dry gas meter calibration factor (0.980)

- P_{bar} = barometric pressure at measurement site, inches of mercury (29.91 in.)
- ΔH = sampling rate, measured as differential pressure at the meter orifice, inches of water (1.72 in.)
- T_m = dry gas meter temperature, °F (62.3 °F).

The constant 17.64 was used to convert to standard conditions (84.7 °F, 30.24 in. mercury); 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 44.35 dscf.

Volume of Water Vapor at Standard Conditions (dscf)

The volume of water vapor under standard conditions was calculated by

$$V_{w(std)} = 0.04707 \times V_{lc} = 6.693 \,\,\mathrm{dscf} \tag{4-7}$$

where:

 $V_{w(std)}$ = volume of water vapor at standard conditions, dry standard cubic feet (dscf) V_{lc} = volume of liquid catch (142.2 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

$$H_2 O\% V = 100 \times \frac{V_{w(std)}}{V_{w(std)} + V_{m(std)}} = 13.11\% V$$
(4-8)

Using values measured using EPA Method 4 and values calculated previously, the moisture content was calculated to be 13.11 %V.

Calculation of Dry Mole Fraction of Flue Gas

The dry mole fraction of flue gas is calculated by

$$M_{fd} = 1 - \frac{\mathrm{H}_2 \mathrm{O}\%\mathrm{V}}{100} = 0.869 \tag{4-9}$$

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 0.869.

Setup of the Dilution Sampling System

The hogged fuel boiler No. 2 sampling location was the vertical wall of a boiler duct, with the sampling port 95 feet above ground level (schematic diagram of test site in Figure 4). The area surrounding the sampling port was an enclosed circular housing with an average width of 48 in. Access to this location was by a catwalk-type platform. The large pieces of the dilution sampling system (i.e., the dilution sampling system itself, 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 3).

The enclosed housing shown in Figure 4 allowed minimal space around the dilution sampling unit and the control unit. The control unit for the dilution sampling system was located just inside the enclosed housing doorway and was connected to the dilution sampling unit by 10 feet of flexible stainless steel tubing. The dilution sampling system positioned at the sampling location is shown during operation in Figure 7.

Figure 8 shows the sampling probe installed in the 6 in. flanged port used for sampling. The control module (Figure 9) was located just inside the enclosed housing doorway, and was connected to the dilution sampling unit. An Electric Low Pressure Impactor (ELPI), manufactured by Dekati (Figure 10), with associated laptop computer was also connected to the sampling module together with other sample collection arrays; sample collection arrays are visible in the background. The dilution system sampling module with all sample collection arrays and instruments attached is shown in Figure 11: note the ELPI in the foreground and the various sample collection arrays (the white filter holders are readily



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



Figure 8. Dilution System Sampling Probe Installed in 6 in. id Flanged Port.



Figure 9. Dilution System Control Module Positioned at the Sampling Location.



Figure 10. ELPI Positioned at the Sampling Location.



Figure 11. Dilution System with All Sample Collection Arrays and Instruments Attached.

visible) attached to the various ports of the dilution system sampling module. Because of the lack of available space in the immediate vicinity of the sampling location, sample recovery (with the exception of the denuders) was conducted inside the ERG mobile laboratory located on the host facility property. Figure 12 shows the denuders being recovered at the sample collection location. The denuders had to be recovered and recharged every 30 minutes. Consequently, the denuders sample collection arrays were transported intact to the recovery area in the ERG mobile laboratory and disassembled. Samples were then labeled, packaged for transport, and placed in a chest-style freezer. Sample logs with sample identification are shown in Appendix B; copies of the chain of custody documentation are also included 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



Figure 12. Recovery and Recharge Area for Denuders Used in the Dilution Sampling System.

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. A stopwatch was started as the reading passed 27 in., 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.

leakage rate =
$$\frac{\Delta P}{\Delta T} \times V \times CF \le 0.1 \, \text{ft}^3 / \text{min}$$
 (4-10)

where:

leakage rate = rate of leakage (ft³/min) ΔP = change in pressure (12 in. water) ΔT = time increment (240 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 $0.1 \text{ ft}^3/\text{ min}$, or more than 1 min 53 sec for a pressure change of 5 in. water. For this test, an average time of 2 min was

required for a 5-in. pressure change to occur. The resulting leak rate was 0.094 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 7).

Unit	Blank Value (ppbC)	
Veriflows		
EPA Unit #418 (Source Veriflow)	5.0	
ERG-1 Ambient Veriflow	1.0	
EPA Unit #315 (Dilution Veriflow)	0.0	
Canisters		
4005	0.0	
4004	2.0	
1482	0.0	
1484	0.0	
1478	0.0	
4037	4.0	
4044	0.0	
3552	0.0	

Table 7. Blank Values for Veriflows and Canisters

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 depended on 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, 11/27/01; Test Run 2, 11/28/01; Test Run 3, 11/29/01), sample collection arrays were attached to various ports on the dilution sampling system, as shown in Figure 13. 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 μ m. 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



Figure 13. Sample Collection Arrays Used for Testing at the Hogged Fuel Boiler.

- *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.
- *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 sintered stainless steel 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 collec tion 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.

Denuder Sampling

In the field, denuders were used in series as pairs on Residence Chamber Port #10. On Test Day 1, the paired denuders were changed and extracted every half hour across the duration of testing, as shown in Table 8. The paired denuders were removed from the sample collection array and separated. Each denuder was 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. Denuder extracts for each halfhour sampling episode were combined, but each half-hour sampling episode generated a separate sample (i.e., 13 denuder extract samples generated). After extraction, the denuders and caps were dried using high purity nitrogen and capped until ready for re-use. A different sampling scheme was used for the paired denuders on Test Days 2 and 3. The first pair of denuders collected sample for a half hour, the second set of paired denuders collected sample for 1 hour, the third pair for 2 hours, and the fourth pair for 4 hours, as shown in Table 8. A denuder sampling log is included in Appendix B.

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 μ m) 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.

Test	Pair Number	Duration
Number		(min)
1	1	35
	2	30
	3	30
	4	30
	5	30
	6	30
	7	30
	8	30
	9	27
	10	30
	11	30
	12	30
	13	30
Total	13 samples	392 min
2	1	30
	2	60
	3	120
	4	240
Total	4 samples	450 min
3	1	30
	2	60
	3	120
	4	240
Total	4 samples	450 min

Table 8. Denuder Sampling Scheme

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 sizedependent 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 O₂ and CO₂ 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 to 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 14 through 22. 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. The dilution ratio averaged 45.5 for the three tests conducted on the hogged fuel boiler.

Run Parameter	Value
Start Time	8:37:06 A.M.
End Time	4:35:46 P.M.
Run Time	478.67 min
Barometric Pressure	29.53 in. Hg
Nozzle Size	#9, 0.299 in. id (160 °C, 2153.4 ft/min)
Canister Flow	dilution canister, 8.125 cm ³ /min residence chamber canister 8.125 cm ³ /min ambient canister, 9.375 cm ³ /min

Table 9. Run Time Summary Information, Test Run 1 (11/27/01)

continued

Table 9. (concluded)

Measurement Parameter	Value

Venturi Flow	30.52 aL/min ^a (18.75 sL/min ^b)
PT-101°	-1.35 in. WC ^d
TE-104 ^e	198.31 °C
Dilution Flow	880.96 aL/min (843.92 sL/min)
PT-102	-1.75 in. WC
TE-108	27.11 °C
Blower Flow	742.52 aL/min (682.13 sL/min)
PT-103	-16.67 in. WC
TE-105	29.93 °C
Dilution Ratio	46.12
TE-101	187.85 °C
TE-102	200.28 °C
TE-103	not used

Sample Flow Rates

			Start/	Fle	0W	Average Flow
Sample	Location	Port	End	(sL/min)	(aL/min)	(sL/min)
PM _{2.5}	Dilution Air	_	start	17.19	17.30	17 10
PM _{2.5}	Dilution Air	_	end	17.19	17.30	17.19
PM _{2.5}	Residence Chamber	10	start	16.89	16.99	16 50
PM _{2.5}	Residence Chamber	10	end	16.29	16.39	10.39
PM _{2.5}	Residence Chamber	8	start	17.19	17.30	17.10
PM _{2.5}	Residence Chamber	8	end	17.19	17.30	17.19
PM _{2.5}	Residence Chamber	6	start	17.19	17.30	17.10
PM _{2.5}	Residence Chamber	6	end	17.19	17.30	17.19
PM _{2.5}	Residence Chamber	4	start	17.04	17.14	17.04
PM _{2.5}	Residence Chamber	4	end	17.04	17.14	17.04
PM _{2.5}	Residence Chamber	2	start	17.04	17.14	17.04
PM _{2.5}	Residence Chamber	2	end	17.04	17.14	17.04
DNPH	Residence Chamber	3	start	0.80	0.81	0.90
DNPH	Residence Chamber	3	end	0.80	0.81	0.80
DNPH	Dilution Chamber	3	start	0.83	0.83	0.02
DNPH	Dilution Chamber	3	end	0.83	0.83	0.83

^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

Run Parameter	Value
Start Time	8:18:04 A.M.
End Time	4:18:14 P.M.
Run Time	480.03 min
Barometric Pressure	29.62 in. Hg
Nozzle Size	#9, 0.299 in. id (160 °C, 2153.4 ft/min)
Canister Flow	dilution canister, 8.125 cm ³ /min residence chamber canister 8.125 cm ³ /min

Table 10. Run Time Summary Information, Test Run 2 (11/28/01)

Measurement Parameter Value

Venturi Flow	30.54 aL/min ^a (18.72 sL/min ^b)
PT-101 ^c	-1.44 in. WC ^d
TE-104 ^e	20.52 °C
Dilution Flow	881.27 aL/min (843.82 sL/min)
PT-102	-1.78 in. WC
TE-108	28.15 °C
Blower Flow	742.46 aL/min (681.84 sL/min)
PT-103	-16.55 in. WC
TE-105	31.10 °C
Dilution Ratio	46.13
TE-101	190.55 °C
TE-102	200.01 °C
TE-103	not used

Sample Flow Rates

			Start/	Fl	ow	Average Flow
Sample	Location	Port	End	(sL/min)	(aL/min)	(sL/min)
PM _{2.5}	Dilution Air		start	17.21	17.27	1714
PM _{2.5}	Dilution Air		end	17.06	17.12	17.14
PM _{2.5}	Residence Chamber	10	start	16.01	16.07	16.00
PM _{2.5}	Residence Chamber	10	end	16.16	16.22	16.09
PM _{2.5}	Residence Chamber	8	start	17.06	17.12	1714
PM _{2.5}	Residence Chamber	8	end	17.21	17.27	17.14
PM _{2.5}	Residence Chamber	6	start	17.06	17.12	17.06
PM _{2.5}	Residence Chamber	6	end	17.06	17.12	17.06
PM _{2.5}	Residence Chamber	4	start	17.21	17.27	1714
PM _{2.5}	Residence Chamber	4	end	17.06	17.12	1/.14
						continued

Table 10. (concluded)

Sample Flow Rates

			Start/	Fle	OW	Average Flow
Sample	Location	Port	End	(sL/min)	(aL/min)	(sL/min)
PM _{2.5}	Residence Chamber	2	start	17.36	17.42	17.20
PM _{2.5}	Residence Chamber	2	end	17.21	17.27	17.29
DNPH	Residence Chamber	3	start	0.83	0.83	0.82
DNPH	Residence Chamber	3	end	0.80	0.81	0.82
DNPH	Dilution Chamber	3	start	0.85	0.85	0.95
DNPH	Dilution Chamber	3	end	0.85	0.85	0.85

^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 (11/29/01)

Run Parameter	Value
Start Time	8:00:00 A.M.
End Time	4:00:30 P.M.
Run Time	480.50 min
Barometric Pressure	29.68 in. Hg
Nozzle Size	#9 0.299 in. id (160 °C, 2153.4 ft/min)
Canister Flow	dilution canister, 8.125 cm ³ /min residence chamber canister 8.125 cm ³ /min

Measurement Parameter Value

Venturi Flow	30.54 aL/min ^a (18.77 sL/min ^b)
PT-101°	-1.48 in. WC ^d
TE-104 ^e	200.10 °C
Dilution Flow	878.49 aL/min (845.52 sL/min)
PT-102	-1.79 in. WC
TE-108	27.23 °C
Blower Flow	742.39 aL/min (684.68 sL/min)
PT-103	-16.86 in. WC
TE-105	30.18 °C
Dilution Ratio	46.10
TE-101	190.64 °C
TE-102	199.89 °C
TE-103	not used

continued

Table 11. (concluded)

Sample Flow Rates

			Start/	Fl	OW	Average Flow
Sample	Location	Port	End	(sL/min)	(aL/min)	(sL/min)
PM _{2.5}	Dilution Air		start	17.24	17.24	17.24
PM _{2.5}	Dilution Air		end	17.24	17.24	17.24
PM _{2.5}	Residence Chamber	10	start	16.04	16.04	16.04
PM _{2.5}	Residence Chamber	10	end	16.04	16.04	10.04
PM _{2.5}	Residence Chamber	8	start	17.09	17.09	17.00
PM _{2.5}	Residence Chamber	8	end	17.09	17.09	17.09
PM _{2.5}	Residence Chamber	6	start	17.24	17.24	17 17
PM _{2.5}	Residence Chamber	6	end	17.09	17.09	1/.1/
PM _{2.5}	Residence Chamber	4	start	17.24	17.24	17 17
PM _{2.5}	Residence Chamber	4	end	17.09	17.09	1/.1/
PM _{2.5}	Residence Chamber	2	start	17.24	17.24	17.24
PM _{2.5}	Residence Chamber	2	end	17.24	17.24	17.24
DNPH	Residence Chamber	3	start	0.87	0.87	0.94
DNPH	Residence Chamber	3	end	0.80	0.80	0.84
DNPH	Dilution Chamber	3	start	0.99	0.99	0.07
DNPH	Dilution Chamber	3	end	0.94	0.94	0.97

^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 14. Blower Flow, Day 1 (11/27/01).



Figure 15. Dilution Flow, Day 1 (11/27/01).



Figure 16. Venturi Flow, Day 1 (11/27/01).



Figure 17. Blower Flow, Day 2 (11/28/01).



Figure 18. Dilution Flow, Day 2 (11/28/01).



Figure 19. Venturi Flow, Day 2 (11/28/01).



Figure 20. Blower Flow, Day 3 (11/29/01).



Figure 21. Dilution Flow, Day 3 (11/29/01).



Figure 22. Venturi Flow, Day 3 (11/29/01).

Dilution System Sample Collection Arrays: Train 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 and field sample log with sample identification are supplied in Appendix B.

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 L.

PM_{2.5} Mass

Teflon membrane (Gelman Teflon) filters of 2 μ m 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- μ m 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- μ L 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 μ L 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 prefired quartz filters was determined by National Institute for Occupational Safety and Health (NIOSH) Method 5040 (NIOSH, 1994)⁷ 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 CO₂ in a bed of granular MnO₂ 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 CO₂ 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 μ m 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 anteisoalkanes 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 listed in Table 12 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)".⁸ 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. MDLs⁹ for the carbonyl analysis are shown in Table 12.

		Method Detection Limits ⁸
Compound	CAS No.	(µg)
formaldehyde	50-00-0	0.0838
acetaldehyde	75-07-0	0.0916
acetone	67-64-1	0.0428
propionaldehyde	123-38-6	0.0934
crotonaldehyde	4170-30-3	0.1283
butyraldehyde	123-72-8	0.0956
benzaldehyde	100-52-7	0.0959
isovaleraldehyde	590-86-3	0.1076
valeraldehyde	110-62-3	0.1758
o-tolualdehyde	529-20-4	0.1439
<i>m</i> -tolualdehyde	620-23-5	0.1439
<i>p</i> -tolualdehyde	104-87-0	0.1439
hexaldehyde	66-25-1	0.1377
2,5-dimethylbenzaldehyde	5779-94-2	0.1337 ^a
diacetyl	432-03-8	0.0154 ^a
methacrolein	78-85-3	0.0125ª
2-butanone	78-93-3	0.0125ª
glyoxal	107-22-2	0.0412 ^a
acetophenone	98-86-2	0.0250^{a}
methylglyoxal	78-98-8	0.0244^{a}
octanal	124-13-0	0.0100^{a}
nonanal	124-19-6	0.0182ª

Table 12. Carbonyl Compounds Analyzed by High Performance LiquidChromatography: Method Detection Limits

^a Estimated value.

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 23, 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 $\pm 15\%$ 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 (SNMOCs) 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)".¹⁰ The analysis of SNMOCs was performed according to the procedures of "Technical Assistance Document for Sampling and Analysis of Ozone Precursors".⁸ Detection limits⁹ for air toxics are shown in Table 13 and for the SNMOCs in Table 14.

Particle Size Distribution Data

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

Table 13. Method Detection Limits for Air Toxics Compounds (Analytical Method TO-15)¹⁰

		Method Detection Limit ^{9, a}
Compound	CAS No.	(µg/m ³)
Acetylene	74-86-2	0.24
Propylene	115-07-1	0.17
Dichlorodifluoromethane	75-71-8	0.40
Chloromethane	74-87-3	0.24
Dichlorotetrafluoroethane	1320-37-2	0.70
Vinyl chloride	75-01-4	0.31
1,3-Butadiene	106-99-0	0.31
Bromomethane	74-83-9	0.70
Chloroethane	75-00-3	0.42
Acetonitrile	75-05-8	0.84
Acetone	67-64-1	1.23
Trichlorofluoromethane	75-69-4	0.45
Acrylonitrile	107-13-1	0.91
1,1-Dichloroethene	75-35-4	0.79
Methylene chloride	75-09-2	0.42
Trichlorotrifluoroethane	26523-64-8	1.07
trans-1,2-Dichloroethylene	56-60-5	0.47
1,1-Dichloroethane	75-34-3	0.65
Methyl tert-butyl ether	1634-04-1	1.29
Methyl ethyl ketone	78-93-3	0.88
Chloroprene	126-99-8	0.73
cis-1,3-Dichloroethylene	156-59-2	0.79
Bromochloromethane	74-97-5	1.26

continued

Table 13. (concluded)

Compound	CAS No.	Method Detection Limit ^{9, a} (µg/m³)
Chloroform	67-66-3	0.49
Ethyl <i>tert</i> -butyl ether	637-92-3	1.25
1,2-Dichloroethane	107-06-2	0.48
1,1,1-Trichloroethane	71-55-6	0.65
Benzene	71-43-2	0.25
Carbon tetrachloride	56-23-5	1.01
<i>tert</i> -Amyl methyl ether	994-05-8	1.00
1,2-Dichloropropane	78-87-5	0.65
Ethyl acrylate	140-88-5	1.31
Bromodichloromethane	75-27-4	0.80
Trichloroethylene	79-01-6	0.75
Methyl methacrylate	80-62-6	1.47
cis-1,2-Dichloropropene	10061-01-5	0.82
Methyl isobutyl ketone	108-10-1	1.36
trans-1,2-Dichloropropene	10061-02-6	1.00
1,1,2-Trichloroethane	79-00-5	0.65
Toluene	108-88-3	0.45
Dibromochloromethane	124-48-1	1.36
1,2-Dibromoethane	106-93-4	1.23
<i>n</i> -Octane	111-65-9	0.56
Tetrachloroethylene	127-18-4	0.81
Chlorobenzene	108-90-7	0.55
Ethylbenzene	100-41-4	0.35
<i>m-, p-</i> Xylene	108-38-3/106-42-3	0.87
Bromoform	75-25-2	1.65
Styrene	100-42-5	0.59
1,1,2,2-Tetrachloroethane	79-34-5	0.82
o-Xylene	95-47-6	0.43
1,3,5-Trimethylbenzene	108-67-8	0.69
1,2,4-Trimethylbenzene	95-63-6	0.69
<i>m</i> -Dichlorobenzene	541-73-1	0.60
Chloromethylbenzene	100-44-7	0.72
<i>p</i> -Dichlorobenzene	106-46-7	1.08
o-Dichlorobenzene	95-50-1	0.72
1,2,4-Trichlorobenzene	120-82-1	0.89
Hexachloro-1,3-butadiene	87-68-3	1.28

^a MDLs reported here are based on nominal injection volume of 200 mL of gas.

		Method Detection Limits ⁸
Compound	CAS No.	$(\mu g/m^3)$
Ethylene	74-85-1	0.50
Acetylene	74-86-2	0.47
Ethane	74-84-0	0.54
Propylene	115-07-1	0.44
Propane	74-98-6	0.46
Propyne	74-99-7	0.42
Isobutane	75-28-5	0.43
Isobutene/1-butene	115-11-7/106-98-0	0.21
1,3-Butadiene	106-99-0	0.40
<i>n</i> -Butane	106-97-8	0.43
trans-2-Butene	624-64-6	0.42
cis-2-Butene	590-18-1	0.42
3-Methyl-1-butene	563-45-1	0.32
Isopentane	78-78-4	0.33
1-Pentene	109-67-1	0.32
2-Methyl-1-butene	563-46-2	0.45
<i>n</i> -Pentane	109-66-0	0.33
Isoprene	78-79-4	0.31
trans-2-Pentene	646-04-8	0.33
cis-2-Pentene	627-20-3	0.33
2-Methyl-2-butene	513-35-9	0.32
2,2-Dimethylbutane	75-83-2	0.46
Cyclopentene	142-29-0	0.31
4-Methyl-1-pentene	691-37-2	0.45
Cyclopentane	287-92-3	0.32
2,3-Dimethylbutane	79-29-8	0.46
2-Methylpentane	107-83-5	0.46
3-Methylpentane	96-14-0	0.46
2-Methyl-1-pentene	763-29-1	0.46
1-Hexene	592-41-6	0.46
2-Ethyl-1-butene	760-21-4	0.45
<i>n</i> -Hexane	110-54-3	0.46
trans-2-Hexene	4050-45-7	0.46
cis-2-Hexene	7688-21-3	0.46
Methylcyclopentane	96-37-7	0.45
2,4-Dimethylpentane	108-08-7	0.35
Benzene	71-43-2	0.42
Cyclohexane	110-82-7	0.45
2-Methylhexane	591-76-4	0.40

 Table 14. Method Detection Limits for Speciated Nonmethane Organic Compounds

continued

Table 14. (concluded)

		Method Detection Limits ⁸
Compound	CAS No.	$(\mu g/m^3)$
2,3-Dimethylpentane	565-59-3	0.40
3-Methylhexane	589-34-4	0.40
1-Heptene	592-76-7	0.39
2,2,4-Trimethylpentane	540-84-1	0.51
<i>n</i> -Heptane	142-82-5	0.40
Methylcyclohexane	108-87-2	0.39
2,2,3-Trimethylpentane	564-02-3	0.51
2,3,4-Trimethylpentane	565-75-3	0.51
Toluene	108-88-3	0.37
2-Methylheptane	592-27-8	0.51
3-Methylheptane	589-81-1	0.51
1-Octene	111-66-0	0.50
<i>n</i> -Octane	111-65-9	0.51
Ethylbenzene	100-41-4	0.52
<i>m</i> -, <i>p</i> -Xylene	108-38-3/106-42-3	0.47
Styrene	100-42-5	0.46
o-Xylene	95-47-6	0.47
1-Nonene	124-11-8	0.40
<i>n</i> -Nonane	111-84-2	0.41
Isopropylbenzene	98-82-8	0.38
α-Pinene	80-56-8	0.39
<i>n</i> -Propylbenzene	103-65-1	0.38
<i>m</i> -Ethyltoluene	620-14-4	0.38
<i>p</i> -Ethyltoluene	622-96-8	0.38
1,3,5-Trimethylbenzene	108-67-8	0.38
o-Ethyltoluene	611-14-3	0.38
β-Pinene	127-91-3	0.39
1,2,4-Trimethylbenzene	95-63-6	0.38
1-Decene	872-05-9	0.33
<i>n</i> -Decane	124-18-5	0.33
1,2,3-Trimethylbenzene	526-73-8	0.38
<i>m</i> -Diethylbenzene	141-93-5	0.32
<i>p</i> -Diethylbenzene	105-05-5	0.32
1-Undecene	821-95-4	0.49
<i>n</i> -Undecane	1120-21-4	0.50
1-Dodecene	112-41-4	0.49
<i>n</i> -Dodecane	112-40-3	0.50
1-Tridecene	2437-56-1	0.49
<i>n</i> -Tridecane	629-50-5	0.50
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.

Emission Factors for PM_{2.5} Mass and Gas-Phase Carbonyls and Nonmethane Organic Compounds

Emission factors (mass of species emitted per unit mass of fuel consumed) for PM₂₅ mass, gas-phase carbonyl compounds, and gas-phase NMOCs are shown in Table 15. Examples of the emission factor calculations are provided in Appendix C. Supporting analytical data for the PM_{2.5}, carbonyl, and NMOC results are provided in Appendices D, E, and F, respectively. Concentrations of PM_{2.5}, carbonyl compounds, and NMOCs in the diluted stack gas were corrected for the concentrations of these species in the cleaned dilution air. Significant concentrations of *n*-hexane, methylene chloride, and acetone were also observed in the gas samples collected from the dilution sampler during all three test days with unusually high concentrations of these compounds observed on the second test day. However, the presence of these compounds may be artifactual. Different sets of the XAD-coated annular denuders were extracted near the sampling location using these same three solvents, and the denuders were placed into service on an alternating schedule to avoid exceeding the capacity of a single set of denuders during a test run. Therefore, the presence of these three compounds in the stack gas samples collected by the dilution sampler and in the ambient air sample collected on the stack are considered suspect and are likely due to contamination arising from on-site extraction of the organic denuders. Values for NMOC (both speciated and total), carbonyl compounds (both speciated and total), and air toxics compounds have been recalculated deleting these compounds on the second test day (11/28/01). DNPH-coated silica gel cartridge and SUMMA canister field blank samples for carbonyl compounds and NMOC, respectively, were obtained only during the first test day but did not show significant levels of either acetone or *n*-hexane. Methylene chloride was also observed in much higher amounts in the stack gas on Test Day 2. Values for the PM₂₅ mass emission factors were very consistent for the three test days and averaged 49.99 mg/kg fuel.

Emission Factor	11/27/01	11/28/01	11/29/01	Mean	Standard Deviation
PM _{2.5} Mass Emission Factor (mg/kg fuel burned)	51.95	49.82	48.19	49.99	1.89
Speciated Carbonyl Compounds Mass Emission Factor (mg/kg fuel burned)	3.46	0.90 ^a	1.12	1.83	1.42
Total (speciated + unspeciated) Carbonyl Compounds Mass Emission Factor (mg/kg fuel burned)	3.46 ^b	2.74ª	1.99	2.73	0.74
Speciated NMOC Mass Emission Factor (mg/kg fuel burned)	12.24	25.32 ^a	22.97	20.18	6.89
Total (speciated + unspeciated) NMOC Mass Emission Factor (mg/kg fuel burned)	11.30	34.07 ^a	13.28	19.55	12.61

Table 15. Fine Particle, Carbonyl, and Nonmethane Organic Compound Emission Factors from a Hogged Fuel Boiler at a Pulp and Paper Facility

^a Suspected artifactual compounds (acetone and *n*-hexane) were deleted in the calculation of emission factors.

^b On Test Day 1, the difference between residence chamber air and dilution air was slightly negative for unspeciated carbonyl compounds, indicating more carbonyl compounds in the dilution air. The value of zero is used to determine total carbonyl compounds.

Gas-Phase Carbonyl Compounds Profile

Analytical results in terms of the mass fractions of individual gas-phase carbonyl emissions for each of the three test days are shown in Table 16. Mass fractions were calculated by dividing the mass of an individual compound by the total mass of speciated plus unspeciated carbonyl compounds. The suspected artifactual value for acetone on Test Day 2 was omitted from the calculations. The "RC-DA" notation in the tabular column headings indicates that amounts of individual carbonyl compounds found in the diluted stack gas samples were background corrected by subtracting the amounts of the same carbonyl compounds found in the dilution air. Tabulated "Total Unspeciated" carbonyl compounds represent the total mass of compounds characterized as carbonyl compounds but not specifically identified because no analytical standards were available. Amounts of the unspeciated carbonyl compounds account for a significant portion of the reported total carbonyl compound mass in each case. Uncertainties in the reported averages are the standard deviation of the three replicate test results. Supporting data for carbonyls can be found in Appendix E.

	Compound	CAS No.	Field Blank (µg)	Carbonyls RC-DA 11/27/01 (µg)	Mass Fraction 11/27/01	Carbonyls RC-DA 11/28/01 (µg)	Mass Fraction 11/28/01	Carbonyls RC-DA 11/29/01 (µg)	Mass Fraction 11/29/01	Mean Mass Fraction	Uncertainty
	formaldehyde	50-00-0	0.0360	0.2770	0.0567	0.4400	0.0924	0.2400	0.0848	0.0484	0.0412
	acetaldehyde	75-07-0	0.0650	ND^{a}	ND	0.9220	0.1937	0.4520	0.1597	0.0558	0.0901
	acetone	67-64-1	0.1810	3.9360	0.8057	ND^b	ND	0.6700	0.2367	0.6682	0.3818
	propionaldehyde	123-38-6	ND	0.1260	0.0258	0.0690	0.0145	0.0510	0.0180	0.0148	0.0129
	crotonaldehyde	4170-30-0	ND	ND	ND	ND	ND	ND	ND	ND	ND
	butyr/isobutyraldehyde	123-72-8	0.0520	0.0830	0.0170	0.0680	0.0143	0.0710	0.0251	0.0142	0.0125
	benzaldehyde	100-52-7	ND	0.0680	0.0139	0.0430	0.0090	0.0360	0.0127	0.0090	0.0075
	isovaleraldehyde	590-86-3	ND	ND	ND	ND	ND	ND	ND	ND	ND
	valeraldehyde	110-62-3	ND	0.0690	0.0141	0.0470	0.0099	0.0320	0.0113	0.0086	0.0073
61	o-tolualdehyde	529-20-4	ND	ND	ND	ND	ND	ND	ND	ND	ND
	<i>m</i> -tolualdehyde	620-23-5	ND	ND	ND	ND	ND	ND	ND	ND	ND
	<i>p</i> -tolualdehyde	104-87-0	ND	ND	ND	0.0330	0.0069	ND	ND	0.0001	0.0002
	hexaldehyde	66-25-1	0.0180	0.1080	0.0221	0.0540	0.0113	0.0210	0.0074	0.0100	0.0111
	2,5-dimethylbenzaldehyde	5779-94-2	ND	ND	ND	ND	ND	ND	ND	ND	ND
	diacetyl	431-03-8	ND	0.0040	0.0008	ND	ND	ND	ND	0.0003	0.0005
	methacrolein	78-85-3	ND	0.0020	0.0004	ND	ND	ND	ND	0.0001	0.0002
	2-butanone	78-93-3	0.0160	0.0360	0.0074	0.0660	0.0139	0.0380	0.0134	0.0071	0.0064
	glyoxal	107-22-2	0.0830	0.0060	0.0012	ND	ND	ND	ND	0.0004	0.0007
	acetophenone	98-86-2	ND	0.0390	0.0080	0.0280	0.0059	0.0300	0.0106	0.0063	0.0054
	methylglyoxal	78-98-8	0.0480	0.0500	0.0102	0.0620	0.0130	0.0030	0.0011	0.0039	0.0055
	octanal	124-13-0	ND	0.0810	0.0166	0.0310	0.0065	ND	ND	0.0056	0.0095
	nonanal	124-19-6	0.1250	ND	ND	0.1100	0.0231	0.0030	0.0011	0.0007	0.0006
											continued

 Table 16. Gas-Phase Carbonyl Compounds Profile, Hogged Fuel Boiler (Carbonyl Compounds Collected in Diluted Stack

 Gas Corrected for Carbonyl Compounds in Dilution Air)

Table 16. (Concluded)

		Field Blank	Carbonyls RC-DA 11/27/01	Mass Fraction	Carbonyls RC-DA 11/28/01	Mass Fraction	Carbonyls RC-DA 11/29/01	Mass Fraction	Mean Mass	
Compound	CAS No.	(µg)	(µg)	11/27/01	(µg)	11/28/01	(µg)	11/29/01	Fraction	Uncertainty
Sum, Speciated		0.6240	4.8850	1.0000	1.9730	0.4145	1.6970	0.5497	0.8421	0.2535
Sum, Unspeciated		0.8730	c		2.7865	0.5855	1.2745	0.4503	0.2368	0.3019
Total (speciated + unspeciated)		1.4970	4.8850		4.7595		2.9215			
										Standard
									Mean	Deviation
Emission Factor, mg/kg fuel	(Speciated)		3.4555		0.8991		1.1230		1.83	1.42
Emission Factor, mg/kg fuel	(Total)		3.4555		2.7411		1.9920		2.73	0.74

^a ND = not detected.

^b Carbonyl values are skewed by an artifactual, high value for acetone on Day 2 of testing (November 28, 2001). This value has been deleted. ^c The difference between RC and DA for unspeciated carbonyl compounds was slightly negative on the first test day.

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Gas-Phase Air Toxic Compounds—Whole Air Samples

The ERG concurrent analysis produces analytical results for both air toxics and speciated/unspeciated NMOCs; these results are presented separately. Method detection limits for the air toxics compounds are shown in Table 13, with values typically $1.65 \ \mu g/m^3$ or less. Most of the values for the small number of air toxic compounds actually observed at the hogged fuel boiler are at the lower end of the calibration curve for this analysis; analytical results are shown in Table 17. Analytical results for an ambient canister taken at the test location are included for reference. The concentrations observed in the ambient air on Test Day 1 (the only day an ambient sample was taken) are higher than the concentrations observed in the stack for nearly all of the air toxic compound emissions on any test day. Methylene chloride was found at fairly high concentrations in the ambient air sample taken on Test Day 1 and in the stack emissions on Test Day 2. Test Day 2 was also the day the high concentrations of *n*-hexane and acetone, considered to be artifactual, were detected in the stack gas samples. Supporting data for the air toxics are presented in Appendix G.

Compounds Detected	CAS No.	Ambient (µg/m³)	RC-DA 11/27/01 (µg/m ³)	RC-DA 11/28/01 (μg/m ³)	RC-DA 11/29/01 (µg/m ³)
acetylene	74-86-2	0.39	0.31	0.30	0.48
propylene	115-07-1	ND^{a}	0.30	0.08	ND
dichlorodifluoromethane	75-71-8	2.58	ND	ND	ND
chloromethane	74-87-3	1.80	ND	ND	ND
trichlorofluoromethane	75-69-4	1.40	ND	ND	ND
methylene chloride	75-09-2	485.21	61.59	ND^{b}	8.67
trichlorotrifluoroethane	26253-64-8	0.60	ND	ND	ND
1,1,1-trichloroethane	71-55-6	0.13	ND	ND	ND
benzene	71-43-2	2.24	9.35	10.94	9.59
carbon tetrachloride	56-23-5	0.61	ND	ND	ND
toluene	108-88-3	0.74	0.52	0.38	0.33
ethylbenzene	100-41-4	0.14	0.20	0.30	0.22
<i>m</i> -, <i>p</i> -xylene	108-38-3/106-42-3	0.67	ND	ND	ND
o-xylene	95-47-6	0.16	ND	ND	ND
1 2 4-trimethylbenzene	95-63-6	0.20	0.23	ND	ND

Table 17. Summarized Analytical Results for Air Toxics Compounds Observed on Each of the Three Test Days (11/27/01 through 11/29/01)

^a ND = not detected.

^b Consistent with other gas-phase compounds, artifactual methylene chloride is deleted on Test Day 2.

Gas-Phase Speciated Nonmethane Organic Compounds Profile

Analysis of whole air samples of dilution air and residence chamber air using ERG's concurrent analysis generated analytical data for SNMOCs, as well as unspeciated NMOCs. Analytical results are presented as mass fractions of total NMOC (speciated plus unspeciated). Mass emission rates of total SNMOCs and total (speciated plus unspeciated) NMOCs are also provided. Reported results include a correction for any amounts of NMOC found in the air used to dilute the sampled stack gas. The "RC-DA" notation in the table column headings indicates this correction, which was obtained by subtracting the amounts found in the dilution air (DA) from the amounts found in the samples collected from the sampler residence chamber (RC). Uncertainties associated with the averages in the tables are standard deviations of the three test day results. Analytical results are reported in Table 18. Supporting data for the NMOC analysis are shown in Appendix F.

PM_{2.5} Elemental/Organic Carbon, Major Inorganic Ion, and Major Element Profile

Emissions of EC/OC, major inorganic ions, and major elements are reported in Table 19 as mass fraction of measured $PM_{2.5}$ mass. Uncertainties in the reported mass fraction averages are expressed as the standard deviation of the replicate results.

Particle Size Distribution Data

The ELPI system was operated in a "charged" mode on all three test days (11/27/01, 11/28/01, and 11/29/01) 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.

The accumulated results of the individual runs are summarized in the following tables, diagrams, and figures. Table 20 lists the collected mass in each of twelve stages for each test day. The mean particle diameter of each stage is listed in increasing size order from 42.78 to 8328.12 nm. Figures 23, 24, and 25 show 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 graph of particle mass by channel is also shown in these figures.

Con	npound	CAS No.	SNMOC RC-DA 11/27/01 (μg)	Mass Fraction 11/27/01	SNMOC RC-DA 11/28/01 (µg)	Mass Fraction 11/28/01	SNMOC RC-DA 11/29/01 (μg)	Mass Fraction 11/29/01	Mean Mass Fraction	Uncertainty
ethylene		74-85-1	0.0024	0.0137	0.0030	0.0057	0.0028	0.0139	0.0111	0.0047
acetylene		74-86-2	0.0016	0.0090	0.0016	0.0029	0.0023	0.0114	0.0078	0.0044
ethane		74-84-0	0.0016	0.0093	0.0023	0.0044	0.0023	0.0111	0.0082	0.0035
propylene		115-07-1	0.0026	0.0148	0.0025	0.0047	0.0020	0.0097	0.0097	0.0050
propane		74-98-6	0.0020	0.0115	0.0019	0.0035	0.0024	0.0118	0.0089	0.0047
propyne		74-99-7	ND^{a}	ND	ND	ND	ND	ND	ND	ND
isobutane		75-28-5	0.0011	0.0060	0.0007	0.0013	0.0011	0.0053	0.0042	0.0025
isobutene/1	-butene	115-11-7/106-98-0	0.0037	0.0212	0.0024	0.0045	0.0025	0.0124	0.0127	0.0083
1,3-butadie	ne	106-99-0	ND	ND	ND	ND	ND	ND	ND	ND
<i>n</i> -butane		106-97-8	0.0020	0.0113	0.0021	0.0039	0.0026	0.0126	0.0093	0.0047
S trans-2-but	ene	624-64-6	0.0012	0.0066	0.0009	0.0016	0.0011	0.0051	0.0045	0.0026
cis-2-buten	e	590-18-1	0.0019	0.0106	0.0017	0.0031	0.0015	0.0074	0.0071	0.0037
3-methyl-1-	-butene	563-45-1	ND	ND	ND	ND	ND	ND	ND	ND
isopentane		78-78-4	0.0022	0.0124	ND	ND	0.0025	0.0122	0.0082	0.0071
1-pentene		109-67-1	0.0011	0.0060	0.0019	0.0035	0.0015	0.0074	0.0056	0.0020
2-methyl-1-	-butene	563-46-2	ND	ND	ND	ND	ND	ND	ND	ND
<i>n</i> -pentane		109-66-0	0.0020	0.0110	0.0022	0.0041	0.0013	0.0065	0.0072	0.0035
isoprene		78-79-4	0.0008	0.0044	ND	ND	ND	ND	0.0015	0.0025
trans-2-pen	itene	646-04-8	0.0015	0.0084	0.0012	0.0023	0.0014	0.0069	0.0058	0.0032
cis-2-penter	ne	627-20-3	0.0015	0.0084	0.0013	0.0025	0.0018	0.0088	0.0065	0.0035
2-methyl-2-	-butene	513-35-9	ND	ND	ND	ND	ND	ND	ND	ND
2,2-dimethy	ylbutane	75-83-2	0.0035	0.0201	0.0036	0.0068	0.0076	0.0374	0.0214	0.0153
cyclopenter	ne	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
cyclopentar	ne	287-92-3	0.0013	0.0073	0.0013	0.0025	0.0014	0.0067	0.0055	0.0026

Table 18. Speciated and (Speciated + Unspeciated) NMOC Data for All Three Test Days, with Mass Fraction, Mean, and Uncertainty

			SNMOC		SNMOC		SNMOC			
			RC-DA	Mass	RC-DA	Mass	RC-DA	Mass	Mean	
		CACN	11/27/01	Fraction	11/28/01	Fraction	11/29/01	Fraction	Mass	T T / • /
	Compound	CAS No.	(µg)	11/27/01	(µg)	11/28/01	(µg)	11/29/01	Fraction	Uncertainty
	2,3-dimethylbutane	79-29-8	0.0026	0.0146	0.0028	0.0052	0.0027	0.0132	0.0110	0.0051
	2-methylpentane	107-83-5	0.0414	0.2343	0.0392	0.0731	0.0282	0.1380	0.1485	0.0811
	3-methylpentane	96-14-0	0.0020	0.0110	0.0348	0.0650	0.0027	0.0132	0.0297	0.0306
	2-methyl-1-pentene	763-29-1	ND	ND	ND	ND	ND	ND	ND	ND
	1-hexene	592-41-6	0.0029	0.0165	0.0036	0.0067	0.0023	0.0114	0.0116	0.0049
	2-ethyl-1-butene	760-21-4	ND	ND	ND	ND	ND	ND	ND	ND
	<i>n</i> -hexane	110-54-3	0.0086	0.0488	1.4510 ^b	ND	0.0191	0.0932	0.0473	0.0466
	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	0.0018	0.0104	0.2064	0.3851	0.0038	0.0185	0.1380	0.2141
	2,4-dimethylpentane	108-08-7	0.0014	0.0079	0.0020	0.0037	0.0023	0.0114	0.0077	0.0039
	benzene	71-43-2	0.0326	0.1844	0.0416	0.0776	0.0356	0.1740	0.1453	0.0589
	cyclohexane	110-82-7	0.0021	0.0117	0.0019	0.0035	0.0024	0.0116	0.0089	0.0047
66	2-methylhexane	591-76-4	0.0033	0.0188	0.0008	0.0015	0.0032	0.0156	0.0120	0.0092
•	2,3-dimethylpentane	565-59-3	0.0027	0.0152	0.0033	0.0061	0.0035	0.0173	0.0129	0.0060
	3-methylhexane	589-34-4	0.0014	0.0079	0.0012	0.0023	0.0016	0.0078	0.0060	0.0032
	1-heptene	592-76-7	0.0095	0.0538	ND	ND	ND	ND	0.0179	0.0311
	2,2,4-trimethylpentane	540-84-1	0.0013	0.0073	ND	ND	0.0232	0.1134	0.0402	0.0635
	<i>n</i> -heptane	142-82-5	0.0014	0.0077	0.0020	0.0036	0.0010	0.0050	0.0054	0.0021
	methylcyclohexane	108-87-2	0.0014	0.0079	0.0018	0.0033	0.0014	0.0067	0.0060	0.0024
	2,2,3-trimethylpentane	564-02-3	ND	ND	ND	ND	ND	ND	ND	ND
	2,3,4-trimethylpentane	565-75-3	0.0015	0.0086	0.0012	0.0023	0.0012	0.0057	0.0055	0.0032
	toluene	108-88-3	0.0025	0.0139	0.0018	0.0033	0.0018	0.0086	0.0086	0.0053
	2-methylheptane	592-27-8	0.0010	0.0055	0.0012	0.0023	0.0010	0.0050	0.0042	0.0017
	3-methylheptane	589-81-1	0.0011	0.0064	0.0016	0.0030	0.0013	0.0063	0.0052	0.0019
	1-octene	111-66-0	ND	ND	ND	ND	ND	ND	ND	ND

Table 18. (continued)

Commented	CASNe	SNMOC RC-DA 11/27/01	Mass Fraction	SNMOC RC-DA 11/28/01	Mass Fraction	SNMOC RC-DA 11/29/01	Mass Fraction	Mean Mass Euroction	
Compound	CAS NO.	(µg)	0.0120	(µg)	11/28/01	(µg)	11/29/01	Fraction	
<i>n</i> -octane	111-65-9	0.0025	0.0139	0.0025	0.0047	0.0024	0.0116	0.0101	0.0048
ethylbenzene	100-41-4	0.0011	0.0062	0.0011	0.0021	ND	ND	0.0028	0.0031
<i>m</i> -xylene/ <i>p</i> -xylene	108-38-3/106-42-3	0.0021	0.0117	0.0029	0.0054	0.0012	0.0061	0.0077	0.0035
styrene	100-42-5	ND	ND	ND	ND	ND	ND	ND	ND
o-xylene	95-47-6	0.0055	0.0309	0.0060	0.0112	0.0059	0.0288	0.0236	0.0108
1-nonene	124-11-8	ND	ND	ND	ND	ND	ND	ND	ND
<i>n</i> -nonane	111-84-2	0.0016	0.0090	0.0027	0.0050	0.0021	0.0103	0.0081	0.0028
isopropylbenzene	98-82-8	0.0009	0.0053	0.0018	0.0033	0.0013	0.0063	0.0050	0.0015
alpha-pinene	80-56-8	ND	ND	ND	ND	ND	ND	ND	ND
<i>n</i> -propylbenzene	103-65-1	ND	ND	0.0009	0.0017	0.0014	0.0067	0.0028	0.0035
<i>m</i> -ethyltoluene	620-14-4	0.0007	0.0038	0.0009	0.0016	0.0009	0.0044	0.0032	0.0015
<i>p</i> -ethyltoluene	622-96-8	0.0011	0.0064	0.0009	0.0017	0.0010	0.0050	0.0044	0.0024
1,3,5-trimethylbenzene	108-67-8	ND	ND	ND	ND	0.0009	0.0044	0.0015	0.0025
S o-ethyltoluene	611-14-3	0.0015	0.0086	ND	ND	ND	ND	0.0029	0.0050
beta-pinene	127-91-3	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-trimethylbenzene	95-63-6	0.0009	0.0051	0.0010	0.0019	0.0008	0.0040	0.0037	0.0016
1-decene	872-05-9	ND	ND	ND	ND	ND	ND	ND	ND
<i>n</i> -decane	124-18-5	0.0016	0.0093	0.0016	0.0030	0.0011	0.0055	0.0059	0.0032
1,2,3-trimethylbenzene	526-73-8	ND	ND	ND	ND	ND	ND	ND	ND
<i>m</i> -diethylbenzene	141-93-5	ND	ND	ND	ND	ND	ND	ND	ND
<i>p</i> -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
<i>n</i> -undecane	1120-21-4	0.0001	0.0007	0.0013	0.0025	ND	ND	0.0010	0.0013
1-dodecene	112-41-4	ND	ND	ND	ND	ND	ND	ND	ND
<i>n</i> -dodecane	112-40-3	0.0009	0.0051	0.0001	0.0001	ND	ND	0.0017	0.0029
1-tridecene	2437-56-1	ND	ND	ND	ND	ND	ND	ND	ND

Table 18. (continued)

Compound	CAS No.	SNMOC RC-DA 11/27/01 (µg)	Mass Fraction 11/27/01	SNMOC RC-DA 11/28/01 (µg)	Mass Fraction 11/28/01	SNMOC RC-DA 11/29/01 (μg)	Mass Fraction 11/29/01	Mean Mass Fraction	Uncertainty
<i>n</i> -tridecane	629-50-5	ND	ND	ND	ND	ND	ND	ND	ND
Total Speciated		0.1768	1.0001	0.4015	0.7491	0.1955	0.9556	0.9016	0.1339
Total Unspeciated		0.0000	0.0000	0.1344	0.2508	0.0091	0.0445	0.0984	0.1338
Total (speciated + unspecia	ated) ^c	0.1768		0.5359		0.2046			
									Standard
							_	Mean	Deviation
Speciated Emission Factor	(mg/kg fuel burned)	12.2357		25.3226 ^b		22.9732	_	20.18	6.98
Total (speciated + unspeciated) Emission Factor (mg/kg fuel burned)		11.3011		34.0711 ^b		13.2803		19.55	12.61

Table 18. (concluded)

^a ND = not detected. ^b The high artifactual level of *n*-hexane has been deleted for this test day. ^c Total NMOC with unknowns in μ g/m³ is an estimate based on propane only.

	11/27/01	11/28/01	11/29/01	Mean	Uncertainty
PM _{2.5} Composition (mass fraction)					
Organic Carbon	0.0588	0.0628	0.0638	0.0618	0.0026
Elemental Carbon	0.0140	0.0172	0.0212	0.0175	0.0036
Elements (mass fraction)					
Silicon	0.1778	0.1674	0.1710	0.1721	0.0053
Aluminum	0.1641	0.1513	0.1538	0.1564	0.0068
Potassium	0.0690	0.0612	0.0738	0.0680	0.0064
Iron	0.0450	0.0474	0.0448	0.0457	0.0014
Sulfur	0.0308	0.0250	0.0301	0.0286	0.0032
Calcium	0.0242	0.0224	0.0244	0.0237	0.0011
Titanium	0.0163	0.0158	0.0162	0.0161	0.0003
Chlorine	0.0091	0.0086	0.0106	0.0094	0.0010
Sodium	0.0085	0.0091	0.0100	0.0092	0.0008
Phosphorus	0.0055	0.0054	0.0062	0.0057	0.0004
Magnesium	0.0052	0.0049	0.0054	0.0052	0.0003
Zinc	0.0027	0.0032	0.0022	0.0027	0.0005
Vanadium	0.0011	0.0012	0.0010	0.0011	0.0001
Major Water-Soluble Ions (mass frac	ction)				
Sulfate	0.0868	0.0833	0.0858	0.0853	0.0018
Potassium	0.0226	0.0201	0.0280	0.0236	0.0040
Chloride	0.0142	0.0158	0.0143	0.0148	0.0009

Table 19. Fine Particle Chemical Composition of Emissions from a Hogged FuelBoiler at a Pulp and Paper Facility

^a ND = Not Detected

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. After mass determination, the foils were also available for organic mass determinations. Plots of particle counts versus size, particle mass versus size, and particle mass versus stage are shown for each test day in Figures 23, 24, and 25. 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.

Table 20. Particle Size Distribution Data

November 27, 2001

	Stage ^a	1	2	3	4	5	6	7	8	9	10	11	12
	Di, ^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	2.90×10 ⁴	7.38×10^{4}	6.77×10 ⁴	2.05×10^{4}	2.34×10 ³	6.91×10^{2}	5.23×10^{2}	0.000	1.25×10^{2}	12.8	1.17	5.60×10 ⁻¹
	M, ^d mg/m ³	0.0004	0.0047	0.0169	0.0181	0.0075	0.0099	0.0270	ND ^e	0.0967	0.0443	0.0196	0.0307
	dM/dlog(Dp), mg/m ³	1.19×10 ⁻³	1.98×10 ⁻²	8.30×10 ⁻²	9.70×10 ⁻²	4.02×10 ⁻²	4.68×10 ⁻²	1.42×10 ⁻¹	0.000	5.30×10 ⁻¹	2.11×10 ⁻¹	8.68×10 ⁻²	1.69×10 ⁻¹
	November 28, 2001	l											
	Stage	1	2	3	4	5	6	7	8	9	10	11	12
	Di, 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	1.98×10^{4}	6.23×10 ⁴	6.78×10^{4}	2.55×10^{4}	4.75×10 ³	8.12×10^{2}	5.14×10^{2}	3.74×10^{2}	1.48×10^{2}	10.6	6.45×10 ⁻¹	1.21
~1	M, mg/m ³	0.0002	0.0039	0.0170	0.0224	00153	0.0116	0.0265	0.0864	0.1149	0.0367	0.0108	0.0665
0	dM/dlog(Dp), mg/m ³	8.10×10 ⁻⁴	1.67×10 ⁻²	8.32×10 ⁻²	1.20×10 ⁻¹	8.16×10 ⁻²	5.51×10 ⁻²	1.39×10 ⁻¹	4.07×10 ⁻¹	6.30×10 ⁻¹	1.75×10 ⁻¹	4.79×10 ⁻²	3.67×10 ⁻¹
	November 29, 2001	l											
	Stage	1	2	3	4	5	6	7	8	9	10	11	12
	Di, 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	1.99×10 ⁴	5.48×10^{4}	6.62×10 ⁴	2.74×10^{4}	6.53×10 ³	1.09×10 ³	5.37×10 ²	3.65×10 ²	1.30×10^{2}	8.75	1.04	1.60
	M, mg/m ³	0.0003	0.0035	0.0166	0.0241	0.0210	0.0155	0.0277	0.0843	0.1008	0.0302	0.0174	0.0879
	dM/dlog(Dp), mg/m ³	8.14×10 ⁻⁴	1.47×10 ⁻²	8.12×10 ⁻²	1.30×10 ⁻¹	1.12×10 ⁻¹	7.37×10 ⁻²	1.46×10 ⁻¹	3.97×10 ⁻¹	5.53×10 ⁻¹	1.44×10 ⁻¹	7.69×10 ⁻²	4.85×10 ⁻¹

^a Stage shows the individual stages of the 12-stage ELPI.

^b Di is the midpoint value used in the distribution calculations; Di is the geometric mean of the boundaries of each stage.

^c Particle counts are expressed as log dN/dlogDp, 1/cm³, or as log dM/dlogDp, mg/cm³, 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 (Di) of each stage.

^e ND = not detected.







Figure 23. Plots of Particle Counts vs. Size, Particle Mass vs. Size, and Particle Mass per Stage for Test Day 1 (11/27/01).







Figure 24. Plots of Particle Counts vs. Size, Particle Mass vs. Size, and Particle Mass per Stage for Test Day 2 (11/28/01).







Figure 25. Plots of Particle Counts vs. Size, Particle Mass vs. Size, and Particle Mass per Stage for Test Day 3 (11/28/01).

PM_{2.5} Semivolatile Organic Compounds

Thermal evolution analysis by NIOSH Method 5040 of fine PM samples collected on quartz filters revealed the presence of organic carbon averaging about 6 wt.% of the PM_{2.5} over the three test days. This result implies the presence of some organic compounds in the particle-phase material. Fine PM samples collected on quartz filters and gas-phase semivolatile organic compounds collected on PUF plugs and organic denuders were extracted from the collection media with a solvent system consisting of benzene:hexane:isopropanol (for filter samples) or methylene chloride:hexane:acetone (for PUFs and denuders) followed by GC/MS analysis of the extracts. This analysis approach revealed the presence of only trace quantities of a few organic species, none of which were above the quantitation limits for the analysis method employed. Quantitation limits for the semivolatile species were taken to be the lowest concentrations of standards used to establish the GC/MS analysis calibration curves. The concentration ranges of these standards are shown in Appendix K.

Table 21 lists those organic compounds that were positively identified above detection limits and above the amounts found in the cleaned dilution air in the fine PM, all of which are relatively high molecular weight hydrocarbons. These results were obtained by GC/MS analysis of the solvent extract of composited quartz filters from Sampling Ports #R4 and #R8 on the dilution sampler residence chamber for all three test days. These filters were not fronted by XAD-coated annular denuders. No quantifiable gas-phase organic compounds were found on the denuders on Port #R10 or on the PUF plugs following the quartz filters on any of the test days. Compositing the quartz filters for all three test days was necessary in order to achieve even the semi-quantitative results reported. Although exact quantitation of the individual trace compounds was not possible, on a relative scale, the straight-chain *n*-alkanes marked with an asterisk (*) in Table 21 were present in the largest amounts, generally 30 to 50 times higher than the rest.

Table 21. Organic Compounds Positively Identified in the PM_{2.5} Emissions from the Hogged Fuel Boiler

<i>n</i> -Docosane	<i>n</i> -Tricosane*	<i>n</i> -Triacontane	<i>n</i> -Tetracosane
iso-Tetracosane	<i>n</i> -Pentacosane*	iso-Pentacosane	anteiso-Pentacosane
<i>n</i> -Hexacosane*	iso-Hexacosane	anteiso-Hexacosane	<i>n</i> -Heptacosane*
iso-Heptacosane	anteiso-Heptacosane	<i>n</i> -Octacosane*	iso-Octacosane
anteiso-Octacosane	<i>n</i> -Nonacosane*	<i>n</i> -Hentriacontane	

Measurement of O₂ and CO₂

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:

- 11/27/01: $O_2 = 7.4\%$ V; $CO_2 = 11.3\%$ V;
- 11/28/01: $O_2 = 6.8\%$ V; $CO_2 = 11.9\%$ V; and
- 11/29/01: $O_2 = 5.9\%$ V; $CO_2 = 13.6\%$ V.



Figure 26. O₂ and CO₂ Concentrations for Hogged Fuel Boiler No. 2 on Test Day 1 (11/27/01).



Figure 27. O₂ and CO₂ Concentrations for Hogged Fuel Boiler No. 2 on Test Day 2 (11/28/01).

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Figure 28. O₂ and CO₂ Concentrations for Hogged Fuel Boiler No. 2 on Test Day 3 (11/29/01).

Quality Assurance/Quality Control

The sampling and analysis procedures performed for this study adhered to approved EPA Quality Assurance Project Plans (QAPPs) QTRAK No. 99051¹⁰ and QTRAK No. 99002¹¹, respectively. MOPs (EPA) and SOPs (ERG), which describe the quality control (QC) checks performed for each procedure, are listed in Appendix L. QAPPs, MOPs, SOPs, 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 22 through 29.

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 22.

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

Table 22. Field Sampling Equipment Quality Control Measures¹⁰

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 23. Supporting calibration and QC data are a part of the project file at ERG.

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

Table 23. Carbonyl Analysis: Quality Control Criteria

(continued)

D. (Quality	D	Acceptance	Corrective	Criteria
Parameter	Control Check	Frequency	Criteria	Action	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 $\pm 2\%$ 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

Table 23. (continued)

(continued)

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	$\begin{array}{l} Measured \\ concentration \\ \leq 5 \times MDL \end{array}$	Locate contamina- tion and document levels of contamina- tion in file	Yes
Duplicate Analyses	Duplicate samples	As collected	±20% difference	Check integration; check instrument function; re- analyze duplicate samples	Yes
Replicate Analyses	Replicate injections	Duplicate samples only	≤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

Table 23. (concluded)

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 24.

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 $\pm 40\%$ 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

Table 24. Quality Control Procedures for the Concurrent Analysis for Air Toxics and SNMOCs

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 $(r^2) \ge 0.995$	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

Table 24. (concluded)

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 25 through 29; supporting data are included in the project file in the EPA laboratory.

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 25. PM Mass Measurements: Quality Control Criteria

Table 26. 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

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 $r^2 \ge 0.999$	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 $\pm 5\%$ of standard retention time	Check system temperature and eluent	Yes
Calibration Check	Analyze 1 standard	Once every 4–10 samples	85–115% 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	≤10% RPD for concentrations greater than 1.0 mg/L	Check instrument function, re- analyze samples	Yes

Table 27. Water-Soluble Ion Analysis: Quality Control Criteria

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	$<0.2 \ \mu g \ C/cm^2$	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 28. (Quality (Control Proced	dures for O	rganic/Elementa	al Carbon	Analysis of F	°М _{2.5}
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				Criteria
Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	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); $\geq 30\%$ (219); $\geq 1\%$ (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 $\pm 2\%$ of established retention time window	Check inlet and column flows and the various GC/MS temperature zones	Yes

Table 29. Quality Control Procedures for Gas Chromatography-Mass SpectrometryAnalysis of Semivolatile Organic Compounds

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The EPA Project Officer is N. Dean Smith, mail dro	op E343-02, phone (919) 541	-2708			
		2.00			
The report provides a profile of the chemical composition of particulate matter (PM) with aerodynamic diameter 2.5 μ m or less (PM _{2.5}) emitted from an auxiliary boiler at a pulp and paper facility using the Kraft pulping process. The auxiliary boiler was fired with a mixture of wood bark (hogged wood waste) and bituminous coal and was rated to generate a maximum of 889 Mbtu/hour. It was equipped with a control system that included a multicyclone-electroscrubber system installed on the flue gas duct and bag filters installed on the vents of the coal bins, scrubber ash silo, and boiler ash silo. 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.					
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