

Source Sampling Fine Particulate Matter Institutional Oil-Fired Boiler

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Section 1 Introduction

In July 1997, the U.S. Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for ambient particulate matter of aerodynamic diameter 2.5 μm or less (PM-2.5). Implementation of the new standards has been delayed to allow EPA time to better understand the factors underlying the observed correlation between ambient fine PM and adverse human health effects and to better evaluate risk management options.

States are required under the federal consolidated emission reporting rule (CERR) to report emissions information to U.S. EPA for inventory and planning purposes, including PM_{2.5} and ammonia. The purpose of the CERR is to simplify reporting, offer options for data collection and exchange, and unify reporting dates for various categories of criteria pollutant emission inventories. This rule consolidates the emission inventory reporting requirements found in various parts of the Clean Air Act (CAA). Consolidation of reporting requirements enables state and local agencies to better explain to program managers and the public the necessity for a consistent inventory program, increases the efficiency of the emission inventory program, and provide more consistent and uniform data. One concern with this reporting requirement is there are no reliable emission factors to use for estimating PM_{2.5} or NH₃. Sources should be able to provide more accurate emission estimates than are currently available in emission inventories or AP-42. This is especially concerning to Title V sources that are required to certify the emissions estimate.

Fine particles can be directly emitted from sources or, like ozone, can be formed in the atmosphere from precursor gases. The most common source of directly emitted PM_{2.5} is incomplete combustion of fuels containing carbon (fossil or biomass), which produces carbonaceous particles consisting of a variety of organic substances and black carbon (soot), as well as gaseous carbon monoxide, VOCs and NO_x. Certain high energy industrial processes also emit primary PM_{2.5}. Examples of direct PM_{2.5} sources include diesel and gasoline vehicles, open

burning, residential wood burning, forest fires, power generation, and industrial metals production and processing. The major gaseous precursors of secondary PM_{2.5} include SO₂, NO_x, certain VOCs and NH₃. Secondary formation of PM_{2.5} involves complex chemical and physical processes. The major sources of secondary PM_{2.5} forming gases (SO₂, NO_x, certain VOCs, NH₃) include nearly every source category of air pollutants. Major SO₂ sources in the U.S. include coal-fired power plants and industrial boilers and smelters. EPA required states upwind of PM_{2.5} nonattainment areas to control and reduce emissions of sulfur dioxide (SO₂) or nitrogen oxides (NO_x). Measurement of the primary PM_{2.5} content and the chemicals that participate in secondary fine particulate formation is important in PM control and attainment of NAAQS. Consequently, EPA has concluded that small contributions of pollution transport to downwind nonattainment areas should be considered significant from an air quality standpoint because these contributions could prevent or delay downwind areas from achieving the health-based standards.

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 (OAQPS) to assist the States in determining regulatory nonattainment areas and to develop State Implementation Plans (SIPs) to bring those areas into compliance with the law for PM-2.5 regulations. One component of the monitoring network was seven supersites: i.e., urban airsheds in which intensive coordinated PM-related research was carried out to better understand the atmospheric formation, composition, and sources of fine PM.

To further support development of better emission factors and an understanding of the formation of fine particulate after emissions leave stationary sources, the Emissions Characterization and Prevention Branch (ECPB) of the Air Pollution Prevention and Control Division (APPCD) implemented research to characterize PM-2.5 emissions from specific source categories. This research focuses on updating and improving source emission rates and profiles for PM-2.5 with the aim of improving the quality of data used for dispersion and receptor modeling and of providing quality emissions data for risk management strategies.

This program has concentrated its PM source sampling efforts on the sources and types of PM-2.5 where data are most needed, with a primary focus on the collection of fine particles emitted by combustion sources, both stationary and mobile. To ensure that the collected PM is representative of the PM collected by ambient monitors downstream of the source, PM samples were collected using a dilution sampling method to simulate the processes of cooling and condensation that occur when material leaves a stack as hot exhaust gas and to provide a means to comply with the requirements of the Consolidated Emissions Reporting Rule.

The mission of the ECPB of the APPCD is to characterize source emissions and develop and evaluate ways to prevent those emissions. Source characterizations as defined here include the measurement of PM mass emission rates, source PM profiles (PM chemical composition and associated chemical mass emission rates), and emission rates of ambient aerosol precursors such as SO_x, NO_x, and NH₃.

PM mass emission rates 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. Source characterization data are used in receptor models which enable apportionment of ambient concentrations of PM to the various sources that emitted the particles and in atmospheric dispersion models that compute the formation of secondary organic aerosols. Source types for testing in this program were selected on the basis of the quantity of fine PM emitted by the source as determined from existing emission inventories and on the basis of the quality of existing PM-2.5 source profiles for each source type. This report presents the results of testing one source type so selected, an institutional scale oil-fired boiler (SCC 1-02-005-01)¹.

Description of Testing and Testing Objectives

This test report describes the measurement and characterization of fine particulate matter (fine PM) emissions and volatile organic compound (VOC) emissions from an institutional scale #2 distillate oil-fired boiler with a rated capacity of 60,000 lbs/h (18.7 MW, 67.3 GJ/h)¹. This

category of boilers was responsible for an estimated 1245.4 kJ (ca. 45.6%) of distillate oil consumption in the U.S. in 1990². The boiler tested in this study was one of three boilers in a university power plant that provided space and water heating to a number of buildings on the university campus. Sampling was conducted in the exhaust duct of one boiler prior to the point at which all three boiler exhausts were combined into a single exhaust stream to the power plant stack. The boiler employed low-NO_x burners for control of NO_x emissions, but no devices for control of particulate matter were utilized.

The report presents results of the test efforts in two ways:

- As mass emission factors (i.e., mass of emitted species per unit mass of fuel consumed), and
- Mass fraction composition of the particle and gas phase emissions.

Mass emission factors are useful for emission inventories and for atmospheric dispersion models that yield estimates of ambient pollutant concentrations via considerations of atmospheric transport and transformation of emitted species. Compositional data are used in source-receptor models to enable the apportionment of ambient air pollutants to the responsible pollutant sources.

Source-receptor models such as the Chemical Mass Balance (CMB) model require as input both the chemical composition of the ambient air samples and the composition of the emissions of all major sources contributing to the ambient pollutants. The oil-fired boiler emission tests described here are among a number of such tests of significant emission sources aimed at updating and improving the quality of source emission profiles in EPA's source profile database (SPECIATE), which is available for use by state and local environmental agencies and others for source-receptor modeling.

Sampling the hot stack gas emissions in the present study involved withdrawing a known amount of sample from the exhaust duct of the boiler and cooling and diluting the sample stream

with cleaned ambient air to near ambient conditions prior to collecting the particle- and gas-phase emissions. A custom-fabricated dilution sampler following the design by Hildemann et al.³ was used. This sampler was constructed entirely of electropolished stainless steel and contained no rubbers, greases, or oils to ensure no introduction of organic contaminants in the samples. Ambient air used to dilute the stack gas was pre-cleaned by means of a HEPA filter, a large bed of activated carbon (carbonaceous material contained in a 30-gallon drum), and a Teflon membrane filter prior to mixing with the stack gas. By sampling in this way, the particle emissions are deemed to be more representative of the material as it exists in the ambient air downwind of the source.

The boiler was tested in two separate campaigns. An initial test series (i.e., campaign #1) was conducted in January 2001. The primary objective of the first campaign effort was to chemically characterize the fine PM emissions (i.e., PM-2.5, particles equal to or less than 2.5 μm aerodynamic diameter) and to develop emission factors for EPA's SPECIATE data base. Many past efforts have focused on the coarse fraction of emitted PM (PM-10) or only the filterable portion of emitted PM. Condensible PM, which can form when a hot exhaust stream is diluted and cooled with ambient air, has not often been characterized in previous work. Also, earlier chemical characterization studies of PM were often limited to the elemental composition of the material with the nature of the organic content of carbonaceous PM unidentified.

This initial test series included a trial run to determine an appropriate test duration and to ensure all systems were operating properly. The trial run was followed by three replicate sampling runs, one run on each of three successive days. Samples of gas phase organic compound emissions were collected concurrently with the fine PM samples in test campaign #1, and results of these gaseous emissions determinations are also reported here for completeness.

A second test series (i.e., campaign #2) was conducted in July 2002 in collaboration with the EPA's OAQPS, Emissions Monitoring and Analysis Division (EMAD). The second campaign had a dual purpose:

- To provide referee comparative data to EMAD to help in the development of a more compact and portable dilution sampler suitable for routine regulatory compliance stack gas sampling and for source emissions profiling; and
- To compare the PM_{2.5} results of the two test campaigns conducted at winter and summer boiler operating conditions, respectively.

A prototype of the EMAD sampler design was operated concurrently with the Hildemann-designed sampler so that results of the two devices could be compared under the same boiler operating conditions.

Some of the experimental design matrix was changed for the second campaign to focus effort on measurements that provided comparison between the Hildemann designed sampler and the EMAD prototype sampler. Measurements focused on contributions to PM_{2.5} and its formation. Semivolatile organic compound sampling and analysis was added to assess a fuller range of condensible organic compounds. Organic and elemental carbon as well as inorganic components contributing to particulate formation were included in both campaigns enabling consistent PM_{2.5} comparisons between campaigns and between the sampling trains.

This report presents only the results derived from the Hildemann-designed dilution sampler for the two test campaigns. The EMAD sampling system and procedure can be found at <http://www.epa.gov/ttn/emc/ctm.html> in conditional test method CTM-039.

Organization of Report

This report is organized into five additional sections plus references and appendices. Section 2 provides the 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 research to ensure generation of high quality data. Section 7 presents the references cited in this report.

Section 2 Conclusions

Salient results from both the winter 2001 and summer 2002 test campaigns (campaign #1 and campaign #2, respectively) at the institutional-scale oil-fired boiler are summarized in Table 2-1. Complete tabulated results with associated uncertainties are provided in Section 5 of this report, along with the combustion parameters data (i.e., O₂, CO, H₂O, fuel consumption).

Table 2-1. Results Summary for Industrial Scale Oil-Fired Boiler

Test Date	Campaign #1		Campaign #2			
	1/16/01	1/17/01	1/18/01	7/9/02	7/10/02	7/11/02
Emission Factors (mg/kg fuel):						
PM-2.5 mass ^a	26.9	32.1	39.8	40.4	42.7	178.0
Particle mass semivolatile organic species	NS	NS	NS	1.0	0.66	7.9
Gas-phase semivolatile organic species	NS	NS	NS	89.5	75.4	123.1
Nonmethane volatile organic compounds						
Speciated	3.0	18.7	32.7	NS	NS	NS
Total	2.4	18.0	35.3	NS	NS	NS
Gas-phase carbonyls						
Speciated	0.25	0.30	0.50	NS	NS	NS
Total	.27	0.30	0.55	NS	NS	NS
PM Composition (wt. %):						
Elemental carbon (EC)	1.8	10.5	34.0	5.8	3.1	1.6
Organic carbon (OC)	NQ	0.5	NQ	43.3	45.7	63.1
Sulfate	58.0	56.9	45.5	6.8	10.7	3.5
Ammonium	NQ	NQ	NQ	2.0	2.6	0.46
Sulfur	5.2	3.4	8.3	2.7	3.7	1.3
Silicon	NQ	NQ	NQ	0.89	0.75	0.24

NQ = below quantitation limit; NS = not sampled

^a Filterable only.

The filterable PM-2.5 mass emission factor was fairly consistent throughout both test campaigns with the exception of one day during campaign #2 (7/11/02) for which the emission factor was nearly five times higher than the average of the other five test days. Excluding the single day of markedly higher emissions, the average PM-2.5 mass emission factor was 36.4 mg per kg of fuel (0.81 $\mu\text{g}/\text{kJ}$) with a range of 26.9 to 42.7 mg/kg (0.60 - 0.96 $\mu\text{g}/\text{kJ}$). The single day of substantially higher PM-2.5 emissions gave an emission factor of 178.0 mg per kg of fuel (3.99 $\mu\text{g}/\text{kJ}$). No unusual event on that day was identified to explain the higher PM-2.5 emissions for that test. However, during both campaign #1 and campaign #2 the boiler was operated at very low load where combustion conditions are difficult to maintain. Under such conditions, erratic behavior in boiler operation and emissions may occur.

A PM-2.5 emission factor for industrial-scale distillate oil-fired boilers with no PM emission controls has been estimated by the EPA as 283 - 313 mg/kg of fuel with fuel sulfur contents ranging from 0.05 - 0.09 wt %, respectively.⁴ It should be noted that these EPA estimates do not consider the condensible portion of fine PM. From this study, the average PM-2.5 emission factor for campaign #1 when the fuel contained 0.09% sulfur was 32.9 mg/kg, nearly an order of magnitude less than the estimated EPA value. The average PM-2.5 emission factor for campaign #2 when the fuel contained 0.05% sulfur was 41.6 mg/kg (excluding the single high emission day) or 87.0 mg/kg with all three test results averaged. These values are 6.8 and 3.3 times less than the current EPA estimated emission factor, respectively.

The PM-2.5 mass emission factor was fairly consistent for both test campaigns, whereas the composition of the PM-2.5 was very different for the two campaigns. Sulfate comprised 45.5 to 58.0% by mass of the PM-2.5 emitted during campaign #1 but accounted for only 3.5 to 10.8% of the PM-2.5 mass during campaign #2. Conversely, there was much more carbon in the PM-2.5 emitted during campaign #2, most of which was organic carbon (43.3 to 63.1% of the PM-2.5 mass). The organic carbon (OC) content of the fine PM was highest for Test Day #3 of campaign #2 (7/11/02), for which the PM-2.5 emission factor was also the highest of all tests.

Most of the speciated and quantified OC associated with the fine PM was made up of the C₁₆ through C₃₁ *n*-alkanes (63.8 wt % of the speciated PM organics). *n*-Tetracosane (C₂₄) was the single most prominent *n*-alkane with the other C₁₆ - C₃₁ species in a near-Gaussian distribution by carbon number around C₂₄. Benzene di- and tri-carboxylic acids comprised the second largest category of organic constituents found in the fine PM (21.4 wt % of the quantified species). Polynuclear aromatic hydrocarbons (PAHs) and *n*-alkanoic acids made up most of the remaining 14.8% of the quantified and speciated particle-phase organic compounds. The benzene di- and tri-carboxylic acids and chrysene were the only semivolatile organic species confined to the particle phase. All of the other semivolatile species were found in both the gas and particle phases with the predominant amounts in the gas phase. The only two elements in the PM found at levels above method quantitation limits were silicon and sulfur.

Two factors may have contributed to this marked difference in PM composition. The sulfur content of the fuel oil was 1.8 times higher during the campaign #1 tests than during the campaign #2 tests (0.09 vs 0.05 wt %, respectively). This factor could have contributed to a higher sulfate content during the campaign #1 tests. During the campaign #2 tests, the fuel feed rate averaged 37.6% lower than for the campaign #1 tests, and the excess oxygen levels were much higher (campaign #2 = 15.7 to 20.5%; campaign #1 = 7.6 to 9.2% excess oxygen). During campaign #1, the boiler was fired at 37 - 42% of its rated capacity; during campaign #2, the boiler was fired at only 25% capacity. A lower combustion efficiency associated with the low combustion load during the summertime is likely responsible for the PM emissions being enriched in OC.

A quantitative analysis of individual organic compounds associated with the organic carbon content of the fine PM was not possible for the campaign #1 owing to breakthrough of the organic species in the PM sampling arrays during the tests. For the campaign #1 tests, XAD-coated annular denuders were used in front of pre-fired quartz filters in an attempt to minimize adsorption of gas-phase organic species on the quartz filters and a consequent positive artifact in the PM mass and PM organic carbon content. Polyurethane foam (PUF) plugs were employed behind the quartz filters to collect any particle-phase semivolatiles that were air stripped from

the filters during sampling. Sampling durations were long (i.e., 10 hours per test) in an attempt to gather sufficient fine PM for analysis of particle-phase organics. However, the lengthy sampling periods resulted in exceeding the capacity of the denuders and PUF plugs. Therefore, an unknown quantity of organic compounds passed through the arrays and could not be accounted for.

During the campaign #2 test, the denuders were omitted from the sample collection arrays, and an attempt was made to correct for the positive Organic Carbon (OC) artifact in the PM collected on the quartz filters by subtracting from each of these filters the amount of OC collected on a quartz filter placed behind a Teflon membrane filter. This correction was based on the presumption that the Teflon filter collected particle-phase organic compounds and the backup quartz filter behind the Teflon filter collected adsorbed gas-phase organics equivalent to those adsorbed on the undenuded primary quartz filter. Even with this substantial correction, the PM collected during the summer campaign contained much more OC than the PM collected during the winter campaign.

Gas-phase organic nonmethane volatile organic compounds (NMOC) and carbonyl compound emissions were measured only during the campaign #1 tests, when the boiler was operating at more typical load conditions. For the campaign #1 tests, total NMOC (speciated + unspeciated) and PM-2.5 mass emission factors increased with increasing fuel consumption rates (2.42, 17.96, and 35.30 mg/kg for successive test days), but total gas-phase carbonyl compound emission factors exhibited the opposite trend.

A Scanning Mobility Particle Sizer (SMPS) operated on all three test days during the campaign #1 tests and collected data on particle size distribution in the range below 2.5 μm (the range monitored was 10 nm to 392 nm), with one complete scan over the entire range every three minutes. Both the particle size distribution and particle number count observed on Day 1 (January 16, 2001) differed with respect to the other two test days. The number of counts observed in each channel was approximately four orders of magnitude lower on Day 1 than on the other two test days. The SMPS instrumental operating parameters appeared to be normal,

and there was no obvious indication of instrumental malfunction. On the second and third test days, the number counts and distribution profiles were similar to the distributions centered at 46 nm and 50 nm, respectively.

During campaign #2, particle size data were collected using an Electrical Low Pressure Impactor (ELPI). The particle size distribution suggests bimodal behavior. Note that the SMPS gives an electrical mobility diameter and the ELPI gives an aerodynamic diameter, so the two values should not necessarily agree.

Results of this study indicate that the fine PM composition emitted from an institutional-scale oil-fired boiler can be markedly different depending on the combustion load and the characteristics of the fuel. Therefore, to the extent possible, source-receptor modeling should consider these conditions when selecting profiles and fitting species for source apportionment modeling. In this study, the boiler tested produced a wide variation in particle size and composition dependent on the fuel combustion and fuel composition. Industrial-scale boilers used to generate process steam and utility boilers used to generate power may be less susceptible to changing demand and therefore emit a fine PM with a more consistent composition.

Section 3 Methods and Materials

Description of the Testing Program

Two field tests (campaign #1, January 16-18, 2001; and campaign #2, July 7-9, 2002) were conducted at an institutional-scale boiler fired with #2 distillate oil and located on the campus of North Carolina A&T University in Greensboro, NC. Quality control procedures were implemented to obtain source emissions measurements of high and known quality. 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 institutional-scale oil-fired boiler. Gaseous and fine particulate material collected during the sampling was also characterized. ERG coordinated all field test activities; laboratory testing activities were divided between EPA and ERG according to the scheme shown in Table 3-1.

The objectives of the testing activities were to evaluate the sampling equipment and to characterize the fine particulate emissions from an institutional oil-fired boiler. 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 a particle size analyzer. Fine particle emission profiles can be used in molecular marker-based source apportionment models, which have been shown to be powerful tools to study the source contributions to atmospheric fine particulate matter.

Table 3-1. Sampling Medium Used for Collection of Samples, Analysis Performed, Analytical Method, and Responsible Laboratory

Sampling Medium	Analysis	Method	Laboratory
Teflon Filter	PM-2.5 mass	Gravimetric (GRAV)	EPA
Teflon Filter	Elemental Analysis	X-ray fluorescence (XRF)	EPA
Teflon Filter	Inorganic Ions	Ion Chromatography (IC)	EPA
Quartz Filter	Elemental Carbon/ Organic Carbon	Thermal-Optical Evolution (TOE)	EPA
Quartz filter XAD-4 denuder PUF	Organic species	Gas Chromatography/ Mass Spectrometry (GC/MS)	EPA
DNPH-impregnated silica gel tubes ^a	Carbonyl compounds	High Performance Liquid Chromatography (HPLC) Method TO-11A	ERG
SUMMA canisters ^a	Air Toxics Speciated Nonmethane Organic Compounds	GC/MS Method TO-15 ERG Concurrent Analysis	ERG
Particle Size Analyzer	Particle Sizes	Scanning Mobility Particle Sizer (SMPS) Electrical Low Pressure Impactor (ELPI)	ERG

^aDNPH tubes and SUMMA canisters were used for campaign #1 only.

To assist in the characterization of the stationary source and to obtain chemical composition data representative of particle emissions after cooling and mixing with the atmosphere, ERG performed the following activities at the test site:

- Performed preliminary measurements using EPA Methods 1-4 to evaluate source operating conditions and parameters;
- Installed the pre-cleaned dilution sampling system, sample collection trains, and ancillary equipment at the field site without introduction of contaminants;
- Calibrated flow meters before and after sampling, monitoring and adjusting gas flows (as necessary) throughout the tests;

- Acquired process data for the test periods, including temperatures, pressures, flows, fuel consumption, etc.;
- Determined the type of combustion fuel and rate of consumption during the source testing;
- Collected six sets of stationary source samples (three per test campaign) as prescribed in the Site-Specific Test Plans, including field blanks (one per test campaign); and
- Recovered the dilution sampling unit and sample collection trains for analysis for specific parameters and return of the dilution sampling unit to EPA.

For Test campaign #1, ERG transported the dilution sampling system to the test site to collect integrated samples, performed whole air analysis of 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 pre-test cleaning of the dilution system, for analysis of semivolatile organic compounds from XAD-4 denuders and polyurethane foam (PUF) modules resulting from the test efforts and for characterization of the particulate-phase emissions and mass loading on quartz and Teflon filters. For Test campaign #2, ERG transported the dilution sampling system to the test site to collect integrated samples and evaluated particle size distribution data. EPA was responsible for pre-test cleaning of the dilution system, for analysis of semivolatile organic compounds from polyurethane foam (PUF) modules resulting from the test efforts and for characterization of the particulate-phase emissions and mass loading on quartz and Teflon filters.

Description of Test Equipment

Dilution Sampling System

The dilution sampling system used in the source test was based on the original design by Dr. L. M. Hildemann³, 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 touchscreen interface connected to the main controller was used to monitor current conditions and allow setpoints 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 to fine particles as they might in ambient air. The sampler is also designed and fabricated to minimize any contamination of samples, especially organic compound contamination, and to minimize particle losses to the sampler walls.

Figure 3-1 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 for dilution of source emissions. Acid gases (if present) will not be completely removed 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 sampler downstream of the dilution air orifice meter. The key zones of the dilution sampling system and their function are discussed below.

Sample Inlet Zone—

Stack Emissions Inlet: designed to allow source exhaust gas to be sampled through an inlet cyclone separator to remove particles with nominal aerodynamic diameters $> 10 \mu\text{m}$. The PM-10 cyclone prevents large particles from entering the sampler to plug or damage the equipment. Three ports are dedicated to sampling of the dilution air before it mixes with the source gas.

Heated Inlet Line: 3/4" 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 15-50 Lpm (typically 30 Lpm).

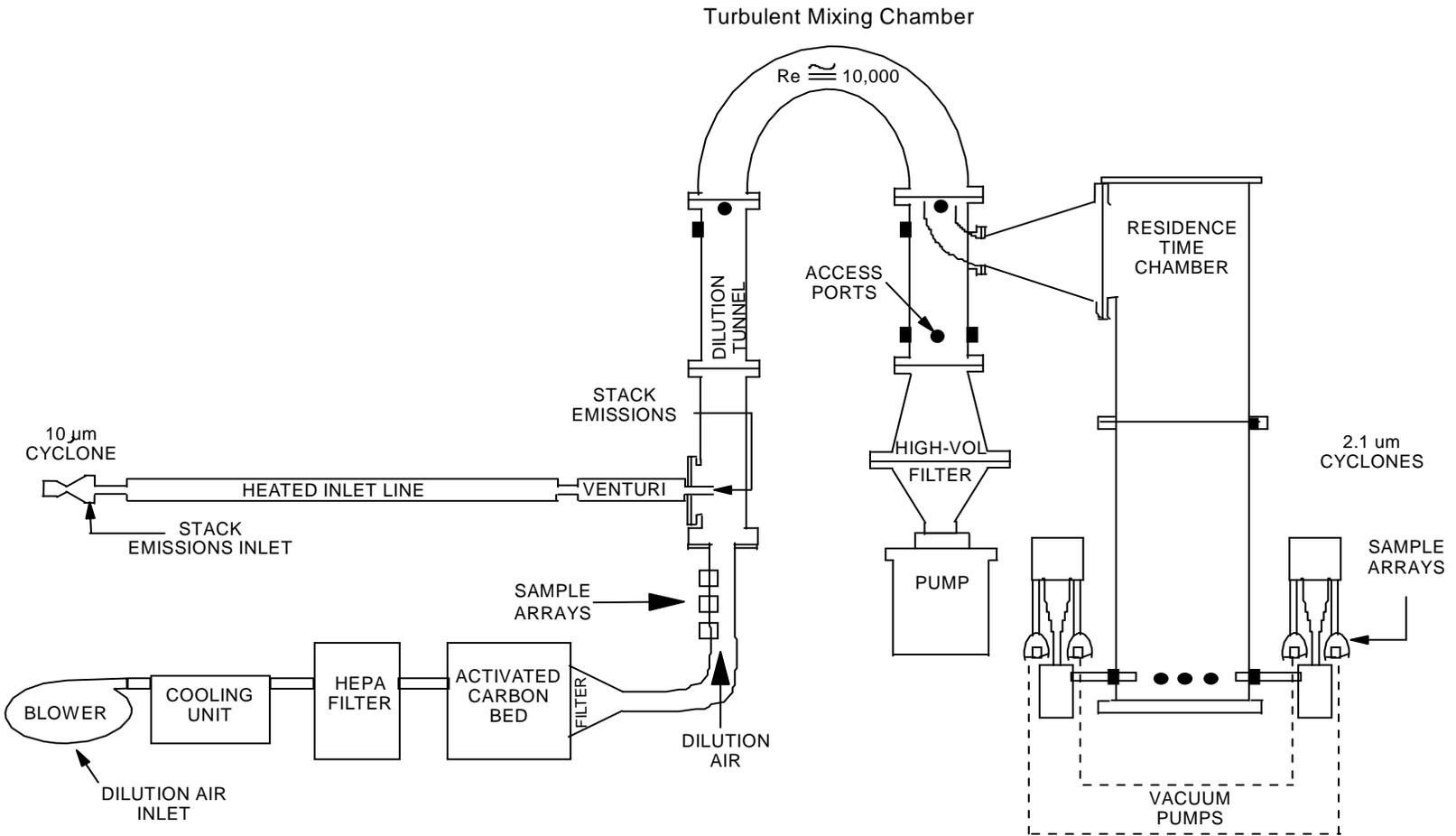


Figure 3-1. Diagram of the dilution sampler and dilution air conditioning system.

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—

Consists of an entrance zone, U-bend, and exit zone.

Inside diameter: 6 in., yielding a Reynolds number of ~10,000 at a flow rate of 1000 Lpm.

Dilution air enters the mixing chamber in the direction parallel to the flow.

Hot source emission gas enters the chamber perpendicular to the dilution airflow, 4.5 in. downstream of the dilution air inlet.

The combined flow travels 38 in. before entering the U-bend.

After the residence chamber transfer line, the mixing chamber continues for 18 in., then expands to an in-line high-volume sampler filter holder. Collected particulate has not experienced time to equilibrate with the gas phase at the diluted condition.

Sample and instrumentation ports are installed on the turbulent mixing chamber at various locations.

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 ~100 Lpm) 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;

 Three ports for instrumentation.

Sample Collection Zone—

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

Since 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 mainly used 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 58-75 sec: 2-3 sec for the turbulent mixing chamber and 56-72 sec for the residence chamber.

Dilution Sampling System Control Instrumentation

Instrumentation for control and analysis of the dilution sampling system is shown in Figure 3-2. Differential pressure measurements made across the venturi and orifice meters are used to determine the dilution airflow rate, the sample gas flow rate, and the exhaust gas flow rate. Since flow equations used for determination of the flow across venturi and orifice meters correct for flowing temperature and pressure, the flowing temperature and pressure of the venturi and orifice meters must be recorded during sampling operations. Thermocouples for monitoring temperature are placed at each flow meter as well as at the inlet PM-10 cyclone, at various points on the sample inlet line, at the inlet to the mixing chamber U-bend, and at the outlet of the residence time chamber. An electronic relative humidity probe is used to determine the relative humidity of the sample gas. The dilution sampling system is equipped with automated data logging capabilities to better monitor source testing operations and to minimize manpower requirements during sampling operations. Dilution sampler flows and temperatures are monitored and controlled automatically at set points established by the operator using a QSI Corporation QTERM-K65 electronic touch-screen interface. The dilution sampling system was operated by three testing staff members during the test at the institutional oil-fired boiler facility.

In operation, the source sample flow, the dilution airflow, and the total airflow (not including the sample collection arrays) were each measured by separate flow meters and pressure

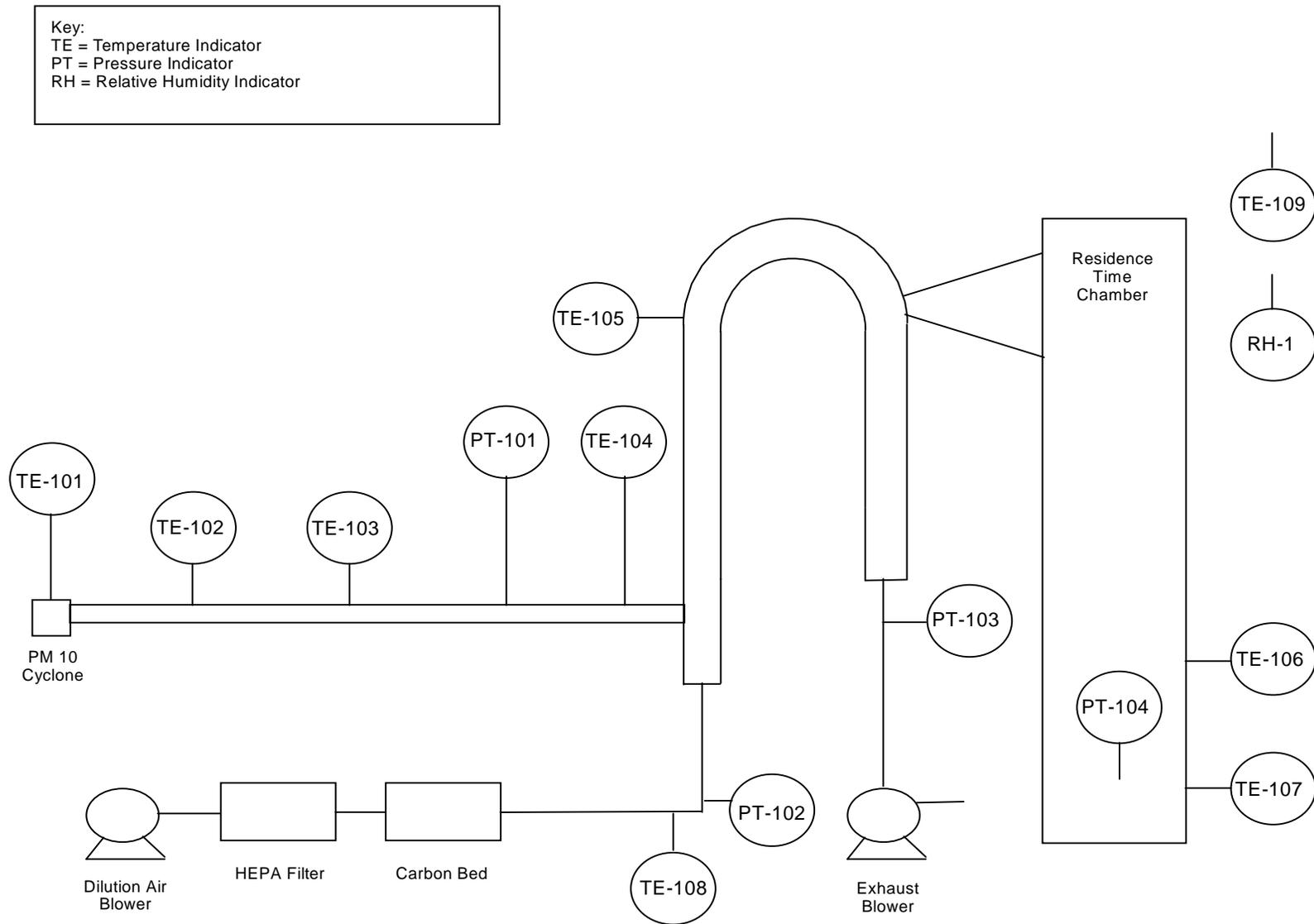


Figure 3-2. Instrumentation for control and analysis of the dilution sampler.

transducers. A venturi measured the source sample flow and orifices were used for the dilution and total flows. A ring compressor was used to push the dilution air through a HEPA filter, a carbon adsorber, and a final filter into the turbulent mixing chamber. The compressor motor was modulated by a variable frequency drive to match the desired dilution flow based on a set point entry. A separate blower (connected to a speed controller adjusted to achieve the desired sample flow based on a set point entry) at the end of the sampler 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 entered by the operator.

Sample Collection Arrays

Virtually any ambient sampling equipment (including filters, denuders, PUF cartridges, DNPH-impregnated 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 arrays is uniquely configured for each testing episode.

Process Description/Site Operation:

With the concurrence of the EPA work assignment manager, an institutional oil-fired boiler located at North Carolina A&T University in Greensboro, NC, that was used to heat multiple dormitories was selected as the test site. The boiler, constructed by the Nebraska Boiler Company, was permitted for operation with either #2 distillate oil or #6 residual oil. For the duration of both tests (January 16-18, 2001, and July 7-9, 2002), the fuel used during testing was #2 distillate oil.

The watertube boiler tested was one of four boilers used to supply space and water heating for several university buildings. The test boiler flue gas was connected through a common duct with the other three boilers to a common exhaust fan and stack as shown in Figure 3-3. The test boiler had a rated capacity of 67.3 GJ/h, was capable of utilizing either #2 distillate oil, #6 residual oil, or natural gas as fuel, and was equipped with a burner designed to reduce NO_x emissions by reducing the peak flame temperature at the flame base. Low NO_x operation of the burner was accomplished by staging the combustion process with specially designed fuel nozzle injectors and an air recirculator. There were no control devices for control of particulate matter emissions from the boiler. Emissions sampling was conducted at a sampling port located in the exhaust gas duct from the boiler prior to the junction of that duct with exhaust ducts from the other two boilers. Exhaust gases from all boilers were fed together to a single stack from the university power plant.

The analysis of the #2 distillate oil used as fuel for the North Carolina A&T boiler is shown in Table 3-2 for both test campaigns; slight differences in the analyzed values were observed.

Table 3-2. Analysis of the #2 Distillate Oil Used to Fuel the Institutional Boiler

Component	Campaign #1 January 16-18, 2001	Campaign #2 July 7-9, 2002
sulfur	0.09%	0.05%
heat value	19,374 BTU per pound	19,193 BTU per pound
ash	< 0.01%	< 0.01%
carbon	85.93%	86.53%
hydrogen	13.66%	12.75%
nitrogen	0.03%	0.02%
oxygen	0.26%	0.65%
chlorine	Not Determined	303.8 ppm

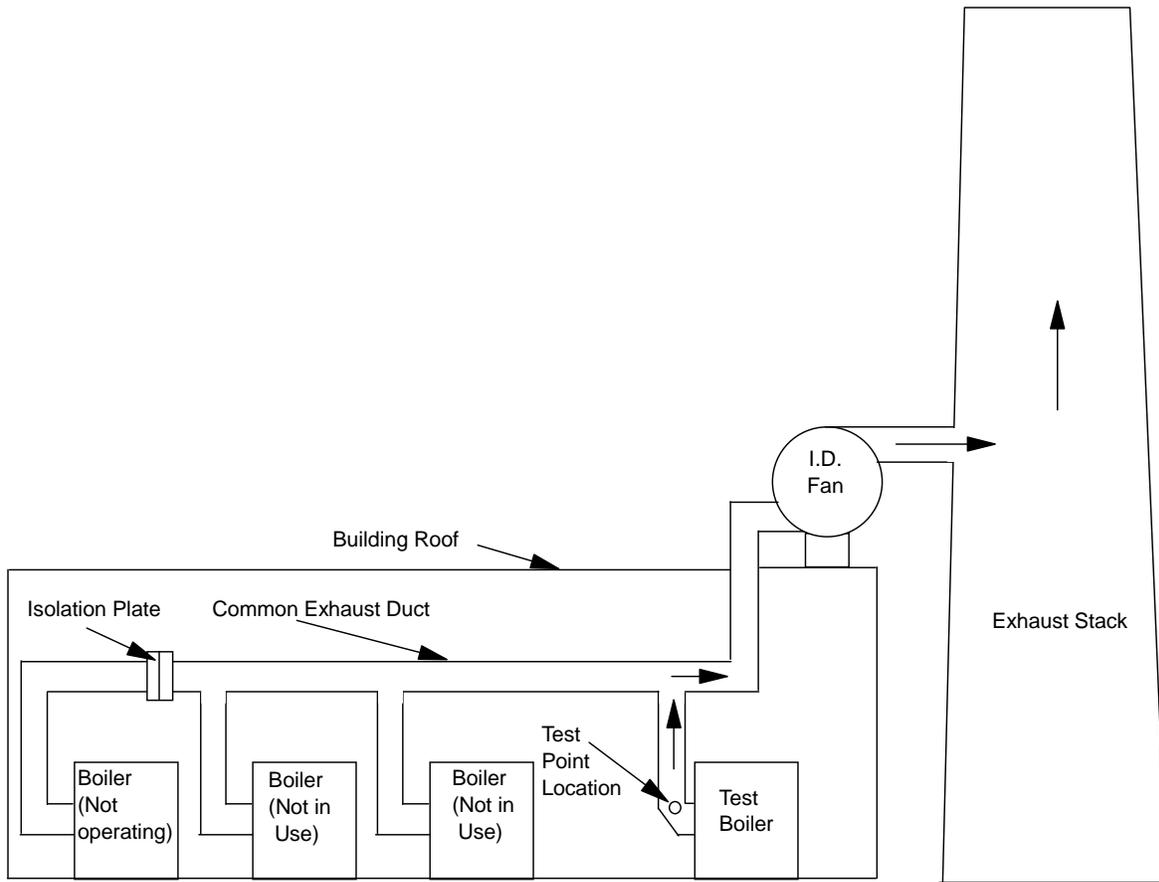


Figure 3-3. Schematic Diagram of Test Boiler Exhaust to Stack Connection

The fuel use for both test campaigns by test days is summarized in Table 3-3.

Table 3-3. Fuel Use Data for Testing Days: #2 Distillate Oil

Campaign #	Test #	Test Date	Test Duration (min)	Fuel Use (gal/min)	Total Fuel (gal)
1	1	1/16/01	600.33	3.428	2058
	2	1/17/01	600.50	3.615	2171
	3	1/18/01	600.17	4.134	2481
2	1	7/09/02	600.60	2.314	1390
	2	7/10/02	600.67	2.331	1400
	3	7/11/02	600.00	2.333	1400

Both test campaigns were scheduled to minimize disruption to the normal operation of the test facility and to enable as much simultaneous data collection important to all parties as possible. ERG scheduled the sampling test at the chosen facility and obtained permission and cooperation of the site/institution/management.

Description of the Oil-Fired Boiler Tested at North Carolina A&T (Greensboro, NC)

The burner tested at North Carolina A&T (Greensboro, NC) was manufactured by Forney Corporation and assembled on a 60,000 lbs/hr Nebraska D-type water tube boiler. The NOXMISER Low NO_x burner is designed to reduce NO_x emissions by reducing the peak flame temperature at the flame base. The formation of NO_x during the combustion process was:

- Exponentially proportional to peak flame temperature;
- Proportional to time duration at peak flame temperature; and
- Proportional to the square root of the number of oxygen molecules available at the primary zone where the peak temperature occurs.

Low NO_x operation is accomplished by staging the combustion process with specially designed fuel nozzle injectors and an air recirculator. This mode of operation results in lower peak flame

temperature yet stable flame with minimum flue gas recirculation and low carbon monoxide emissions.

The combustion air forced draft fan, a direct-drive high performance airfoil fan designed for a speed of 3500 rpm, is sized to provide all the required combustion air and flue gas for recirculation. The combustion air forced draft fan is equipped with a 100% width inlet cone. The airflow control damper is located between the windbox and forced draft fan; the damper assembly is linked to the burner jack shaft.

The burner wind box, designed to provide equal air distribution into the air register, contains the zone divider and the primary and secondary air slide damper assembly. The air slide damper assembly provides a manual adjustment to the distribution of the total air between the primary and secondary air zones.

A flame safeguard system, designed to provide proper burner sequencing for safe burner operation, sequences the burner from purge, low fire ignition of the pilot, and main flame automatically. The flame safeguard system monitors main flame, limit switches, and boiler operating interlocks applicable to boiler operation, and interfaces with fuel shutoff valves and oil pumps.

The burner consists of the subassemblies listed below:

- Basic Burner
 - The basic burner is completely assembled with fuel and air control devices with necessary control linkages and levers. Electrical components are pre-wired, using Sealtite conduit, to a junction box. Oil and atomizing air piping trains are a part of the basic burner.
- A burner refractory throat tile seal-welded to the boiler furnace plate, with plastic refractory packed between the burner refractory throat and the furnace wall;
- Burner positioned to the boiler front plate with support to center the burner with the refractory throat inside diameter;

- Flame safeguard system, in its own enclosure, with a conduit and wiring to the forced draft fan motor and separate conduits and wiring to junction box #1 (located at the burner) and junction box #2 (located at the gas train assembly), as well as the boiler limit switches. House power was connected to the flame safeguard enclosure fuse block;
- Gas train assembly with gas vent lines installed per applicable codes, piped to the designated safe and nonhazardous location;
- Piping connecting the fuel gas train outlets to the burner flow control valve inlet, with fuel oil and atomizing medium supplied to the burner on a combination fuel-firing boiler; and
- A stack gas fuel inlet nozzle located approximately five stack diameters downstream of the boiler smoke box outlet, with a fuel gas recirculation line running from the stack inlet nozzle to the flue gas recirculation fan inlet.

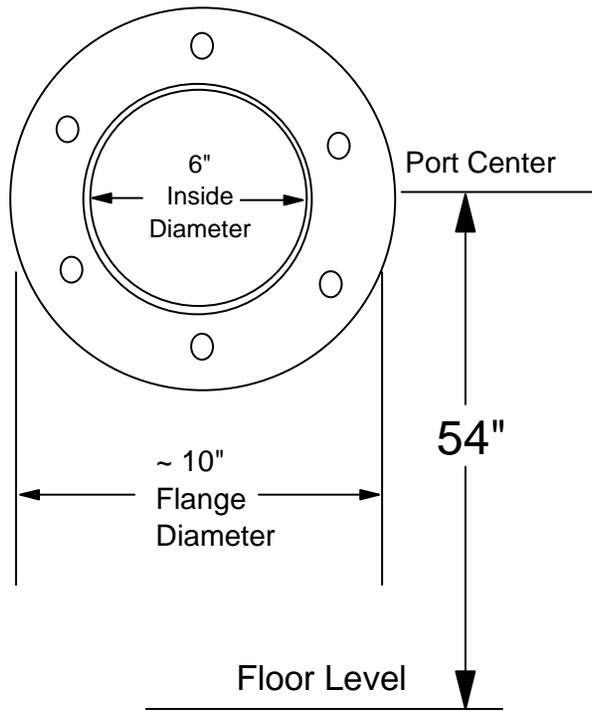
Proper burner setup is essential for safe operation and optimum burner performance; the burner was started up by an authorized service engineer.

Pre-Test Surveys

A thorough survey of the test site was performed prior to each test campaign. The purpose of the surveys was to determine that the test equipment would fit in the test location, to identify and gain access to the utilities needed to operate the dilution system and its ancillary equipment, to arrange for installation of a sample collection port (installation for campaign #1 - the same port was used for campaign #2), to arrange for installation of power for operation of the dilution sampling system (installation for campaign #1 only) and to evaluate the means for positioning the sampler at the desired location. The same sampling location and port were utilized in both campaigns. A schematic diagram of the sampling port is shown in Figure 3-3; a photograph of the port, as installed, with cap plate, is shown in Figure 3-4. The relationship of the sampling port relative to the boiler and the exhaust ductwork is discussed in Section 4.

A new power panel and feeder to provide power to two quad outlets and a 50-amp, 2-pole circuit, including a breaker in the existing main panel, was also installed prior to campaign #1. ERG conducted pre-test site surveillance and site preparation to ensure readiness of the site for

Front View



Side View

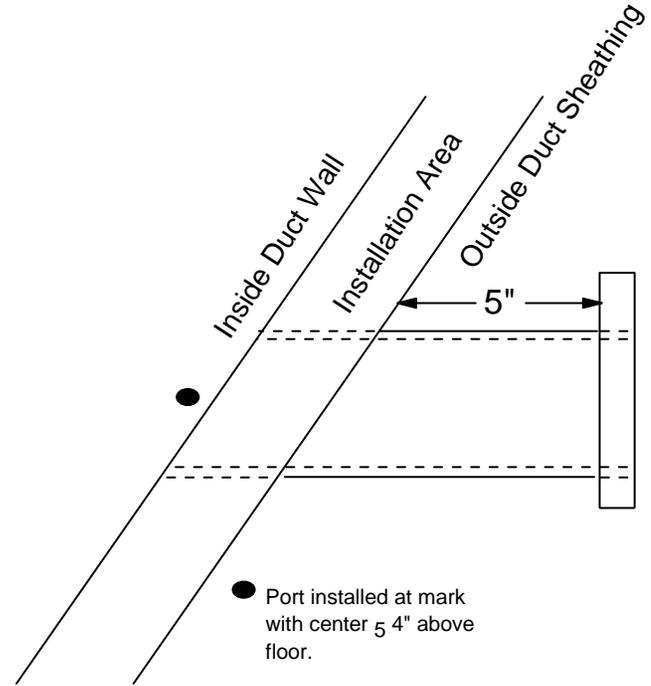


Figure 3-4. Diagram of the sampling port.

the start of the scheduled sampling activities. The pre-test survey considered access to utilities and personnel, as well as legal and safety requirements. ERG obtained source data such as exhaust gas flow rate and velocity, exhaust gas temperature and water vapor content, and approximate particulate matter concentration, parameters useful for estimating appropriate dilution ratios and duration of sample collection.

The sampling port was positioned to allow the dilution sampling unit to sit on a sturdy hydraulic lift cart, which could be rolled into place and raised to allow the probe access to the sampling port. The cart sat on the floor of the boiler room, with its wheels firmly anchored. Access to the test facility was attained by a ground-level door that was sufficiently wide to accommodate the dilution sampling unit. The two modules (dilution air supply/control module and sampler module) were positioned at the sampling location, (Figure 3-5), by rolling the units through the ground-level door at the test facility (Figure 3-6); testing occurred at ground level inside the facility (Figure 3-7), with the dilution system elevated to allow access to the sampling port.

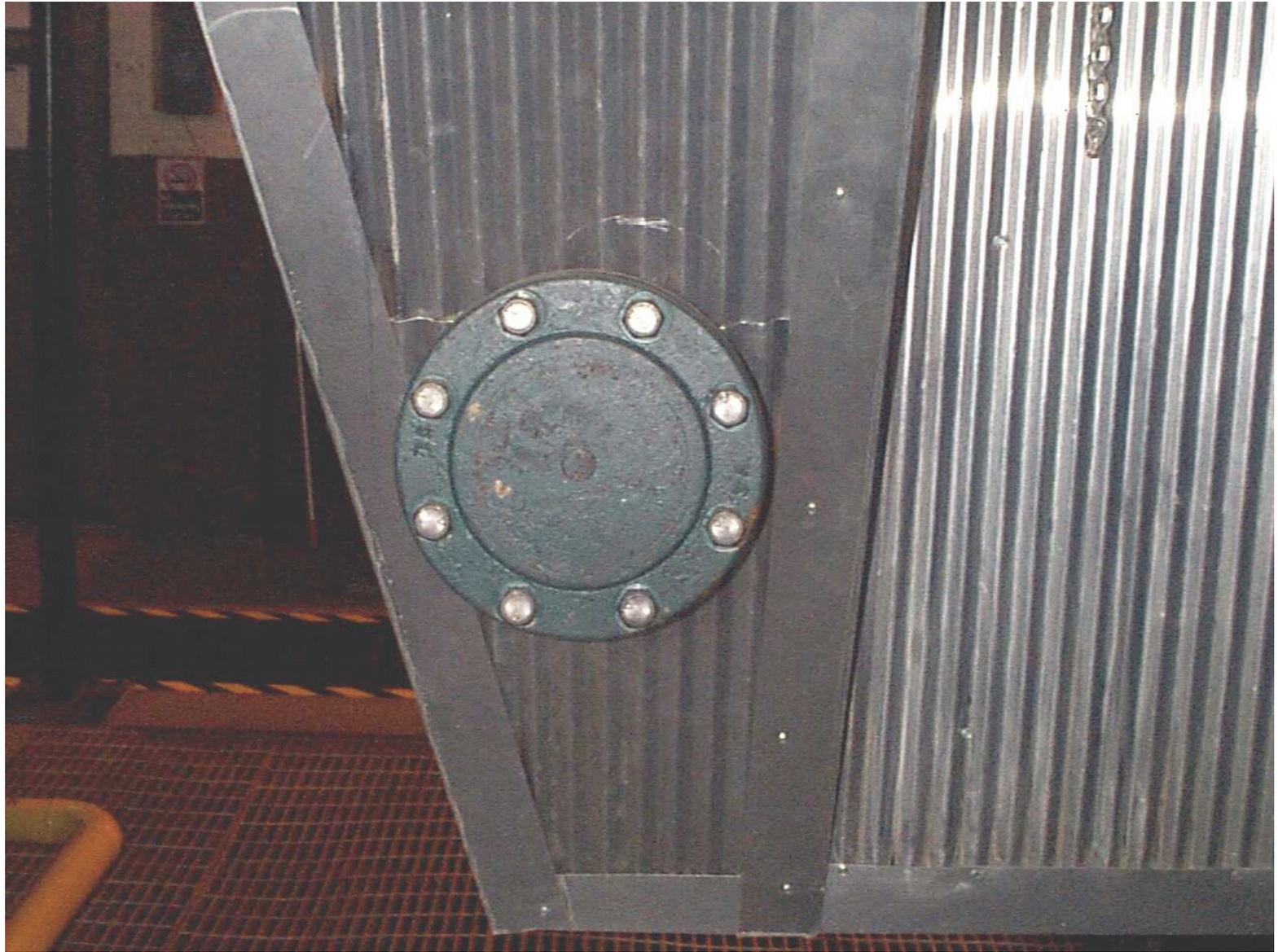


Figure 3-5. Sampling port with cap plate.



Figure 3-6. Ground level access to the test facility.



Figure 3-7. Testing area, ground level.

Section 4

Experimental Procedures

To sample undiluted hot exhaust gas streams, the EPA/ECPB dilution sampling system (schematic diagram in Figure 3-1), sample collection arrays, sample substrates, and a dilution air cleaning system were used by ERG. To minimize introduction of contaminants, EPA pre-cleaned and pre-assembled the dilution sampler and sample collection arrays in a clean environment prior to transport to the test site. The sampler and dilution air cleaning system were assembled on separate portable aluminum frames equipped with wheels and tie-down lugs for transport to and from the site. ERG maintained the sampler and sample collection arrays in a contaminant-free condition prior to collection of institutional oil-fired boiler samples and field blanks.

A sampler blank test was run prior to transporting the sampler to the test site for each campaign to ensure that the system had been cleaned properly and was leak free. The blank test was run in the laboratory by completely assembling the sampling system, including the sample collection arrays connected to the residence chamber and all instrumentation. The blank test was conducted for a time period consistent with the expected duration of the source tests (10 hours). Following the blank test, the sampler was shut down in reverse order from startup, 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 deployment of the dilution sampling system at the test site and initiation of sampling with the dilution sampling system and associated sample collection arrays, EPA Methods 1-4⁵⁻⁸ were used to establish key experimental parameters for the test conditions.

Application of EPA Methods 1-4

Traverse Point Determination Using EPA Method 1

EPA Method 1⁵, “Sample and Velocity Traverses for Stationary Sources,” was used to establish the number and location of sampling traverse points necessary for isokinetic and flow sampling. These parameters are based upon how much duct distance separates the sampling ports from the closest downstream and upstream flow disturbances.

The selected sample collection location did not meet the minimum requirements of EPA Method 1 for length of straight run or for orientation of the port with respect to the plane of bends in the ductwork. However, this location was the only position on the duct work with sufficient space for physical location of the sampling system. The duct work was rectangular. The inside stack dimensions were length, 48 in.; width, 22 in. The port was located 3 ft. downstream from the exit of the boiler breech area and 20 ft. upstream of the common exhaust duct. Traverse point locations are shown in Table 4-1. A table of metric unit conversions is shown in Appendix A. Sampling at the test site was performed at the point determined by Method 1 to represent the average velocity in the oil-fired boiler exhaust stack (Figure 3-4).

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

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

Where:

PS	=	absolute gas pressure, inches of mercury
P _{bar}	=	barometric pressure, inches of mercury
P _g	=	gauge pressure, inches of water (static pressure)

Table 4-1. EPA Method 1—Traverse Point Location for Institutional Boiler Exhaust (A Rectangular Duct)

Traverse Point Number	Fraction of Inside Stack Dimension Length (%)	Distance from Inside Stack Wall (in.)	Traverse Point Location from Outside Sampling Port^a (in.)
1	2.6	1.250	8.250
2	8.2	3.875	10.875
3	14.6	7.000	14.000
4	27.6	13.250	20.125
5	34.2	16.375	23.375
6	65.8	31.500	38.500
7	77.4	37.250	44.125
8	85.4	41.000	48.000
9	91.8	44.125	51.125
10	97.4	46.750	53.750

^a The thickness of the stack wall plus the port flange was 7.0 in.

The value 13.6 represents the specific gravity of mercury (1 inch of mercury = 13.6 inches of water). For the stack tested, the absolute gas pressure under these conditions was 29.68 inches of mercury.

Volumetric Flow Rate Determination Using EPA Method 2

Volumetric flow rate was measured according to EPA Method 2⁶, “Velocity — S-Type Pitot”. A Type K 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 Type-S 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

Type-S pitot tube is presented in detail in Section 3.1.1 of *Quality Assurance Handbook for Air Pollution Measurement Systems*. Volume III. Stationary Source Specific Methods.⁹ Only Type-S pitot tubes meeting the required EPA specifications were used. Pitot tubes were inspected and documented as meeting EPA specifications prior to field sampling.

Calculation of Average Flue Gas Velocity

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

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

Where:

V_s	=	average flue gas velocity, ft/sec
K_p	=	Pitot constant (85.49)
C_p	=	Pitot coefficient (dimensionless), typically 0.84 for Type S
ΔP_{avg}	=	average flue gas velocity head, inches of water
460	=	zero degrees Fahrenheit expressed as degrees Rankine
T_s	=	flue gas temperature, degrees Fahrenheit
P_s	=	absolute stack pressure (barometric pressure at measurement site plus stack static pressure), in. Hg
M_s	=	wet molecular weight, pounds per pound-mole

The flue gas velocity calculated for each traverse point and the average velocity are shown in Table 4-2.

Table 4-2. Campaign-Specific Flue Gas Velocity for Each Traverse Point

Traverse Point (As Calculated in Table 4-1)	Campaign #1 Velocity, ft/min	Campaign #2 Velocity, ft/min
1	0.0	293.9
2	0.0	339.1
3	0.0	321.0
4	0.0	340.0
5	423.3	366.7
6	598.0	390.3
7	792.4	423.4
8	732.3	298.4
9	0.0	230.7
10	0.0	230.7
Average Velocity	(4-point \bar{x}) 636.51	(10-point \bar{x}) 323.42

For campaign #1, the point of average velocity has the closest relationship to traverse point #6. For campaign #2, the point of average velocity has the closest relationship to traverse point #3.

Determination of Volumetric Flow Rate for Stack Gas

Because stack gas flow rate velocity could be measured at only four of ten traverse points for the testing performed for campaign #1 (whereas stack flow could be measured at all ten traverse points for campaign #2), stack volumetric flow rates could not be determined on the same basis in both test campaigns. Stack gas flow rates were therefore calculated for both campaigns on the basis of carbon content of fuel feed, as shown in Table 4-3. The values shown in Table 4-3 for flue gas flow rate were used in subsequent calculations for emission factors.

Table 4-3. Carbon-Based Calculation of Flue Gas Flow Rates

Volume occupied by 1 mole of gas at 273.16 K and 1 atm (29.92 “ Hg) [Standard Temperature and Pressure]

$$PV = nRT \quad V = nRT/P$$

$$V = [(1 \text{ mol}) * (0.082056 \text{ L atm K}^{-1} \text{ mol}^{-1}) * (273.16 \text{ K})]/1 \text{ atm}$$

Molar volume at 273 K, 1 atm

$$V = 22.4144 \text{ L/g-mol}$$

$$1 \text{ ft}^3 = 28.317 \text{ L}$$

Therefore, 22.4144 L/mol = 791.55 ft³/kg-mol, and corrected to the test conditions 849.66 ft³/kg-mol.

Parameter	Sampling Campaign #1			Sampling Campaign #2		
	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
Fuel volumetric flow rate (gal/min)	3.43	3.62	4.14	2.32	2.33	2.33
Fuel density (kg/gal)	3.19	3.19	3.19	3.19	3.19	3.19
Fuel mass feed rate (kg/min)	10.9417	11.5478	13.2066	7.4008	7.4327	7.4327
Carbon in fuel (wt %)	85.93	85.93	85.93	86.53	86.53	86.53
Carbon feed rate (kg/min)	9.4022	9.9230	11.3484	6.404	6.4315	6.4315
Carbon feed rate (kmol/min)	0.7829	0.8623	0.9449	0.5337	0.5360	0.5360
CO ₂ in flue gas (vol %, wet)	16.20	15.67	15.47	10.70	10.40	9.90
CO in flue gas (vol %, wet)	0.03	0.03	0.03	0.03	0.03	0.03
Ideal gas conversion (0 °C, 1 atm) (scf/kmol)	849.66	849.66	849.66	849.66	849.66	849.66
Gaseous carbon in flue gas (kmol/scf)	0.000191	0.000184	0.000182	0.000126	0.000123	0.000123
Organic carbon on quartz filter (µg/cm ²)	0.31	2.39	2.37	20.337	20.267	66.04
Elemental carbon on quartz filter (µg/cm ²)	0.59	2.51	10.31	1.47	0.66	1.47
Total carbon on filter ^a (µg)	12.105	65.905	170.546	293.304	281.468	908.010

Table 4-3. (Continued)

Parameter	Sampling Campaign #1			Sampling Campaign #2		
	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
Sample flow (sLpm)	8.255	8.242	8.489	8.239	8.195	8.251
Test run time (min)	600.33	600.50	600.17	600.60	600.67	600.00
PM concentration at filter (kmol/scf)	5.785×10^{-11}	3.139×10^{-10}	7.891×10^{-11}	1.397×10^{-9}	1.348×10^{-9}	4.323×10^{-10}
Dilution ratio	46.81	48.67	45.91	44.31	44.37	44.95
PM carbon in flue gas (kmol/scf)	2.695×10^{-9}	1.528×10^{-8}	3.623×10^{-9}	6.191×10^{-8}	5.980×10^{-8}	1.943×10^{-8}
Total carbon in flue gas (kmol/scf)	0.000191	0.000184	0.000182	0.000126	0.000123	0.000117
Flue gas flow rate by carbon content (scfm)	4065	4159	4827	3935	4066	4270
Flue gas flow rate by pitot (scfm)	4666			2371		
Difference in flow measurements	-1.3%			39.7%		

^aFilter area on which particulate matter was collected was 13.45 cm².

No structural changes to the ductwork were made between the two test campaigns. The percent load at which the boiler was operated was different for the two campaigns. During the campaign #2 tests, the fuel feed rate averaged 37.6% lower than the campaign #1 tests, and the excess oxygen levels were much higher (campaign #2 = 15.7 to 20.5%; campaign #1 = 7.6 to 9.2% excess oxygen). During campaign #1, the boiler was fired at 37 - 42% of its rated capacity; during campaign #2, the boiler was fired at only 25% capacity. The differences in load resulted in different stack velocities for the two campaigns (see Section 4, Table 4-2). As the point at which the sampling port used for these tests had to be installed (due to physical constraints) was very close to the breech area exit of the boiler, the upstream and downstream distances specified in EPA Method 1 could not be attained (see Section 3). Consequently, the stack gas at the different velocities behaved differently in the duct work resulting in a different flow profile. As the point of average velocity was determined using EPA Methods 1 - 4 for both tests, representativeness and comparability are considered to be appropriate.

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 5⁸ (U.S. EPA, 1989d) 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 in liters/minute. At the average velocity calculated using the four-point average for campaign #1, the recommended nozzle size was 0.552 in. At the average velocity calculated using the 10-point average for campaign #2, the recommended nozzle size was 0.505 in.

Measurement of O₂ and CO₂ Concentrations

The O₂ and CO₂ concentrations were determined by use of a Fyrite bulb during the traverse.

Stationary Gas Distribution (as Percent Volume)

The following values were measured for the stationary gases:

	<u>Campaign #1</u>	<u>Campaign #2</u>
Measured O ₂ vol % (wet)	6.0	8.1
Measured CO ₂ vol % (wet)	15.0	11.0
(Provided) CO vol % (wet)	0.03	0.03

The percentage of nitrogen (N₂) was calculated according to the following equation:

$$\begin{aligned}
 \text{N}_2 \text{ vol \%} &= 100 - (\text{O}_2 \text{ vol \%} + \text{CO}_2 \text{ vol \%} + \text{CO vol \%}) \\
 &= 100 - (6.0 + 15.0 + 0.03) \\
 &= 78.97 \text{ (campaign \#1)} \\
 &= 100 - (8.1 + 11.0 + 0.03) \\
 &= 80.87 \text{ (campaign \#2)}
 \end{aligned}
 \tag{4-3}$$

Dry Molecular Weight of Flue Gas

The dry molecular weight of the flue gas (M_d) was calculated according to the following equation:

$$\begin{aligned}
 M_d &= (\text{CO}_2 \text{ vol \%} * 0.44) + (\text{O}_2 \text{ vol \%} * 0.32) + [(\text{CO vol \%} + \text{N}_2 \text{ vol \%}) * 0.28] \\
 &= (15.0 * 0.44) + (6.0 * 0.32) + [(0.03 + 78.97) * 0.28] \\
 &= 6.60 + 1.92 + 22.12 \\
 &= 30.64 \text{ lb/lb-mole (campaign \#1)} \\
 &= 30.08 \text{ lb/lb-mole (campaign \#2)}
 \end{aligned}
 \tag{4-4}$$

Where:

$$\begin{aligned}
 M_d &= \text{molecular weight of flue gas, dry basis (lb/lb-mole)} \\
 \text{CO}_2 \text{ vol \%} &= \text{percent CO}_2 \text{ by volume, dry basis}
 \end{aligned}$$

O ₂ vol %	=	percent O ₂ by volume, dry basis
CO vol %	=	percent CO by volume, dry basis
N ₂ vol %	=	percent N ₂ by volume, dry basis
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 according to the following equation:

$$\begin{aligned}
 M_s &= (M_d * M_{fd}) + (0.18 * \text{H}_2\text{O vol \%}) \\
 &= 29.25 \text{ wet lb/lb-mole (campaign \#1)} \quad (4-5) \\
 &= 28.65 \text{ wet lb/lb-mole (campaign \#2)}
 \end{aligned}$$

Where:

M_s	=	wet molecular weight of flue gas, wet lb/lb-mole
M_d	=	molecular weight of flue gas, dry basis (lb/lb-mole)
M_{fd}	=	dry mole fraction of effluent gas, calculated as $[1 - \text{H}_2\text{O vol \%} / 100]$
0.18	=	molecular weight of H ₂ O, divided by 100
%H ₂ O	=	percent H ₂ O, by volume.

Determination of Average Moisture Using EPA Method 4

EPA Method 4⁷, “Moisture Content”, was used to determine the average moisture content of the stack gas. A gas sample was extracted from the source, moisture was removed from the sample stream, and the moisture content was determined gravimetrically. Before sampling, the initial weight of the impingers was recorded. When sampling was completed, the final weights of the impingers were recorded and the weight gain was calculated. The weight gain and the volume of gas sampled were used to calculate the average moisture content (percent) of the stack gas. The calculations were performed by computer. Method 4 was incorporated into the techniques that were used for all of the manual sampling methods used during the test.

The measurements shown in Table 4-4 were made on January 15, 2001, for campaign #1 and on July 7, 2002, for campaign #2, using Method 4 to determine moisture recovery.

Table 4-4. Moisture Recovery for Method 4

Measured on January 15, 2001, for Campaign #1

Impinger Number	Impinger Solution	Weight of Impinger Contents (g)	Impinger Tip Configuration	Impinger Weight		
				Final (g)	Initial (g)	Weight Gain (g)
1	Water	100	S&G	702.3	625.1	77.2
2	Water	100	S&G	672.0	642.1	29.9
3	Empty	0	S&G	597.2	590.0	7.2
4	Silica Gel	300	S&G	749.1	748.3	3.8
Total Weight Gain (g)						118.1

Measured on July 7, 2002, for Campaign #2

Impinger Number	Impinger Solution	Weight of Impinger Contents (g)	Impinger Tip Configuration	Impinger Weight		
				Final (g)	Initial (g)	Weight Gain (g)
1	Water	100	S&G	674.5	607.6	66.9
2	Water	100	S&G	609.0	575.9	33.1
3	Empty	0	S&G	492.7	484.8	7.9
4	Silica Gel	300	S&G	732.3	720.3	12.0
Total Weight Gain (g)						119.9

Volume of Dry Gas Sampled at Standard Conditions (dscf)

The volume of dry gas sampled under standard conditions was calculated using the following equation:

$$V_{m(\text{std})} = 17.64 * Y * V_m * P_{\text{bar}} + \frac{\Delta H}{460 + T_m} \quad (4-6)$$

Where:

$V_{m(\text{std})}$	=	volume of dry gas sampled at standard conditions, dry standard cubic feet (dscf)
Y	=	dry gas meter calibration factor (0.98)
V_m	=	volume of gas metered, cubic feet, dry
P_{bar}	=	barometric pressure at measurement site, inches of mercury
ΔH	=	Sampling rate, measured as differential pressure at the meter orifice, inches of water
T_m	=	dry gas meter temperature, degrees Fahrenheit

The constant 17.64 was used for conversion to standard conditions $(68^\circ\text{F} + 460^\circ\text{R})/29.92$ in. Hg; 460 is zero degrees Fahrenheit in degrees Rankine. Using measured values from the field data sheet, the volume of dry gas sampled at standard conditions ($V_{m(\text{std})}$) was calculated to be 43.011 dscf for campaign #1, 42.034 dscf for campaign #2.

Volume of Water Vapor at Standard Conditions (dscf)

The volume of water vapor under standard conditions was calculated using the following equation:

$$V_{w(\text{std})} = 0.04707 * V_{\text{lc}} \quad (4-7)$$

Where:

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

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 4-4 above), the volume of water vapor at standard conditions is calculated to be 5.559 scf for campaign #1, 5.644 scf for campaign #2.

Calculation of Moisture/Water Content (as % Volume)

The moisture content of the gaseous stack emissions is calculated using the following equation:

$$\text{H}_2\text{O vol \%} = 100 * \frac{V_{w(\text{std})}}{V_{w(\text{std})} + V_{m(\text{std})}} \quad (4-8)$$

Using values measured using EPA Method 4 and values calculated previously, the moisture content was calculated to be 10.993 percent volume for campaign #1 and 11.838 percent volume for campaign #2.

Calculation of Dry Mole Fraction of Flue Gas

The dry mole fraction of flue gas is calculated using the following equation:

$$M_{fd} = 1 - \frac{\text{H}_2\text{O vol \%}}{100} \quad (4-9)$$

Where:

M_{fd} = dry mole fraction of effluent gas.

Using the percent moisture determined above, the dry mole fraction of effluent gas is calculated as 0.8901 for campaign #1 and 0.8816 for campaign #2.

Setup of the Dilution Sampling System

The site location was a boiler room at the NC A&T facility, with the 6-inch flanged sampling port installed in the exhaust duct work to allow the dilution sampling unit to sit on a sturdy hydraulic lift cart, which could be rolled into place and raised to allow the probe of the dilution sampling system (Figure 3-2) access to the sampling port. The dilution system control module, the sampling module, and all ancillary equipment were delivered to the test site by truck. The two modules (dilution air supply/control module and sampling module) were positioned at the sampling location by rolling the units through a ground-level door, then elevating the sampling module to the appropriate height for access to the sampling port using the sturdy hydraulic lift to raise and lower the sampling assembly. A power panel and feeder to provide power to two quad outlets and a 50-amp, 2-pole circuit, including a breaker in the existing main panel, had also been installed by the facility prior to campaign #1.

The location provided convenient access to the stack and sampling port, as shown in Figure 3-4, and sufficient space for the equipment and personnel for both testing campaigns. The dilution air system module positioned at the sampling location in the boiler room is shown during testing operations in Figure 4-1. Figure 4-2 shows the sampling probe installed in the 6-in. I.D. flanged port used for sampling. The dilution air supply/control module (Figure 4-3) was located in the boiler room, approximately 12 feet from the sampling module and around the corner of the boiler. A TSI SMPS (Figure 4-4), with associated laptop computer, was also connected to the sampling module (visible behind the TSI display in Figure 4-4), together with the sample collection arrays for campaign #1. An Electrical Low Pressure Impactor (ELPI) (Figure 4-5), with an associated laptop computer, was connected to the sampling module together with the sample collection arrays for campaign #2. The dilution system sampling module, together with other sample collection arrays and instruments attached, is shown in Figure 4-6 for campaign #1. The dilution system sampling module, together with other sample collection arrays and instruments attached, is shown in Figure 4-7 for campaign #2.



Figure 4-1. Dilution sampling system elevated on mobile lift for access to the sampling port.

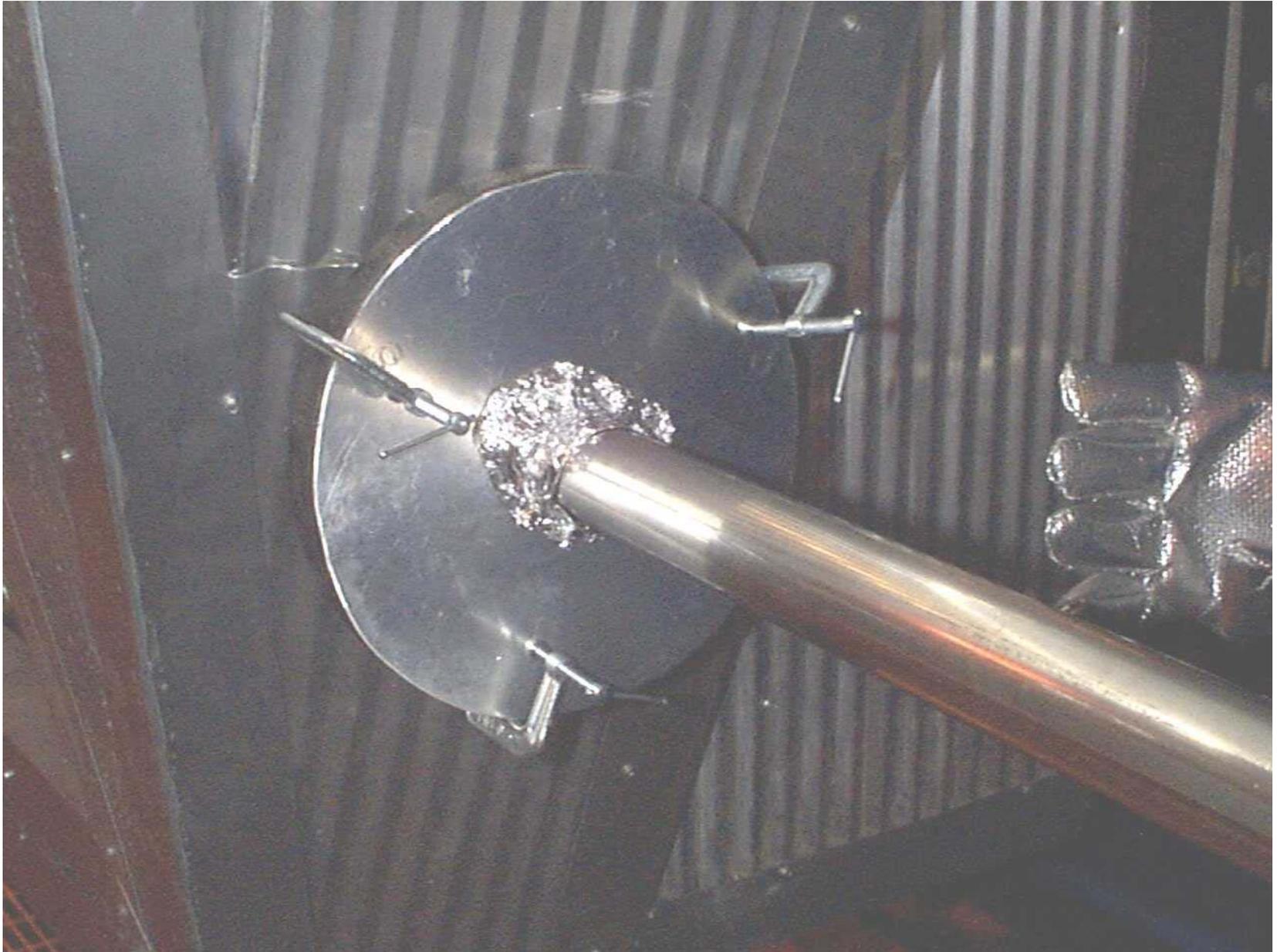


Figure 4-2. Dilution system sampling probe installed in 6 in. I.D. flanged port.



Figure 4-3. Dilution system control module positioned at the sampling location.



Figure 4-4. TSI particle sizer positioned at the sampling location (January 16, 2001) for Campaign #1.

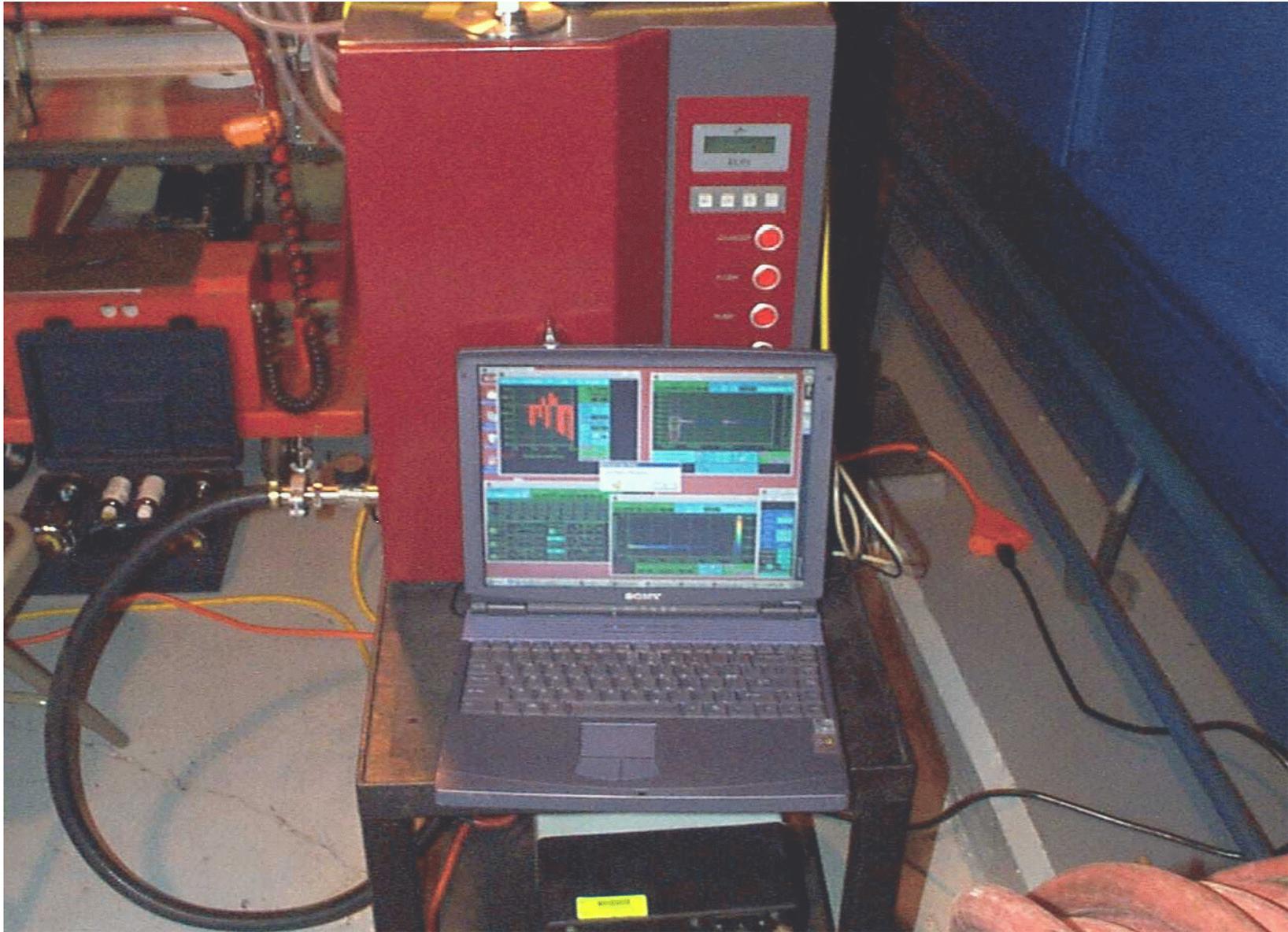


Figure 4-5. ELPI particle sizer positioned at the sampling location (July 7, 2002) for Campaign #2.



Figure 4-6. Dilution system with all sample collection arrays and instruments attached for Campaign #1.

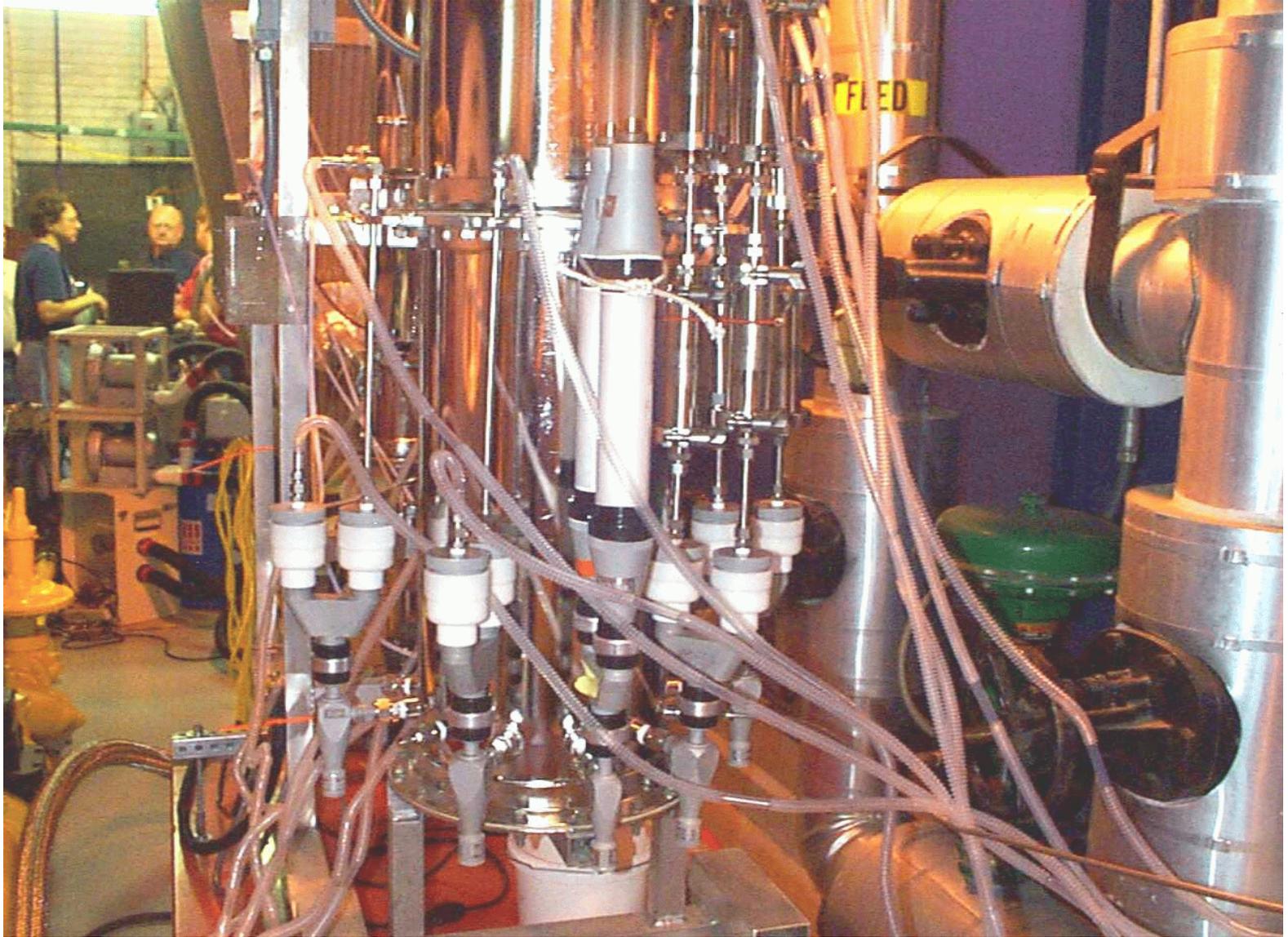


Figure 4-7. Dilution system sampling module, together with sample collection arrays, for Campaign #2.

Figures 4-8 and 4-9 present the recovery area used during both testing campaigns. Figure 4-9 shows the analyst recovering a PUF sampling module. Figure 4-10 shows the removal of a filter from a sample collection array prior to packaging for transport to the laboratory.

Pre-Test Leak Check

To perform a pre-test leak check on the assembled dilution system in the field, the inlet end of the probe was plugged with a Swagelok fitting. Solvent-cleaned solid plates were inserted in place of the orifice plates at the orifice meter run flanges and sealed off using gaskets on each side. A new preweighed quartz 8-in. x 10-in. filter was inserted into the filter holder and carefully sealed in place using screw fittings. A vacuum pump was attached to the residence chamber and a Magnehelic gauge was attached to an available port. The valve between the pump and the chamber was opened and the vacuum was monitored as the system was evacuated. As the reading passed 27 in., the valve between the pump and the chamber was closed. The leak rate was timed between 25 to 20 in. H₂O and again from 20 to 15 in. H₂O, and the two times were averaged. Using the recorded data, the leakage rate in cubic feet/minute was calculated according to Equation 4-10.

$$\text{leakage rate} = \frac{\Delta P}{\Delta T} \times V \times \text{CF} \quad (4-10)$$

Where:

leakage rate	=	rate of leakage (ft ³ /min)
ΔP	=	change in pressure (in. H ₂ O)
ΔT	=	time increment (sec)
V	=	volume of the evacuated dilution sampler (15.3 ft ³)
CF	=	unit conversion factors
	-	60 sec/min
	-	1 atm/406.8 in. H ₂ O



Figure 4-8. Sample recovery area.



Figure 4-10. Teflon filter being removed from the holder in preparation for packaging for transport to the laboratory.

The criteria for an acceptable leak are ≤ 0.1 cfm, or ≥ 1 min 53 sec, equivalent to a pressure increase of 5 in. H₂O. For campaign #1, an average time of 1 min 58 sec was required for a 5-in. pressure change to occur (resulting leak rate: 0.100 cfm). For campaign #2, an average time of 1 min 59 sec was required for a 5-in. pressure change to occur (resulting leak rate: 0.095 cfm). These leak rates both met the acceptance criteria.

Orifice Flow Check

Critical orifice flows on the sampling pumps were checked without sample collection arrays in place using a rotameter to verify that the channels on sample collection array pumps were at the specified flow rate of 16.7 L/min. Rotameters were calibrated with an NIST-traceable electronic bubble flow meter.

Determination of Test Duration

To maximize the collection of particulate material, the decision was made to extend the run time for the longest duration (~10 hours) allowed by the facility.

Canister/Veriflow Blanks

Canisters and Veriflows were utilized only for campaign #1. 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 < 10 parts per billion carbon (ppbC, Table 4-5).

Table 4-5. Blank Values for Veriflows and Canisters (Campaign #1)

Unit	Blank Value, ppbC
Veriflows	
Unit #418 (Source)	0.0
Unit #315 (Dilution Air)	0.0
ERG-3 (Ambient)	0.7
Canisters	
3950	1.1
3953	4.4
4031	1.4
4040	1.03
3965	1.0
1404	1.0
4028	0.0
4039	0.0
4024	1.5
5000	3.7

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 the 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 (sLpm) 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 conditions (aLpm) and compared to those produced by the dry gas meter corrected to the venturi conditions. An Excel macro automatically selected a correct calibration value to be applied based on the flowing temperature.

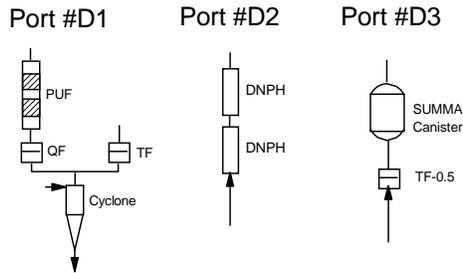
Since the actual venturi flow was dependent upon the operating conditions, the setpoint value displayed and entered on the viewing screens needed to be adjusted to achieve the desired flow. Information to be entered included desired flow, flowing temperature, flowing pressure, and barometric pressure;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

Sample Collection Arrays: Campaign #1

Prior to actual testing (Test Run #1, January 16, 2001; Test Run #2, January 17, 2001; Test Run #3, January 18, 2001), sample collection arrays were attached to various ports on the dilution sampling system, as shown in Figure 4-11. Up to ten sampling ports were available, attached to either the dilution chamber (designated Ports #D1, #D2, and #D3) or the residence chamber (designated Ports #R2, #R3, #R4, #R5, #R6, #R8, and #R10); the available sampling ports are shown in Figure 3-1. The following sample collection arrays were used on all three test days for campaign #1; the sample collection arrays with two denuders in series were used only on the first test day (Figure 4-11A):

- **Dilution Chamber Sample Collection for Campaign #1**
 - *Dilution Chamber Collection Array D1*
Collection array D1 collects gas phase semivolatile organic compounds, particle-bound organic materials, and metals. The array consists of a cyclone separator to remove particulate matter with aerodynamic diameter greater than 2.5 μm . The gas stream is split into two legs. Leg 1 contains a quartz filter followed by two PUF units in series. The other leg of array D1 consists of a Teflon filter.
 - *Dilution Chamber Array D2*
Collection array D2 collects gas-phase carbonyl compounds using a pair of carbonyl collection cartridges in series in a pump.
 - *Dilution Chamber Array D3*
Collection array D3 collects fine particulate matter and gas-phase organic compounds. This array consists of a single filter unit followed by a SUMMA canister.

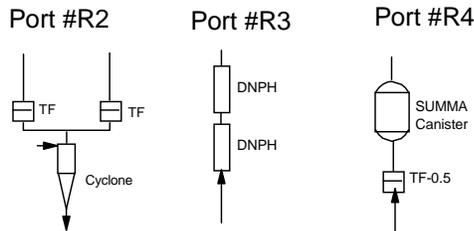
Dilution chamber



Total Sample Substrates

QF	7
TF-0.5	2
TF	5
PUF	14
Denuder*	6
SUMMA	2
DNPB	4
*Denuders collected one test day only.	

Residence chamber



Total Field Blank Substrates

QF	1
TF	1
PUF	1
DNPB	1

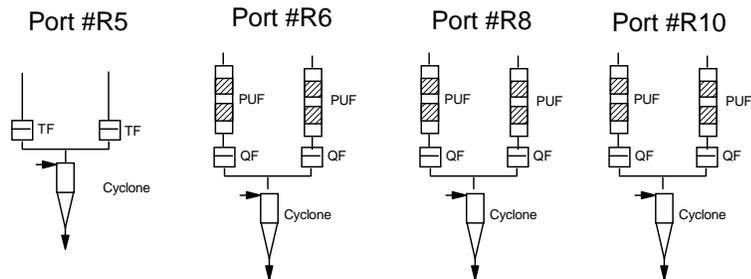
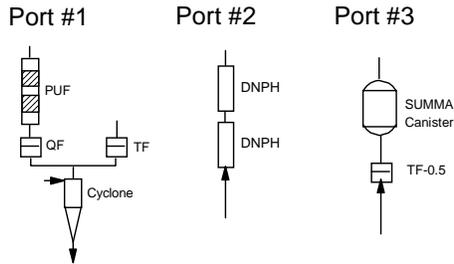


Figure 4-11. Schematic diagram of sample collection arrays used in field test (January 16-18, 2001) for Campaign #1.

Dilution chamber

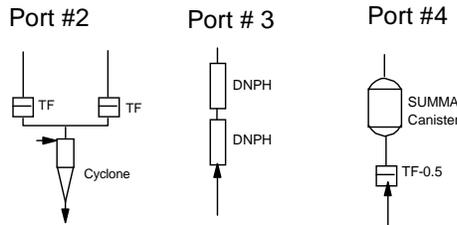


Total Sample Substrates

QF	7
TF-0.5	2
TF	5
PUF	14
Denuder*	6
SUMMA	2
DNP	4

*Denuders collected one test day only.

Residence chamber



Total Field Blank Substrates

QF	1
TF	1
PUF	1
DNP	1

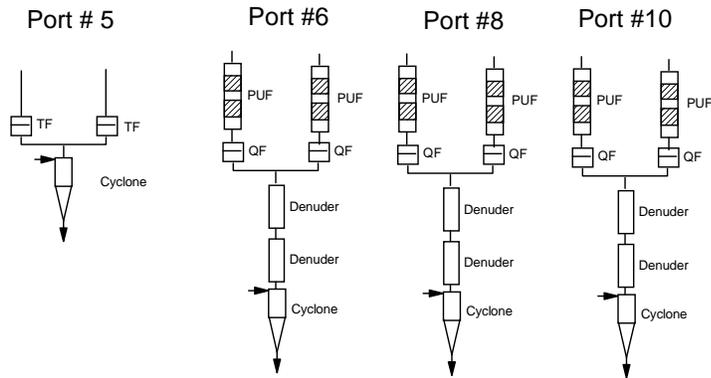


Figure 4-11A. Schematic diagram of sample collection arrays used in field test (January 16-18, 2001) for Campaign #1, showing denuders used on only one test day.

- **Residence Chamber Collection Arrays for Campaign #1**
 - *Residence Chamber Collection Array R2*
Collection array R2 collects fine particulate matter. The array consists of a 2.5- μm cyclone followed by two identical legs containing Teflon filters.
 - *Residence Chamber Collection Array R3*
Collection array R3 collects fine particulate matter and gas-phase carbonyl compounds. This array consists of a pair of carbonyl collection cartridges in series and a pump.
 - *Residence Chamber Collection Array R4*
Collection array R4 collects fine particulate matter and gas-phase organic compounds. This array consists of a single filter unit followed by a SUMMA canister.
 - *Residence Chamber Collection Array R5*
Collection array R5 collects fine particulates. The array consists of a 2.5- μm cyclone followed by two identical legs containing Teflon filters.
 - *Residence Chamber Collection Arrays R6, R8, and R10*
Collection arrays R6, R8, and R10 collect fine particulate matter on quartz filters for total carbon and elemental carbon analysis. These sampling arrays consist of a 2.5- μm cyclone followed by two identical legs each containing a quartz filter followed by two PUF plugs in series. On one test day, two XAD-4-coated denuders in series will be used with each array to collect semivolatile organic compounds.

In addition to the sample collection arrays, a TSI continuous particle size analyzer was used on the residence chamber. The scanning mobility particle sizer (SMPS) includes a TSI Model 3081 Electrostatic Classifier in tandem with a TSI Model 3025A Ultrafine Condensation Particle Counter. This device scanned the range of 9-421 nanometers (nm) in a scan cycle of approximately 3 minutes, with data collected continuously onto a laptop computer with real-time data display and saving. The SMPS was connected to the residence chamber at port #R7 to continuously monitor particle size distribution.

Sample Collection Arrays: Campaign #2

Prior to actual testing (Test Run #1, July 9, 2002; Test Run #2, July 10, 2002; and Test Run #3, July 11, 2002), sample collection arrays were attached to various ports on the dilution sampling system, as shown in Figure 4-12. Up to ten sampling ports were available, attached to either the dilution chamber (designated port #D1) or the residence chamber (designated ports #R2, 3, 4, 5, 6, 8, and 10); the available sampling ports are shown in Figure 4-12, the schematic diagram of the dilution sampling system. The following sample collection arrays were used on all three test days for campaign #2:

- **Dilution Chamber Sample Collection for Campaign #2**
 - *Dilution Chamber Collection Array D1*
Collection array D1 collects gas phase semivolatile organic compounds, particle-bound organic materials (both organic and inorganic). The array consists of a cyclone separator to remove particulate matter with aerodynamic diameter greater than 2.5 μm . The gas stream is split into two legs. Leg one contains a quartz filter followed by two PUF units in series. The other leg of array D1 consists of a Teflon filter.

- **Residence Chamber Collection Arrays for Campaign #2**
 - *Residence Chamber Collection Arrays R6, R8 and R10*
Collection arrays R6, R8 and R10 collect fine particulate matter and semivolatile organic compounds for analysis of elemental carbon/organic carbon (EC/OC) and speciated organic compounds. The array consists of a 2.5- μm cyclone followed by two identical legs containing quartz filters and four PUF plugs in series (two PUF modules containing two PUF plugs each on each leg).

Sampling Arrays - Oil Boiler Tests (NC A&T, 6/2002)

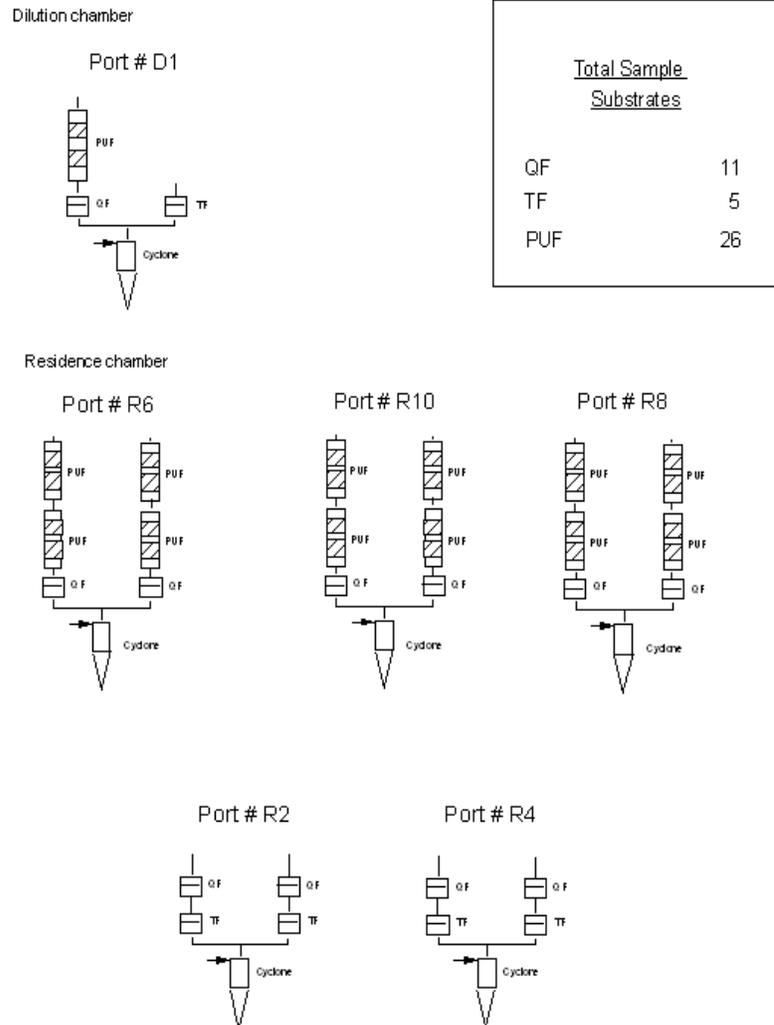


Figure 4-12. Schematic diagram of sample collection arrays used in field test (July 9-11, 2002) for Campaign #2.

- *Residence Chamber Collection Arrays R2 and R4*
Collection arrays R2 and R4 collected PM-2.5 on Teflon filters for determination of mass, elements and inorganic ions. The Teflon filters are followed by quartz filters to determine any semivolatile organic compounds stripped from the Teflon filters during sampling.

In addition to the sample collection arrays, an ELPI was connected to the residence chamber at port R3 to continuously monitor particle size distribution.

Measurement of O₂ and CO₂ Process Concentrations

For campaign #1, measurements of O₂ were made using the certified facility O₂ analyzer every 15 min for the duration of each test day to determine average O₂ concentrations during test conditions. For campaign #2, measurement of O₂ and CO₂ were made using Fyrite bulbs every 30 min across the duration of the tests to determine average O₂ and CO₂ concentrations during testing.

Operation of the Dilution Sampling System and Sample Collection Arrays

To prepare the dilution sampling system for a full test run, sampling probe temperature setpoints were set equal to or slightly above the measured stack temperature. The system was equilibrated at temperature. Sample collection arrays were loaded with appropriate media, and flow/leak checks were performed with each sample collection 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 in the stack. Sample collection array pumps were started, and for campaign #1 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 pressure change in the canister to ensure that filters were not overloaded in the course of sampling. Start time and other pertinent data were recorded. At the end of the predetermined 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 sampling 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 of campaign #1 are shown in Tables 4-6 through 4-8; blower flow, dilution flow, and venturi flow for tests #1, #2, and #3 of campaign #1 are shown graphically in Figures 4-13 through 4-21. Experimental parameters for tests #1, #2, and #3 of campaign #2 are shown in Tables 4-9 through 4-11; blower flow, dilution flow, and venturi flow for tests #1, #2, and #3 of campaign #2 are shown graphically in Figures 4-22 through 4-30.

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 were carefully packaged for transport 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 sampling system, the sampling aperture was covered to avoid introduction of any contaminants into the dilution sampler. The ends of the sample collection array were capped and the array placed in a secure container for transport to the sample recovery area.

Table 4-6. Run Time Summary Information, Test Run #1, Campaign #1

Test Run #1 (January 16, 2001)			
Start Time	9:25:09 a.m.		
End Time	7:25:29 p.m.		
Run Time	600.33 min		
Barometric Pressure	29.68 in. Hg		
Nozzle Size	0.390		
Parameter	Average		
Venturi Flow	30.47 aLpm		
	18.53 sLpm		
PT-101	-0.92 in. WC		
TE-104	205.53 °C		
Dilution Flow	876.58 aLpm		
	847.89 sLpm		
PT-102	-1.37 in. WC		
TE-108	25.23 °C		
Blower Flow	918.41 aLpm		
	839.02 sLpm		
PT-103	-17.59 in. WC		
TE-105	28.20 °C		
Dilution Ratio	46.81		
TE-101	189.98 °C		
TE-102	198.11 °C		
TE-103	198.14 °C		
Sample Flow Rates			
Actual Flow aLpm	Corrected Flow sLpm	Notes	Average Flow sLpm
17.22	16.96	PM 2.5 sample on dilution air: start	16.88
17.07	16.81	PM 2.5 sample on dilution air: end	
16.92	16.66	PM 2.5 sample on residence chamber port 10: start	16.51
16.62	16.36	PM 2.5 sample on residence chamber port 10: end	
17.22	16.96	PM 2.5 sample on residence chamber port 8: start	16.96

Table 4-6. (Continued)

Sample Flow Rates

Actual Flow aLpm	Corrected Flow sLpm	Notes	Average Flow sLpm
17.22	16.96	PM 2.5 sample on residence chamber port 8: end	
16.92	16.66	PM 2.5 sample on residence chamber port 6: start	16.51
16.62	16.36	PM 2.5 sample on residence chamber port 6: end	
17.22	16.96	PM 2.5 sample on residence chamber port 4: start	16.96
17.22	16.96	PM 2.5 sample on residence chamber port 4: end	
17.22	16.96	PM 2.5 sample on residence chamber port 2: start	16.96
17.22	16.96	PM 2.5 sample on residence chamber port 2: end	
0.90	0.89	DNPH sample on residence chamber port 3: start	0.96
1.05	1.03	DNPH sample on residence chamber port 3: end	
1.47	1.45	DNPH sample on dilution air port 3: start	1.45
1.47	1.45	DNPH sample on dilution air port 3: end	
Canisters	Start Pressure	End Pressure	
#4024, Dilution	29.0 in. Hg	5.0 in. Hg	
#4039, Source	29.0 in. Hg	8.0 in. Hg	
#5000, Ambient ^a	29.0 in. Hg	0.0 in. Hg	
#1404, Blank	29.0 in. Hg	29.0 in. Hg	

^a The ambient sample was collected on the first test day of campaign #1 at the inlet of the charcoal scrubber subsystem of the EPA Dilution Sampling System. The data from the analysis of the ambient canister sample were reported but no correction of the monitoring data for ambient levels was performed. The ambient information was supplied to provide an indicator of the performance of the dilution sampling system scrubber efficiency in removing the ambient background from the air used for sample dilution at the test site.

PT = pressure transducer

TE = thermocouple

aLpm = actual liters per minute

sLpm = standard liters per minute

WC = water column

Table 4-7. Run Time Summary Information, Test Run #2, Campaign #1

Test Run #2 (January 17, 2001)			
Start Time	7:50:00 a.m.		
End Time	5:50:30 p.m.		
Run Time	600.50 min		
Barometric Pressure	29.83 in. Hg		
Nozzle Size	0.390 in.		
Parameter	Average		
Venturi Flow	29.37 aLpm		
	17.88 sLpm		
PT-101	-0.96 in. WC		
TE-104	207.51 °C		
Dilution Flow	870.64 aLpm		
	848.35 sLpm		
PT-102	-1.34 in. WC		
TE-108	24.57 °C		
Blower Flow	877.00 aLpm		
	833.41 sLpm		
PT-103	-13.30 in. WC		
TE-105	27.67 °C		
Dilution Ratio	48.67		
TE-101	194.54 °C		
TE-102	207.63 °C		
TE-103	209.57 °C		
Sample Flow Rates			
Actual Flow aLpm	Corrected Flow sLpm	Notes	Average Flow sLpm
17.40	17.39	PM 2.5 sample on dilution air: start	17.31
17.25	17.24	PM 2.5 sample on dilution air: end	
16.49	16.48	PM 2.5 sample on residence chamber port 10: start	16.48
16.49	16.48	PM 2.5 sample on residence chamber port 10: end	
17.10	17.08	PM 2.5 sample on residence chamber port 8: start	17.08

Table 4-7. (Continued)

Sample Flow Rates

Actual Flow aLpm	Corrected Flow sLpm	Notes	Average Flow sLpm
17.10	17.08	PM 2.5 sample on residence chamber port 8: end	
16.49	16.48	PM 2.5 sample on residence chamber port 6: start	16.48
16.49	16.48	PM 2.5 sample on residence chamber port 6: end	
17.10	17.08	PM 2.5 sample on residence chamber port 4: start	17.08
17.10	17.08	PM 2.5 sample on residence chamber port 4: end	
17.25	17.24	PM 2.5 sample on residence chamber port 2: start	17.16
17.10	17.08	PM 2.5 sample on residence chamber port 2: end	
0.99	0.99	DNPH sample on residence chamber port 3: start	0.96
0.93	0.93	DNPH sample on residence chamber port 3: end	
0.93	0.93	DNPH sample on dilution air port 3: start	0.93
0.93	0.93	DNPH sample on dilution air port 3: end	
Canisters	Start Pressure	End Pressure	
#4031, Dilution	29.0 in. Hg	5.0 in. Hg	
#4040, Source	29.0 in. Hg	4.0 in. Hg	

PT = pressure transducer

TE = thermocouple

aLpm = actual liters per minute

sLpm = standard liters per minute

WC = water column

Table 4-8. Run Time Summary Information, Test Run #3, Campaign #1

Test Run #3 (January 18, 2001)				
Start Time	7:35:06 a.m.			
End Time	5:35:16 p.m.			
Run Time	600.17 min			
Barometric Pressure	29.74 in. Hg			
Nozzle Size	0.390 in.			
Parameter	Average			
Venturi Flow	31.26 aLpm			
	19.02 sLpm			
PT-101	-0.99 in. WC			
TE-104	206.60 °C			
Dilution Flow	875.34 aLpm			
	850.66 sLpm			
PT-102	-1.39 in. WC			
TE-108	24.44 °C			
Blower Flow	885.81 aLpm			
	836.70 sLpm			
PT-103	-14.68 in. WC			
TE-105	27.44 °C			
Dilution Ratio	45.91			
TE-101	196.98 °C			
TE-102	203.77 °C			
TE-103	206.10 °C			
Sample Flow Rates				
Actual Flow aLpm	Corrected Flow sLpm	Notes		Average Flow sLpm
17.36	17.13	PM 2.5 sample on dilution air: start		17.13
17.36	17.13	PM 2.5 sample on dilution air: end		
16.60	16.38	PM 2.5 sample on residence chamber port 10: start		16.38
16.60	16.38	PM 2.5 sample on residence chamber port 10: end		
17.20	16.98	PM 2.5 sample on residence chamber port 8: start		16.98
		PM 2.5 sample on residence chamber port 6:start		16.98
17.20	16.98			

Table 4-8. (Continued)

Actual Flow aLpm	Corrected Flow sLpm	Notes	Average Flow sLpm
17.20	16.98	PM 2.5 sample on residence chamber port 6: end	
17.20	16.98	PM 2.5 sample on residence chamber port 4: start	16.98
17.20	16.98	PM 2.5 sample on residence chamber port 4: end	
17.20	16.98	PM 2.5 sample on residence chamber port 2: start	16.98
17.20	16.98	PM 2.5 sample on residence chamber port 2: end	
1.14	1.12	DNPH sample on residence chamber port 3:start	1.12
1.14	1.12	DNPH sample on residence chamber port 3: end	
1.18	1.17	DNPH sample on dilution air port 3: start	1.17
1.18	1.17	DNPH sample on dilution air port 3: end	
Canisters	Start Pressure	End Pressure	
#3953, Dilution	29.0 in. Hg	5.0 in. Hg	
#3950, Source	29.0 in. Hg	3.0 in. Hg	

PT = pressure transducer

TE = thermocouple

aLpm = actual liters per minute

sLpm = standard liters per minute

WC = water column

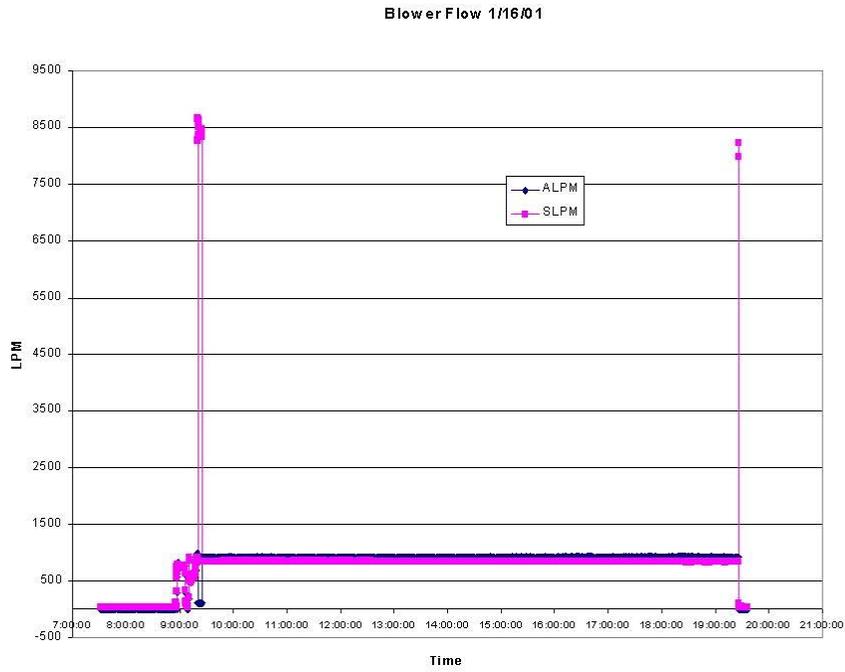


Figure 4-13. Blower flow, Test 1—Day 1, January 16, 2001, Campaign #1.

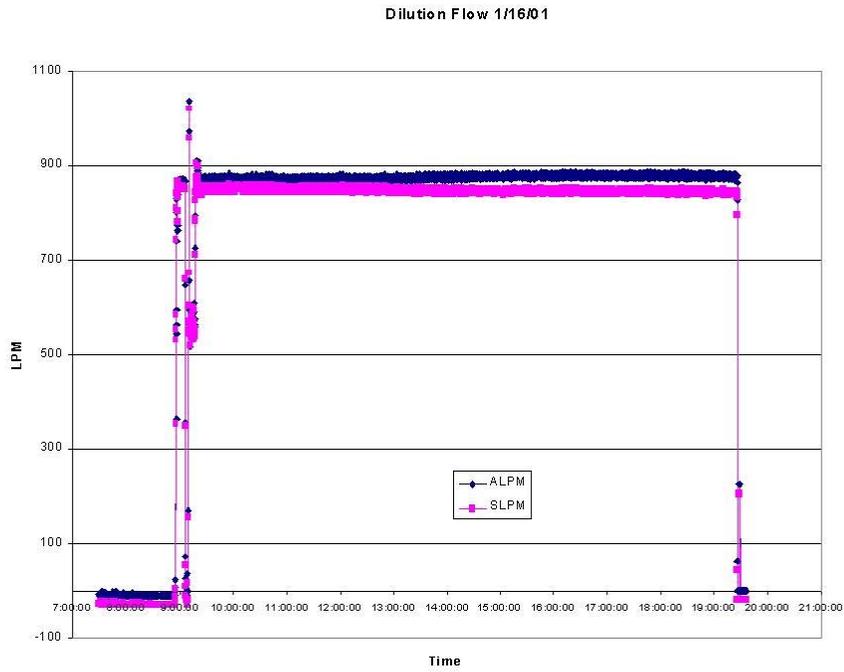


Figure 4-14. Dilution flow, Test 1—Day 1, January 16, 2001, Campaign #1.

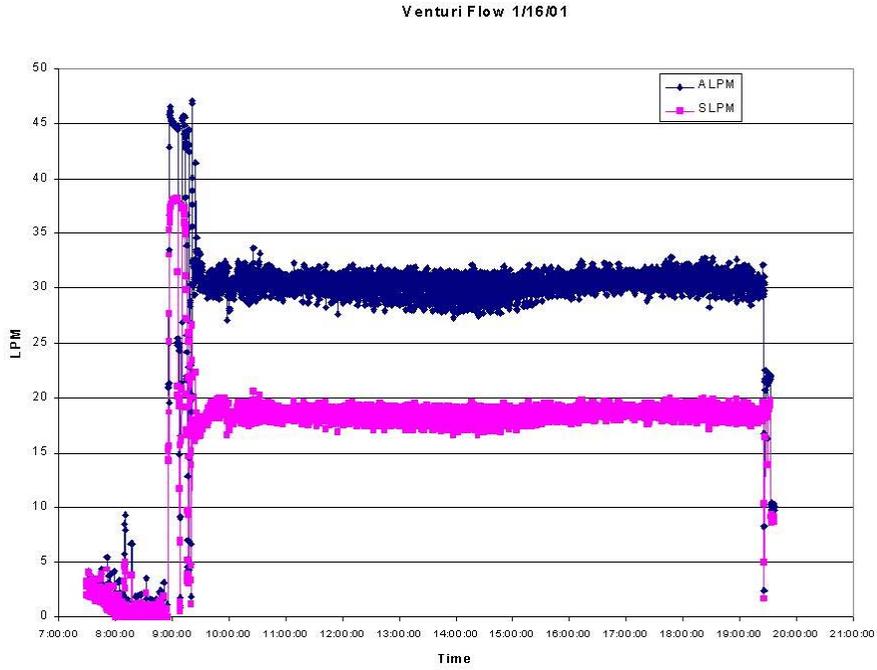


Figure 4-15. Venturi flow, Test 1—Day 1, January 16, 2001, Campaign #1.

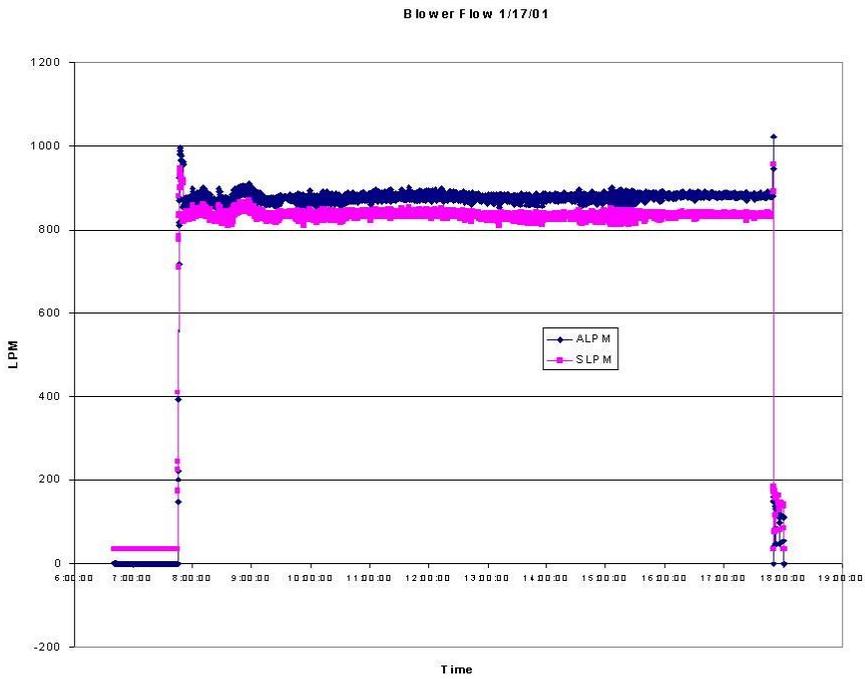


Figure 4-16. Blower flow, Test 2—Day 2, January 17, 2001, Campaign #1.

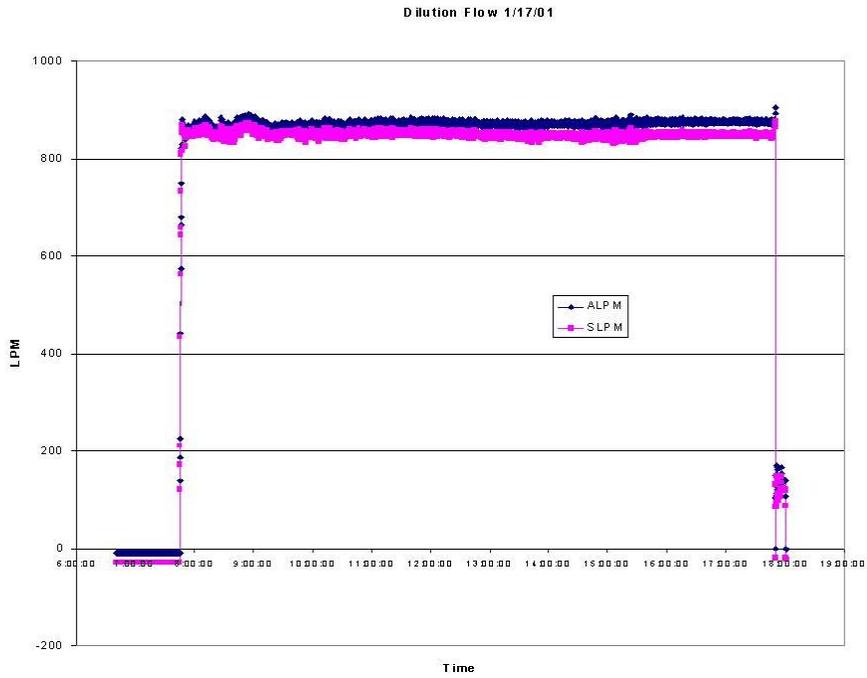


Figure 4-17. Dilution flow, Test 2—Day 2, January 17, 2001 Campaign #1.

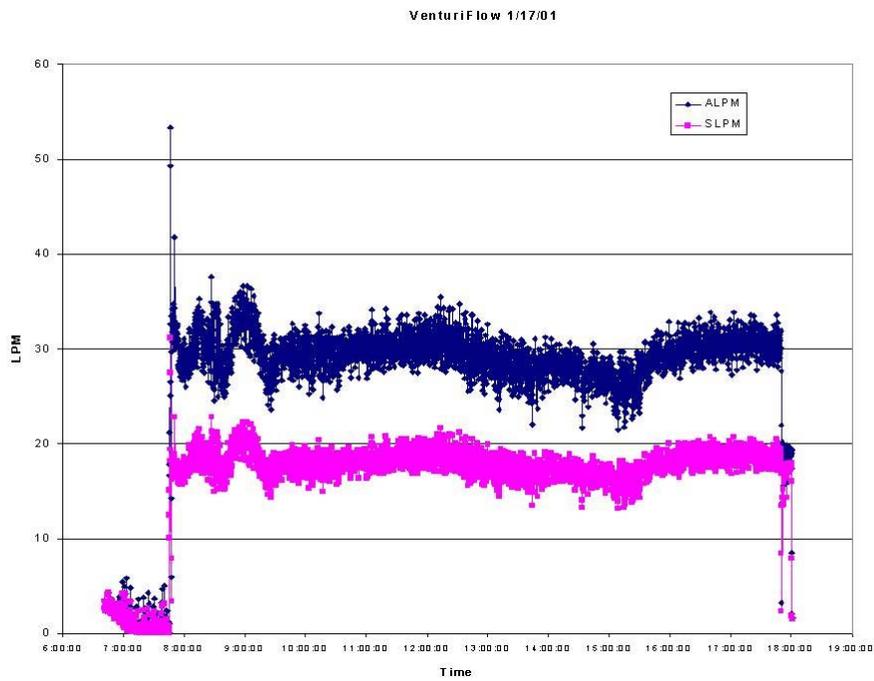


Figure 4-18. Venturi flow, Test 2—Day 2, January 17, 2001, Campaign #1.

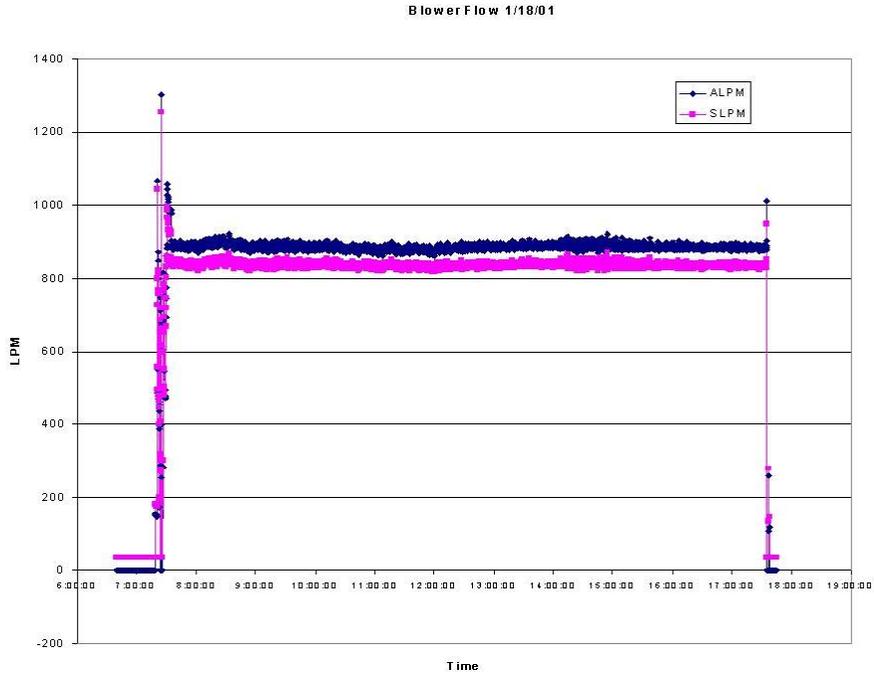


Figure 4-19. Blower flow, Test 3—Day 3, January 18, 2001, Campaign #1.

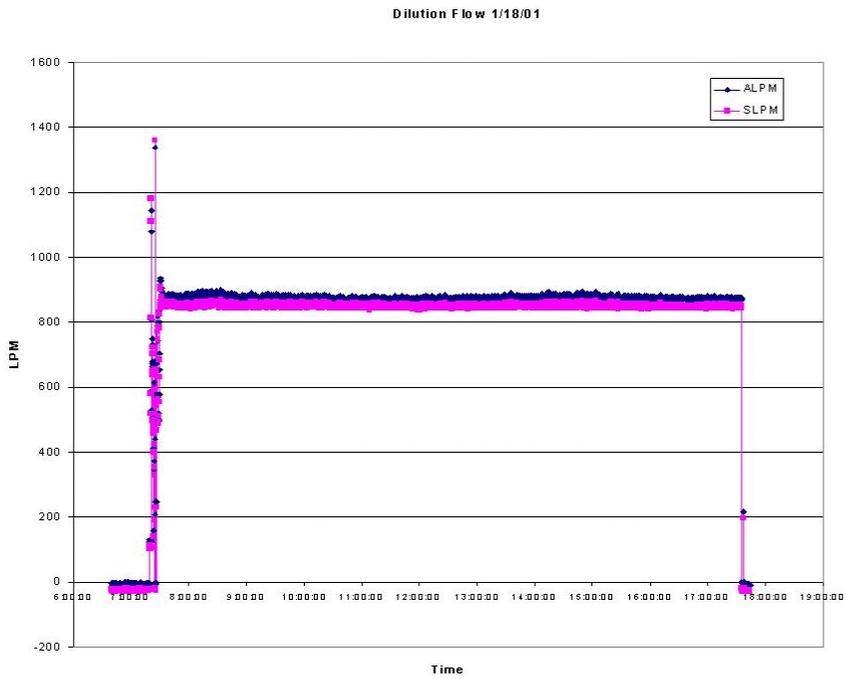


Figure 4-20. Dilution flow, Test 3—Day 3, January 18, 2001, Campaign #1.

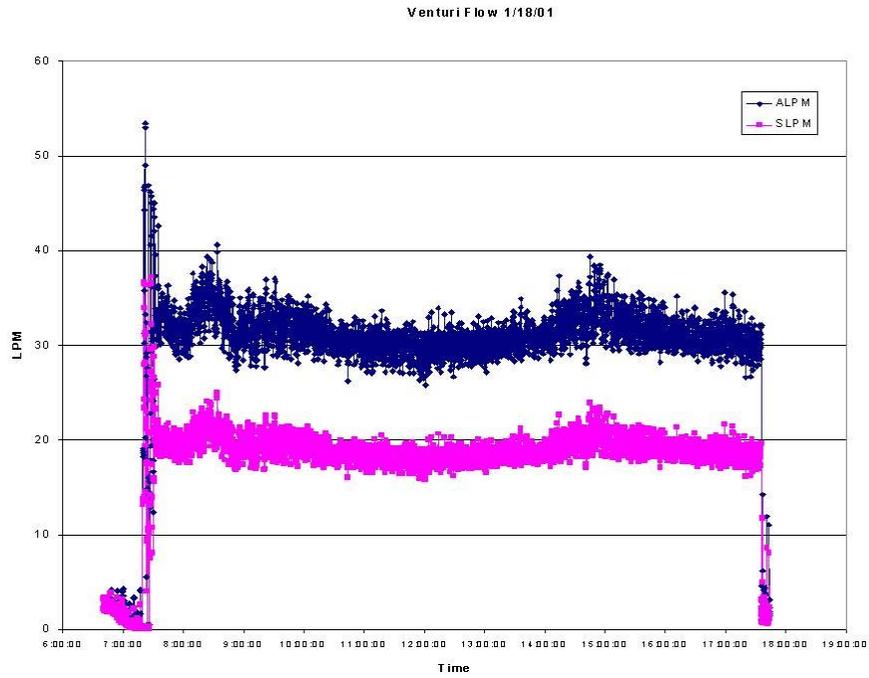


Figure 4-21. Venturi flow, Test 3—Day 3, January 18, 2001, Campaign #1.

Table 4-9. Run Time Summary Information, Test Run #1, Campaign #2

Test Run #1 (July 9, 2002)				
Start Time	8:01:08 a.m.			
End Time	6:01:44 p.m.			
Run Time	600.60 min			
Barometric Pressure	28.79 inches Hg			
Nozzle Size	0.505 inches			
Parameter	Average			
Venturi Flow	30.03 aLpm			
	18.85 sLpm			
PT-101	-0.77 inches WC			
TE-104	176.89 °C			
Dilution Flow	908.65 aLpm			
	816.28 sLpm			
PT-102	-1.42 inches WC			
TE-108	38.82 °C			
Blower Flow	789.12 aLpm			
	680.59 sLpm			
PT-103	-16.54 inches WC			
TE-105	41.37 °C			
Dilution Ratio	44.33			
TE-101	171.45 °C			
TE-102	176.73 °C			
TE-103	176.48 °C			
Actual Flow sLpm	Corrected Flow aLpm	Notes		Average Flow sLpm
16.43	17.78	PM 2.5 sample on dilution air–start		16.43
16.43	17.78	PM 2.5 sample on dilution air–end		
16.43	17.78	PM 2.5 sample on residence chamber port 10–start		16.43
16.43	17.78	PM 2.5 sample on residence chamber port 10–end		
16.58	17.93	PM 2.5 sample on residence chamber port 8–start		16.58
16.58	17.93	PM 2.5 sample on residence chamber port 8–end		
16.43	17.78	PM 2.5 sample on residence chamber port 6–start		16.43
16.43	17.78	PM 2.5 sample on residence chamber port 6–end		

Table 4-9. (Continued)

Actual Flow sLpm	Corrected Flow aLpm	Notes	Average Flow sLpm
8.91	9.64	PM 2.5 sample on residence chamber port 5–start	9.04
9.16	9.91	PM 2.5 sample on residence chamber port 5–end	
16.29	17.62	PM 2.5 sample on residence chamber port 4–start	16.22
16.14	17.46	PM 2.5 sample on residence chamber port 4–end	
16.58	17.93	PM 2.5 sample on residence chamber port 2–start	16.51
16.43	17.78	PM 2.5 sample on residence chamber port 2–end	

PT = pressure transducer

TE = thermocouple

aLpm = actual liters per minute

sLpm = standard liters per minute

WC = water column

Table 4-10. Run Time Summary Information, Test Run #2, Campaign #2

Test Run #2 (July 10, 2002)			
Start Time	7:06:05 a.m.		
End Time	5:06:45 p.m.		
Run Time	600.67 min		
Barometric Pressure	28.67 inches Hg		
Nozzle Size	0.505 inches		
Parameter	Average		
Venturi Flow	30.00 aLpm		
	18.79 sLpm		
PT-101	-0.80 inches WC		
TE-104	176.03 °C		
Dilution Flow	911.02 aLpm		
	814.43 sLpm		
PT-102	-1.42 inches WC		
TE-108	39.00 °C		
Blower Flow	783.42 aLpm		
	673.14 sLpm		
PT-103	-16.32 inches WC		
TE-105	41.45 °C		
Dilution Ratio	44.37		
TE-101	171.71 °C		
TE-102	177.13 °C		
TE-103	176.68 °C		
Sample Flow Rates			
Actual Flow sLpm	Corrected Flow aLpm	Notes	Average Flow sLpm
16.51	18.00	PM 2.5 sample on dilution air–start	16.44
16.37	17.85	PM 2.5 sample on dilution air–end	
16.37	17.85	PM 2.5 sample on residence chamber port 10–start	16.37
16.37	17.85	PM 2.5 sample on residence chamber port 10–end	
16.37	17.85	PM 2.5 sample on residence chamber port 8–start	16.37
16.37	17.85	PM 2.5 sample on residence chamber port 8–end	

Table 4-10. (Continued)**Sample Flow Rates**

Actual Flow sLpm	Corrected Flow aLpm	Notes	Average Flow sLpm
16.37	17.85	PM 2.5 sample on residence chamber port 6–end	
9.12	9.95	PM 2.5 sample on residence chamber port 5–start	9.19
9.25	10.08	PM 2.5 sample on residence chamber port 5–end	
16.22	17.69	PM 2.5 sample on residence chamber port 4–start	16.15
16.08	17.53	PM 2.5 sample on residence chamber port 4–end	
16.37	17.85	PM 2.5 sample on residence chamber port 2–start	16.37
16.37	17.85	PM 2.5 sample on residence chamber port 2–end	

PT = pressure transducer

TE = thermocouple

aLpm = actual liters per minute

sLpm = standard liters per minute

WC = water column

Table 4-11. Run Time Summary Information, Test Run #3, Campaign #2

Test Run #3 (July 11, 2002)	
Parameter	Average
Start Time	7:17:03 a.m.
End Time	5:17:03 p.m.
Run Time	600.00 min
Barometric Pressure	28.64 inches Hg
Nozzle Size	0.505 inches
Venturi Flow	30.02 aLpm
	18.78 sLpm
PT-101	-0.98 inches WC
TE-104	176.12 °C
Dilution Flow	900.09 aLpm
	824.70 sLpm
PT-102	-1.45 inches WC
TE-108	31.22 °C
Blower Flow	774.50 aLpm
	681.74 sLpm
PT-103	-16.20 inches WC
TE-105	33.61 °C
Dilution Ratio	44.95
TE-101	169.72 °C
TE-102	177.18 °C
TE-103	176.86 °C

Table 4-11. (Continued)**Sample Flow Rates**

Actual Flow sLpm	Corrected Flow aLpm	Notes	Average Flow sLpm
16.41	17.80	PM 2.5 sample on dilution air–start	16.41
16.41	17.80	PM 2.5 sample on dilution air–end	
16.55	17.96	PM 2.5 sample on residence chamber port 10–start	16.48
16.41	17.80	PM 2.5 sample on residence chamber port 10–End	
16.55	17.96	PM 2.5 sample on residence chamber port 8–start	16.48
16.41	17.80	PM 2.5 sample on residence chamber port 8–end	
16.70	18.11	PM 2.5 sample on residence chamber port 6–start	16.56
16.41	17.80	PM 2.5 sample on residence chamber port 6–end	
9.27	10.06	PM 2.5 sample on residence chamber port 5–start	9.15
9.02	9.79	PM 2.5 sample on residence chamber port 5–end	
16.12	17.49	PM 2.5 sample on residence chamber port 4–start	16.12
16.12	17.49	PM 2.5 sample on residence chamber port 4–end	
16.55	17.96	PM 2.5 sample on residence chamber port 2–start	16.55
16.55	17.96	PM 2.5 sample on residence chamber port 2–end	

PT = pressure transducer

TE = thermocouple

aLpm = actual liters per minute

sLpm = standard liters per minute

WC = water column

Blower Flow 7/9/2002

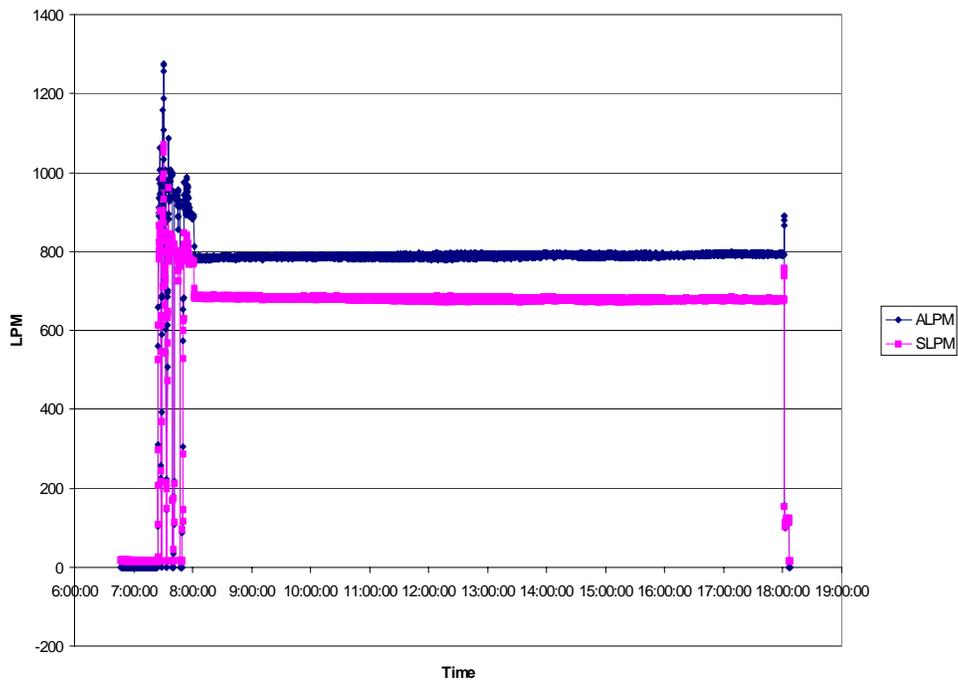


Figure 4-22. Blower flow, Test 1–Day 1, July 9, 2002, Campaign #2.

Dilution Flow 7/9/2002

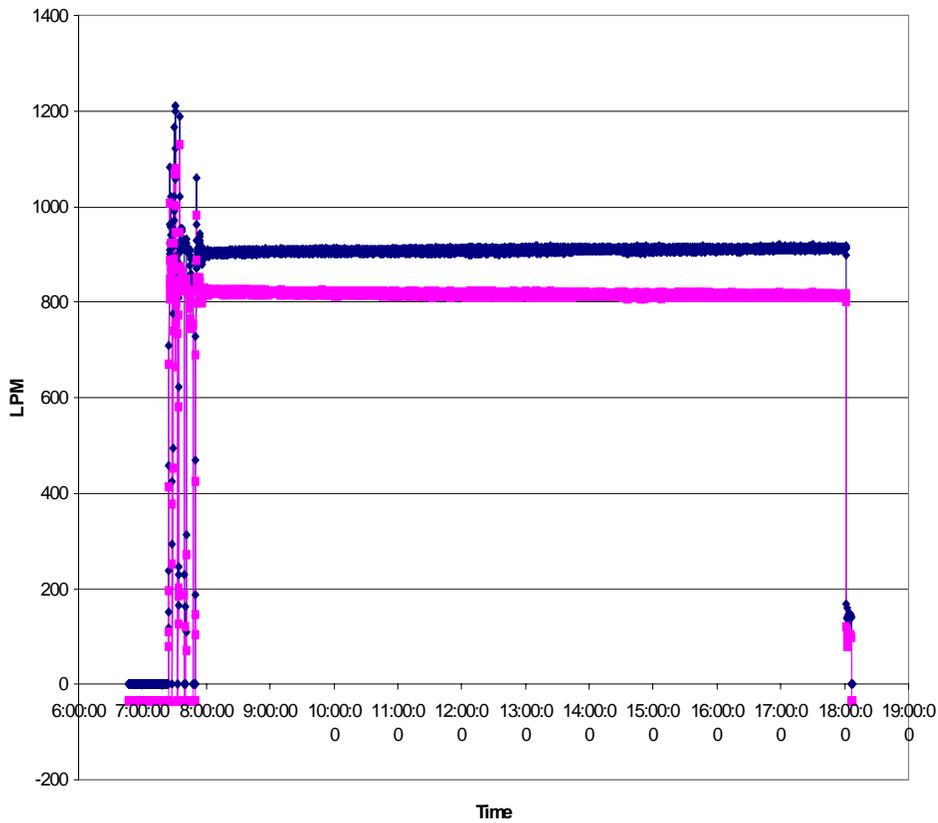


Figure 4-23. Dilution flow, Test 1–Day 1, July 9, 2002, Campaign #2.

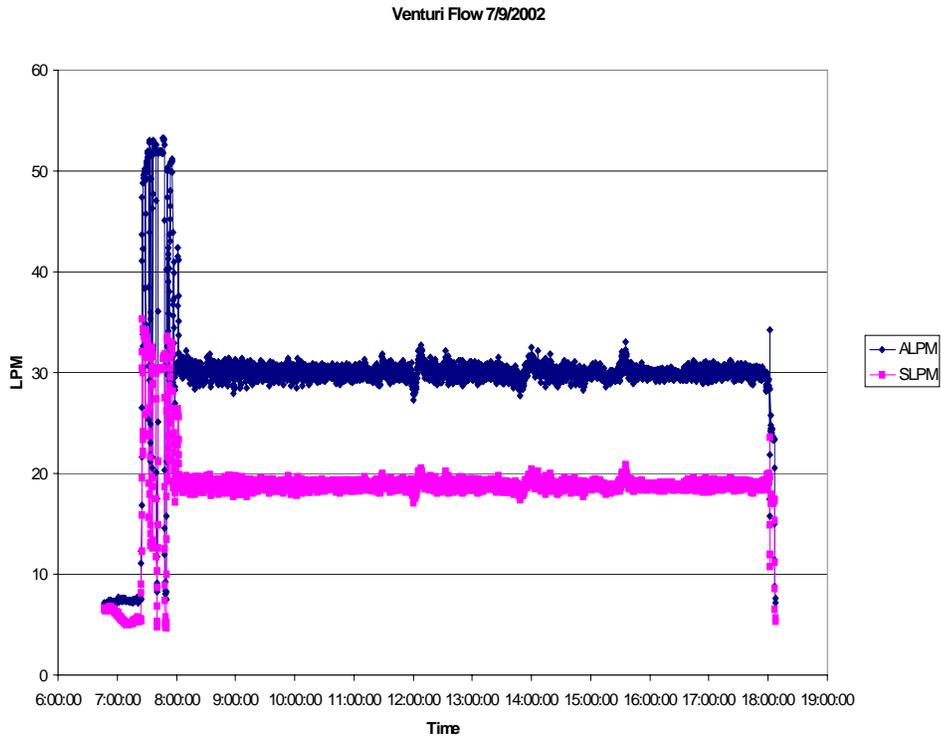


Figure 4-24. Venturi flow, Test 1–Day 1, July 9, 2002, Campaign #2.

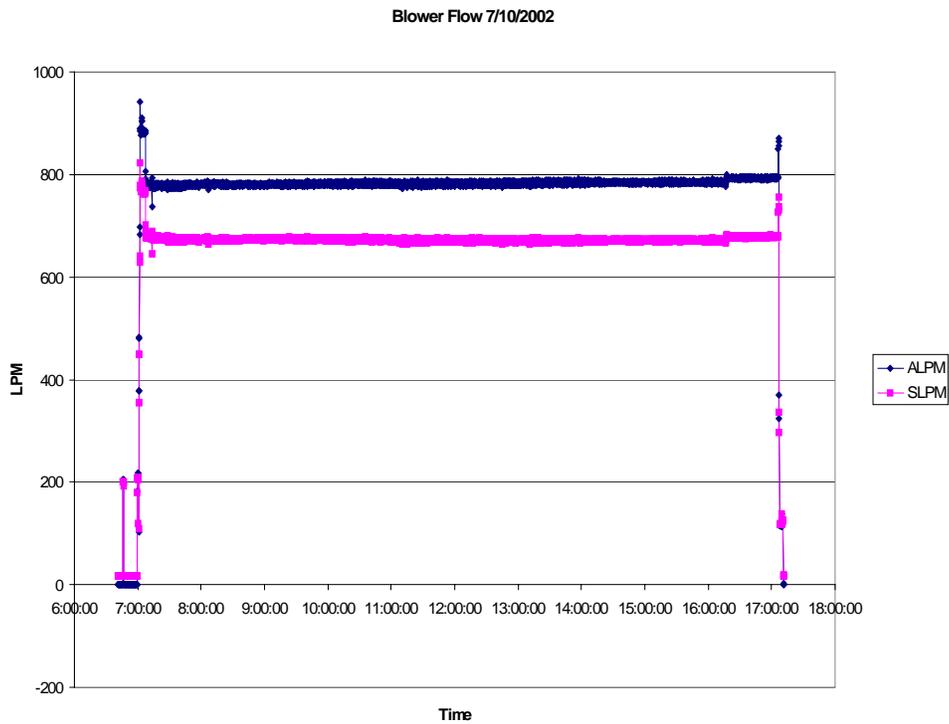


Figure 4-25. Blower flow, Test 2–Day 2, July 10, 2002, Campaign #2.

Dilution Flow 7/10/2002

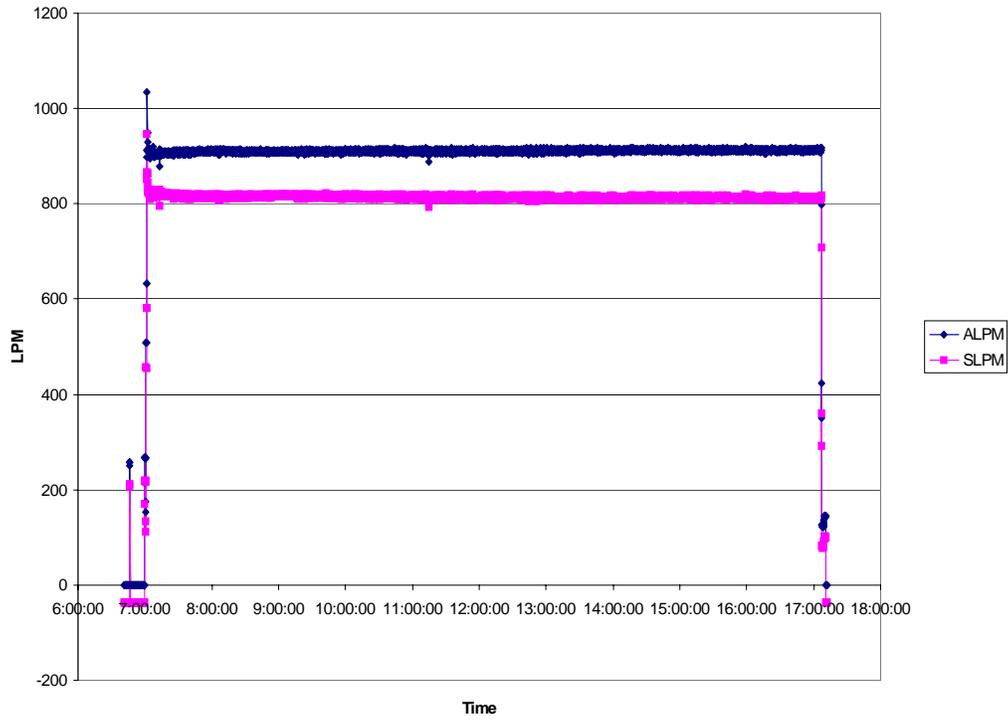


Figure 4-26. Dilution flow, Test 2–Day 2, July 10, 2002, Campaign #2.
Venturi Flow 7/10/2002

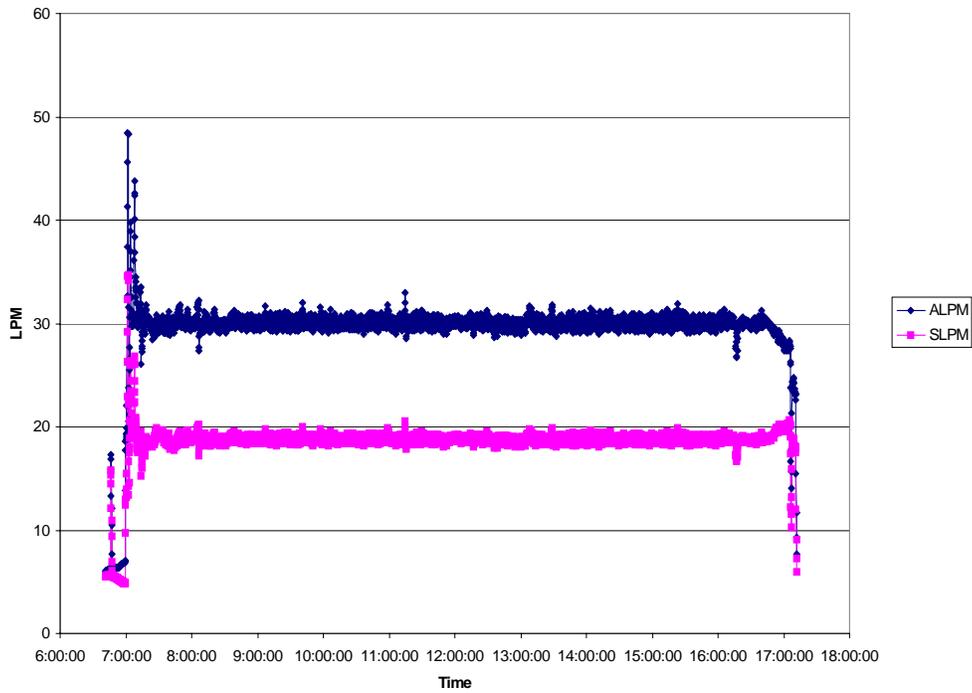


Figure 4-27. Venturi flow, Test 2–Day 2, July 10, 2002, Campaign #2.

Blower Flow 7/11/2002

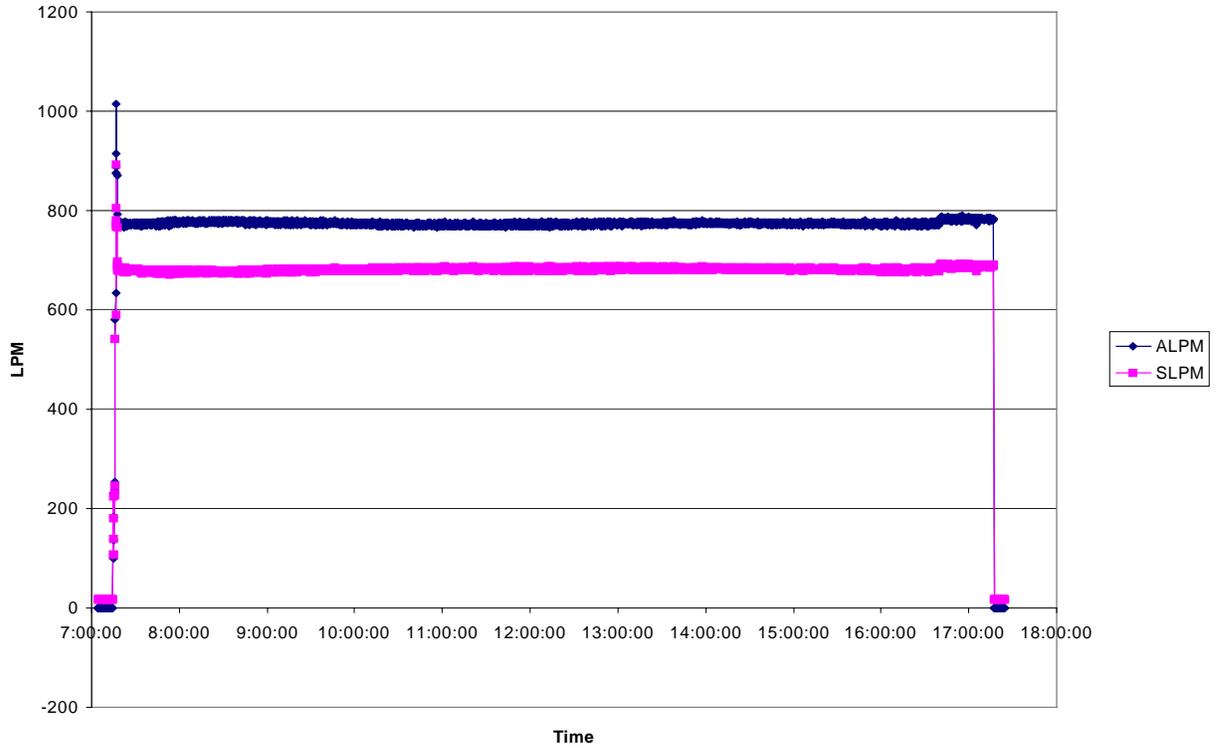


Figure 4-28. Blower flow, Test 3–Day 3, July 11, 2002, Campaign #2.

Dilution Flow 7/11/2002

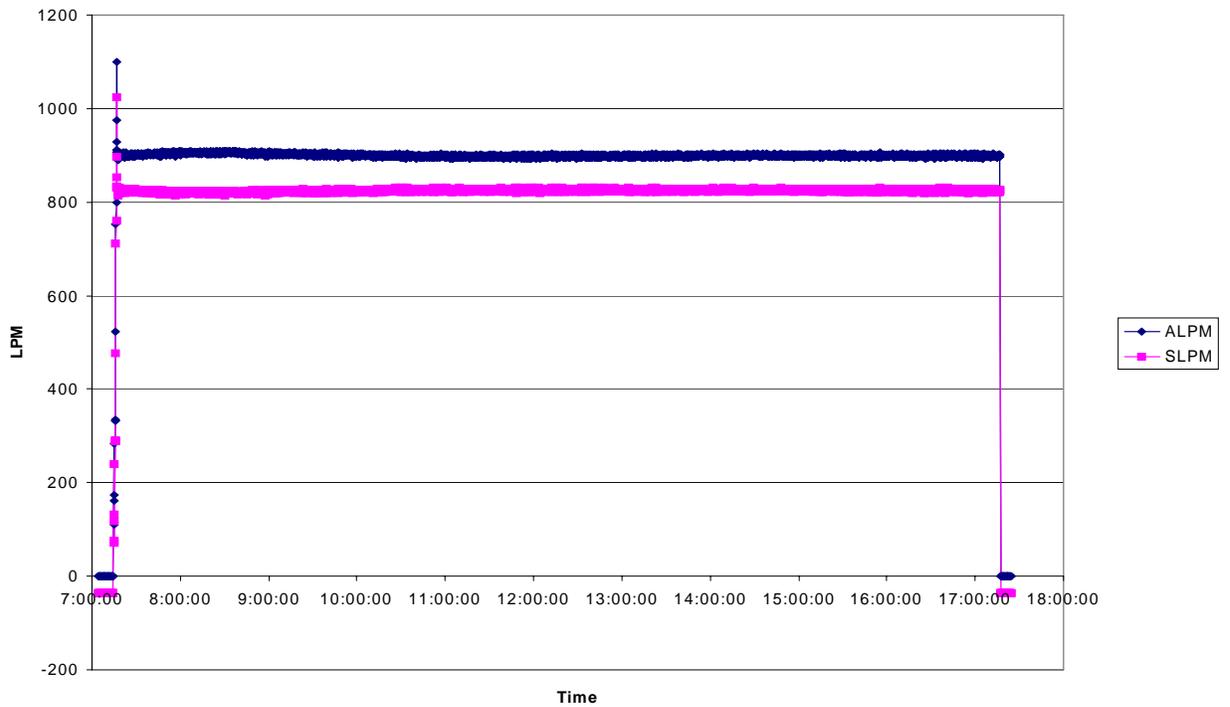


Figure 4-29. Dilution flow, Test 3–Day 3, July 11, 2002, Campaign #2.

Venturi Flow 7/11/2002

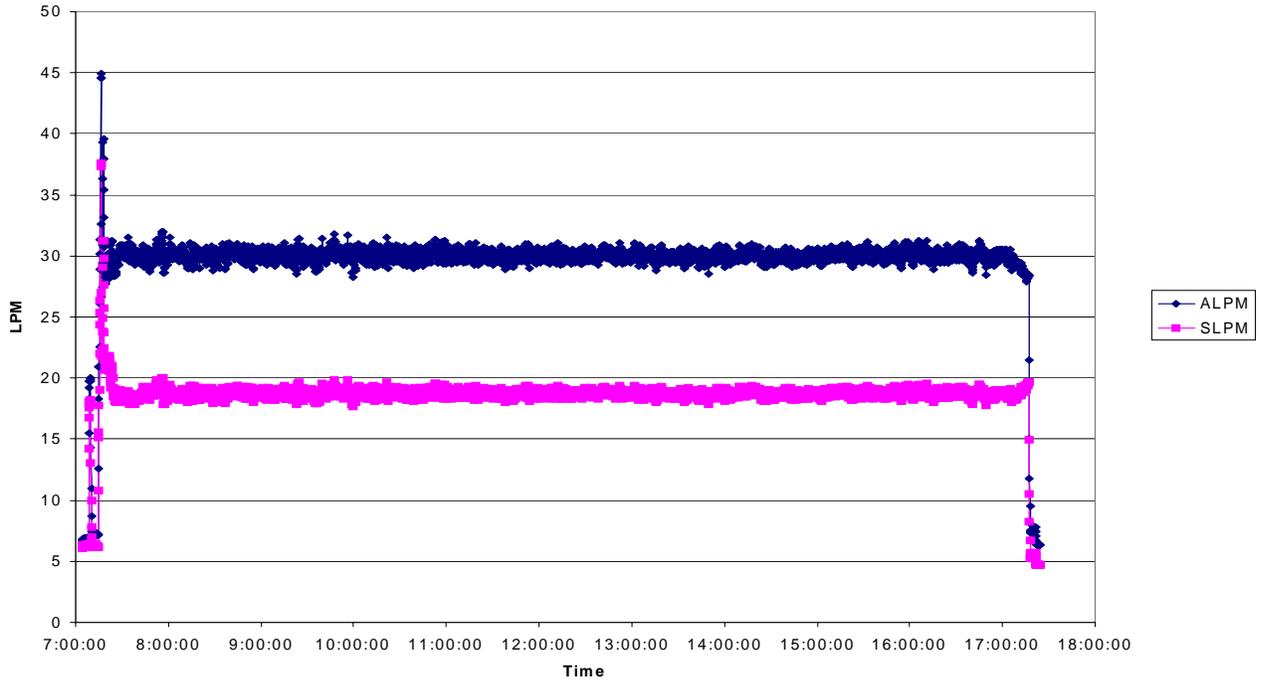


Figure 4-30. Venturi flow, Test 3–Day 3, July 11, 2002, Campaign #2.

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

- Polyurethane foam (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 pre-numbered custom filter container with a locking lid. The appropriate label was affixed to the filter container and chain of custody documentation initiated. The filter holder assembly was re-assembled without the filter, placed in a 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 plastic bag, labeled, and chain of custody documentation initiated.
- Carbonyl sampling tube assemblies 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 system and capped; chain of custody documentation was generated.

At a later time, extraction of the denuders was performed on-site. 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 pre-cleaned glass jar for paired denuders, the jar was labeled, 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 re-use.

Denuders, PUF modules, and filters were all bagged and stored on site in a chest freezer. Canisters and carbonyl tubes were transported to the ERG laboratory for analysis; the filters, PUF modules, and denuder extracts were transported to the EPA laboratory for analysis.

Chain of custody documentation for both test campaigns is supplied in Appendix E; field sample logs are presented in Appendix F.

Laboratory Experimental Methodology

The analytical methodology used in EPA and ERG laboratories to perform the analyses is summarized in Table 3-1.

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, respectively; the analyses described in the following sections were performed.

PM-2.5 Mass

Teflon membrane (Gelman Teflo) filters of 2- μm pore diameter were used to collect fine PM samples for mass determinations. Filters before and after sample collection were maintained at 20-23 °C and a relative humidity of 30-40% for a minimum of 24 hours prior to weighing on a micro-balance. Sample mass was determined by the difference in weight of a filter before and after sample collection.

Elemental Analysis

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

with the analysis. Only elements which 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 ethanol (350-500 μ L). 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 x 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 x 250 mm) column with an 8- μ m 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 (EC) and organic carbon (OC) content of PM samples collected on pre-fired quartz filters was determined by NIOSH Method 5040¹⁰ using a Sunset Laboratory instrument with a 30-m, 0.32-mm I.D. Rtx - 5MS (Crossbond 5% diphenyl - 95% dimethyl polysiloxane) capillary column, with a 1 μ m film thickness. In this method, a 1.0- x 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 an increase in the transmittance of a laser light beam through the filter occurs. 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 elemental (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 with a 2:1 mixture 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 isotropically labeled (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 blowdown 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 blowdown. A separate portion of the methylated extract was derivatized a second time using Sylon BFT reagent to convert compounds such as levoglucosan and cholesterol to their trimethylsilyl (TMS) derivatives. Both derivatizations 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 5MS 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 min. 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 over 100 authentic compound standards. Iso- and anteiso-alkanes were identified using secondary standards derived from paraffin candle wax. Additional compounds were identified as “probable” based on a comparison of the GC retention times and mass spectra with commercially available spectral libraries. Quantification of the individual compounds involved referencing each compound against one or more of the deuterated internal standards spiked into the sample to correct for losses of the analytes which 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 3-point or 5-point calibration curves from which the concentrations of the analytes were determined.

Carbonyl Compounds

Carbonyl compounds were sampled and analyzed in campaign #1 only. 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 compounds listed in Table 4-12 using a modified version of EPA Compendium Method TO-11A¹¹, “Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)”. The analytical instrument was a Varian 5000 High Performance Liquid Chromatograph (HPLC) with a multiwavelength detector operated at 360 nanometers (nm). The HPLC was configured with a 25-cm, 4.6-mm I.D., C18 silica

Table 4-12. Carbonyl Compounds Analyzed by High Performance Liquid Chromatography

Compound	CAS No.
Formaldehyde	50-00-0
Acetaldehyde	75-07-0
Acetone	67-64-1
Propionaldehyde	123-38-6
Crotonaldehyde	4170-30-3
Butyraldehyde	123-72-8
Benzaldehyde	100-52-7
Isovalderaldehyde	590-86-3
Valeraldehyde	110-62-3
<i>o</i> -Tolualdehyde	529-20-4
<i>m</i> -Tolualdehyde	620-23-5
<i>p</i> -Tolualdehyde	104-87-0
Hexaldehyde	66-25-1
2,5-Dimethylbenzaldehyde	5779-94-2
Diacetyl	432-03-8
Methacrolein	78-85-3
2-Butanone	78-93-3
Glyoxal	107-22-2
Acetophenone	98-86-2
Methylglyoxal	78-98-8
Octanal	124-13-0
Nonanal	124-19-6

analytical column with a 5-micron particle size. Twenty-five (25) μ L aliquots were injected into the HPLC with an automatic sample injector.

The chromatography data acquisition system was used to retrieve data from the HPLC; 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.

Daily calibration checks were performed to ensure that the analytical procedures were in control. Daily quality control checks were performed after every ten samples on the days that

samples were analyzed, with compound responses within $\pm 15\%$ relative to the responses from 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 injection of the quality control standard was performed. If the second quality control check 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 analyzed. All samples analyzed with the unacceptable quality control checks would be re-analyzed.

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

Canister sampling and analysis were performed for campaign #1 only. The combined analysis^{12,13} for air toxics and speciated nonmethane organic compounds was performed on a gas chromatograph(GC)/flame ionization detector(FID)/mass selective detector (MSD), using a Hewlett-Packard 5971 MSD and a Hewlett-Packard 5890 Series II GC with a 60-m by 0.32-mm i.d. and a 1 μm film thickness J&W DB-1 capillary column followed by a 2:1 splitter 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 $-50\text{ }^{\circ}\text{C}$ with liquid nitrogen at the beginning of the sample injection. This temperature was held for five minutes and then increased at the rate of $15\text{ }^{\circ}\text{C}$ per minute up to $0\text{ }^{\circ}\text{C}$. The oven temperature was then ramped at $6\text{ }^{\circ}\text{C}/\text{minute}$ to $150\text{ }^{\circ}\text{C}$, then ramped at $20\text{ }^{\circ}\text{C}/\text{minute}$ to $225\text{ }^{\circ}\text{C}$ and held for 8 min. 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)” for the compounds shown in Table 4-13. The analysis of SNMOC was performed according to the procedures of “Technical Assistance Document for Sampling and Analysis of Ozone Precursors¹³” for the compounds shown in Table 4-14. Detection limits for air toxics and for the speciated nonmethane organic compounds are shown in Appendix C. Method detection limits were determined according to the Federal Register procedure.¹⁴

Particle Size Distribution Data

The SMPS was operated and collected data during both test days. Data were reduced using the TSI software package.

Table 4-13. Air Toxics Compounds Determined by Analytical Method TO-15

Compound	CAS No.
Acetylene	74-86-2
Propylene	115-07-1
Dichlorodifluoromethane	75-71-8
Chloromethane	74-87-3
Dichlorotetrafluoroethane	1320-37-2
Vinyl chloride	75-01-4
1,3-Butadiene	106-99-0
Bromomethane	74-83-9
Chloroethane	75-00-3
Acetonitrile	75-05-8
Acetone	67-64-1
Trichlorofluoromethane	75-69-4
Acrylonitrile	107-13-1
1,1-Dichloroethene	75-35-4
Methylene chloride	75-09-2
Trichlorotrifluoroethane	26523-64-8
<i>trans</i> -1,2-Dichloroethylene	56-60-5
1,1-Dichloroethane	75-34-3
Methyl <i>tert</i> -butyl ether	1634-04-1
Methyl ethyl ketone	78-93-3
Chloroprene	126-99-8
<i>cis</i> -1,3-Dichloroethylene	156-59-2
Bromochloromethane	74-97-5
Chloroform	67-66-3
Ethyl <i>tert</i> -butyl ether	637-92-3
1,2-Dichloroethane	107-06-2
1,1,1-Trichloroethane	71-55-6
Benzene	71-43-2
Carbon tetrachloride	56-23-5
<i>tert</i> -Amyl methyl ether	994-05-8
1,2-Dichloropropane	78-87-5
Ethyl acrylate	140-88-5
Bromodichloromethane	75-27-4
Trichloroethylene	79-01-6
Methyl methacrylate	80-62-6
<i>cis</i> -1,2-Dichloropropene	10061-01-5

Table 4-13. (Continued)

Compound	CAS No.
Methyl isobutyl ketone	108-10-1
<i>trans</i> -1,2-Dichloropropene	10061-02-6
1,1,2-Trichloroethane	79-00-5
Toluene	108-88-3
Dibromochloromethane	124-48-1
1,2-Dibromoethane	106-93-4
<i>n</i> -Octane	111-65-9
Tetrachloroethylene	127-18-4
Chlorobenzene	108-90-7
Ethylbenzene	100-41-4
<i>m</i> -, <i>p</i> -Xylene	108-38-3/106-42-3
Bromoform	75-25-2
Styrene	100-42-5
1,1,2,2-Tetrachloroethane	79-34-5
<i>o</i> -Xylene	95-47-6
1,3,5-Trimethylbenzene	108-67-8
1,2,4-Trimethylbenzene	95-63-6
<i>m</i> -Dichlorobenzene	541-73-1
Chloromethylbenzene	100-44-7
<i>p</i> -Dichlorobenzene	106-46-7
<i>o</i> -Dichlorobenzene	95-50-1
1,2,4-Trichlorobenzene	120-82-1
Hexachloro-1,3-butadiene	87-68-3

Table 4-14. Speciated Nonmethane Organic Compounds Determined According to the Procedures of EPA Research Operating Procedure “Research Protocol Method for Analysis of C₂-C₁₂ Hydrocarbons in Ambient Air by Gas Chromatography with Cryogenic Concentration”

Compound	CAS No.
Ethylene	74-85-1
Acetylene	74-86-2
Ethane	74-84-0
Propylene	115-07-1
Propane	74-98-6
Propyne	74-99-7
Isobutane	75-28-5
Isobutene/1-butene	115-11-7/106-98-0
1,3-Butadiene	106-99-0
<i>n</i> -Butane	106-97-8
<i>trans</i> -2-Butene	624-64-6
<i>cis</i> -2-Butene	590-18-1
3-Methyl-1-butene	563-45-1
Isopentane	78-78-4
1-Pentene	109-67-1
2-Methyl-1-butene	563-46-2
<i>n</i> -Pentane	109-66-0
Isoprene	78-79-4
<i>trans</i> -2-Pentene	646-04-8
<i>cis</i> -2-Pentene	627-20-3
2-Methyl-2-butene	513-35-9
2,2-Dimethylbutane	75-83-2
Cyclopentene	142-29-0
4-Methyl-1-pentene	691-37-2
Cyclopentane	287-92-3
2,3-Dimethylbutane	79-29-8
2-Methylpentane	107-83-5
3-Methylpentane	96-14-0
2-Methyl-1-pentene	763-29-1
1-Hexene	592-41-6
2-Ethyl-1-butene	760-21-4
<i>n</i> -Hexane	110-54-3
<i>trans</i> -2-Hexene	4050-45-7
<i>cis</i> -2-Hexene	7688-21-3
Methylcyclopentane	96-37-7

Table 4-14. (Continued)

Compound	CAS No.
2,4-Dimethylpentane	108-08-7
Benzene	71-43-2
Cyclohexane	110-82-7
2-Methylhexane	591-76-4
2,3-Dimethylpentane	565-59-3
3-Methylhexane	589-34-4
1-Heptene	592-76-7
2,2,4-Trimethylpentane	540-84-1
<i>n</i> -Heptane	142-82-5
Methylcyclohexane	108-87-2
2,2,3-Trimethylpentane	564-02-3
2,3,4-Trimethylpentane	565-75-3
Toluene	108-88-3
2-Methylheptane	592-27-8
3-Methylheptane	589-81-1
1-Octene	111-66-0
<i>n</i> -Octane	111-65-9
Ethylbenzene	100-41-4
<i>m</i> -, <i>p</i> -Xylene	108-38-3/106-42-3
Styrene	100-42-5
<i>o</i> -Xylene	95-47-6
1-Nonene	124-11-8
<i>n</i> -Nonane	111-84-2
Isopropylbenzene	98-82-8
α -Pinene	80-56-8
<i>n</i> -Propylbenzene	103-65-1
<i>m</i> -Ethyltoluene	620-14-4
<i>p</i> -Ethyltoluene	622-96-8
1,3,5-Trimethylbenzene	108-67-8
<i>o</i> -Ethyltoluene	611-14-3
β -Pinene	127-91-3
1,2,4-Trimethylbenzene	95-63-6
1-Decene	872-05-9
<i>n</i> -Decane	124-18-5
1,2,3-Trimethylbenzene	526-73-8
<i>m</i> -Diethylbenzene	141-93-5

Table 4-14. (Continued)

Compound	CAS No.
<i>p</i> -Diethylbenzene	105-05-5
1-Undecene	821-95-4
<i>n</i> -Undecane	1120-21-4
1-Dodecene	112-41-4
<i>n</i> -Dodecane	112-40-3
1-Tridecene	2437-56-1
<i>n</i> -Tridecane	629-50-5

Section 5 Results and Discussion

Analyses for each campaign were performed in either the EPA or ERG laboratories as shown in Table 3-1, using the analytical procedures described in Section 4. Results of these analyses are discussed in this section.

PM Mass, Elemental/Organic Carbon, Major Inorganic Ions, and Major Elements

Emissions of PM mass, elemental/organic carbon (EC/OC), major elements, and major inorganic ions as components of the fine particulate matter are reported in Table 5-1 both as weight percent and as mass fraction of measured PM-2.5 mass. Results reported in Table 5-1 show the following:

- The PM-2.5 mass emission factor was fairly consistent throughout both test campaigns with the exception of one day during campaign #2 (7/11/02) for which the emission factor was nearly 5 times higher than the average of the other 5 test days. Excluding the single day of markedly higher emissions, the average PM-2.5 mass emission factor was 36.4 mg per kg of fuel (0.81 $\mu\text{g}/\text{kJ}$) with a range of 26.9 to 42.7 mg/kg (0.60 - 0.96 $\mu\text{g}/\text{kJ}$). The single day of substantially higher PM-2.5 emissions gave an emission factor of 178.0 mg per kg of fuel (3.99 $\mu\text{g}/\text{kJ}$). No unusual event on that day was identified to explain the higher PM-2.5 emissions for that test. However, during campaign #2 (which occurred in July) the boiler was operated at very low load where combustion conditions are difficult to maintain. Under such conditions, erratic behavior in boiler operation and emissions may occur.
- Although the PM-2.5 mass emission factor was fairly consistent for both test campaigns, the composition of the PM-2.5 was very different for the two campaigns. Sulfate comprised 45.5 to 58.0% by mass of the PM-2.5 emitted during campaign #1, but accounted for only 3.5 to 10.8% of the PM-2.5 mass during campaign #2.

Table 5-1. Summary of Oil-Fired Institutional Boiler Results

Parameter	Campaign #1 (1/01)			Campaign #2 (7/02)		
	Test #1	Test #2	Test #3	Test #1	Test #2	Test #3
Fuel Feed Rate (kg/min)	10.94	11.55	13.21	7.40	7.43	7.43
Fuel Carbon ^a (wt %)	85.93	85.93	85.93	86.53	86.53	86.53
Fuel Sulfur ^a (wt %)	0.09	0.09	0.09	0.05	0.05	0.05
Flue Gas Composition						
Flue Gas O ₂ (volume %, wet)	4.8	5.3	5.5	8.1	9.0	8.9
Flue Gas CO ₂ (volume %, wet)	16.2	15.7	15.5	11.0	10.7	10.4
Flue Gas CO (volume %, wet)	0.03	0.03	0.03	0.0	0.03	0.03
Flue Gas O ₂ (volume %, dry)	5.4	6.0	6.2	10.2	10.1	9.1
Flue Gas CO ₂ (volume %, dry)	18.2	17.6	17.4	12.1	11.8	11.2
Flue Gas CO (volume %, dry)	0.034	0.034	0.034	0.0	0.034	0.034
Flue Gas N ₂ (volume %, dry)	76.4	76.4	76.4	77.6	78.1	79.7
Excess Air (%)	36.1	41.4	43.6	97.6	94.4	74.8
PM-2.5 Emission Factor (mg/kg fuel)	26.86 ± 3.44	32.09 ± 1.89	39.77 ± 0.88	40.36 ± 1.27	42.67 ± 2.51	178.02 ± 2.51

Table 5-1. (Continued)

Mean PM-2.5 Emission Factor (mg/kg fuel) 32.91 ± 5.93

Mean PM-2.5 Emission Factor (mg/kg fuel) 87.02 ± 67.3

PM-2.5 Composition (wt %)

Elemental Carbon	1.8	10.5	34.0	5.8 ± 1.4	3.1 ± 0.7	1.6 ± 0.2
Mean Elemental Carbon	15.4 ± 16.6 wt %			Mean Elemental Carbon 4.0 ± 2.2 wt %		
Organic Carbon	0	0.5	0	43.3 ± 5.9	45.7 ± 12.0	63.1 ± 4.3
Mean Organic Carbon	0.17 ± 0.29 wt %			Mean Organic Carbon 50.7 ± 10.1 wt %		
Sulfate	58.0 ± 6.1	56.9 ± 5.3	45.5 ± 4.2	6.8 ± 0.2	10.7 ± 0.1	3.5 ± 0.0
Mean Sulfate	53.5 ± 7.4 wt %			Mean Sulfate wt %		
Ammonium	NQ	NQ	NQ	2.0 ± 0.2	2.6 ± 0.1	0.46 ± 0.0
Mean Ammonium	NQ			Mean Ammonium 1.7 ± 1.0 wt %		
Sulfur	5.2 ± 2.2	3.4 ± 0.2	8.3 ± 6.0	2.7 ± 0.2	3.7 ± 0.1	1.3 ± 0.1
Mean Sulfur	5.6 ± 3.6			Mean Sulfur 2.6 ± 1.1 wt %		
Silicon	NQ	NQ	NQ	0.89 ± 0.10	0.75 ± 0.10	0.24 ± 0.00
Mean Silicon	NQ			Mean Silicon 0.63 ± 0.31 wt %		

PM-2.5 Composition (mass fraction)

Elemental Carbon	0.018	0.105	0.34	0.066	0.038	0.017
Mean Elemental Carbon	0.15 ± 0.17 mass fraction			Mean Elemental Carbon 0.040 ± 0.025 mass fraction		
Organic Carbon	0	0.005	0	0.433	0.452	0.631
Mean Organic Carbon	0.0017 ± 0.0029 mass fraction			Mean Organic Carbon 0.505 ± 0.109		

Table 5-1. (Continued)**PM-2.5 Composition (mass fraction)**

Sulfate	0.58 ± 0.061	0.569 ± 0.053	0.455 ± 0.042	0.068 ± 0.002	0.107 ± 0.001	0.035 ± 0.000
Mean Sulfate	0.535 ± 0.069 mass fraction			Mean Sulfate 0.070 ± 0.036 mass fraction		
Ammonium	NQ	NQ	NQ	0.02 ± 0.002	0.026 ± 0.001	0.046 ± 0.000
Mean Ammonium	NQ			Mean Ammonium 0.017 ± 0.011 mass fraction		
Sulfur	0.052 ± 0.022	0.034 ± 0.002	0.083 ± 0.063	0.027 ± 0.002	0.037 ± 0.001	0.013 ± 0.001
Mean Sulfur	0.056 ± 0.025 mass fraction			Mean Sulfur 0.026 ± 0.012 mass fraction		
Silicon	NQ	NQ	NQ	0.0089 ± 0.0010	0.0075 ± 0.0000	0.0024 ± 0.0000
Mean Silicon	NQ			Mean Silicon 0.0063 ± 0.0034 mass fraction		

^a Fuel was sampled one time per campaign and the results applied to all the test runs in each of the two campaigns.

NQ = Below quantitation limit.

- Conversely, there was much more carbon in the PM-2.5 emitted during campaign #2, most of which was organic carbon (43.3 to 63.1% of the PM-2.5 mass). The organic carbon (OC) content of the fine PM was highest for Test Day #3 of campaign #2 (7/11/02), for which the PM-2.5 emission factor was also the highest of all tests.
- Two factors may have contributed to the marked difference in PM composition. The sulfur content of the fuel oil was 1.8 times higher during the campaign #1 test series than during the campaign #2 tests (0.09 vs 0.05 wt %, respectively). This factor could have contributed to a higher sulfate content in the campaign #1 tests. In the campaign #2 tests, the fuel feed rate averaged 37.6% lower than in the campaign #1 tests and the excess oxygen levels were much higher (campaign #2 = 15.7 to 20.5%; campaign #1 = 7.6 to 9.2% excess oxygen). During the campaign #1 tests, the boiler was fired at 37 - 42% of its rated capacity, while during the campaign #2 tests, the boiler was fired at only 25% capacity. A lower combustion efficiency associated with the low combustion load during the summertime is likely responsible for the PM emissions being enriched in organic carbon.

Supporting data for Table 5-1 are found in the following appendices:

- Appendix J, Data Tables for Individual PM-2.5 Mass Measurements, Both Campaigns;
- Appendix K, Data Tables for PM-2.5 Mass Emission Factors, Both Campaigns;
- Appendix L, Data Tables for Individual PM-2.5 EC/OC Samples, Both Campaigns;
- Appendix M, Data Tables for Individual PM-2.5 Elemental Samples, Both Campaigns; and
- Appendix N, Data Tables for Individual PM-2.5 Inorganic Ion Samples, Both Campaigns.

General Equation for Uncertainty

If a result, R , is calculated from a set of measurements, x_1, x_2, \dots, x_n , it can be expressed as:

$$R = R(x_1, x_2, \dots, x_n) \quad (5-1)$$

The uncertainty in the calculated result, w_R , is given as:

$$w_R = \left[\left(\frac{\partial R}{\partial x_1} w_1 \right)^2 + \left(\frac{\partial R}{\partial x_2} w_2 \right)^2 + \dots + \left(\frac{\partial R}{\partial x_n} w_n \right)^2 \right]^{\frac{1}{2}} \quad (5-2)$$

where w_1 , w_2 , and w_3 are the uncertainties in each of the respective measurements.

Uncertainty in PM Mass Emission Factor Estimation

The three-day average emission factor, E_a , is calculated by:

$$E_a = \frac{E_1 + E_2 + E_3}{3} \quad (5-3)$$

where E_1 , E_2 , and E_3 are the emission factors for Day-1, Day-2, and Day-3, respectively. Thus, the uncertainty in E_R can be obtained as:

$$\begin{aligned} w_R &= \left[\left(\frac{\partial E_a}{\partial E_1} w_1 \right)^2 + \left(\frac{\partial E_a}{\partial E_2} w_2 \right)^2 + \left(\frac{\partial E_a}{\partial E_3} w_3 \right)^2 \right]^{\frac{1}{2}} \\ &= \left[\left(\frac{1}{3} w_1 \right)^2 + \left(\frac{1}{3} w_2 \right)^2 + \left(\frac{1}{3} w_3 \right)^2 \right]^{\frac{1}{2}} \end{aligned} \quad (5-4)$$

where w_1 , w_2 , w_3 are the uncertainties in PM emission factors for Day-1, Day-2, and Day-3, respectively. In this report the values for uncertainties w_1 , w_2 , and w_3 are taken to be the standard deviations (S_1 , S_2 , and S_3) for the daily emission factor averages.

Uncertainty in PM-2.5 Organic Carbon Concentration

The OC concentration in PM-2.5 is given by:

$$OC = \frac{C_f - C_b - C_d}{C_p} \times 100\% \quad (5-5)$$

where C_f , C_b , and C_d represent the daily average OC concentrations on the primary (front) quartz filters (QF), backup QFs, and dilution chamber QF, and C_p represents the daily average PM concentrations on the Teflon filters (TF). These concentrations are obtained by dividing the sample mass by the volume of flow in the sampling array. The uncertainty in the day-average OC concentration in the PM is then derived as:

$$w_R = \left[\left(\frac{\partial C}{\partial C_f} w_f \right)^2 + \left[\left(\frac{\partial C}{\partial C_b} w_b \right)^2 + \left(\frac{\partial C}{\partial C_p} w_p \right)^2 \right]^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad (5-6)$$

$$= \left[\left(\frac{w_f}{C_p} \right)^2 + \left(\frac{w_b}{C_p} \right)^2 + \left(\frac{C_f - C_b - C_d}{C_p^2} w_p \right)^2 \right]^{\frac{1}{2}}$$

where w_f , w_b , and w_p represent the uncertainties in day-average OC concentrations in the front QF, backup QF, and day-average PM concentration. These uncertainties are taken to be the standard deviations (S_f , S_b , and S_p) of the respective daily averages. There was no standard deviation associated with the OC concentration for the dilution air sample because of only one QF and one TF was used to sample the dilution air each day.

The uncertainty for the three-day average of OC concentration is calculated using the same equation as for three-day average PM emission factor.

Uncertainty in Gas-Phase Semivolatile Organic Species Emission Factors

Uncertainties of three-day averages of emission factors for gas-phase semivolatile organic species analyzed on the PUF samples were calculated using an equation in the same form as that for the three-day average PM emission factor (Equation 4).

Uncertainty in Particle-Phase Semivolatile Organic Species Emission Factors

Since the QF samples were composited for each day of the first two days, the average and standard deviation of the first two days was first calculated. The three-day average is then given by:

$$E_a = \frac{E_{1+2} + E_3}{2} \quad (5-7)$$

where E_{1+2} is the average emission factor for the first two days. The uncertainty for the three-day average is calculated as:

$$\begin{aligned} w_R &= \left[\left(\frac{\partial E_a}{\partial E_{1+2}} w_{1+2} \right)^2 + \left(\frac{\partial E_a}{\partial E_3} w_3 \right)^2 \right]^{\frac{1}{2}} \\ &= \left[\left(\frac{1}{3} w_{1+2} \right)^2 + \left(\frac{1}{3} w_2 \right)^2 \right]^{\frac{1}{2}} \end{aligned} \quad (5-8)$$

where w_{1+2} and w_3 are the standard deviations for the first two days and for the third day, respectively.

Uncertainty in PM-2.5 Elemental and Ion Concentrations

Element and inorganic ion concentrations in the PM-2.5 for each test day are reported as averages of replicate samples taken on each test day. Uncertainties reported for these averages represent the standard deviation of the replicate sample analyses.

Speciated Gas- and Particle-Phase Organic Compounds

Semivolatile organic compounds were not determined during campaign #1 because the gas-phase semivolatiles exceeded the collection capacity of the XAD-coated denuders and the PUF plugs. Sampling for ten hours in an attempt to maximize collection of PM for organic compound analysis resulted in overloading the denuders and PUF plugs so that an undetermined quantity of gas-phase material was allowed to escape collection and analysis.

For campaign #2, 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 dichloromethane:hexane:acetone (for PUFs and denuders) followed by GC/MS analysis of the extracts. Table 5-2 lists those organic compounds which 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. Compositing the quartz filters was necessary in order to achieve even the results reported; the compositing scheme for the quartz filters is presented in the Sample log in Appendix F. All PUF plug pairs were analyzed individually; none were composited. Emission factors for the gas-phase semivolatiles from the oil-fired industrial boiler are shown in Table 5-2, together with the calculated uncertainty. Particle-phase semivolatiles expressed as mass fractions are shown in Table 5-3, and as emission factors, in Table 5-4.

Most of the speciated and quantified organic carbon associated with the fine PM was made up of the C₁₆ through C₃₁ *n*-alkanes (63.8 wt.% of the speciated PM organics). *n*-Tetracosane (C₂₄) was the single most prominent *n*-alkane with the other C₁₆-C₃₁ species in a near-Gaussian distribution by carbon number around C₂₄. Benzene di- and tri-carboxylic acids

comprised the second largest category of organic constituents found in the fine PM (21.4 wt % of the quantified species). Polynucleararomatic hydrocarbons (PAHs) and *n*-alkanoic acids made up most of the remaining 14.8% of the quantified and speciated particle phase organic compounds. The benzene di- and tri-carboxylic acids and chrysene were the only semivolatile organic species confined to the particle-phase. All of the other semivolatile species were found in both the gas and particle phases with the predominant amounts in the gas phase. The only two elements in the PM which were found at levels above method quantitation limits were silicon and sulfur.

Supporting data for the semivolatile organic compounds are found in the following appendices:

- Appendix O, Data Tables for Individual or Composited Particle-Phase (Quartz Filter) Semivolatile Organic Compound Samples; and
- Appendix P, Data Tables for Individual Gas-Phase (PUF) Semivolatile Organic Compound Samples.

Table 5-2. Gas Phase Semivolatiles: Emission Factors from an Institutional Oil-Fired Boiler (Campaign #2, July 2002)

Compound	Emission Factor (mg/kg fuel)	Uncertainty (mg/kg fuel)
dimethyl phthalate	0.000	0.000
diethyl phthalate	0.076	0.031
naphthalene	0.667	0.167
2-methylnaphthalene	3.688	0.846
1-methylnaphthalene	2.526	0.530
2,7-dimethylnaphthalene	3.499	0.514
1,3-dimethylnaphthalene	2.561	0.580
2,6-dimethylnaphthalene	3.715	0.576
additional dimethylnaphthalenes	2.559	0.466
acenaphthylene	0.047	0.013
acenaphthene	0.066	0.086
fluorene	0.516	0.114
1-methylfluorene	0.857	0.281
additional methylfluorenes (peak 1)	0.960	0.326
additional methylfluorenes (peak 2)	0.274	0.096
phenanthrene	1.258	0.263
additional dimethylphenanthrenes	0.127	0.061
anthracene	0.127	0.253
methylanthracene - peak 1	1.188	0.473
methylanthracene - peak 2	1.702	0.431
methylanthracene - peak 3	0.843	0.222
methylanthracene - peak 4	0.672	0.156
octylcyclohexane	0.043	0.036
norpristane	3.219	1.593
decylcyclohexane	0.338	0.050
pristane	2.986	1.204
phytane	2.163	1.314
tridecylcyclohexane	0.040	0.070

Table 5-2. (Continued)

Compound	Emission Factor (mg/kg fuel)	Uncertainty (mg/kg fuel)
dibutyl phthalate	0.140	0.070
butyl benzyl phthalate	0.078	0.078
<i>bis</i> (2-ethylhexyl) phthalate	0.063	0.034
dioctyl phthalate	0.074	ND
fluoranthene	0.065	0.041
pyrene	0.058	0.041
chrysene	0.002	0.002
benzo[a]anthracene	ND	ND
benzo[k]fluoranthene	ND	ND
benzo[b]fluoranthene		
benzo[a]pyrene		
nonadecylcyclohexane	0.002	0.003
squalane		
indeno[1,2,3-cd]pyrene		
dibenzo[a,h]anthracene		
benzo[ghi]perylene		
coronene		
cholestane - peak 1		
cholestane - peak 2		
cholestane - peak 3		
cholestane - peak 4		
ABB-2OR-24S-methylcholestane		
ABB-2OR-ethylcholestane		
17A(H)-22,29,30- <i>tris</i> (norhopane)		
17(B)-21A(H)-norhopane		
17B(H)-21B(H)-hopane		
17B(H)-21A(H)-hopane		
17A(H)-21B(H)-hopane		

Table 5-2. (Continued)

Compound	Emission Factor (mg/kg fuel)	Uncertainty (mg/kg fuel)
<i>n</i> -decane (<i>n</i> -C10)		
<i>n</i> -undecane (<i>n</i> -C11)	0.014	0.011
<i>n</i> -dodecane (<i>n</i> -C12)	0.855	0.130
<i>n</i> -tridecane (<i>n</i> -C13)	0.686	0.054
9H-fluoren-9-one	0.127	0.028
<i>n</i> -tetradecane (<i>n</i> -C14)	2.405	0.539
<i>n</i> -pentadecane (<i>n</i> -C15)	6.089	1.963
<i>n</i> -hexadecane (<i>n</i> -C16)	8.948	2.201
<i>n</i> -heptadecane (<i>n</i> -C17)	7.787	2.854
1-octadecene	0.002	0.003
<i>n</i> -octadecane (<i>n</i> -C18)	4.242	2.384
2-methylnonadecane	0.000	0.000
3-methylnonadecane	0.000	0.000
<i>n</i> -nonadecane (<i>n</i> -C19)	3.331	2.032
<i>n</i> -eicosane (<i>n</i> -C20)	2.965	1.603
<i>n</i> -heneicosane (<i>n</i> -C21)	2.424	1.084
<i>n</i> -docosane (<i>n</i> -C22)	2.034	0.689
<i>n</i> -tricosane (<i>n</i> -C23)	1.959	0.504
<i>iso</i> -docosane (C22)		
<i>anteiso</i> -docosane (C22)		
pyrene	0.080	0.010
anthraquinone		
naphthalic anhydride		
methylfluoranthene		
retene		
cyclopenta[<i>c,d</i>]acepyrene		
benzanthraquinone		
1-methylchrysene		

Table 5-2. (Continued)

Compound	Emission Factor (mg/kg fuel)	Uncertainty (mg/kg fuel)
<i>n</i> -tetracosane (<i>n</i> -C24)	0.926	0.231
<i>iso</i> -tricosane (C23)		
<i>anteiso</i> -tricosane (C23)		
<i>n</i> -pentacosane (<i>n</i> -C25)	0.501	0.178
<i>iso</i> -tetracosane (C24)		
<i>anteiso</i> -tetracosane (C24)		
<i>n</i> -hexacosane (<i>n</i> -C26)	0.405	0.154
<i>iso</i> -pentacosane (C25)		
<i>anteiso</i> -pentacosane (C25)		
<i>n</i> -heptacosane (<i>n</i> -C27)	0.506	0.228
<i>iso</i> -hexacosane (C26)		
<i>anteiso</i> -hexacosane (C26)		
<i>iso</i> -heptacosane (C27)		
<i>anteiso</i> -heptacosane (C27)		
<i>iso</i> -octacosane (C28)		
<i>anteiso</i> -octacosane (C28)		
<i>n</i> -octacosane (<i>n</i> -C28)	0.609	0.303
<i>n</i> -nonacosane (<i>n</i> -C29)	0.483	0.238
<i>iso</i> -nonacosane (C29)		
<i>anteiso</i> -nonacosane (C29)		
squalene	0.273	0.382
indeno[1,2,3-cd]fluoranthene		
dibenzo[a,e]pyrene		
<i>n</i> -triacontane (<i>n</i> -C30)	1.641	0.823
<i>n</i> -hentriacontane (<i>n</i> -C31)	1.317	0.806
<i>iso</i> -triacontane (C30)		
<i>anteiso</i> -triacontane (C30)		
<i>iso</i> -hentriacontane (C31)		

Table 5-2. (Continued)

Compound	Emission Factor (mg/kg fuel)	Uncertainty (mg/kg fuel)
<i>anteiso</i> -hentriacontane (C31)		
<i>iso</i> -dotriacontane (C32)		
<i>anteiso</i> -dotriacontane (C32)		
<i>n</i> -dotriacontane (<i>n</i> -C32)	0.693	0.249
<i>n</i> -tritriacontane (<i>n</i> -C33)	0.438	0.212
<i>n</i> -tetratriacontane (<i>n</i> -C34)	0.522	0.263
<i>iso</i> -tritriacontane (C33)		
<i>anteiso</i> -tritriacontane (C33)		
<i>n</i> -pentatriacontane (<i>n</i> -C35)		
<i>n</i> -hexatracontane (<i>n</i> -C36)	0.649	0.223
<i>n</i> -tetracontane (<i>n</i> -C40)	0.145	0.099
hexanoic acid	0.482	0.097
succinic acid	0.040	0.007
octanoic acid	0.522	0.096
glutaric acid	0.012	0.009
nonanoic acid	0.884	0.272
adipic acid	0.002	0.004
decanoic acid	0.412	0.061
undecanoic acid	0.544	0.148
pimelic acid		
suberic acid		
dodecanoic acid	0.366	0.127
azelaic acid	0.036	0.062
tridecanoic acid		
pinonic acid		
phthalic acid		
1,4-benzenedicarboxylic acid		
1,3-benzenedicarboxylic acid		

Table 5-2. (Continued)

Compound	Emission Factor (mg/kg fuel)	Uncertainty (mg/kg fuel)
1,2-benzenedicarboxylic acid, 4-methyl		
1,2,4-benzenetricarboxylic acid		
benzenetetracarboxylic acid		
abietic acid		
pimaric acid		
sandaracopimaric acid		
isopimaric acid		
dehydroabietic acid		
sebacic acid		
tetradecanoic acid	0.366	0.251
pentadecanoic acid	0.239	0.169
palmitoleic acid	0.151	0.238
hexadecanoic acid	0.985	0.636
heptadecanoic acid	0.068	0.035
linoleic acid	0.030	0.018
oleic acid	0.070	0.103
linolenic acid	0.000	0.000
octadecanoic acid	0.525	0.226
nonadecanoic acid		
eicosanoic acid	0.021	0.008
docosanoic acid	0.021	0.011
tricosanoic acid		
tetracosanoic acid	0.054	0.027
pentacosanoic acid		
hexacosanoic acid		
heptacosanoic acid		
octacosanoic acid		
nonacosanoic acid		

Table 5-2. (Continued)

Compound	Emission Factor (mg/kg fuel)	Uncertainty (mg/kg fuel)
triacontanoic acid		
Total	96.03	27.76

Table 5-3. Particle-Phase Semivolatiles from an Institutional Oil-Fired Boiler: Mass Fractions (Campaign #2, July 2002)

Compound	Summer Campaign Average Mass Fraction	Uncertainty (%)
dimethyl phthalate	ND	ND
diethyl phthalate	0.00234	0.00082
naphthalene	ND	ND
2-methylnaphthalene	0.00128	0.00082
1-methylnaphthalene	0.00064	0.00036
2,7-dimethylnaphthalene	0.00146	0.00094
1,3-dimethylnaphthalene	0.00290	0.00162
2,6-dimethylnaphthalene	0.00140	0.00088
additional dimethylnaphthalenes		
acenaphthylene		
acenaphthene		
fluorene		
1-methylfluorene	0.00385	0.00069
additional methylfluorenes (peak 1)		
additional methylfluorenes (peak 2)		
phenanthrene	0.01509	0.00190
additional dimethylphenanthrenes	0.01376	0.00112
anthracene		
methylanthracene - peak 1	0.03651	0.00498
methylanthracene - peak 2	0.04635	0.00635
methylanthracene - peak 3	0.02841	0.00354
methylanthracene - peak 4	0.02411	0.00339
octylcyclohexane		
norpristane		
decylcyclohexane		
pristane	0.00702	0.00132

Table 5-3. (Continued)

Compound	Average Mass Fraction	Uncertainty (%)
phytane	0.02373	0.00490
tridecylcyclohexane	0.01745	0.00187
dibutyl phthalate	0.00848	0.00876
butyl benzyl phthalate	0.01038	0.00887
<i>bis</i> (2-ethylhexyl) phthalate	0.04065	0.03904
dioctyl phthalate		
fluoranthene	0.00191	0.00130
pyrene	0.03512	0.00358
chrysene	0.00881	0.00095
benzo[a]anthracene		
benzo[k]fluoranthene		
benzo[b]fluoranthene		
benzo[a]pyrene		
nonadecylcyclohexane		
squalane		
indeno[1,2,3-cd]pyrene		
dibenzo[a,h]anthracene		
benzo[ghi]perylene		
coronene		
cholestane - peak 1		
cholestane - peak 2		
cholestane - peak 3		
cholestane - peak 4		
ABB-2OR-24S-methylcholestane		
ABB-2OR-ethylcholestane		
17A(H)-22,29,30- <i>tris</i> (norhopane)		
17(B)-21A(H)-norhopane		

Table 5-3. (Continued)

Compound	Average Mass Fraction	Uncertainty (%)
17B(H)-21B(H)-hopane		
17B(H)-21A(H)-hopane		
17A(H)-21B(H)-hopane		
<i>n</i> -decane (<i>n</i> -C10)		
<i>n</i> -undecane (<i>n</i> -C11)		
<i>n</i> -dodecane (<i>n</i> -C12)		
<i>n</i> -tridecane (<i>n</i> -C13)	0.00052	0.00066
9H-fluoren-9-one	0.00069	0.00138
<i>n</i> -tetradecane (<i>n</i> -C14)	0.00004	0.00008
<i>n</i> -pentadecane (<i>n</i> -C15)		
<i>n</i> -hexadecane (<i>n</i> -C16)	0.00436	0.00124
<i>n</i> -heptadecane (<i>n</i> -C17)	0.01469	0.00412
1-octadecene		
<i>n</i> -octadecane (<i>n</i> -C18)	0.02085	0.00564
2-methylnonadecane		
3-methylnonadecane		
<i>n</i> -nonadecane (<i>n</i> -C19)	0.05049	0.00901
<i>n</i> -eicosane (<i>n</i> -C20)	0.15462	0.04156
<i>n</i> -heneicosane (<i>n</i> -C21)	0.16568	0.04720
<i>n</i> -docosane (<i>n</i> -C22)	0.20432	0.04845
<i>n</i> -tricosane (<i>n</i> -C23)	0.25152	0.03866
<i>iso</i> -docosane (C23)		
<i>anteiso</i> -docosane (C23)		
pyrene		
anthraquinone		
naphthalic anhydride	0.08036	0.00869
methylfluoranthene		

Table 5-3. (Continued)

Compound	Average Mass Fraction	Uncertainty (%)
benzanthraquinone		
1-methylchrysene		
<i>n</i> -tetracosane (<i>n</i> -C24)	0.41407	0.03666
<i>iso</i> -tricosane (C24)		
<i>anteiso</i> -tricosane (C24)		
<i>n</i> -pentacosane (<i>n</i> -C25)	0.22033	0.01569
<i>iso</i> -tetracosane (C25)		
<i>anteiso</i> -tetracosane (C25)		
<i>n</i> -hexacosane (<i>n</i> -C26)	0.18047	0.01074
<i>iso</i> -pentacosane (C26)		
<i>anteiso</i> -pentacosane (C26)		
<i>n</i> -heptacosane (<i>n</i> -C27)		
<i>iso</i> -hexacosane (C27)	0.13140	0.00846
<i>anteiso</i> -hexacosane (C27)		
<i>iso</i> -heptacosane (C28)		
<i>anteiso</i> -heptacosane (C28)		
<i>iso</i> -octacosane (C29)		
<i>anteiso</i> -octacosane (C29)		
<i>n</i> -octacosane (<i>n</i> -C28)	0.10031	0.00794
<i>n</i> -nonacosane (<i>n</i> -C29)	0.06173	0.00555
<i>iso</i> -nonacosane (C30)		
<i>anteiso</i> -nonacosane (C30)		
squalene	0.09177	0.03406
indeno[1,2,3-cd]fluoranthene		
dibenzo[a,e]pyrene		
<i>n</i> -triacontane (<i>n</i> -C30)	0.00135	0.00097
<i>n</i> -hentriacontane (<i>n</i> -C31)	0.00142	0.00160

Table 5-3. (Continued)

Compound	Average Mass Fraction	Uncertainty (%)
<i>iso</i> -triacontane (C31)		
<i>anteiso</i> -triacontane (C31)		
<i>iso</i> -hentriacontane (C32)		
<i>anteiso</i> -hentriacontane (C32)		
<i>iso</i> -dotriacontane (C33)		
<i>anteiso</i> -dotriacontane (C33)		
<i>n</i> -dotriacontane (<i>n</i> -C32)	0.00041	0.00064
<i>n</i> -tritriacontane (<i>n</i> -C33)	0.00064	0.00036
<i>n</i> -tetratriacontane (<i>n</i> -C34)		
<i>iso</i> -tritriacontane (C34)		
<i>anteiso</i> -tritriacontane (C34)		
<i>n</i> -pentatriacontane (<i>n</i> -C35)	0.00093	0.00043
<i>n</i> -hexatracontane (<i>n</i> -C36)		
<i>n</i> -tetracontane (<i>n</i> -C40)		
hexanoic acid	0.00351	0.00054
succinic acid	0.01805	0.00188
octanoic acid	0.00416	0.00051
glutaric acid	0.01289	0.00355
nonanoic acid	0.00578	0.00027
adipic acid	0.00943	0.00520
decanoic acid	0.00422	0.00213
undecanoic acid	0.00803	0.00439
pimelic acid	0.00798	0.00083
suberic acid	0.00859	0.00158
dodecanoic acid	0.00674	0.00389
azelaic acid	0.00437	0.00093
tridecanoic acid		
pinonic acid	0.01795	0.02539

Table 5-3. (Continued)

Compound	Average Mass Fraction	Uncertainty (%)
phthalic acid	0.00079	0.00112
1,4-benzenedicarboxylic acid	0.04304	0.00223
1,3-benzenedicarboxylic acid	0.07511	0.00351
1,2-benzenedicarboxylic acid, 4-methyl		
1,2,4-benzenetricarboxylic acid	0.43862	0.02279
benzenetetracarboxylic acid	0.11274	0.01355
abietic acid		
pimaric acid		
sandaracopimaric acid		
isopimaric acid		
dehydroabietic acid		
sebacic acid		
tetradecanoic acid	0.00879	0.00743
pentadecanoic acid	0.01823	0.01804
palmitoleic acid		
hexadecanoic acid	0.13150	0.05328
heptadecanoic acid	0.01520	0.00328
linoleic acid	0.01516	0.00417
oleic acid	0.00550	0.00071
linolenic acid		
octadecanoic acid	0.08921	0.01976
nonadecanoic acid		
eicosanoic acid	0.00331	0.00076
docosanoic acid	0.00311	0.00073
tricosanoic acid		
tetracosanoic acid	0.00267	0.00203
pentacosanoic acid		
hexacosanoic acid		

Table 5-3. (Continued)

Compound	Average Mass Fraction	Uncertainty (%)
heptacosanoic acid		
octacosanoic acid		
nonacosanoic acid		
triacontanoic acid		
Total	3.56	0.34

Table 5-4. Particle-Phase Semivolatiles from an Institutional Oil-Fired Boiler: Emission Factors (Campaign #2, July 2002)

Compound	Emission Factor ($\mu\text{g}/\text{kg}$ fuel)	Uncertainty ($\mu\text{g}/\text{kg}$ fuel)
dimethyl phthalate		
diethyl phthalate	3.10	0.90
naphthalene		
2-methylnaphthalene	0.69	0.52
1-methylnaphthalene	0.36	
2,7-dimethylnaphthalene	0.79	0.61
1,3-dimethylnaphthalene	1.57	1.08
2,6-dimethylnaphthalene	0.76	0.57
additional dimethylnaphthalenes		
acenaphthylene		
acenaphthene		
fluorene		
1-methylfluorene	4.34	0.81
additional methylfluorenes (peak 1)		
additional methylfluorenes (peak 2)		
phenanthrene	14.69	1.81
additional dimethylphenanthrenes	16.01	1.25
anthracene		
methylanthracene - peak 1	41.41	5.21
methylanthracene - peak 2	52.29	5.99
methylanthracene - peak 3	32.39	3.75
methylanthracene - peak 4	27.32	3.60
octylcyclohexane		
norpristane		
decylcyclohexane		
pristane	7.82	1.39
phytane	26.02	4.69

Table 5-4. (Continued)

Compound	Emission Factor ($\mu\text{g}/\text{kg}$ fuel)	Uncertainty ($\mu\text{g}/\text{kg}$ fuel)
tridecylcyclohexane	9.66	
dibutyl phthalate	13.42	9.71
butyl benzyl phthalate	15.83	9.59
<i>bis</i> (2-ethylhexyl) phthalate	30.13	35.33
dioctyl phthalate		
fluoranthene	1.89	1.64
pyrene	37.83	4.26
chrysene	7.90	0.39
benzo[a]anthracene		
benzo[k]fluoranthene		
benzo[b]fluoranthene		
benzo[a]pyrene		
nonadecylcyclohexane		
squalane		
indeno[1,2,3-cd]pyrene		
dibenzo[a,h]anthracene		
benzo[ghi]perylene		
coronene		
cholestane - peak 1		
cholestane - peak 2		
cholestane - peak 3		
cholestane - peak 4		
ABB-2OR-24S-methylcholestane		
ABB-2OR-ethylcholestane		
17A(H)-22,29,30- <i>tris</i> (norhopane)		
17(B)-21A(H)-norhopane		
17B(H)-21B(H)-hopane		
17B(H)-21A(H)-hopane		

Table 5-4. (Continued)

Compound	Emission Factor ($\mu\text{g}/\text{kg fuel}$)	Uncertainty ($\mu\text{g}/\text{kg fuel}$)
17A(H)-21B(H)-hopane		
<i>n</i> -decane (<i>n</i> -C10)		
<i>n</i> -undecane (<i>n</i> -C11)		
<i>n</i> -dodecane (<i>n</i> -C12)		
<i>n</i> -tridecane (<i>n</i> -C13)	0.27	0.47
9H-fluoren-9-one	1.09	1.89
<i>n</i> -tetradecane (<i>n</i> -C14)	0.07	0.11
<i>n</i> -pentadecane (<i>n</i> -C15)		
<i>n</i> -hexadecane (<i>n</i> -C16)	4.28	1.47
<i>n</i> -heptadecane (<i>n</i> -C17)	15.52	4.84
1-octadecene		
<i>n</i> -octadecane (<i>n</i> -C18)	21.94	6.64
2-methylnonadecane		
3-methylnonadecane		
<i>n</i> -nonadecane (<i>n</i> -C19)	46.48	9.19
<i>n</i> -eicosane (<i>n</i> -C20)	168.23	50.85
<i>n</i> -heneicosane (<i>n</i> -C21)	182.46	58.66
<i>n</i> -docosane (<i>n</i> -C22)	225.50	55.96
<i>n</i> -tricosane (<i>n</i> -C23)	283.78	41.33
<i>iso</i> -docosane (C23)		
<i>anteiso</i> -docosane (C23)		
pyrene		
anthraquinone		
naphthalic anhydride	72.43	11.82
methylfluoranthene		
retene		
cyclopenta[c,d]acepyrene		
benzanthraquinone		

Table 5-4. (Continued)

Compound	Emission Factor (µg/kg fuel)	Uncertainty (µg/kg fuel)
1-methylchrysene		
<i>n</i> -tetracosane (<i>n</i> -C24)	403.25	40.02
<i>iso</i> -tricosane (C24)		
<i>anteiso</i> -tricosane (C24)		
<i>n</i> -pentacosane (<i>n</i> -C25)	209.06	16.78
<i>iso</i> -tetracosane (C25)		
<i>anteiso</i> -tetracosane (C25)		
<i>n</i> -hexacosane (<i>n</i> -C26)	160.30	11.33
<i>iso</i> -pentacosane (C26)		
<i>anteiso</i> -pentacosane (C26)		
<i>n</i> -heptacosane (<i>n</i> -C27)	105.60	8.65
<i>iso</i> -hexacosane (C27)		
<i>anteiso</i> -hexacosane (C27)		
<i>iso</i> -heptacosane (C28)		
<i>anteiso</i> -heptacosane (C28)		
<i>iso</i> -octacosane (C29)		
<i>anteiso</i> -octacosane (C29)		
<i>n</i> -octacosane (<i>n</i> -C28)	81.32	8.35
<i>n</i> -nonacosane (<i>n</i> -C29)	41.14	5.41
<i>iso</i> -nonacosane (C30)		
<i>anteiso</i> -nonacosane (C30)		
squalene	73.59	40.25
indeno[1,2,3-cd]fluoranthene		
dibenzo[a,e]pyrene		
<i>n</i> -triacontane (<i>n</i> -C30)	1.58	1.15
<i>n</i> -hentriacontane (<i>n</i> -C31)	1.56	1.90
<i>iso</i> -triacontane (C31)		
<i>anteiso</i> -triacontane (C31)		

Table 5-4. (Continued)

Compound	Emission Factor ($\mu\text{g}/\text{kg}$ fuel)	Uncertainty ($\mu\text{g}/\text{kg}$ fuel)
<i>iso</i> -hentriacontane (C32)		
<i>anteiso</i> -hentriacontane (C32)		
<i>iso</i> -dotriacontane (C33)		
<i>anteiso</i> -dotriacontane (C33)		
<i>n</i> -dotriacontane (<i>n</i> -C32)	0.65	0.76
<i>n</i> -tritriacontane (<i>n</i> -C33)	0.36	
<i>n</i> -tetratriacontane (<i>n</i> -C34)		
<i>iso</i> -tritriacontane (C34)		
<i>anteiso</i> -tritriacontane (C34)		
<i>n</i> -pentatriacontane (<i>n</i> -C35)	0.51	
<i>n</i> -hexatracontane (<i>n</i> -C36)		
<i>n</i> -tetracontane (<i>n</i> -C40)		
hexanoic acid	4.16	0.63
succinic acid	21.42	2.12
octanoic acid	4.94	0.58
glutaric acid	15.30	4.19
nonanoic acid	6.86	0.23
adipic acid	11.19	6.16
decanoic acid	5.01	2.53
undecanoic acid	9.53	5.20
pimelic acid	7.60	0.32
suberic acid	8.47	1.65
dodecanoic acid	8.00	4.61
azelaic acid	2.42	
tridecanoic acid		
pinonic acid	21.30	30.13
phthalic acid	0.94	1.33
1,4-benzenedicarboxylic acid	36.74	0.22

Table 5-4. (Continued)

Compound	Emission Factor (µg/kg fuel)	Uncertainty (µg/kg fuel)
1,3-benzenedicarboxylic acid	64.33	2.12
1,2-benzenedicarboxylic acid, 4-methyl		
1,2,4-benzenetricarboxylic acid	437.83	23.28
benzenetetracarboxylic acid	115.71	15.47
abietic acid		
pimaric acid		
sandaracopimaric acid		
isopimaric acid		
dehydroabietic acid		
sebacic acid		
tetradecanoic acid	10.43	8.81
pentadecanoic acid	21.64	21.40
palmitoleic acid		
hexadecanoic acid	156.06	63.02
heptadecanoic acid	18.04	3.84
linoleic acid	17.99	4.91
oleic acid	6.53	0.81
linolenic acid		
octadecanoic acid	101.47	23.19
nonadecanoic acid		
eicosanoic acid	3.93	0.89
docosanoic acid	2.81	0.60
tricosanoic acid		
tetracosanoic acid	3.16	2.40
pentacosanoic acid		
hexacosanoic acid		
heptacosanoic acid		
octacosanoic acid		

Table 5-4. (Continued)

Compound	Emission Factor ($\mu\text{g}/\text{kg}$ fuel)	Uncertainty ($\mu\text{g}/\text{kg}$ fuel)
nonacosanoic acid		
triacontanoic acid		
Total	3058.78	481.44

Gas-Phase Carbonyl Compounds

Analytical results for the carbonyl field samples for each of the three test days of campaign #1 are shown in Table 5-5 (A, B, C). The DNPH-impregnated silica gel tubes were sampled as pairs (in series), using the back tube of each pair as a check for breakthrough. Final values are reported as the difference between the sum of the paired tubes sampling the residence chamber and the sum of the paired tubes sampling the Dilution Air. At the bottom of each table, the entry reported as “Total Speciated” is the total mass (front tube plus back tube) of the sum of the specifically identified compounds; the final value represents the difference between the

Table 5-5A. Carbonyl Compounds Analyzed by High Performance Liquid Chromatography (Campaign #1, January 16, 2001)

Compound	CAS No.	Residence Chamber Pair (µg)	Dilution Air (µg)	Residence Chamber Minus Dilution Air (µg)	% Total^a
formaldehyde	50-00-0	0.6150	0.0745	0.5405 ± 0.06	34.06 ± 3.75
acetaldehyde	75-07-0	0.3575	0.1980	0.1595 ± 0.00 ^b	10.05 ± 0.11
acetone	67-64-1	0.3585	0.2260	0.1325 ± 0.01	8.35 ± 0.35
propionaldehyde	123-38-6	ND	ND	ND	ND
crotonaldehyde	4170-30-0	ND	ND	ND	ND
butyraldehyde	123-72-8	0.0560	0.0470	0.0090 ± 0.00	0.57 ± 0.03
benzaldehyde	100-52-7	0.0450	0.0200	0.0250 ± 0.00	1.58 ± 0.05
isovaleraldehyde	590-86-3	0.0090	ND	0.0090 ± 0.00	0.57 ± 0.08
valeraldehyde	110-62-3	ND	0.0015	ND	ND
<i>o</i> -tolualdehyde	529-20-4	ND	0.0120	ND	ND
<i>m</i> -tolualdehyde	620-23-5	ND	0.0015	ND	ND
<i>p</i> -tolualdehyde	104-87-0	ND	ND	ND	ND
hexaldehyde	66-25-1	0.0560	0.0560	ND	ND
2,5-dimethylbenzaldehyde	5779-94-2	ND	ND	ND	ND
diacetyl	431-03-8	ND	ND	ND	ND
methacrolein	78-85-3	ND	ND	ND	ND
2-butanone	78-93-3	0.0720	0.0640	0.0080 ± 0.00	0.50 ± 0.04
glyoxal	107-22-2	0.2730	0.1990	0.0740 ± 0.00	4.66 ± 0.13
acetophenone	98-86-2	0.0060	ND	0.0060	0.38 ± 0.02
methylglyoxal	78-98-8	0.0880	0.0700	0.0180 ± 0.00	1.13 ± 0.14
octanal	124-13-0	0.0140	0.0250	ND	ND
nonanal	124-19-6	0.2100	0.2430	ND	ND
Total Speciated			2.1600	1.2375	0.9225

Table 5-5A. (Continued)

Compound	CAS No.	Residence Chamber Pair (µg)	Dilution Air (µg)	Residence Chamber Minus Dilution Air (µg)
Total Unspeciated		1.5375	0.8730	0.6645
Total Speciated + Unspeciated		3.6975	2.1105	1.5870
Mass emission rate of Speciated Carbonyls				0.84 mg/kg fuel
Mass emission rate of Total Carbonyls (Speciated + Unspeciated) (1/16/01)				1.42 mg/kg fuel

ND = Not Detected

^aPercent of each compound expressed as a percentage of Total Speciated + Unspeciated Carbonyl Compounds.

^bCalculated value for analytical uncertainty is less than 0.01.

Table 5-5B. Carbonyl Compounds Analyzed by High Performance Liquid Chromatography (Campaign #1, January 17, 2001)

Compound	CAS No.	Residence Chamber Pair (µg)	Dilution Air (µg)	Residence Chamber Minus Dilution Air (µg)	% Total ^a
formaldehyde	50-00-0	0.2870	0.0890	0.1980 ± 0.02	21.39 ± 2.36
acetaldehyde	75-07-0	0.2385	0.1790	0.0595 ± 0.00 ^b	6.429 ± 0.07
acetone	67-64-1	0.4085	0.2380	0.1705 ± 0.007	18.42 ± 0.78
propionaldehyde	123-38-6	ND	0.0005	ND	ND
crotonaldehyde	4170-30-0	ND	ND	ND	ND
butyraldehyde	123-72-8	0.0645	0.0485	0.0160 ± 0.00	1.73 ± 0.10
benzaldehyde	100-52-7	0.0330	0.0150	0.0180 ± 0.00	1.94 ± 0.06
isovaleraldehyde	590-86-3	ND	ND	ND	ND
valeraldehyde	110-62-3	0.0045	0.0015	0.0045 ± 0.00	0.49 ± 0.05
<i>o</i> -tolualdehyde	529-20-4	ND	0.0120	ND	ND
<i>m</i> -tolualdehyde	620-23-5	ND	0.0015	ND	ND
<i>p</i> -tolualdehyde	104-87-0	ND	ND	ND	ND
hexaldehyde	66-25-1	0.0585	0.0450	0.0135 ± 0.00	1.46 ± 0.14
2,5-dimethylbenzaldehyde	5779-94-2	ND	ND	ND	ND
diacetyl	431-03-8	ND	ND	ND	ND
methacrolein	78-85-3	ND	ND	ND	ND
2-butanone	78-93-3	0.0640	0.0560	0.0080 ± 0.00	0.86 ± 0.07
glyoxal	107-22-2	0.2370	0.1720	0.0650 ± 0.00	7.02 ± 0.19
acetophenone	98-86-2	ND	ND	ND	ND
methylglyoxal	78-98-8	0.0840	0.0590	0.0250 ± 0.00	2.70 ± 0.33
octanal	124-13-0	0.0220	0.0070	0.0150 ± 0.00	1.62 ± 0.00
nonanal	124-19-6	0.1550	0.1430	0.0120 ± 0.00	1.30 ± 0.10
Total Speciated			1.6565	1.0520	0.6045
Total Unspeciated			1.0515	0.730	0.3210
Total Speciated + Unspeciated			2.7080	1.7825	0.9255
Mass emission rate of Speciated Carbonyls					0.56 mg/kg fuel
Mass emission rate of Total Carbonyls (Speciated + Unspeciated)					0.86 mg/kg fuel

ND = Not Detected

^aPercent of each compound expressed as a percentage of Total Speciated + Unspeciated Carbonyl Compounds.

^bCalculated value for analytical uncertainty is less than 0.01.

Table 5-5C. Carbonyl Compounds Analyzed by High Performance Liquid Chromatography (Campaign #1, January 18, 2001)

Compound	CAS No.	Residence Chamber Pair (μg)	Dilution Air (μg)	Residence Chamber Minus Dilution Air (\pm Analytical Uncertainty (μg))	% Total^a (\pm Analytical Uncertainty)
formaldehyde	50-00-0	0.2155	0.1140	0.1015 ± 0.01	14.43 ± 1.59
acetaldehyde	75-07-0	0.2885	0.2390	0.0495 ± 0.00^b	7.04 ± 0.08
acetone	67-64-1	0.2230	0.1910	0.0320 ± 0.00	4.55 ± 0.19
propionaldehyde	123-38-6	ND	0.0005	ND	ND
crotonaldehyde	4170-30-0	ND	ND	ND	ND
butyraldehyde	123-72-8	0.0865	0.0590	0.0275 ± 0.00	3.91 ± 0.23
benzaldehyde	100-52-7	0.0130	0.0200	ND	ND
isovaleraldehyde	590-86-3	ND	ND	ND	ND
valeraldehyde	110-62-3	ND	ND	ND	ND
<i>o</i> -tolualdehyde	529-20-4	ND	ND	ND	ND
<i>m</i> -tolualdehyde	620-23-5	ND	ND	ND	ND
<i>p</i> -tolualdehyde	104-87-0	ND	ND	ND	ND
hexaldehyde	66-25-1	0.0515	0.0545	ND	ND
2,5-dimethylbenzaldehyde	5779-94-2	ND	ND	ND	ND
diacetyl	431-03-8	ND	ND	ND	ND
2-butanone	78-93-3	0.0630	0.0590	0.0040 ± 0.00	0.57 ± 0.05
glyoxal	107-22-2	0.2890	0.2100	0.0790 ± 0.00	11.23 ± 0.31
acetophenone	98-86-2	ND	ND	ND	ND
methylglyoxal	78-98-8	0.0700	0.0650	0.0050 ± 0.00	0.71 ± 0.09
octanal	124-13-0	0.0060	0.0090	ND	ND
nonanal	124-19-6	0.1120	0.1320	ND	ND

Table 5-5C. (Continued)

Compound	CAS No.	Residence Chamber Pair (µg)	Dilution Air (µg)	Residence Chamber Minus Dilution Air (± Analytical Uncertainty (µg))
Total Speciated		1.4180	1.1540	0.2640
Total Unspeciated		1.4795	1.0400	0.4395
Total Speciated + Unspeciated		2.8975	2.1940	0.7035
Mass emission rate of Speciated Carbonyls				0.23 mg/kg fuel
Mass emission rate of Total Carbonyls (Speciated + Unspeciated)				0.56 mg/kg fuel

^a Percent of each compound expressed as a percentage of Total Speciated + Unspeciated Carbonyl Compounds.

^b Calculated value for analytical uncertainty is less than 0.01.

residence chamber air and dilution air. At the bottom of each table, the entry reported as “Total Unspeciated” is the total mass (front plus back tube) of the compounds characterized as carbonyl compounds but not identified as a specific compound because no analytical standard was available; the final value represents the difference between residence chamber air and dilution air. The entry reported as “Total Speciated + Unspeciated” includes the total mass (front tube plus back tube) of specifically identified carbonyl compounds as well as unspeciated carbonyl compounds; the final value represents the difference between residence chamber air and dilution air.

Supporting data showing results for each individual carbonyl sampling tube (blanks, front and back tubes) are included in Appendix I.

The total mass of the carbonyl compounds (Speciated, Unspeciated, and (Speciated + Unspeciated)) for each test day is summarized in Table 5-6. The speciated carbonyl compounds decrease with each successive test day, as do the total (Speciated + Unspeciated) carbonyl compounds. The unspeciated carbonyl compounds decrease from Day #1 to Day #2, but increase from Day #2 to Day #3. This behavior says that one or more unidentified carbonyl compounds increase in concentration from Day #2 to Day #3, while the speciated (i.e., identified) carbonyl

compounds decrease in concentration. Fuel consumption increases over the three test days as both

Table 5-6. Total Mass of Carbonyl Compounds for Each Campaign #1 Test Day

Test Day	Fuel Consumption (kg)	Speciated	Unspeciated	Speciated + Unspeciated
January 16, 2001	6,569	0.9225 µg	0.6645 µg	1.5870 µg
Emission Rate		0.84 mg/kg fuel		1.42 mg/kg fuel
January 17, 2001	6,934	0.6045 µg	0.3210 µg	0.9255 µg
Emission Rate		0.56 mg/kg fuel		0.86 mg/kg fuel
January 18, 2001	7,926	0.2640 µg	0.4395 µg	0.7035 µg
Emission Rate		0.23 mg/kg fuel		0.56 mg/kg fuel

speciated and total (Speciated + Unspeciated) carbonyl compounds are decreasing. Emission rates also show a decline over the three test days, even with increased consumption of fuel.

Gas-Phase Air Toxics Whole Air Samples

Air toxics values were determined only for campaign #1. Analytical results for the air toxics canister samples are shown in Table 5-7. The ERG concurrent analysis produces analytical results for both air toxics and nonmethane organic compound ozone precursors; the NMOC results are presented separately. Table 5-7 shows only the air toxics compounds that were observed, with the ambient sample analytical data included for reference. By comparison with the ambient air sample, the concentrations of the air toxics compounds are seen to be very low, with most of the compounds on the air toxics target list not observed in the field samples at measurable levels. No consistent trends for the three test days are evident for these compounds. Samples labeled “Dilution Air (DA)” reflect the dilution air entering the sample dilution system; this dilution air has not been exposed to the stationary source matrix. The second canister for each test day is labeled “Residence Chamber Air” and reflects the diluted stationary source matrix at the end of the residence chamber (RC).

Supporting data for the air toxics analysis are shown in Appendix H.

Table 5-7. Air Toxics Compounds (Campaign #1)

Compounds	CAS No.	Ambient µg/m ³	RC-DA 1/16/01 µg/m ³	RC-DA 1/17/01 µg/m ³	RC-DA 1/18/01 µg/m ³
acetylene	74-86-2	1.52	ND	1.27	ND
propylene	115-07-1	2.20	0.08	0.07	ND
dichlorodifluoromethane	75-71-8	2.45	ND	ND	ND
chloromethane	74-87-3	0.98	ND	ND	0.12
dichlorotetrafluoroethane	1320-37-2	0.13	ND	ND	ND
1,3-butadiene	106-99-0	0.16	ND	ND	ND
trichlorofluoromethane	75-69-4	1.56	0.05	ND	ND
methylene chloride	75-09-2	0.42	0.11	1.00	0.16
trichlorotrifluoroethane	26253-64-8	0.65	ND	ND	ND
methyl <i>tert</i> -butyl ether	1634-04-1	0.15	ND	ND	ND
methyl ethyl ketone	78-93-3	12.31	ND	ND	ND
benzene	71-43-2	1.29	0.19	0.33	0.05
carbon tetrachloride	56-23-5	0.53	ND	0.05	ND
toluene	108-88-3	2.11	0.08	0.05	0.05
<i>n</i> -octane	111-65-9	0.22	0.18	ND	ND
styrene	100-42-5	0.11	ND	ND	ND
<i>o</i> -xylene	95-47-6	0.86	ND	0.04	ND
1,3,5-trimethylbenzene	108-67-8	0.31	0.03	0.13	0.15
1,2,4-trimethylbenzene	95-63-6	0.88	0.18	0.33	0.11
<i>p</i> -dichlorobenzene	106-46-7	0.10	ND	ND	ND
1,2,4-trichlorobenzene	120-82-1	0.28	ND	ND	ND

ND = Not Detected

Gas-Phase Speciated Nonmethane Organic Compounds

Nonmethane organic compounds were determined only for campaign #1. Analysis of whole air samples of dilution air and residence chamber air using ERG’s concurrent analysis generated analytical data for speciated nonmethane organic compounds (SNMOC), shown in Tables 5-8 (A, B, C). Analytical results are calculated as the difference between the weight of the compound collected from the residence chamber minus the weight of the compound collected from the dilution air, expressed as micrograms (µg). The weight percent of total SNMOC (Speciated + Unspeciated) is also calculated. Mass emission rates of speciated SNMOC and total (Speciated + Unspeciated) nonmethane organic compounds are also shown in Table 5-9. Supporting data for the NMOC analysis are found in Appendix G. Samples labeled “Dilution Air” reflect the dilution air entering the sample dilution system; this dilution air has not been exposed to the stationary source matrix. The second canister for each test day is labeled “Residence Chamber Air” and reflects the diluted stationary source matrix at the end of the residence chamber. The general profiles of the collected concentrations of analytes do not

Table 5-8A. SNMOC (Campaign #1, January 16, 2001)

Compound	CAS No.	Residence Chamber minus Dilution Air (μg)	%Total
ethylene	4-84-0	652.00 \pm 13.02	2.65 \pm 0.05
acetylene	74-86-2	9.34 \pm 12.01	0.04 \pm 0.05
ethane	74-85-1	136.89 \pm 10.90	0.56 \pm 0.04
propylene	115-07-1	8.14 \pm 6.90	0.03 \pm 0.03
propane	74-98-6	18751.70 \pm 12.24	76.36 \pm 0.05
propyne	74-99-7	ND	ND
isobutane	75-28-5	511.43 \pm 6.23	2.08 \pm 0.03
isobutene/1-butene	115-11-7/106-98-0	48.81 \pm 4.00	0.20 \pm 0.02
1,3-butadiene	106-99-0	31.20 \pm 5.90	0.13 \pm 0.02
<i>n</i> -butane	106-97-8	275.28 \pm 11.24	1.12 \pm 0.05
<i>trans</i> -2-butene	624-64-6	1.45 \pm 7.23	0.01 \pm 0.03
<i>cis</i> -2-butene	590-18-1	6.65 \pm 10.79	0.03 \pm 0.04
3-methyl-1-butene	563-45-1	ND	ND
isopentane	78-78-4	191.81 \pm 16.13	0.78 \pm 0.07
1-pentene	109-67-1	21.81 \pm 9.01	0.09 \pm 0.04
2-methyl-1-butene	563-46-2	ND	ND
<i>n</i> -pentane	109-66-0	71.29 \pm 11.24	0.29 \pm 0.05
isoprene	78-79-4	ND	ND
<i>trans</i> -2-pentene	646-04-8	11.63 \pm 9.12	0.05 \pm 0.04
<i>cis</i> -2-pentene	627-20-3	22.03 \pm 13.46	0.09 \pm 0.05
2-methyl-2-butene	513-35-9	ND	ND
2,2-dimethylbutane	75-83-2	38.63 \pm 16.46	0.16 \pm 0.07
cyclopentene	142-29-0	6.42 \pm 15.57	0.03 \pm 0.06
4-methyl-1-pentene	691-37-2	ND	ND
cyclopentane	287-92-3	26.90 \pm 7.68	0.11 \pm 0.03
2,3-dimethylbutane	79-29-8	ND	ND
2-methylpentane	107-83-5	54.24 \pm 8.79	0.22 \pm 0.04
3-methylpentane	96-14-0	80.69 \pm 16.80	0.33 \pm 0.07

Table 5-8A. (Continued)

Compound	CAS No.	Residence Chamber minus Dilution Air (μg)	%Total
2-methyl-1-pentene	763-29-1	ND	ND
1-hexene	592-41-6	17.72 \pm 17.01	0.07 \pm 0.07
2-ethyl-1-butene	760-21-4	ND	ND
<i>n</i> -hexane	110-54-3	843.46 \pm 12.90	3.43 \pm 0.05
<i>trans</i> -2-hexene	4050-45-7	ND	ND
<i>cis</i> -2-hexene	7688-21-3	ND	ND
methylcyclopentane	96-37-7	153.95 \pm 10.68	0.63 \pm 0.04
2,4-dimethylpentane	108-08-7	11.74 \pm 13.35	0.05 \pm 0.05
benzene	71-43-2	137.35 \pm 8.45	0.56 \pm 0.03
cyclohexane	110-82-7	ND	ND
2-methylhexane	591-76-4	88.42 \pm 2.22	0.36 \pm 0.01
2,3-dimethylpentane	565-59-3	2.00 \pm 11.12	0.01 \pm 0.05
3-methylhexane	589-34-4	ND	ND
1-heptene	592-76-7	ND	ND
2,2,4-trimethylpentane	540-84-1	38.75 \pm 11.24	0.16 \pm 0.05
<i>n</i> -heptane	142-82-5	32.77 \pm 5.67	0.13 \pm 0.02
methylcyclohexane	108-87-2	27.56 \pm 10.79	0.11 \pm 0.04
2,2,3-trimethylpentane	564-02-3	ND	ND
2,3,4-trimethylpentane	565-75-3	37.63 \pm 7.79	0.15 \pm 0.03
toluene	108-88-3	54.04 \pm 4.45	0.22 \pm 0.02
2-methylheptane	592-27-8	ND	ND
3-methylheptane	589-81-1	1.22 \pm 4.23	0.00 ^a \pm 0.02
1-octene	111-66-0	ND	ND
<i>n</i> -octane	111-65-9	14.52 \pm 2.22	0.06 \pm 0.01
ethylbenzene	100-41-4	ND	ND
<i>m</i> -xylene/ <i>p</i> -xylene	108-38-3/106-42-3	ND	ND
styrene	100-42-5	ND	ND
<i>o</i> -xylene	95-47-6	14.30 \pm 3.00	0.06 \pm 0.01

Table 5-8A. (Continued)

Compound	CAS No.	Residence Chamber minus Dilution Air (μg)	%Total
1-nonene	124-11-8	21.70 \pm 2.34	0.09 \pm 0.01
<i>n</i> -nonane	111-84-2	18.27 \pm 2.34	0.07 \pm 0.01
isopropylbenzene	98-82-8	ND	ND
α -pinene	80-56-8	ND	ND
<i>n</i> -propylbenzene	103-65-1	11.40 \pm 2.22	0.05 \pm 0.01
<i>m</i> -ethyltoluene	620-14-4	90.09 \pm 5.12	0.37 \pm 0.02
<i>p</i> -ethyltoluene	622-96-8	58.88 \pm 5.90	0.24 \pm 0.02
1,3,5-trimethylbenzene	108-67-8	51.48 \pm 3.23	0.21 \pm 0.01
<i>o</i> -ethyltoluene	611-14-3	61.11 \pm 3.45	0.25 \pm 0.01
β -pinene	127-91-3	ND	ND
1,2,4-trimethylbenzene	95-63-6	100.52 \pm 3.23	0.41 \pm 0.01
1-decene	872-05-9	ND	ND
<i>n</i> -decane	124-18-5	ND	ND
1,2,3-trimethylbenzene	526-73-8	58.88 \pm 2.67	0.24 \pm 0.01
<i>m</i> -diethylbenzene	141-93-5	16.94 \pm 1.45	0.07 \pm 0.01
<i>p</i> -diethylbenzene	105-05-5	ND	ND
1-undecene	821-95-4	ND	ND
<i>n</i> -undecane	1120-21-4	140.43 \pm 2.11	0.57 \pm 0.01
1-dodecene	112-41-4	ND	ND
<i>n</i> -dodecane	112-40-3	ND	ND
1-tridecene	2437-56-1	ND	ND
<i>n</i> -tridecane	629-50-5	ND	ND
Total Speciated SNMOC			23.40 $\mu\text{g}/\text{m}^3$
Total Unspeciated SNMOC			2.36 $\mu\text{g}/\text{m}^3$
Total Speciated + Unspeciated SNMOC			25.76 $\mu\text{g}/\text{m}^3$
Mass Emission Rate of Speciated Nonmethane Organic Compounds			0.25 mg/kg fuel
Mass Emission Rate of Total (Speciated + Unspeciated) Nonmethane Organic Compounds			0.27 mg/kg fuel

^aCalculated value less than 0.00.

Table 5-8B. SNMOC (Campaign #1, January 17, 2001)

Compound	CAS No.	Residence Chamber Minus Dilution Air (μg)	% Total
ethylene	4-84-0	1773.89 \pm 12.56	10.80 \pm 0.08
acetylene	74-86-2	1335.54 \pm 11.60	8.12 \pm 0.07
ethane	74-85-1	1974.33 \pm 10.52	12.02 \pm 0.06
propylene	115-07-1	154.47 \pm 6.66	0.94 \pm 0.04
propane	74-98-6	2894.27 \pm 11.81	17.62 \pm 0.07
propyne	74-99-7	ND	ND
isobutane	75-28-5	39.96 \pm 6.01	0.24 \pm 0.04
isobutene/1-butene	115-11-7/106-98-0	131.87 \pm 3.87	0.80 \pm 0.02
1,3-butadiene	106-99-0	ND	ND
<i>n</i> -butane	106-97-8	82.53 \pm 10.84	0.50 \pm 0.07
<i>trans</i> -2-butene	624-64-6	42.90 \pm 6.98	0.26 \pm 0.04
<i>cis</i> -2-butene	590-18-1	48.21 \pm 10.41	0.29 \pm 0.06
3-methyl-1-butene	563-45-1	ND	ND
isopentane	78-78-4	106.50 \pm 15.57	0.65 \pm 0.09
1-pentene	109-67-1	37.38 \pm 8.70	0.23 \pm 0.05
2-methyl-1-butene	563-46-2	ND	ND
<i>n</i> -pentane	109-66-0	64.35 \pm 10.84	0.39 \pm 0.07
isoprene	78-79-4	1.40 \pm 1.29	0.01 \pm 0.01
<i>trans</i> -2-pentene	646-04-8	26.97 \pm 8.80	0.16 \pm 0.05
<i>cis</i> -2-pentene	627-20-3	63.60 \pm 12.99	0.39 \pm 0.08
2-methyl-2-butene	513-35-9	ND	ND
2,2-dimethylbutane	75-83-2	126.88 \pm 15.89	0.77 \pm 0.10
cyclopentene	142-29-0	47.78 \pm 15.03	0.29 \pm 0.09
4-methyl-1-pentene	691-37-2	ND	ND
cyclopentane	287-92-3	37.49 \pm 7.41	0.23 \pm 0.05
2,3-dimethylbutane	79-29-8	54.59 \pm 18.36	0.33 \pm 0.11
2-methylpentane	107-83-5	99.80 \pm 8.48	0.61 \pm 0.05
3-methylpentane	96-14-0	106.18 \pm 16.21	0.65 \pm 0.10
2-methyl-1-pentene	763-29-1	ND	ND

Table 5-8B. (Continued)

Compound	CAS No.	Residence Chamber Minus Dilution Air (μg)	% Total
1-hexene	592-41-6	84.16 \pm 16.42	0.51 \pm 0.10
2-ethyl-1-butene	760-21-4	ND	ND
<i>n</i> -hexane	110-54-3	451.16 \pm 12.45	2.75 \pm 0.08
<i>trans</i> -2-hexene	4050-45-7	ND	ND
<i>cis</i> -2-hexene	7688-21-3	ND	ND
methylcyclopentane	96-37-7	148.22 \pm 10.31	0.90 \pm 0.06
2,4-dimethylpentane	108-08-7	63.71 \pm 12.88	0.39 \pm 0.08
benzene	71-43-2	157.55 \pm 8.16	0.96 \pm 0.05
cyclohexane	110-82-7	ND	ND
2-methylhexane	591-76-4	42.47 \pm 2.15	0.26 \pm 0.01
2,3-dimethylpentane	565-59-3	85.16 \pm 10.74	0.52 \pm 0.07
3-methylhexane	589-34-4	16.79 \pm 9.02	0.10 \pm 0.05
1-heptene	592-76-7	ND	ND
2,2,4-trimethylpentane	540-84-1	58.72 \pm 10.84	0.36 \pm 0.07
<i>n</i> -heptane	142-82-5	84.19 \pm 5.48	0.51 \pm 0.03
methylcyclohexane	108-87-2	32.50 \pm 10.41	0.20 \pm 0.06
2,2,3-trimethylpentane	564-02-3	ND	ND
2,3,4-trimethylpentane	565-75-3	42.69 \pm 7.52	0.26 \pm 0.05
toluene	108-88-3	61.08 \pm 4.29	0.37 \pm 0.03
2-methylheptane	592-27-8	32.18 \pm 4.19	0.20 \pm 0.03
3-methylheptane	589-81-1	47.89 \pm 4.08	0.29 \pm 0.02
1-octene	111-66-0	ND	ND
<i>n</i> -octane	111-65-9	226.36 \pm 2.15	1.38 \pm 0.01
ethylbenzene	100-41-4	32.82 \pm 2.90	0.20 \pm 0.02
<i>m</i> -xylene/ <i>p</i> -xylene	108-38-3/106-42-3	40.38 \pm 4.51	0.25 \pm 0.03
styrene	100-42-5	53.31 \pm 7.41	0.32 \pm 0.05
<i>o</i> -xylene	95-47-6	43.63 \pm 2.90	0.27 \pm 0.02
1-nonene	124-11-8	ND	ND

Table 5-8B. (Continued)

Compound	CAS No.	Residence Chamber Minus Dilution Air (μg)	% Total
<i>n</i> -nonane	111-84-2	100.12 \pm 2.55	0.61 \pm 0.01
isopropylbenzene	98-82-8	37.39 \pm 4.29	0.23 \pm 0.03
α -pinene	80-56-8	ND	ND
<i>n</i> -propylbenzene	103-65-1	26.76 \pm 2.15	0.16 \pm 0.01
<i>m</i> -ethyltoluene	620-14-4	74.33 \pm 4.94	0.45 \pm 0.03
<i>p</i> -ethyltoluene	622-96-8	43.01 \pm 5.69	0.26 \pm 0.03
1,3,5-trimethylbenzene	108-67-8	126.13 \pm 3.11	0.77 \pm 0.02
<i>o</i> -ethyltoluene	611-14-3	95.13 \pm 3.33	0.58 \pm 0.02
β -pinene	127-91-3	114.44 \pm 2.25	0.70 \pm 0.01
1,2,4-trimethylbenzene	95-63-6	174.56 \pm 3.11	1.06 \pm 0.02
1-decene	872-05-9	ND	ND
<i>n</i> -decane	124-18-5	66.13 \pm 2.36	0.40 \pm 0.01
1,2,3-trimethylbenzene	526-73-8	78.99 \pm 2.58	0.48 \pm 0.02
<i>m</i> -diethylbenzene	141-93-5	78.03 \pm 1.40	0.48 \pm 0.01
<i>p</i> -diethylbenzene	105-05-5	67.62 \pm 1.61	0.41 \pm 0.01
1-undecene	821-95-4	ND	ND
<i>n</i> -undecane	1120-21-4	150.48 \pm 2.04	0.92 \pm 0.01
1-dodecene	112-41-4	93.63 \pm 4.51	0.57 \pm 0.03
<i>n</i> -dodecane	112-40-3	3950.78 \pm 4.62	24.05 \pm 0.03
1-tridecene	2437-56-1	ND	ND
<i>n</i> -tridecane	629-50-5	93.63 \pm 4.62	0.57 \pm 0.03
Total Speciated SNMOC			29.48 $\mu\text{g}/\text{m}^3$
Total Unspeciated SNMOC			ND
Total Speciated + Unspeciated SNMOC			29.48 $\mu\text{g}/\text{m}^3$
Mass Emission Rate of Speciated Nonmethane Organic Compounds			0.30 $\mu\text{g}/\text{kg}$ fuel
Mass Emission Rate of Total (Speciated + Unspeciated) Nonmethane Organic Compounds			0.30* $\mu\text{g}/\text{kg}$ fuel

* More unspeciated NMOC was found in dilution air than in residence chamber samples. Unspeciated analysis was determined invalid and not used in this calculation due to an unidentified contaminant.

Table 5-8C. SNMOC (Campaign #1, January 18, 2001)

Compound	CAS No.	Residence Chamber Minus Dilution Air (μg)	% Total
ethylene	4-84-0	418.90 \pm 13.35	1.37 \pm 0.04
acetylene	74-86-2	222.76 \pm 12.32	0.73 \pm 0.04
ethane	74-85-1	ND	ND
propylene	115-07-1	268.93 \pm 7.07	0.88 \pm 0.02
propane	74-98-6	23162.61 \pm 12.55	75.68 \pm 0.04
propyne	74-99-7	ND	ND
isobutane	75-28-5	ND	ND
isobutene/1-butene	115-11-7/106-98-0	48.57 \pm 4.11	0.16 \pm 0.01
1,3-butadiene	106-99-0	ND	ND
<i>n</i> -butane	106-97-8	ND	ND
<i>trans</i> -2-butene	624-64-6	1.14 \pm 7.42	0.00 ^a \pm 0.02
<i>cis</i> -2-butene	590-18-1	ND	ND
3-methyl-1-butene	563-45-1	ND	ND
isopentane	78-78-4	ND	ND
1-pentene	109-67-1	11.24 \pm 9.24	0.04 \pm 0.03
2-methyl-1-butene	563-46-2	ND	ND
<i>n</i> -pentane	109-66-0	1.83 \pm 11.52	0.01 \pm 0.04
isoprene	78-79-4	ND	ND
<i>trans</i> -2-pentene	646-04-8	6.13 \pm 9.36	0.02 \pm 0.03
<i>cis</i> -2-pentene	627-20-3	ND	ND
2-methyl-2-butene	513-35-9	ND	ND
2,2-dimethylbutane	75-83-2	12.38 \pm 16.89	0.04 \pm 0.06
cyclopentene	142-29-0	16.57 \pm 15.97	0.05 \pm 0.05
4-methyl-1-pentene	691-37-2	ND	ND
cyclopentane	287-92-3	6.13 \pm 7.87	0.02 \pm 0.03
2,3-dimethylbutane	79-29-8	7.27 \pm 19.51	0.02 \pm 0.06
2-methylpentane	107-83-5	612.16 \pm 9.01	2.00 \pm 0.03

Table 5-8C. (Continued)

Compound	CAS No.	Residence Chamber Minus Dilution Air (μg)	% Total
3-methylpentane	96-14-0	33.48 \pm 17.22	0.11 \pm 0.06
2-methyl-1-pentene	763-29-1	ND	ND
1-hexene	592-41-6	2.17 \pm 17.46	0.01 \pm 0.06
2-ethyl-1-butene	760-21-4	ND	ND
<i>n</i> -hexane	110-54-3	362.46 \pm 13.23	1.18 \pm 0.04
<i>trans</i> -2-hexene	4050-45-7	ND	ND
<i>cis</i> -2-hexene	7688-21-3	ND	ND
methylcyclopentane	96-37-7	75.13 \pm 10.95	0.25 \pm 0.04
2,4-dimethylpentane	108-08-7	1.14 \pm 13.69	0.00 \pm 0.04
benzene	71-43-2	33.03 \pm 8.67	0.11 \pm 0.03
cyclohexane	110-82-7	1.48 \pm 19.40	0.00 \pm 0.06
2-methylhexane	591-76-4	0.91 \pm 2.28	0.00 \pm 0.01
2,3-dimethylpentane	565-59-3	ND	ND
3-methylhexane	589-34-4	ND	ND
1-heptene	592-76-7	41.76 \pm 9.47	0.13 \pm 0.03
2,2,4-trimethylpentane	540-84-1	6.70 \pm 11.52	0.02 \pm 0.04
<i>n</i> -heptane	142-82-5	22.13 \pm 5.82	0.07 \pm 0.02
methylcyclohexane	108-87-2	11.47 \pm 11.07	0.04 \pm 0.04
2,2,3-trimethylpentane	564-02-3	ND	ND
2,3,4-trimethylpentane	565-75-3	1.14 \pm 7.99	0.00 \pm 0.03
toluene	108-88-3	ND	ND
2-methylheptane	592-27-8	ND	ND
3-methylheptane	589-81-1	ND	ND
1-octene	111-66-0	ND	ND
<i>n</i> -octane	111-65-9	43.81 \pm 2.28	0.14 \pm 0.01
ethylbenzene	100-41-4	ND	ND
<i>m</i> -xylene/ <i>p</i> -xylene	108-38-3/106-42-3	ND	ND

Table 5-8C. (Continued)

Compound	CAS No.	Residence Chamber Minus Dilution Air (μg)	% Total
styrene	100-42-5	58.44 \pm 7.87	0.19 \pm 0.03
<i>o</i> -xylene	95-47-6	12.26 \pm 3.08	0.04 \pm 0.01
1-nonene	124-11-8	0.91 \pm 2.40	0.00 \pm 0.01
<i>n</i> -nonane	111-84-2	32.69 \pm 2.40	0.11 \pm 0.01
isopropylbenzene	98-82-8	1.03 \pm 4.56	0.00 \pm 0.01
α -pinene	80-56-8	ND	ND
<i>n</i> -propylbenzene	103-65-1	ND	ND
<i>m</i> -ethyltoluene	620-14-4	ND	ND
<i>p</i> -ethyltoluene	622-96-8	1.14 \pm 6.04	0.00 \pm 0.02
1,3,5-trimethylbenzene	108-67-8	42.44 \pm 3.31	0.14 \pm 0.01
<i>o</i> -ethyltoluene	611-14-3	21.68 \pm 3.54	0.07 \pm 0.01
β -pinene	127-91-3	104.39 \pm 2.40	0.34 \pm 0.01
1,2,4-trimethylbenzene	95-63-6	44.27 \pm 3.31	0.14 \pm 0.01
1-decene	872-05-9	ND	ND
<i>n</i> -decane	124-18-5	56.19 \pm 2.51	0.18 \pm 0.01
1,2,3-trimethylbenzene	526-73-8	ND	ND
<i>m</i> -diethylbenzene	141-93-5	52.19 \pm 1.48	0.17 \pm 0.00
<i>p</i> -diethylbenzene	105-05-5	36.54 \pm 1.71	0.12 \pm 0.01
1-undecene	821-95-4	ND	ND
<i>n</i> -undecane	1120-21-4	71.16 \pm 2.17	0.23 \pm 0.01
1-dodecene	112-41-4	78.29 \pm 4.79	0.26 \pm 0.02
<i>n</i> -dodecane	112-40-3	2067.01 \pm 4.90	6.75 \pm 0.02
1-tridecene	2437-56-1	ND	ND
<i>n</i> -tridecane	629-50-5	93.95 \pm 4.90	0.31 \pm 0.02
Total Speciated SNMOC			48.28 $\mu\text{g}/\text{m}^3$
Total Unspeciated SNMOC			4.41 $\mu\text{g}/\text{m}^3$
Total Speciated + Unspeciated SNMOC			52.69 $\mu\text{g}/\text{m}^3$
Mass Emission Rate of Speciated Nonmethane Organic Compounds			0.50 mg/kg fuel
Mass Emission Rate of Total (Speciated + Unspeciated) Nonmethane Organic Compounds			0.55 mg/kg fuel

^aCalculated value less than 0.00.

Table 5-9. Total Mass of Nonmethane Organic Compounds for Each Campaign #1 Test Day

	Mass of Fuel Consumed (kg)	Speciated	Unspeciated	Speciated + Unspeciated
January 16, 2001	6,569	1617 mg	163 mg	1780 mg
Emission Rate		0.25 mg/kg fuel		0.27 mg/kg fuel
January 17, 2001	6,934	2085 mg	0 ^a	2085 mg
Emission Rate		0.23 mg/kg fuel		0.28 mg/kg fuel
January 18, 2001	7,926	3961 mg	361 mg	4322 mg
Emission Rate		0.50 mg/kg fuel		0.55 mg/kg fuel

^aWeight of unspeciated NMOC in dilution air was higher than the weight of unspeciated NMOC in the residence chamber air for January 17, 2001.

parallel the results for the carbonyl compounds. Weight % for each analyte was calculated by dividing the value of that analyte by the total speciated plus unspeciated NMOC value. The analytical uncertainty was calculated using the standard deviation of the replicate determinations performed in the determination of the method detection limits. Both the “Total” and “Speciated” NMOC values are calculated on the basis of subtraction of analyte in the dilution air (DA) from the analyte collected in the residence chamber (RC) air. Because the EPA dilution sampling system was operated at a dilution factor of approximately 40 for both campaign #1 and campaign #2, dilution air in 40-fold excess is present in the final sample. In some instances, when the sum of the speciated (or unspeciated) analytes in the dilution air is subtracted from the sum of the speciated (or unspeciated) analytes from the residence chamber, a negative value is obtained. The total value is obtained by adding the sum of the values for the residence chamber minus dilution air for speciated analytes to the sum of unspeciated analytes for the residence chamber minus dilution air. If the (RC-DA) difference is negative, the value for Total NMOC is less than the value for speciated NMOC (as in data from January 16, 2001 and January 17, 2001). Complete NMOC calculations are shown in Appendix G for each day; NMOC emission factor calculations are shown in Appendix B. Note that on January 16, 2001, the mass of analyte in total combustion air for speciated NMOC is 0.025004 µg; for speciated and unspeciated NMOC the value is 0.020531 µg. The total emission factor is therefore less than the speciated emission factor.

The mass of total speciated NMOC results and the total speciated plus unspeciated results have been used to calculate the mass emission rates for SNMOC as well as speciated plus unspeciated NMOC (Table 5-9). Samples taken from the residence chamber were corrected for the SNMOC observed in the dilution air to determine the total SNMOC collected. These values were used to calculate a mass emission rate for SNMOC and speciated plus unspeciated NMOC for each test day. The supporting calculations are shown in Appendix G.

The profile of the concentrations for the SNMOC differs from the profile of the concentrations for the carbonyl compounds. Both speciated and total carbonyl compounds show a decreasing trend over the three test days, while the concentration of the unspeciated carbonyl compounds increases on the third test day. For all SNMOC (speciated, unspeciated, and speciated plus unspeciated), concentrations drop on the second test day and reach their highest level on the third test day. During these compound concentration changes, fuel consumption is increasing on each test day, as shown in Table 5-9.

Particle Size Distribution Data

The SMPS system was operated on all three test days of campaign #1, collecting data on particle size distribution in the range below 2.5 μm (the range monitored was 10 nm to 392 nm), with one complete scan over the entire range every three minutes. The analytical data are presented in Table 5-10 and are presented graphically as a plot of midpoint diameter of the particles vs counts (an indirect version of number of particles in each size range) or as midpoint diameter in nanometers vs number of particles (Figures 5-1 through 5-3).

Table 5-10. Particle Size Diameter Measurements, TSI SMPS (Campaign #1, January 16-18, 2001)

Particle Size Range (10 - 392 nm)

Channel Range (32 - 83)

Channels per decade: 32

Weighted by number

Units: Counts

Channel	Sample Time Midpoint Diameter (nm)	Average Values for All Scans		
		Counts (1/16/01)	Counts (1/17/01)	Counts (1/18/01)
1	10.3663	101.6	96083.3	117694.3
2	11.1397	75.2	156779.5	201348.7
3	11.9709	80.3	245424.3	314480.1
4	12.8640	110.8	355450.4	466870.4
5	13.8237	80.9	484897.1	659765.6
6	14.8551	74.1	647382.2	885842.2
7	15.9634	60.4	841926	1155580
8	17.1544	505	1047940	1451086
9	18.4342	448.8	1247522	1743655
10	19.8096	271.7	1420894	2000971
11	21.2875	259.1	1547679	2221012
12	22.8757	248.2	1593648	2358421
13	24.5824	324.9	1541539	2391306
14	26.4165	492.6	1401504	2292371
15	28.3874	650.5	1188134	2066818
16	30.5053	689.8	924710.5	1748867
17	32.7812	498.1	654602	1364195
18	35.2269	362	411559.7	978867
19	37.8552	337.5	227993.9	638168.4
20	40.6794	337.7	109850.2	372354.5
21	43.7144	341.7	45115.7	193396.2

Table 5-10. (Continued)

Channel	Sample Time	Counts	Counts	Counts
	Midpoint Diameter (nm)	(1/16/01)	(1/17/01)	(1/18/01)
22	46.9759	338.1	16148	89624.2
23	50.4087	279	5514.5	40419.2
24	54.2469	290.8	2282.8	21423.4
25	58.2942	250	2159.4	16296.9
26	62.6434	250.8	1231	15712.8
27	67.317	216.1	1053.1	15653.5
30	83.5363	210.7	822.6	17714.2
31	89.7687	199.5	2625.5	18073.2
32	96.4662	232.2	2181.4	18423.3
33	103.663	206.1	1297	18337.5
34	111.397	185.4	1258.3	18547.1
35	119.709	219.8	952.2	18312.1
36	128.64	167.1	884.4	17837.9
37	138.237	169.2	914.1	17157.6
38	148.551	154.8	785.7	16610.4
39	159.634	164.5	724.8	15352.5
40	171.544	162.6	668.5	14226.8
41	184.342	127.4	649.4	12581.4
42	198.096	146.3	614	11571.9
43	212.875	131.3	761.2	10084.2
44	228.757	121.1	592.7	8847.7
45	245.824	130.8	3130.4	7273.6
46	264.165	148.5	2964.6	6256.8
47	283.874	101.6	765.9	5033.7
48	305.053	94.6	501.2	4185.9
49	327.812	107.2	454.4	3394.8
50	352.269	91.5	458.9	2734.5
51	378.552	109.9	452.7	2189.1

1-16-01

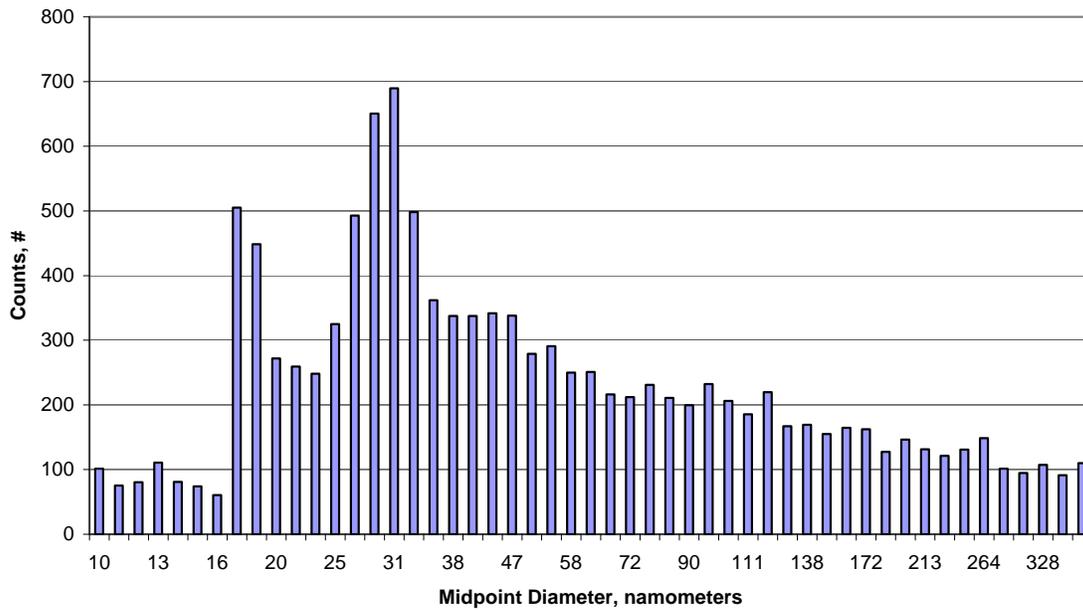


Figure 5-1. Graphical presentation of particle size data, SMPS (January 16, 2001).

1-17-01

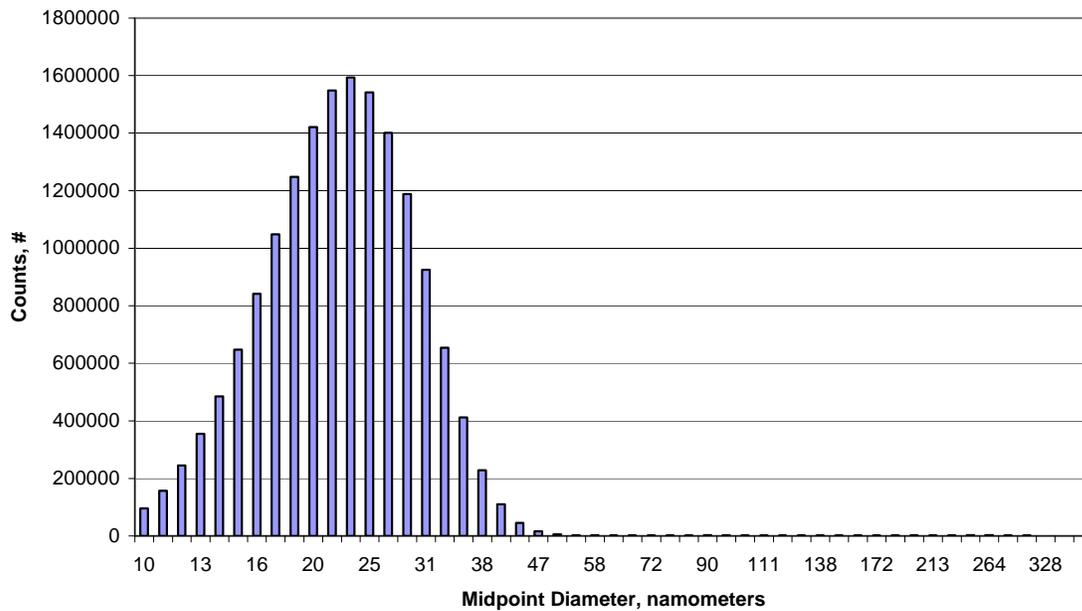


Figure 5-2. Graphical presentation of particle size data, SMPS (January 17, 2001).

The profile observed on Day 1 (January 16, 2001) appears to be an outlier with respect to

1-18-01

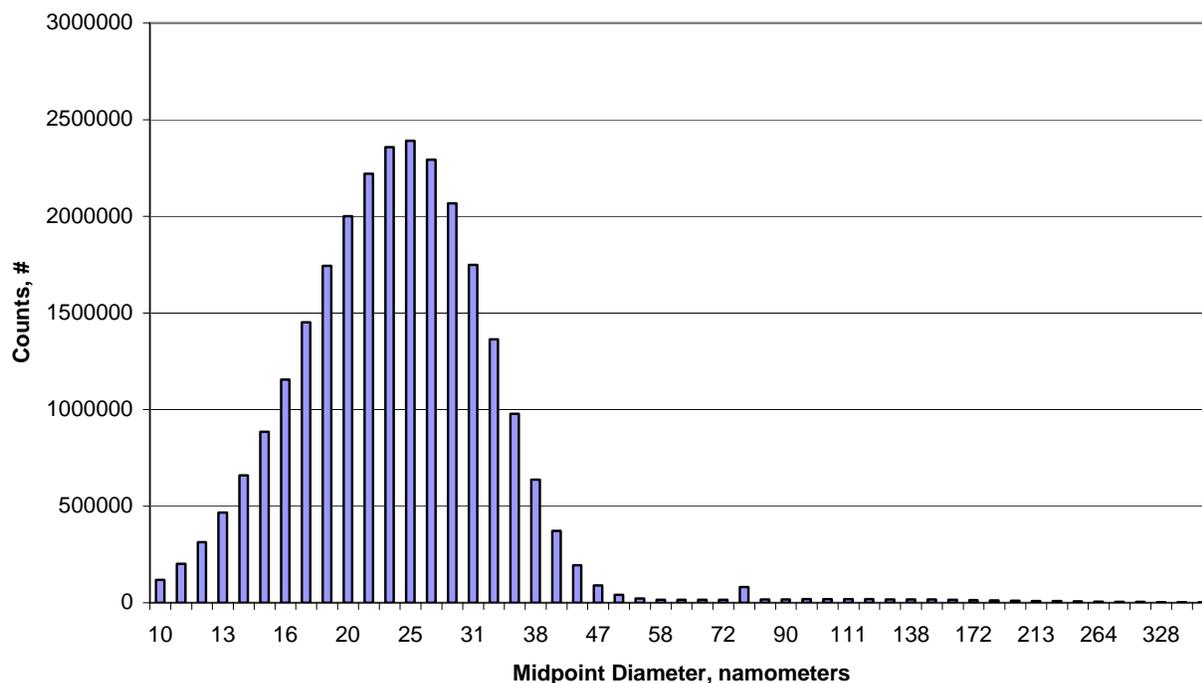


Figure 5-3. Graphical presentation of particle size data, SMPS (January 18, 2001).

the other two test days: the shape of the plot is very different from the plots obtained on the other two days, and the number of counts observed in each channel is approximately four orders of magnitude lower on Day 1 than on the other two test days. The SMPS instrumental operating parameters appeared to be normal and there was no obvious indication of instrumental malfunction. There is not an obvious explanation for the outstandingly low signal level on Day 1. On Day 2 (January 17, 2001) and Day 3 (January 18, 2001), the shapes of the profiles appear to be qualitatively similar. However, the signal maximum on Day 2 is observed at approximately 1.6×10^6 counts, at a midpoint diameter of 23 nm. On Day 3, the signal maximum occurs at approximately 2.4×10^6 counts (50% higher than the signal level on Day 2), at a slightly larger midpoint diameter (approximately 25 nm).

During campaign #2, particle size data were collected using an Electrical Low Pressure Impactor (ELPI). The particle size distribution was bimodal. The greatest amount of mass was found on the second stage, but it is not clear where the peak of the actual mode is located, given the data collected. ELPI data are shown in Table 5-11 and graphically in Figures 5-4, 5-5, and 5-6. The three-day average is shown graphically in Figure 5-7. Note that the SMPS gives an electrical mobility diameter and the ELPI gives an aerodynamic diameter, so the two values should not necessarily agree.

Table 5-11. Gravimetric Data, ELPI (Campaign #2, July 9-11, 2002) PM-2.5 Mass Concentration by Size

Stage	D50 (nm)	Di (nm)	Stage Mass Concentration (mg/m ³)			Mean
			7/9/02	7/10/02	7/11/02	
1	30.0	42.78	0.0061	0.0028	0.0172	0.0087
2	61.0	80.03	0.0064	0.0042	0.0316	0.0140
3	105.0	132.82	0.0040	0.0017	0.0120	0.0059
7	645.0	803.12	0.0007	0.0010	0.0005	0.0008
8	1000.0	1276.71	0.0003	0.0007	0.0007	0.0006
9	1630.0	2010.57	0.0036	0.0014	0.0010	0.0020
10	2480.0	3157.47	0.0023	0.0000	0.0002	0.0008
11	4020.0	5212.98	0.0017	0.0007	0.0000	0.0008
12	6760.0	8328.12	0.0017	0.0012	0.0002	0.0010
13	10260.0		0.0000	0.0007	0.0002	0.0003
Total Mass Concentration (mg/m³)			0.0331	0.0170	0.0741	0.0414

Stage mass concentration (Test 7/9/02)

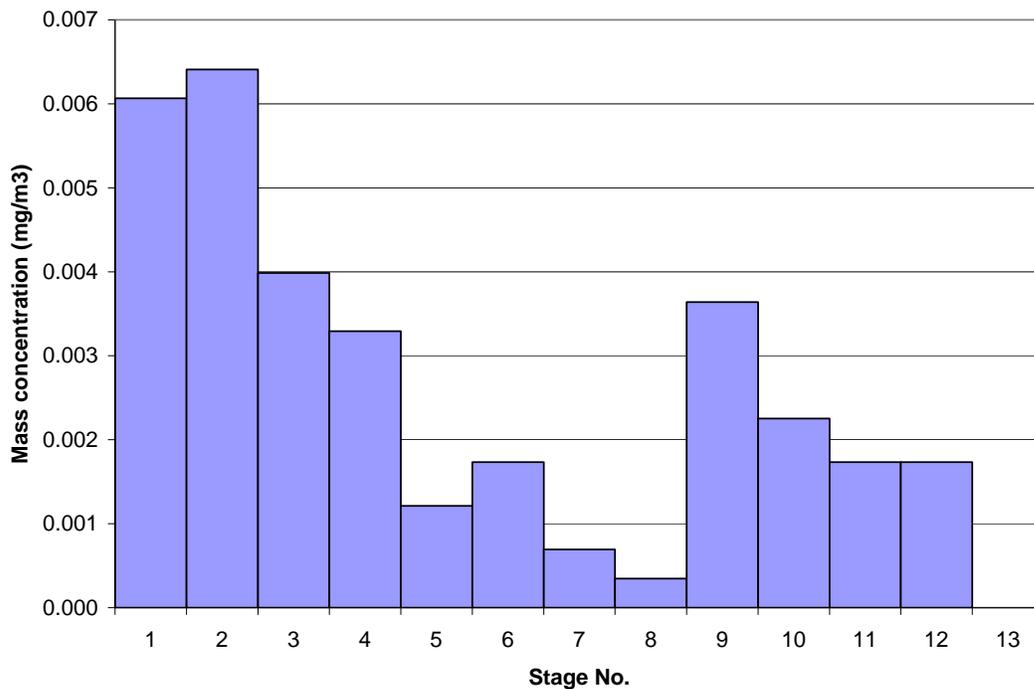


Figure 5-4. ELPI Mass Concentration by Stage (July 9, 2002)

Stage mass concentration (Test 7/10/02)

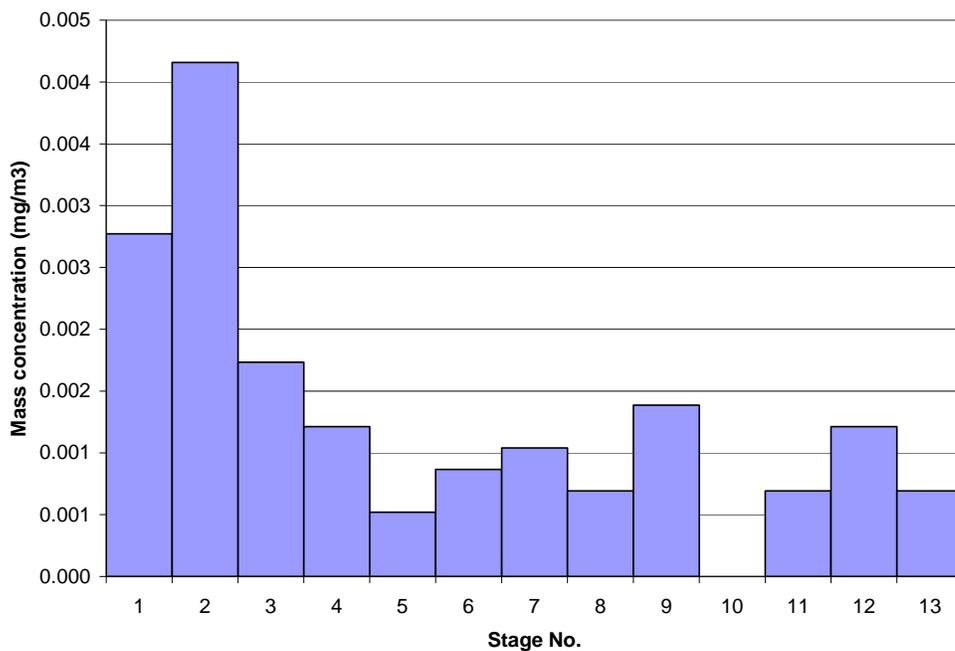


Figure 5-5. ELPI Mass Concentration by Stage (July 10, 2002)

Stage mass concentration (Test 7/11/02)

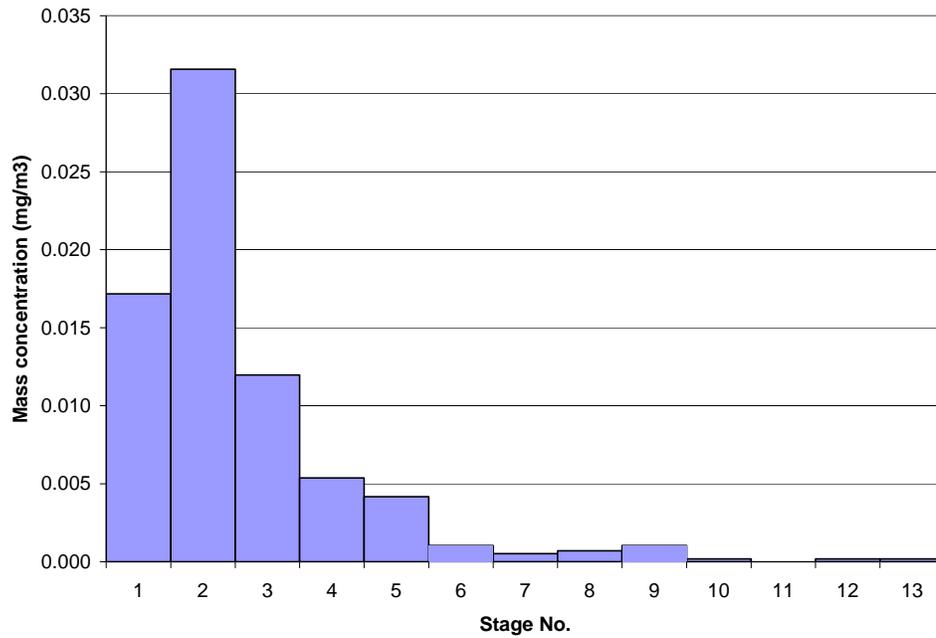


Figure 5-6. ELPI Mass Concentration by Stage (July 11, 2002)

Stage mass concentration (Three-Day Average)

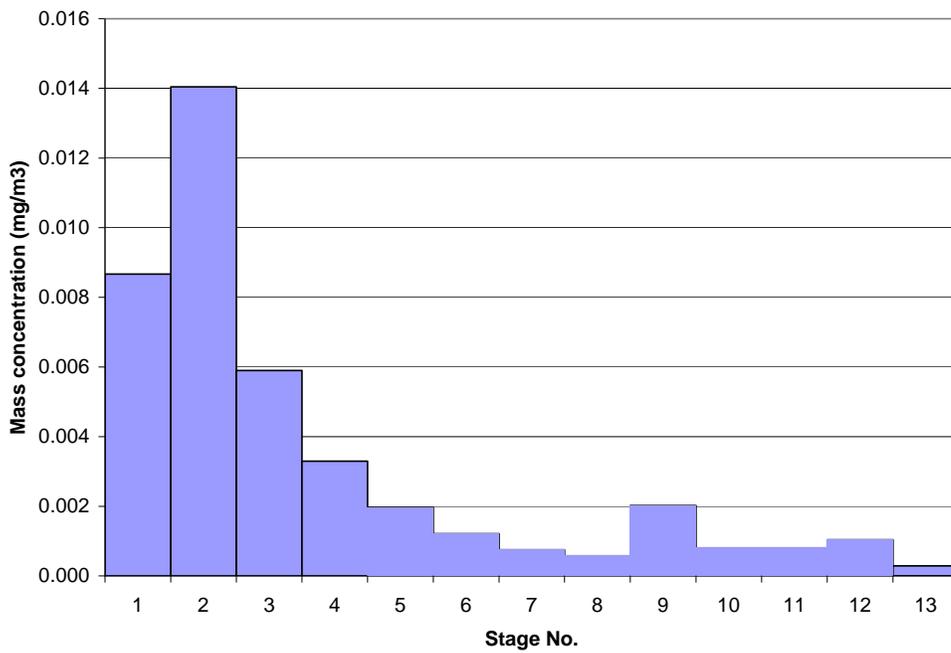


Figure 5-7. ELPI Mass Concentration by Stage (Three-Day Average)

Section 6

Quality Assurance/Quality Control

A detailed description of the objectives and activities of the institutional oil-fired boiler tests is presented in Sections 3 and 4 of this report. Separate quality assurance project plans for the source sampling and PM-2.5 sample analyses were developed for each of the two testing campaigns (i.e., QTRAX numbers 99051¹⁵ and 99002¹⁶) and were approved by EPA/NRMRL. The testing that was conducted adhered to the specifications of these two QAPPS. QA procedures for the analyses of gaseous nonmethane organic compounds and air toxics were followed as prescribed by EPA Compendium Method TO-15¹². Analyses of the gaseous carbonyl compounds adhered to the QA procedures of EPA Compendium Method TO-11A¹¹.

A summary of the quality control measures, acceptance criteria, and whether these criteria were achieved is provided in Tables 6-1 through 6-7 for source sampling activities, concurrent speciated NMOC/air toxics analyses, carbonyl analyses, PM mass measurement, PM elemental analysis, PM inorganic ion analysis, and semivolatile organic compound analysis, respectively.

Sampling and analytical procedures for critical measurements are presented in Section 4. In field sampling with the dilution sampling system, the following quality control procedures were implemented:

- A leak check of the dilution sampling system was performed before field testing was initiated;
- Pitot tubes and meter boxes were calibrated;
- The 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.

Table 6-1. Sample Collection Equipment: Quality Criteria

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 6-2. Carbonyl Analysis: Quality Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
HPLC Column Efficiency	Analyze SSQC	At setup and one 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 $\pm 20\%$ or less Relative Error	Check integration, re-integrate or re-calibrate	Yes
Retention time	Analyze calibration midpoint	Once per 10 samples	Intercept acceptance should be $\leq 10,000$ area counts/compound; correlates to 0.06 mg/mL Acetaldehyde, Benzaldehyde, Hexaldehyde within retention time window established by determining 3σ 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
Calibration Check	Analyze midpoint standard	Once per 10 samples	85-115% recovery	Check integration, re-calibrate or re-prepare standard, re-analyze samples not bracketed by acceptable standard	Yes Yes
Calibration Accuracy	SSQC	Once after calibration in triplicate	85-115% recovery	Check integration; re-calibrate or re-prepare standard, re-analyze samples not bracketed by acceptable standard	Yes
	Analyze 0.1 $\mu\text{g/mL}$ standard	Once after calibration in triplicate	$\pm 25\%$ difference	Check integration; re-calibrate or re-prepare standard, re-analyze samples not bracketed by acceptable standard	Yes

Table 6-2. (Continued)

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

HPLC = High Performance Liquid Chromatography
 SSQC = Second Source Quality Control
 MDL = Method Detection Limit
 RPD = Relative Percent Difference
 MS/MSD = Method Spike/Method Spike Duplicate

Table 6-3. Air Toxics and SNMOC Analysis: Quality Criteria

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
Air Toxics Analysis				
BFB 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	Following any major change, repair, or maintenance if daily quality control check is not acceptable. Calibration is valid for six weeks if calibration check criteria are met.	RSD of response factors $\leq 30\%$ 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 mid-point of calibration range	Daily	Response factor $\leq 30\%$ 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 IS area response $\pm 40\%$ and ± 0.33 min of most recent calibration check	Repeat analysis with new blank; check system for leaks, contamination; re-analyze blank.	Yes
LCS	Daily	Recovery limits 70% - 130% IS RT ± 0.33 min of most recent calibration	Repeat analysis; repeat calibration curve.	Yes
Replicate Analysis	All duplicate field samples	$< 30\%$ RPD for compounds $> 5 \times \text{MDL}$	Repeat sample analysis	Yes
Samples	All samples	IS RT ± 0.33 min of most recent calibration	Repeat analysis	Yes
SNMOC Analysis				Yes
System Blank Analysis	Daily, following calibration check	20 ppbC total	Repeat analysis; check system for leaks; clean system with wet air	Yes

Table 6-3. (Continued)

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
Multiple point calibration (minimum 5); propane bracketing the expected sample concentration range	Prior to analysis and monthly	Correlation coefficient (r^2) ≥ 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 $\pm 30\%$ difference of calibration curve slope	Repeat calibration check; repeat calibration curve.	Yes
Replicate analysis	All duplicate field samples	Total NMOC within $\pm 30\%$ RSD	Repeat sample analysis	Yes

BFB = 1,4-Bromofluorobenzene
RSD = Relative Standard Deviation
RRT = Relative Retention Time
MDL = Method Detection Limit¹⁴
IS = Internal Standard
LCS = Laboratory Control Standard
RPD = Relative Percent Difference

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Table 6-4. PM Mass Measurements: Quality Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
Deposition on Filter during Conditioning	Analyze Laboratory Filter Blank	Bracket sample batch, one at beginning and one at end	Mass within ± 15 mg of previous weight	Adjust mass for deposition	Yes
Laboratory Stability	Analyze Laboratory Control Filter	Bracket sample batch, one at beginning and one 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, one at beginning and one at end	Mass within ± 3 mg of previous weight	Perform internal calibration of balance, perform external calibration of balance	Yes

Table 6-5. Elemental Analysis: Quality Criteria

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

Table 6-6. Water-Soluble Ion Analysis: Quality Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
Linearity Check	Analyze 4-point calibration curve	At setup or when calibration check does not meet acceptance criteria	Correlation coefficient ≥ 0.999	Recalibrate	Yes
System Dead Volume	Analyze water	Bracket sample batch, one at beginning and one at end	Within 5% of previous analysis	Check system temperature, eluent, and columns	Yes
Retention Time	Analyze standard	At setup	Each ion within ± 5% of standard retention time	Check system temperature and eluent	Yes
Calibration check	Analyze one standard	Once every 4-10 samples	85-115% recovery	Recalibrate or re-prepare standard, re-analyze sample not bracketed by acceptable standard	Yes
System Blank	Analyze HPLC grade water	Bracket sample batch, one at beginning and one at end	No quantifiable ions	Re-analyze	Yes
Duplicate analyses	Duplicate Samples	As collected			Yes Yes

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Table 6-6. (Continued)

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
Replicate Analyses	Replicate Injections	Each sample	≤ 10% RPD for concentrations greater than 1.0mg/L	Check instrument function, re-analyze samples	Yes

HPLC = High Performance Liquid Chromatography
 RPD = Relative Percent Difference

Table 6-7. Semivolatile Organic Compounds Analysis: Quality Criteria

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
Mass spectrometer instrument tune check (FC-43)	Daily prior to calibration check	Mass assignments m/z = 69, 219, 502 (± 0.2) Peak widths = 0.59-0.65 Relative mass abundances = 100 % (69); ≥30 % (219); ≥ 1% (502).	Retune mass spectrometer; clean ion source	Yes
Five-point calibration bracketing the expected concentration range	Following maintenance or repair of either gas chromatograph or mass spectrometer or when daily quality control check is not acceptable	Correlation coefficient of either quadratic or linear regression ≥ 0.999	Check integration, re-integrate 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 ≤ detection limit values	Repeat analysis; check system integrity. Reanalyze blank	Yes
Retention time check	Daily	Verify that select compounds are within ±2% of established retention time window	Check inlet and column flows and the various GC/MS temperature zones	Yes

Field sampling equipment quality control requirements that were met in the course of preparing for the field test and execution of testing activities are summarized in Table 6-1.

For this testing program:

- No performance evaluation audits were performed for any of the analytical procedures for the NCA&T field tests. During the development phases of the EPA dilution sampling system and the associated analytical procedures, PE audits were conducted, but not on a test-specific basis.
- Collocated sample collection was not feasible as EPA owns only one dilution sampling system.
- Duplicate or replicate sample collection arrays for the measurement of particulate matter were collected on each of the three test runs for each campaign (see Figure 4-11). However, comparison of individual samples was not achievable because of the need to composite samples to aggregate sufficient quantities of material to perform analytical procedures. There were not sufficient sample collection ports or physical space on the EPA Dilution Sampling System to accommodate duplicate collection of air toxics or carbonyl samples.
- The primary function of testing with the dilution sampling system was collection of PM for determination of mass collected. There is no commercial source of PM standards spiked on filters and there is presently no accepted procedure for the preparation of spiked PM filters.
- TO-15 samples were collected for informational purposes only and the TO-15 results were not used in any calculations of emission factors. A field blank was collected for the TO-15 samples for campaign #1 as presented in the sample chain of custody (COC) forms (see Appendix E). TO-15 sampling/analysis was not performed for campaign #2. Data for the field blanks are presented in Appendix H [Supporting Data for Air Toxics Analysis]; field blanks for TO-15 are erroneously labeled as “Laboratory Blanks”. These samples are clearly identified.
- A field blank was collected for the TO-11A samples for campaign #1 as presented in the sample chain of custody (COC) forms (see Appendix E). TO-11A sampling/analysis was not performed for campaign #2. Data for the field blanks are presented in Appendix I [Supporting Data for Carbonyl Analysis]; field blanks for TO-11A are erroneously labeled as “Laboratory Blanks”. These samples are clearly identified.

The inability to conduct robust sampling QC affects the ability to calculate analytical uncertainties associated with the analysis of individual samples. As a result, uncertainties associated with individual emission factors for individual test days were calculated by the EPA

Work Assignment Manager and reported. It is recommended that procedures for conducting robust sampling QC be developed for future field testing.

Strict chain of custody procedures were followed in collecting and transporting samples and sampling media to and from the field sampling location. Sample substrates (filters, denuders, PUF canister, DNPH cartridges) were prepared in advance in accordance with the number and types of samples designated in the sampling matrix of the approved field test plan. Clean SUMMA collection canisters and DNPH cartridges used to collect carbonyl compounds were prepared and supplied by ERG. The PUF, XAD-4, denuder, and PM-2.5 sampling substrates were prepared and supplied by EPA. Chain of custody forms (Figure 6-1) 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 E.

Sample identification numbers include a code to track:

- Source type;
- Test date;
- 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 sampling 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 analyses.

Carbonyl Compound Analysis

Quality control criteria for the carbonyl analysis performed by ERG are shown in Table 6-2. Supporting analytical calibration and quality control data are a part of the project file at ERG.

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 quality control standard is analyzed daily prior to sample analysis to ensure the validity of the current monthly response factor. Following the daily quality control 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. Quality control procedures for the air toxics and SNMOC analyses are summarized in Table 6-3; supporting analytical calibration and quality control data are a part of the project file at ERG.

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

Quality control criteria for EPA analyses (PM mass, elemental analyses, ion chromatography analysis, and GC/MS analysis are summarized in Tables 6-4 through 6-7; supporting data are included in the project file in the EPA laboratory.

Sample collection completeness was 100% (i.e., all planned samples were collected for both campaign #1 and campaign #2). Most of the solvent extracts of the XAD-coated annular denuders, quartz filters, and PUF plugs from campaign #1 were subjected to analysis for semivolatile organic compounds. However, these results are not reported due to the observation that breakthrough of the sampling substrates had occurred, thus rendering reliable quantitative measurements impossible. For campaign #2, 99% of the samples were analyzed. Of the samples not analyzed, two were quartz which were archived and two were PUF extracts which were misplaced at the EPA laboratory.

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