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Research and Development

SOURCE SAMPLING

FINE PARTICULATE MATTER:

WOOD-FIRED INDUSTRIAL BOILER

Prepared for

Office of Air Quality Planing and Standards

Prepared by

National Risk Management
Research Laboratory
Research Triangle Park, NC 27711

Foreword

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

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E. Timothy Oppelt, Director
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EPA REVIEW NOTICE

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Wood-Fired Industrial Boiler

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Abstract

Fine particulate matter of aerodynamic diameter 2.5 μm or less (PM-2.5) has been implicated in adverse health effects, and a National Ambient Air Quality Standard for PM-2.5 has been promulgated (July 1997) by the U. S. Environmental Protection Agency. A national network of ambient monitoring stations has been established to assist states in determining areas which do not meet the ambient standard for PM-2.5. For such areas, it is important to determine the major sources of the PM-2.5 so states can devise and institute a control strategy to attain the ambient concentrations set by the standard.

One of the tools often used by states in apportioning ambient PM-2.5 to the sources is a source-receptor model. Such a model requires a knowledge of the PM-2.5 chemical composition emitted from each of the major sources contributing to the ambient PM-2.5 as well as the chemical composition of the PM-2.5 collected at the receptor (ambient monitoring) sites. This report provides such a profile for a wood-fired industrial boiler equipped with a multistage electrostatic precipitator control device. Along with the PM-2.5 emission profile, data are also provided for gas-phase emissions of several organic compounds. Data are provided in a format suitable for inclusion in the EPA source profile database, SPECIATE.

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Section 1
Introduction

In July, 1997, the U. S. Environmental Protection Agency (EPA) promulgated a new National Ambient Air Quality Standard (NAAQS) for ambient particulate matter (PM) of aerodynamic diameter 2.5 µm or less (PM-2.5) and revised the existing standard for ambient particles of aerodynamic diameter 10 µm or less (PM-10). The first steps in implementation of the new standard have been to deploy a network of ambient monitors and to collect the three years of data required for designation of areas as nonattainment or attainment of the new standard. This period also will give EPA time to review newer research on the observed correlation between ambient fine particulate matter and adverse human health effects.

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 non-attainment areas and to develop State Implementation Plans (SIPs) to bring those areas into compliance with the law for PM-2.5 and revised PM-10 regulations. One component of the monitoring network will be a few (4-7) "Supersites:" i.e., regional airsheds in which intensive coordinated particulate matter-related research will be carried out in order to attain a better understanding of the links between source emissions and actual human dosages of fine particulate matter.

To support development of this better understanding, the Emissions Characterization and Prevention Branch (ECPB) of the Air Pollution Prevention and Control Division (APPCD) oversees research to characterize PM-2.5 emissions from specific source categories, develops chemical profiles of fine PM constituents from specific sources, and populates the OAQPS SPECIATE database with improved source profiles. Profiles in SPECIATE are used by receptor

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modelers nationwide to conduct modeling analyses to identify specific sources of fine PM found in ambient air by the national network of ambient monitoring stations.

Previous development of source signatures at EPA have focused on analysis of elemental constituents which are usually condensed at stack sampling temperatures. To add improved analytical power to source signatures, ECPB and others are analyzing organic and elemental constituents. Due to very significant shifts in organic gas/particle phase partitioning as a function of temperature, there are large differences between profiles acquired by analysis of raw stack gas samples at stack temperature and those acquired by dilution sampling. Use of a dilution sampler cools the sample and provides additional residence time for developing a stable partitioning of semivolatile species at near-ambient temperatures. The dilution sampler gas/particle phase partitioning provides samples more representative of the fine PM collected by monitoring stations at ambient temperature, especially for the organic components.

This project focuses on updating and improving source emission profiles and emission rates for PM-2.5 with the dual aim of improving the quality of data used for dispersion and receptor modeling of ambient PM-2.5 and of providing quality emissions data for evaluation of risk management strategies. The program has concentrated its PM source sampling efforts on the sources and types of PM-2.5 where data are most lacking and needed, with a primary focus on the collection of fine particles emitted by combustion sources, both stationary and mobile.

Test Objectives

The mission of the ECPB is to characterize source emissions and develop and evaluate ways to prevent those emissions. Source characterization as defined here includes 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 NH_3.

PM mass emission rates are used in emission inventories and as inputs to atmospheric dispersion models which yield estimates of ambient PM concentrations via 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 which emitted the particles. The overall objective of this program is to update and improve source emission profiles and emission rates for PM-2.5 with the dual aim of improving the quality of data used for dispersion and receptor modeling of ambient PM-2.5 and of providing quality emissions data for evaluation of risk management strategies.

Source types for testing in this program were selected on the basis of the quantity of fine PM emitted by the source type as determined from 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, i.e., a wood-fired industrial boiler (Source Classification Code SCC 10200902) with the aim of acquiring a PM-2.5 emissions profile for source receptor modeling purposes.

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 2
Conclusions

Both gas- and particle-phase emissions from the wood-fired boiler were measured. Values reported are for the composition of gas and particulate matter emissions following cooling and dilution of the boiler stack gas rather than the in-stack exhaust gas composition and may therefore be considered representative of the emissions in the exhaust plume near the stack. Diluted source emissions reported in this way are more appropriate than in-stack data for source-receptor models used for apportioning pollutants in the ambient air to the sources of the pollutants.

Mass emission rates for Speciated Nonmethane Organic Compounds and Carbonyl Compounds are shown in Table 2-1. An explanation for the observed significant difference

Table 2-1. Mass Emission Rates for Nonmethane Organic Compounds and Carbonyl Compounds

Parameter	Mass Emission Rate mg/kg Fuel	
	Day #1	Day #2
Speciated Nonmethane Organic Compounds	4.83	0.98
Total Nonmethane Organic Compounds (Speciated + Unspeciated)	7.50	1.85
Speciated Carbonyl Compounds	2.53	0.80
Total Carbonyl Compounds (Speciated + Unspeciated)	2.74	0.94
PM-2.5 mass	3.54	1.23

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in emission rates of both gaseous and PM-2.5 emissions between the two test days could not be deduced with confidence. Both the boiler and sampling system operating parameters were essentially identical for both days. The only apparent variable which may have contributed to the difference was the nature of the chipped wood fuel itself since the fuel was selected from different locations in the large on-site wood chip storage pile during the two days of testing. However, only one composited wood waste sample from the storage pile was analyzed, so any significant differences in boiler feed between the two tests could not be determined.

Elemental and organic carbon content of the PM-2.5 collected on quartz filters was found to be highly dependent on whether an XAD-coated denuder was inserted in the sampling line prior to the filter. The purpose of the denuder was to remove gas-phase semivolatile organic compounds which otherwise might be adsorbed to the quartz filter, thereby resulting in a positive artifact to the particulate matter collected. Without the denuder, the amount of organic carbon found on the quartz filters was 2.6 times the amount found with the denuder, thus providing confirmatory evidence for a positive adsorption artifact. The relatively small amount of PM mass collected on these filters appears to render this adsorption artifact especially noticeable and the adsorbed gaseous organic compounds appear to be primarily responsible for a calculated mass balance of greater than 100 percent when the organic carbon value for the undenuded case is used.

Individual organic compounds comprising the organic carbon fraction of the PM-2.5 emissions consisted mostly of polynuclear aromatic hydrocarbons (PAHs), alkanes (>C15), alkanoic acids (>C8), and the iso- and anteiso-alkanes. Levoglucosan, a marker compound for biomass combustion, was found in the particulate matter but not in the relatively large amounts characteristic of open burning of biomass or wood stove combustion emissions. Resin acids (e.g., pimaric, isopimaric, and sandarapimaric acids) used as markers for softwood combustion and methoxyphenols used as markers for hardwood combustion were not found. Therefore, the organic compound emission profile for the wood-fired industrial boiler is very unlike profiles for residential wood-fired appliances (wood stoves and wood-burning fireplaces) and biomass open

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burning. This observation is not unexpected since the combustion regimes are very different for the two types of sources and since the boiler particulate matter emissions in this case were controlled by a multi-stage electrostatic precipitator whereas residential wood-fired appliance emissions are typically uncontrolled. From this one stationary source test, no unique markers for source apportionment were identified.

Residential wood-fired appliances operate at much lower temperatures compared to industrial boilers, and the combustion process for wood stoves and fireplaces entails repeated cycling from an initial kindling phase through a final smoldering phase over the course of normal operation. Operation of an industrial boiler such as the one studied here involves charging the fuel at a fairly constant rate, and the combustion can be thought of as occurring in two stages: an initial stage in which the wood is gasified under pyrolysis conditions and a second stage in which the pyrolysis gases are essentially completely combusted at high temperature in the presence of excess air.

Section 3

Methods and Materials

Description of the Testing Program

A field test was conducted (August 8-9, 2000) at a wood-fired industrial boiler
(SCC 10200902) equipped with an electrostatic precipitator control device, with quality control
procedures implemented to obtain source emissions measurements of 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 wood-fired industrial 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 a wood-fired boiler equipped with an
electrostatic precipitator. 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 Scanning Mobility Particle Sizer (SMPS). 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.

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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	Carbonyl compounds	High Performance Liquid Chromatography (HPLC) Method TO-11A	ERG
SUMMA® canisters	Air Toxics Speciated Nonmethane Organic Compounds	GC/MS Method TO-15 ERG Concurrent Analysis	ERG
Particle Size Analyzer	Particle Sizes	Ion mobility spectrometer	ERG

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:

- 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;

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- Acquired process data for the test periods, including temperatures, pressures, flows, fuel consumption, etc.;

- Collected two sets of stationary source samples as prescribed in the Site-Specific Test Plan, including one set of field blanks;

- Determined the type of combustion fuel (gross characterization of wood waste material and any auxiliary fuel) and the rate of consumption during the source tests; and

- Recovered the dilution sampling unit and sample collection trains for analysis for specific parameters and return of the dilution sampling unit to EPA.

ERG collected integrated samples and performed whole air analysis of volatile organic compounds from SUMMA®-polished stainless steel canisters and gas-phase carbonyl compounds from 2,4-dinitrophenylhydrazine (DNPH)-impregnated silica gel cartridges, as well as evaluation of particle size distribution data collected. EPA was responsible for cleaning and transport of the dilution sampling system to the test site, for analysis of semivolatile organic compounds from XAD-4® denuders and polyurethane foam (PUF) sampling modules, and for characterization of the particle 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 an original design by L. M. Hildemann (Hildemann et al., 1989), 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.

ECPB built a state-of-the-art dilution sampler to deploy in the performance of this field testing effort. The dilution sampling system dilutes hot exhaust emissions with clean air to simulate atmospheric mixing and particle formation. Control of residence time, temperature, and pressure allows condensible organic compounds to adsorb onto fine particles as they might in ambient air. The sampler is also designed and fabricated to minimize any contamination of samples, especially organic compound contamination, and to have particle losses to the sampler walls of no more than approximately 7 percent.

Figure 3-1 shows a schematic diagram of the dilution sampling system and dilution air conditioning system. As shown, the dilution air conditioning system provides High Efficiency Particulate Arresting (HEPA) and activated carbon-filtered air. Acid gases (if present) will not be completely removed by the dilution air conditioning system, but the presence of acid gases can be monitored in the dilution tunnel immediately downstream of the dilution air inlet. The dilution air conditioning 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 as follows:

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 μm. 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).

Venturi Meter—

> Constructed of low carbon, very highly corrosion-resistant stainless steel; equipped for temperature and pressure measurement. Wrapped with heating coils
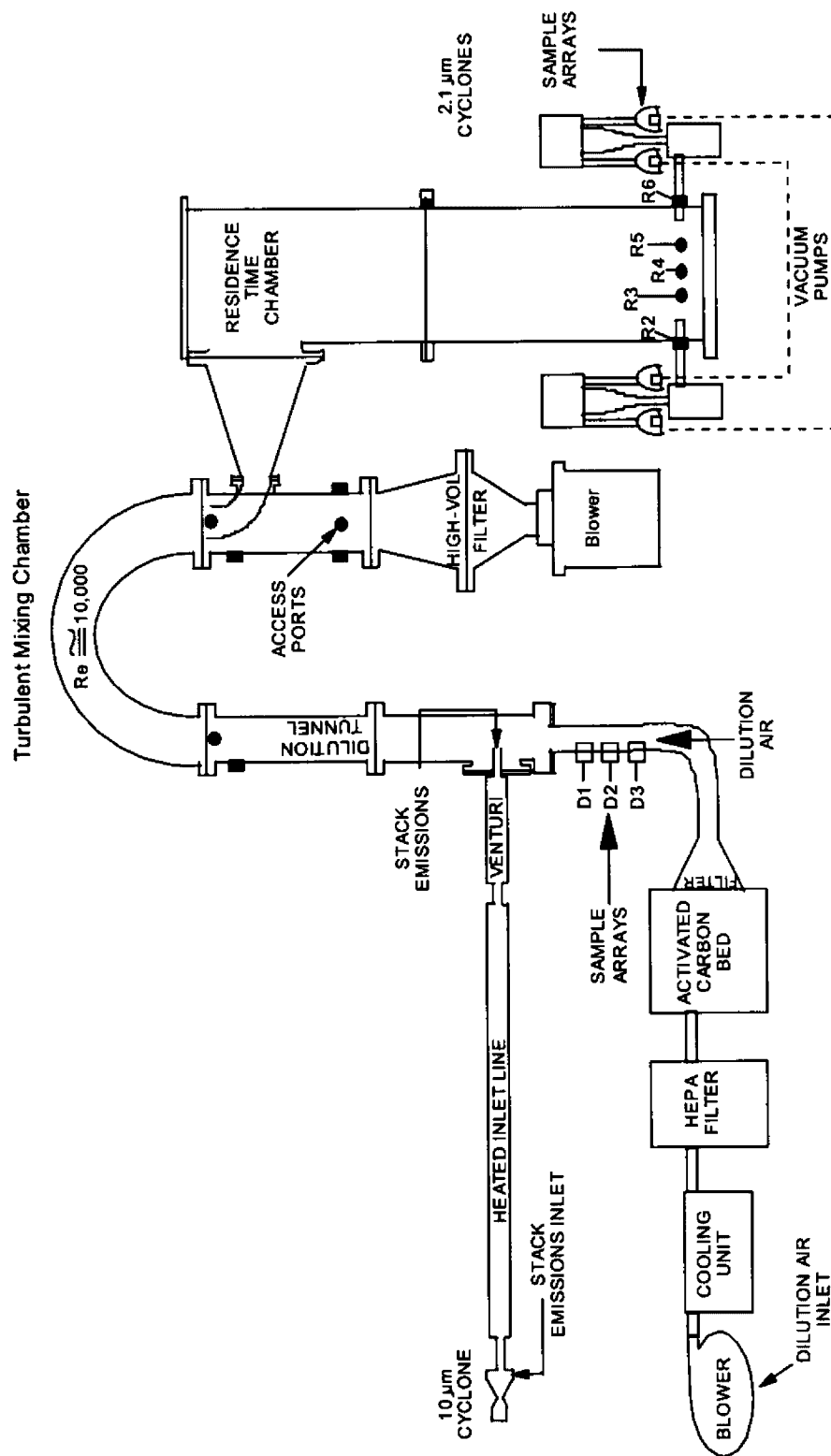
Figure 3-1. Diagram of the dilution sampler and dilution air conditioning system.

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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 air flow, 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. For the test conducted on August 8-9, 2000, the calculated total time the sample spent in the dilution sampling system was 73 seconds: 2.4 seconds for the Turbulent Mixing Chamber and 70.6 seconds for the Residence Chamber.

Sampler 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 air flow rate, the sample gas flow rate, and the exhaust gas flow rate. Since flow equations used for determination of the flow across venturi and orifice meters correct for flowing temperature and pressure, the flowing temperature and pressure of the venturi and orifice meters must be recorded during sampling operations. Thermocouples for monitoring temperature are placed at each flow meter as well as at the inlet PM-10 cyclone, at various points on the sample inlet line, at the inlet to the Mixing Chamber U-bend, and at the outlet of the Residence Time Chamber. An electronic relative humidity probe is used to determine the relative humidity of the sample gas. The sampler 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 setpoints 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 wood-fired industrial boiler.

In operation, the source sample flow, the dilution air flow, and the total air flow (not including the sampling arrays) were each measured by separate flow meters and pressure transmitters. 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 setpoint entry. A separate blower (connected to a speed controller adjusted to achieve the desired sample

Key:
TE = Temperature Indicator
PT = Pressure Indicator
RH = Relative Humidity Indicator
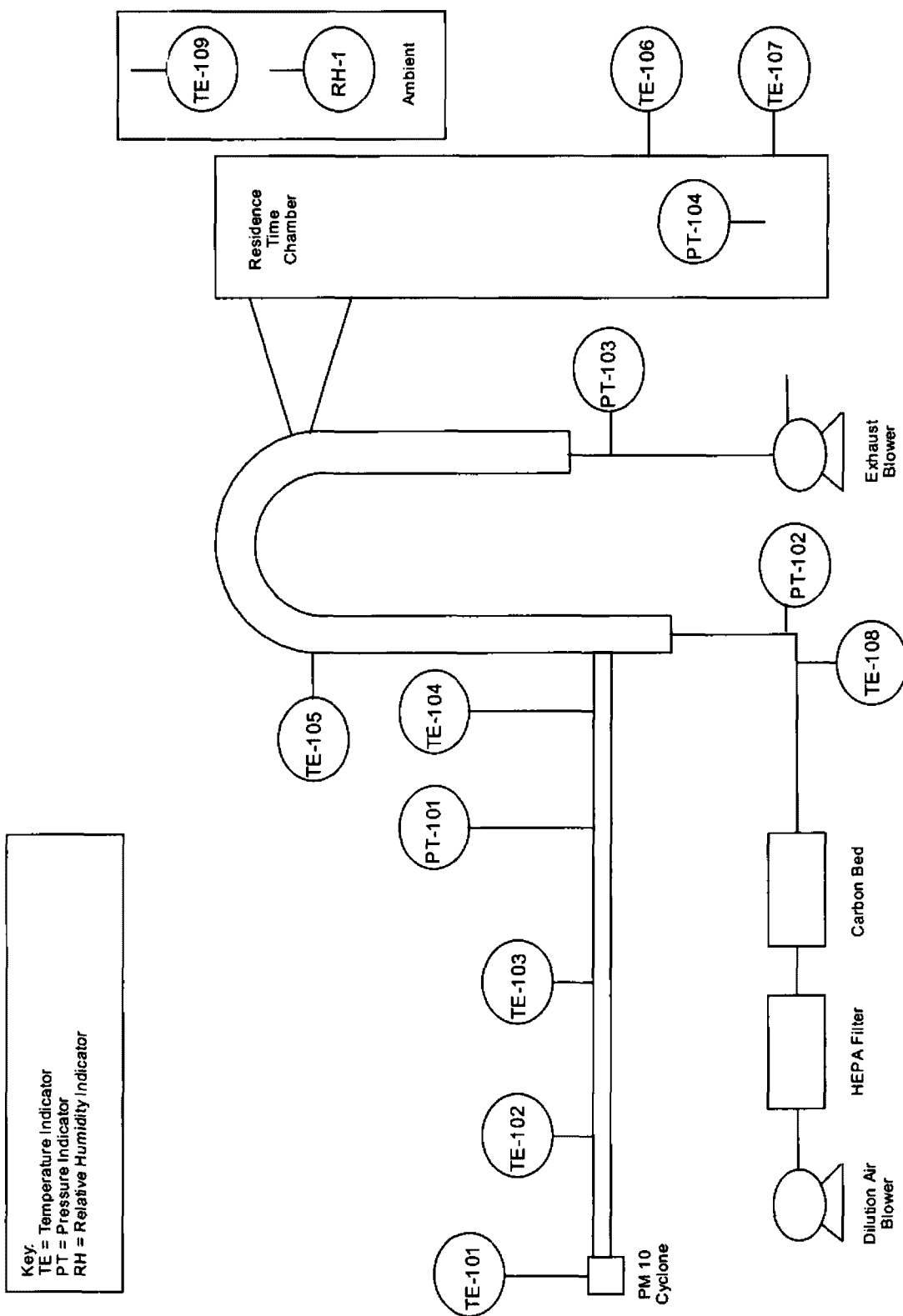
Figure 3-2. Instrumentation for control and analysis of the dilution sampler.

flow based on a setpoint entry) at the end of the sampler pulled the source sample flow through the venturi. Flow through this blower consisted of the dilution air flow 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 industrial wood/bark waste-fired boiler was selected as the test site. The boiler was operated with a continuous screw-feed conveyor belt, with continuous weighing of the wood chips fed to the boiler. The test series was 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/company/management.

Description of the Boiler

The boiler was a relatively modern, field-erected, watertube, pneumatic, vibrating stoker-type unit designed and erected by Steam & Control Systems, Inc. When operating at the design heat input rate, the boiler generates 165,000 lb of steam per hour of continuous 960 psig/760 °F superheated steam.

The boiler utilized wood as the primary fuel and natural gas as start-up and backup fuel. The combustion unit was a pyrolysis system designed to gasify wood in the initial combustion zone at sub-stoichiometric air rates. The initial combustion zone is on the stoker grate. Complete combustion of the off-gases from the pyrolysis process occurs in a secondary combustion zone located above the initial combustion zone.

Emissions were controlled by a multicyclone type dust collector, followed by a multi-stage electrostatic precipitator (ESP). The multicyclone type dust collector was manufactored by Zurn Air Systems and the ESP was a model 34R-1330-37125 Electrostatic Precipitator manufactured by PPC industries.

Description of the Fuel

Boiler fuel consisted of chipped municipal and residential wood waste – i.e., branches, limbs, twigs, tree trunks, stumps, or roots – that had passed through a chipper/shredder and was delivered to the test site via dump truck for storage until use. Types of wood were unrestricted and encompassed any wood that could be grown in a yard, a municipal park, or other vegetated area. The facility utilized a large outdoor wood storage pile that was approximately 800 ft long, 800 ft wide, and 60 ft deep. Because wood chips were delivered continuously on a daily basis and distributed into the pile to ensure that the pile was stable, the age of the wood being burned at any given time varied greatly, depending on where in the pile the wood was being selected for combustion. The moisture content of this wood also varied greatly depending upon the age of

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the wood chips, where the wood chips were located in the wood pile (i.e., depth) and meteorological conditions.

Collection/Analysis of Fuel Samples

While the test team was on site, two samples of wood chips that were composited from all over the wood pile were collected. These wood samples incorporated wood chips from both the top and the bottom of the wood pile, including both old and new wood chips, since a mixture of all the available wood chips is fed to the wood-fired boiler. Analysis results for the wood chips are shown in Table 3-2.

Table 3-2. Results of the Analysis of the Wood Chips

Parameter	As Received %	Dry Basis %
Moisture	38.90	N/A*
Volatile Matter	52.67	86.20
Fixed Carbon	7.38	12.08
Ash	1.05	1.72
Sulfur	0.01	0.02
Carbon	30.85	50.50
Hydrogen	3.55	5.81
Nitrogen	0.15	0.25
Oxygen	25.49	41.69
BTU/lb	5537	9062

*Not applicable.

Pre-Test Survey

A thorough survey of the test site was performed in order 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 sample
collection ports (Figure 3-3) at the outlet of the electrostatic precipitator, and to determine the
means of positioning the sampler at the desired location. A flanged sampling port was installed
at the exact point in the stack where the shape became circular. ERG conducted pre-test site
surveillance and site preparation to ensure readiness of the site for the start of the scheduled
sampling activities. The pre-test survey considered access to utilities and personnel, legal, and
safety requirements. ERG obtained limited 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.

Arrangements were made to position the sampler on a platform at the test location
(Figure 3-4). The sampling location was a flat metal deck (approximately 50 x 50 feet square) on
top of the ESP system approximately 60 feet above ground level, adjacent to the 6 foot O.D.
stack at the ESP outlet where the 6 inch flanged port was installed (Figure 3-4). The dilution
system control module, the sampling module, and all ancillary equipment were delivered to the
test site by EPA. The two modules (dilution air supply/control module and sampler module)
were positioned at the sampling location using a crane supplied and operated by the facility.
Electrical power (250V, single phase, 40A) was provided and installed by the facility.

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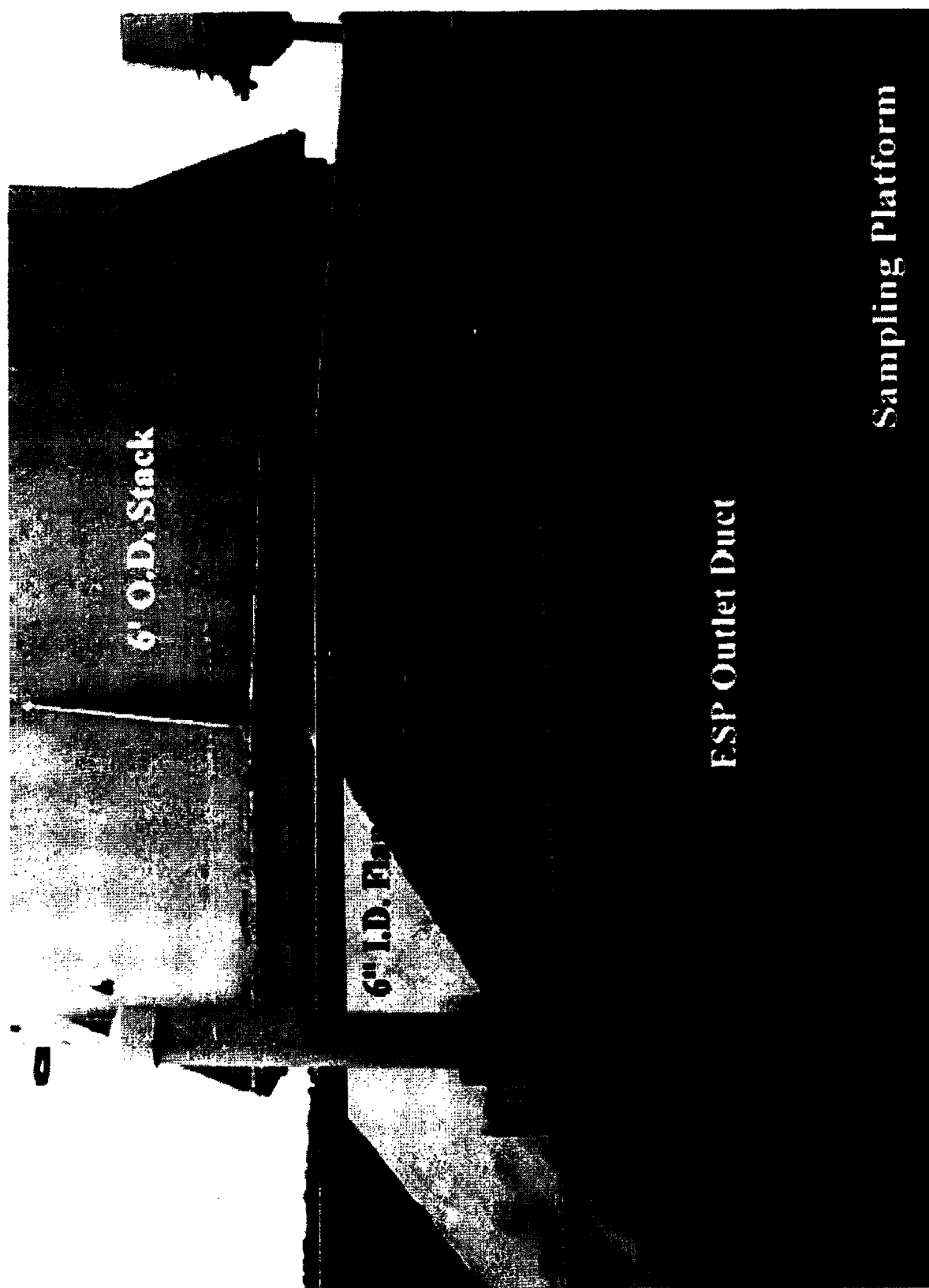
Figure 3-3. Wood-chip fired boiler test facility (SCC 10200902), sampling port
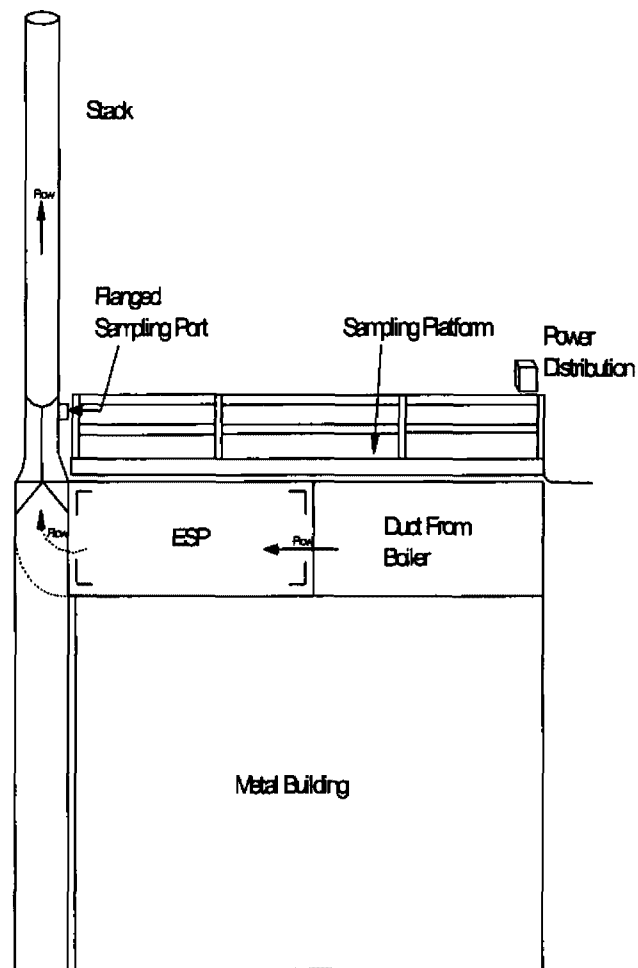
Figure 3-4. Schematic diagram of physical layout of process and sampling location.

Section 4
Experimental Procedures

For sampling undiluted hot exhaust gas streams, the EPA/ECPB dilution sampling system (schematic diagram in Figure 3-1), sample collection arrays, sample substrates, and dilution air cleaning system were used by ERG. EPA arranged for transporting the sampler and ancillary equipment to (and from) the sampling site. To minimize introduction of contaminants, EPA pre-cleaned and pre-assembled the dilution sampler and sampling train 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 and hoisting lugs for transport to and from the site and for positioning on a stack platform. ERG maintained the sampler and sampling trains in a contaminant-free condition prior to collection of source samples and field blanks.

A sampler blank test was run prior to transporting the sampler to the test site 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 sampler, including the sampling train equipment connected to the Residence Time Chamber and all instrumentation. The blank test was conducted for a time period consistent with the expected duration of the source tests (4-6 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.

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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 1-4 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 1, "Sample and Velocity Traverses for Stationary Sources" (U.S. EPA, 1989a) 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 (Figure 3-3) did not meet the minimum requirements of EPA Method 1 for length of straight run, nor for orientation of the port with respect to the plane of bends in the ductwork. However, this location was the only site with sufficient space for physical location of the sampling system. Sampling at the test site was performed at the point determined by Method 1 to represent the average velocity in the electrostatic precipitator exhaust stack (Figure 3-3).

The following stack parameters were measured:

- Inside of Far Wall to Outside of Nipple (Distance A): 74-3/8 in.
- Inside of Near Wall to Outside of Nipple (Distance B): 2-3/8 in.
- Inside Stack Dimensions: 72 in.

Traverse point locations for a circular duct (72 in. diameter) are shown in Table 4-1. A table of metric unit conversions is shown in Appendix A.

Table 4-1. EPA Method 1—Traverse Point Location for Circular Ducts

Traverse Point Number	Fraction of Inside Stack Dimension [a] %	Distance From Stack Wall (in.)	Traverse Point Location (in.)
1	2.6	1-7/8	4-1/4
2	8.2	5-7/8	8-1/4
3	14.6	10-1/2	12-7/8
4	22.6	16-1/4	18-5/8
5	34.2	24-5/8	27
6	65.8	47-3/8	49-3/4
7	77.4	55-3/4	58-1/8
8	85.4	61-1/2	63-7/8
9	91.8	66-1/8	68-1/2
10	97.4	70-1/8	72-1/2

[a] Inside stack diameter, 72 in. Distance from lip of flange to inside stack wall, 2-3/8 in.

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

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

Where:

PS = absolute gas pressure, inches of mercury
P_{bar} = barometric pressure, inches of mercury (29.68 in.)
P_g = gauge pressure, inches of water (static pressure) (0.31 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 29.702 inches of mercury.

Volumetric Flow Rate Determination Using EPA Method 2

Volumetric flow rate was measured according to EPA Method 2, "Velocity - S-Type Pitot" (U.S. GPO, 1989b). 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 report EPA 600/4-77-027b (von Lehmden et al., 1979). 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:

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

(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 Rankin
T_s = flue gas temperature, degrees Fahrenheit

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

Traverse Point (Calculated in Table 4-1)	Velocity (ft/min)
1	1432
2	1544
3	1547
4	1611
5	1549
6	2109
7	2296
8	2340
9	2336
10	2290
Average Velocity	**1905**

The point of average velocity has the closest relationship to Traverse Point #6.

Nozzle Size Determination

It is desirable to sample at or near isokinetic velocities at the probe inlet nozzle. The nozzle size is based on the required sample flow rate. Prior to using an Excel® macro to perform nozzle size calculations according to the procedures of EPA Method 5 (U.S. GPO, 1989d), the

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velocity in the stack (feet per minute) must be determined from the pitot traverses prior to the start of the test run. The additional input required by the macro is sampling rate (liters/minute).

Measurement of O_2 and CO_2 Concentrations

The O_2 and CO_2 concentrations were determined by use of a Fyrite bulb during the traverse.

Stationary Gas Distribution (as Percent Volume)

The following values were measured by continuous emission monitors at the facility; the value for CO was supplied from compliance data collected by the facility.

Measured %O_2	=	10.75%
Measured %CO_2	=	10.5%
Measured %CO	=	0.03%

The percentage of nitrogen (N_2) was calculated according to the following equation:

$$\%N_2 = 100 - (\%O_2 + \%CO_2 + \%CO) = 78.75\% \tag{4-3}$$

Dry Molecular Weight of Flue Gas

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

$$M_d = (\%CO_2 * 0.44) + (\%O_2 * 0.32) + [(\%CO + \%N_2) * 0.28] \tag{4-4}$$
$$= 30.15 \quad lb / lb - mole$$

Where:

M_d = molecular weight of flue gas, dry basis (lb/lb-mole)
%CO_2 = percent CO_2 by volume, dry basis

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%O$_2$	=	percent O$_2$ by volume, dry basis
%CO	=	percent CO by volume, dry basis
%N$_2$	=	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:

$$M_s = (M_d * M_{fd}) + (0.18 * \%H_2O)$$
$$= 27.77 \; wet \; lb / lb - mole \tag{4-5}$$

Where:

M$_s$	=	wet molecular weight of flue gas, wet lb/lb-mole
M$_d$	=	molecular weight of flue gas, dry basis (lb/lb-mole)
M$_{fd}$	=	dry mole fraction of effluent gas, calculated as [1 - %H$_2$O / 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 4, "Moisture Content" (U.S. GPO, 1989c), 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 used for all of the manual sampling methods that were used during the test.

The measurements shown in Table 4-3 were made on August 7, 2000, using Method 4 to determine moisture recovery.

Table 4-3. Moisture Recovery for Method 4 (Measured on August 7, 2000)

Impinger Number	Impinger Solution	Weight of Impinger Contents (g)	Impinger Tip Configuration	Impinger Weight		
				Final (g)	Initial (g)	Weight Gain (g)
1	Water	100	S6	707.3	566.0	141.3
2	Water	100	S6	653.7	598.6	55.1
3	Empty	--	MS6	499.0	488.6	10.4
4	Silica Gel	300	S6	773.2	758.8	14.4
				Total Weight Gain (g)		221.2

Volume of Dry Gas Sampled At Standard Conditions (dscf)

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

$$V_{m(std)} = 17.64 * V_m * P_{bar} + \frac{\frac{\Delta H}{13.6}}{460 + T_m} \quad (4\text{-}6)$$

$$= 42.785 \, dscf$$

Where:

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

V_m = volume of gas metered, cubic feet, dry

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 °F + 460 °R)/29.92 in. Hg; 460 is zero degrees Fahrenheit in degrees Rankin. Using measured values from the field data sheet, the volume of dry gas sampled at standard conditions is calculated to be 42.785 dscf.

Volume of Water Vapor At Standard Conditions (dscf)

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

$$V_{w(std)} = 0.04707 * V_{lc}$$
$$= 10.412 \text{ dscf} \tag{4-7}$$

Where:

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

V_{lc} = volume of liquid catch, cubic feet

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 4-3, above), the volume of water vapor at standard conditions is calculated to be 10.412 dscf.

Calculation of Moisture/Water Content (as % Volume)

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

$$\% \ H_2O = 100 * \frac{V_{w(std)}}{V_{w(std)} + V_{m(std)}} \tag{4-8}$$
$$= 19.4\%$$

Using values measured using EPA Method 4 and values calculated previously, the moisture content was calculated to be 19.4 percent. The value supplied by the facility was 21 percent.

Calculation of Dry Mole Fraction of Flue Gas

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

$$M_{fd} = 1 - \frac{\% H_2O}{100} \qquad (4-9)$$

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 0.806.

Setup of the Dilution Sampling System

The sampling location was a flat metal deck on top of the ESP system approximately 60 feet above ground level, adjacent to the 6 ft O.D. stack at the ESP outlet where the 6 in. flanged port was installed (Figure 3-3). The dilution system control module, the sampling module, and all ancillary equipment were delivered to the test site by EPA. The two modules (dilution air supply/control module and sampler module) were positioned at the sampling location using a crane supplied and operated by the facility. Electrical power (250V, single phase, 40A) was provided and installed by the facility.

The location provided convenient access to the stack and sampling ports, as shown in Figure 3-3, and sufficient space for the equipment and personnel. The dilution air system module positioned at the sampling location on the flat deck is shown during operation in Figure 4-1. Because this test was conducted in the summer, the metal surface of the deck was very hot. Note that the pump was elevated above the deck surface for cooling purposes.

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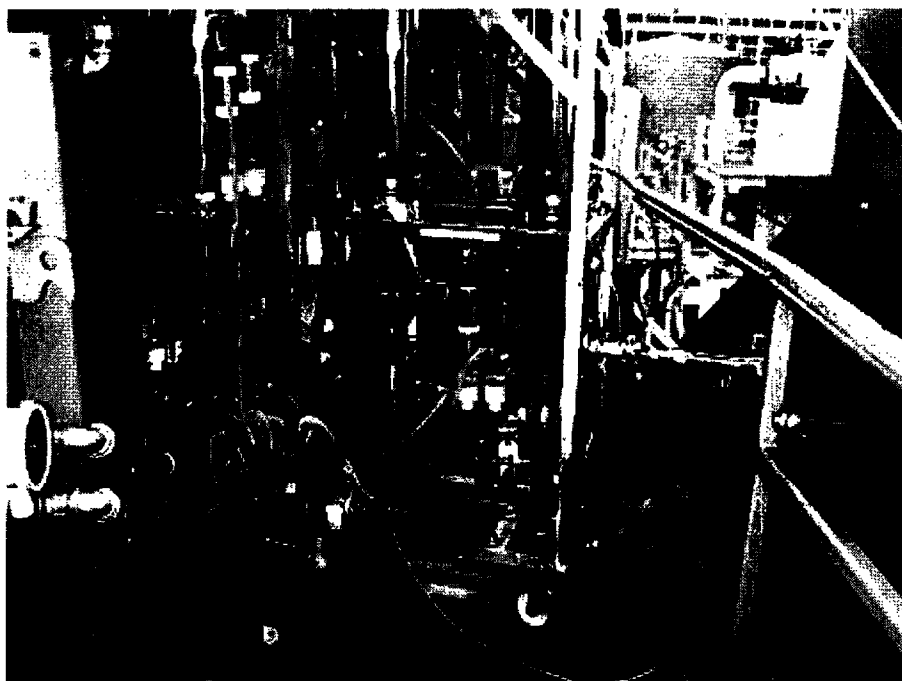
Figure 4-1. Dilution system sampling module positioned at the sampling location.

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 on the deck immediately adjacent to the sampling module. A TSI SMPS (Figure 4-4), with associated laptop computer, was also connected to the sampling module, together with other sampling arrays shown in the background. The dilution system sampling module with all sample collection arrays and instruments attached is shown in Figure 4-5: note the TSI SMPS in the foreground, SUMMA®- polished canister on the deck, and the various sample collection arrays (the white filter holders are readily visible) attached to the various ports of the dilution system sampling module.

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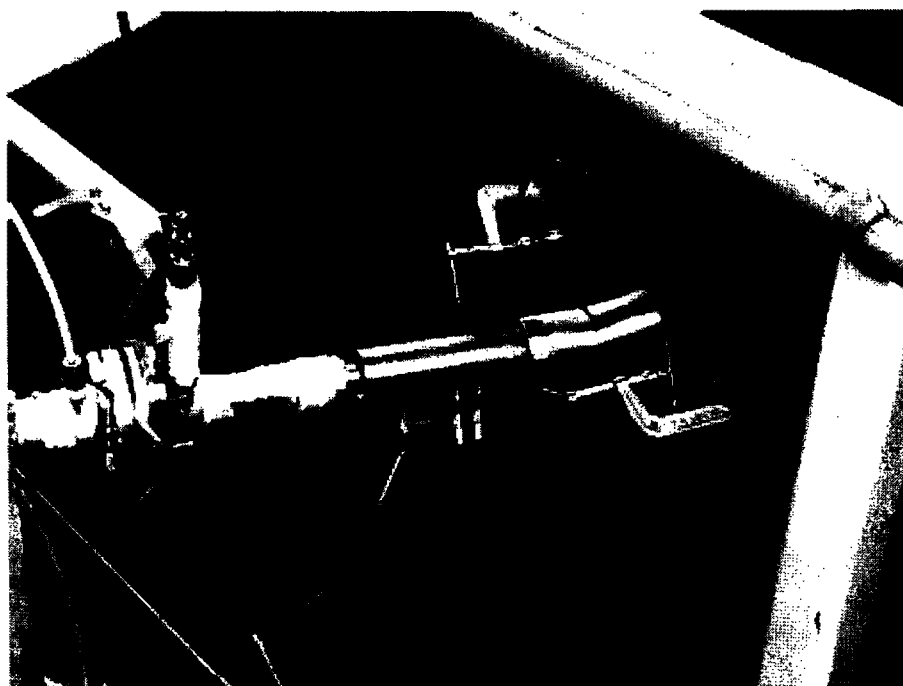
Figure 4-2. Dilution system sampling probe installed in 6 in. I.D. flanged port.
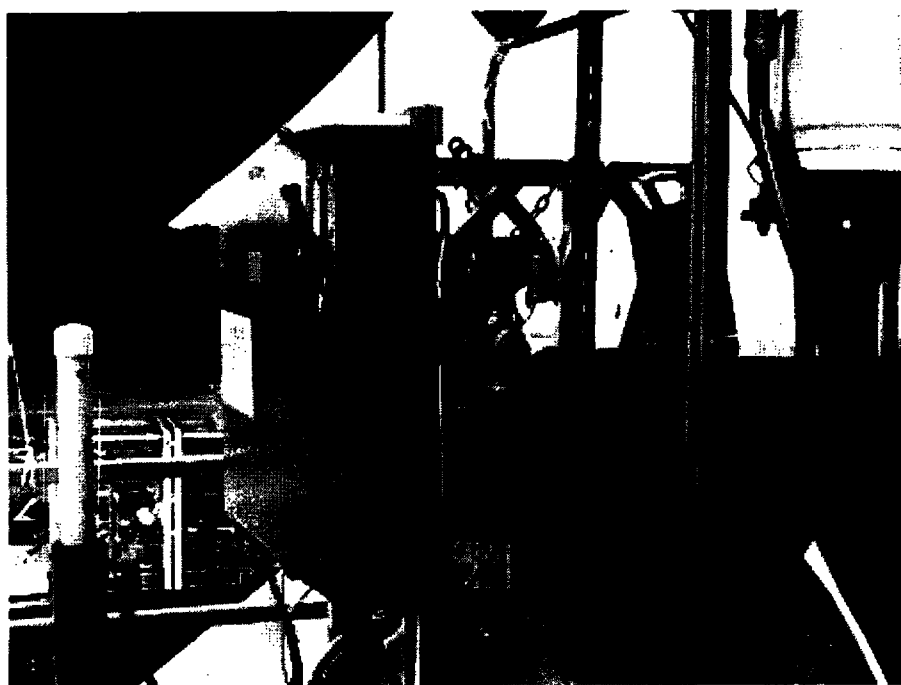
Figure 4-3. Dilution system control module positioned at the sampling location.
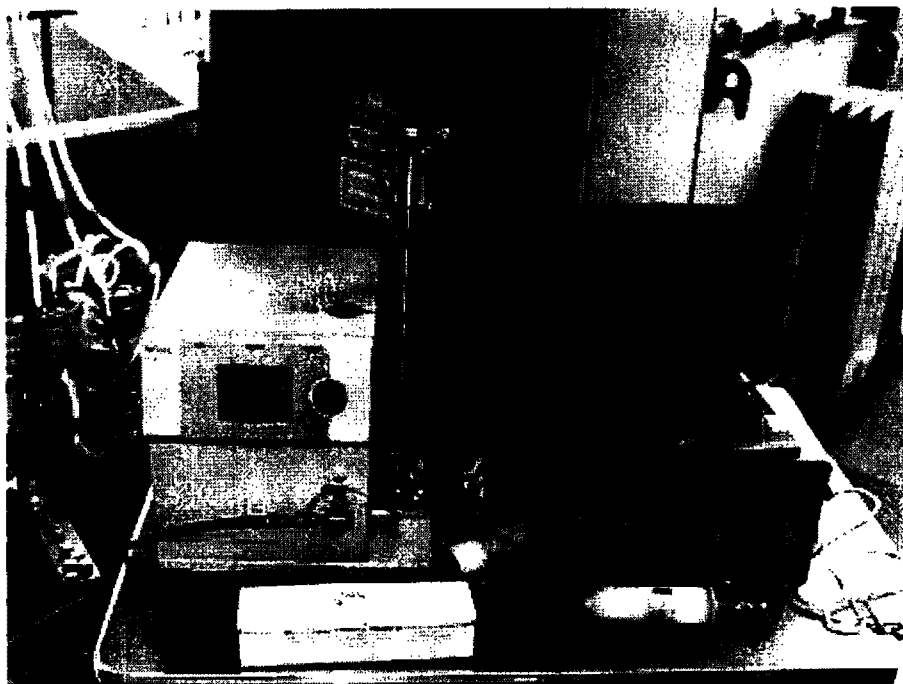
Figure 4-4. TSI SMPS positioned at the sampling location.
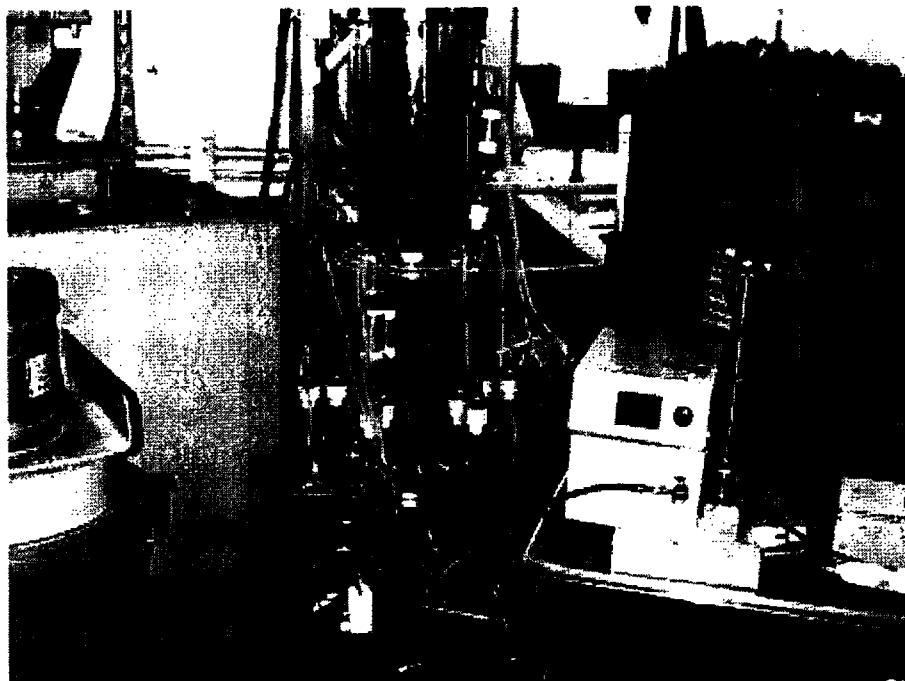
Figure 4-5. Dilution system with all sample collection arrays and instruments attached.

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Pre-Test Leak Check

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

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

Where:

leakage rate	=	rate of leakage (ft^3/min)
ΔP	=	change in pressure (in. water)
ΔT	=	time increment (sec)
V	=	volume of the evacuated chamber ($15.3\ ft^3$)
CF	=	unit conversion factors – 60 sec/min – 1 atm/406.8 in. water

The target time (greater than 1 minute 53 seconds, which equals 0.1 cfm) was achieved. A recorded time that was too fast or the inability to evacuate the sampler to 27 in. water would have been indicative of the presence of a leak, requiring corrective action before the sampler could be operated for the test run.

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 sampling array pumps were at the specified flow rate of 16.7 L/min. Rotameters were calibrated with a NIST-traceable electronic bubble flow meter and the readings were converted to flow (L/min) using a spreadsheet.

Determination of Test Duration

A pre-test was performed prior to the initiation of source testing to establish the length of the test runs. The pre-test was used to assess whether there were any problems with the source testing operations and to obtain an estimate of the substrate loadings during the actual source tests to avoid overloading the substrates. To perform the pre-test, two arrays consisting of two sets of paired filters, one dedicated to determination of collected mass and the other dedicated to the determination of elemental and organic carbon, were attached to the Residence Time Chamber. The dilution sampling system was operated for a period of two hours, and the resulting samples were transported to the EPA laboratories in Research Triangle Park that evening for analysis. The results of the analysis (the loading on the test filters) demonstrated that the maximum achievable integration time should be used for the test runs. The equipment used to collect the integrated canister samples dictated a maximum integration time of six hours for the test runs since the canisters were used to collect an integrated sample over the duration of the test run.

Canister/Veriflow Blanks

Prior to deployment in the field, SUMMA®-polished canisters and Veriflow® canister filling units were cleaned and blank analysis was performed in the laboratory. All units met the cleanliness criterion of < 10 parts per billion carbon (ppbC, Table 4-4).

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Table 4-4. Blank Values for Veriflows® and Canisters

Unit	Blank Value, ppbC
Veriflows®	
Unit #418 (Source), Field Test 1	0.4
Unit #315 (Dilution Air), Field Test 2	0.2
Canisters	
3942	0.3
4040	0.2
3953	0.3
1478	0.9
4043	0.5
1408	0.3
1473	0.3
1425	0.6
4031	1.1

Determination of Flow Rates

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

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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, flow temperature, flow pressure, and barometric pressure; the Excel® macro automatically selected the correct value to be applied based on the flow temperature.

Flow information collected during the pre-test (August 7, 2000) is summarized in Table 4-5. The flows for the blower, dilution, and venturi air are shown graphically in Figures 4-6, 4-7, and 4-8, respectively.

Sample Collection Arrays

Prior to actual testing (Test Run #1 on August 8, 2000, and Test Run #2 on August 9, 2000), sample collection arrays were attached to various ports on the dilution sampler, as shown in Figure 4-9. Up to ten sampling ports were available attached to either the Dilution Chamber or the Residence Chamber (available sampling ports are shown in Figure 3-1). The following arrays were used for Test #1 and Test #2:

- **Port #D1 (Dilution Chamber)**
  The sample collection array used on Port #D1 (Dilution Chamber) included a PM-2.5 cyclone branching off to two sample collection systems: one a quartz filter (QF) followed by a polyurethane foam (PUF) sampling module, the second a Teflon® filter (TF) followed by a KOH-impregnated quartz filter (KOH-QF) for collection of volatile organic acids. This array collected semivolatile organic compounds, particles, and particle phase organic compounds, as well as any semivolatile organic compounds that may have been volatilized from the filters.

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Table 4-5. Run Time Flow Summary Information: Pre-Test, August 7, 2000

Start Time   6:38:38 PM
End Time   8:28:19 PM
Run Time   109.68 minutes
Barometric Pressure   29.63 in. Hg

Parameter	Average
Venturi Flow	30.08 aLpm[c]
	17.26 sLpm[d]
PT-101[a]	-1.09 in. WC[e]
TE-104[b]	233.55 °C
Dilution Flow	891.10 aLpm
	828.58 sLpm
PT-102	-1.34 in. WC
TE-108	36.58 °C
Blower Flow	967.85 aLpm
	874.56 sLpm
PT-103	-14.92 in. WC
TE-105	39.07 °C
Dilution Ratio	49.24
TE-101	224.97 °C
TE-102	227.62 °C

[a]PT = pressure transducer
[b]TE = thermocouple
[c]aLpm = actual liters per minute
[d]sLpm = standard liters per minute
[e]WC = water column
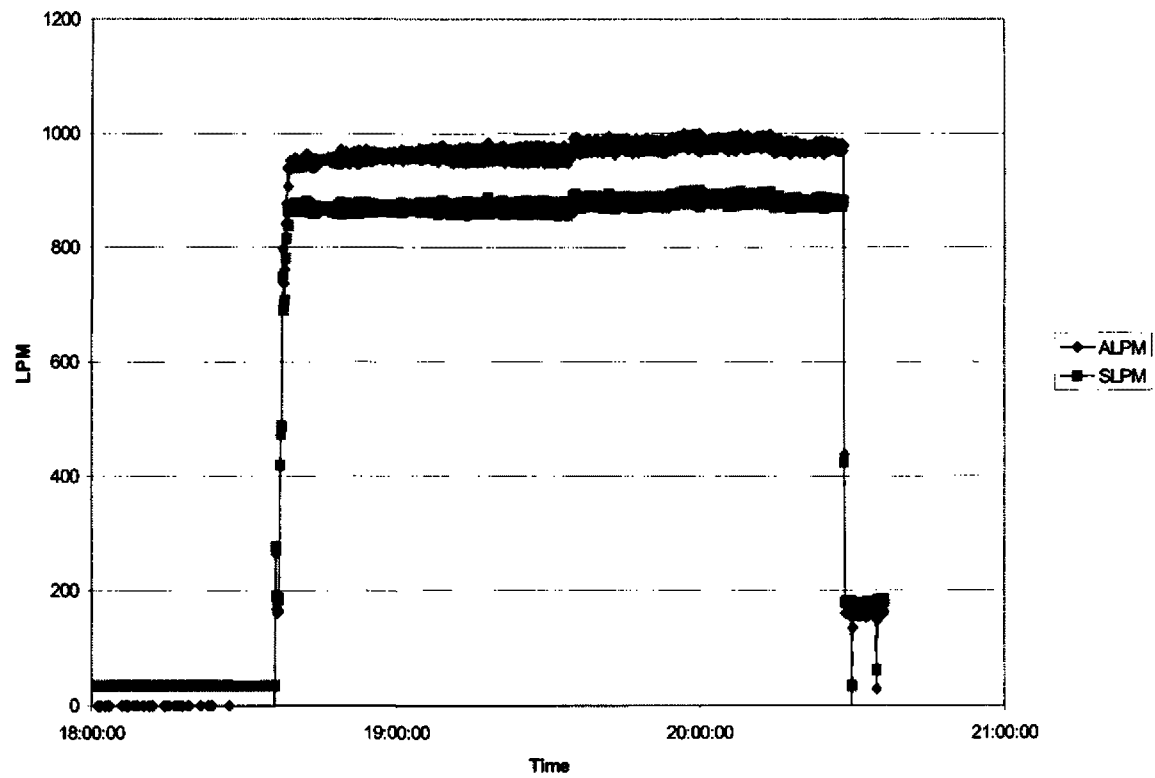
Figure 4-6. Blower flow, pre-test, August 7, 2000.
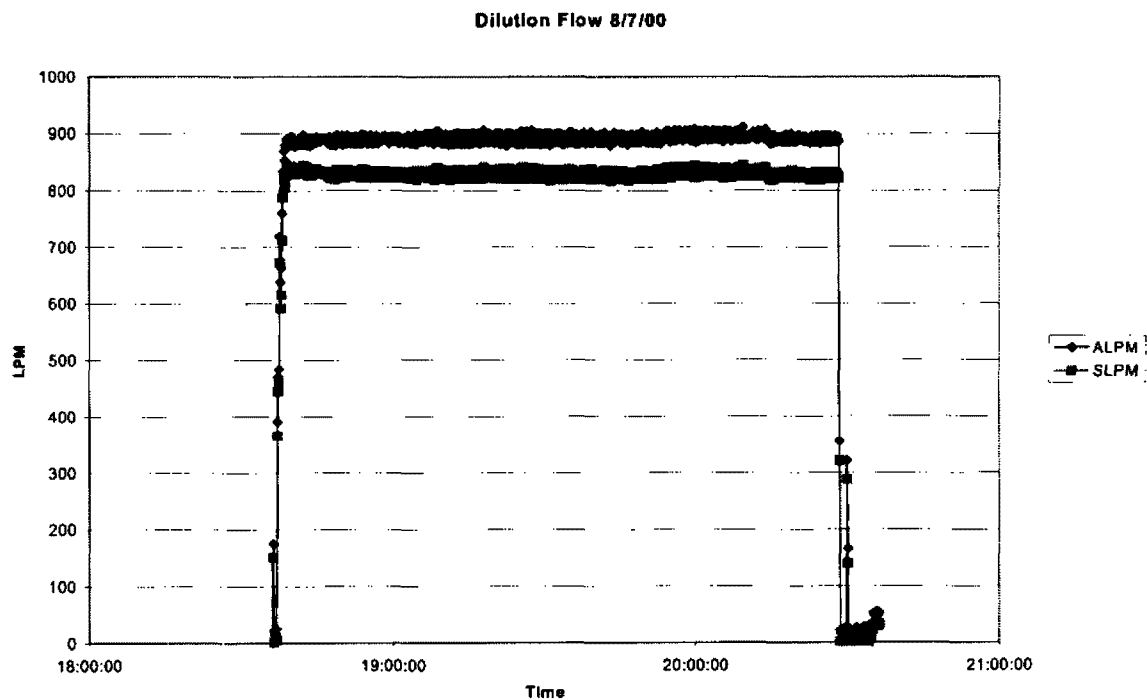
Dilution Flow 8/7/00

Figure 4-7. Dilution flow, pre-test, August 7, 2000.
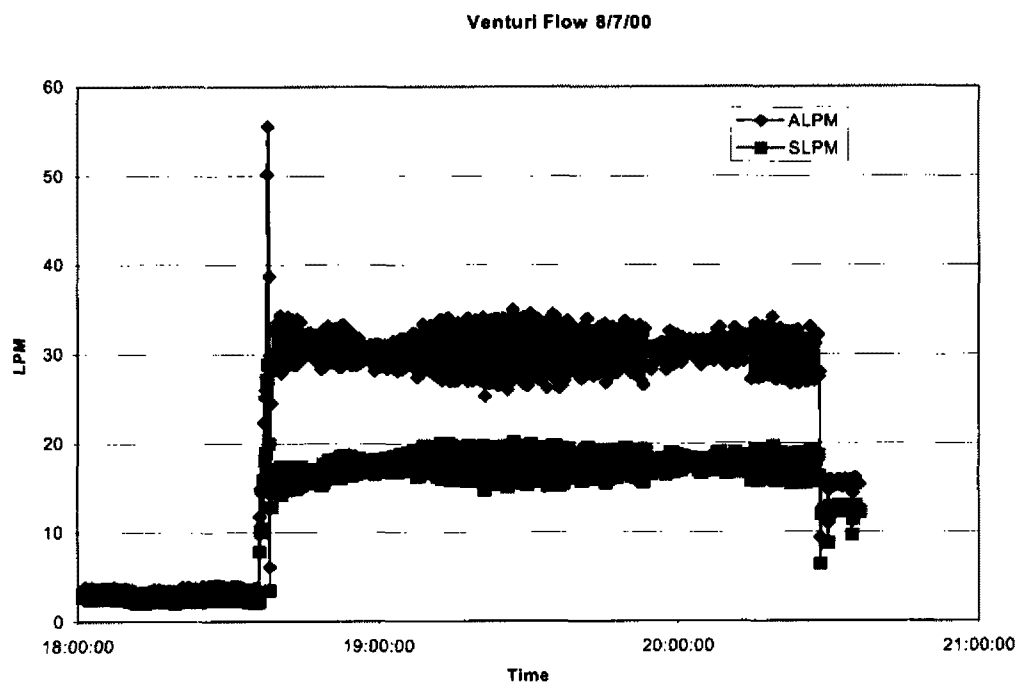
Venturi Flow 8/7/00

Figure 4-8. Venturi flow, pre-test, August 7, 2000.

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Test: 8/8/00

Dilution chamber

Port #D1   Port #D2

PUF   KOH QF
QF   TF
Cyclone
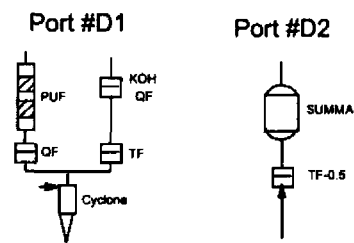
SUMMA
TF-0.5

Field blanks:

QF   1
KOH QF   1
TF   2
PUF   1
DNPH   1

Residence chamber

Port #R2   Port #R3   Port #R4   Port #R5

TF   TF
Cyclone

DNPH
DNPH

PUF   PUF
QF   QF
Cyclone

SUMMA
TF-0.5

Port #R6   Port #R8   Port #R10

KOH QF   KOH QF
TF   TF
Cyclone

TF   ZF
Cyclone

PUF   PUF
QF   QF
Denuder
Denuder
Cyclone
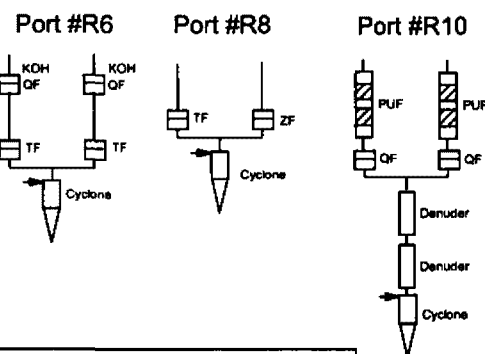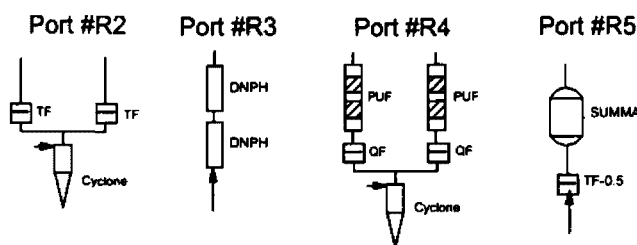
Total Substrates

QF   6
KOH QF   4
TF-0.5   2
TF   9
PUF   11
Denuder   2
SUMMA   2
DNPH   3

Legend

QF	=	Quartz Filter
KOH QF	=	KOH Quartz Filter
TF-0.5	=	Teflone Filter - 0.5
TF	=	Teflone Filter
PUF	=	Polyurethane Foam Sampling Module
Denuder	=	Denuder
SUMMA	=	SUMMA® Canister
DNPH	=	2,4-Dinitrophenylhydrazine -impregnated silica gel cartridge

Figure 4-9. Schematic diagram of sample collection arrays used in field test (August 8-9, 2000).

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- **Port #D2 (Dilution Chamber)**
  The sample collection array used on Port #D2 (Dilution Chamber) included a Teflon® filter followed by a cleaned and blanked SUMMA®-polished stainless steel canister for the collection of volatile organic compounds. The canister collected whole air samples for analysis of air toxics and Speciated Nonmethane Organic Compounds, with a Teflon® filter to protect the canister from particulate contamination.

- **Port #R2 (Residence Chamber)**
  The sample collection array used on Port #R2 (Residence Chamber) included a PM-2.5 cyclone leading into two Teflon® filters in parallel to collect fine particulate matter for determination of PM mass and elemental composition.

- **Port #R3 (Residence Chamber)**
  The sample collection array used on Port #R3 (Residence Chamber) consisted of two DNPH-impregnated silica gel tubes in series for collection of carbonyl compounds.

- **Port #R4 (Residence Chamber)**
  The sample collection array used on Port #R4 (Residence Chamber) consisted of a PM-2.5 cyclone leading into two parallel assemblies consisting of quartz filters followed by PUF plugs. This array collected semivolatile organic compounds, particles, and particle phase organic compounds, as well as any semivolatile organic compounds that may have been volatilized from the filters.

- **Port #R5 (Residence Chamber)**
  The sample collection array used on Port #R5 (Residence Chamber) consisted of a Teflon® filter followed by a cleaned and blanked SUMMA®-polished canister for collection of Volatile Organic Compounds. The canister collected integrated whole air samples for analysis of air toxics and Speciated Nonmethane Organic Compounds, with a Teflon® filter to protect the canister from particulate contamination.

- **Port #R6 (Residence Chamber)**
  The sample collection array used on Port #R6 (Residence Chamber) included a PM-2.5 cyclone leading into two parallel assemblies consisting of Teflon® filters followed by KOH-impregnated quartz filters for collection of fine particulate material and volatile organic acids, respectively.

- **Port #R7 (Residence Chamber)**
  The sample collection assembly used on Port #R7 (Residence Chamber) consisted of an aerodynamic particle-sizing spectrometer to separate particles by size for high-resolution measurements of particle size distribution. The instrumentation utilized was the TSI Model 3025A (Ultra Fine Condensation Particle Counter)

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coupled with the TSI Model 3080 (Electrostatic Classifier), collectively described as the Scanning Mobility Particle Sizer (SMPS).

- **Port #R8 (Residence Chamber)**
The sample collection array used on Port #R8 (Residence Chamber) consisted of a cyclone leading into two parallel Teflon® filters (supplied by a second vendor) for collection of fine particulate matter for determination of major inorganic ions and PM mass.

- **Port #R10 (Residence Chamber)**
The sample collection array used on Port #R10 (Residence Chamber) included a cyclone leading into a set of two 200 mm long XAD-4®-coated denuders in series followed by two parallel quartz filters both leading into PUF sampling modules. These denuder-equipped arrays provide an alternative method for distinguishing gas- and particle-phase semivolatile organic compounds.

Preparation of the Particle Size Distribution Analyzer

The Scanning Mobility Particle Sizer (consisting of the TSI Model 3025A Ultra Fine Condensation Particle Counter combined with the TSI Model 3080 Electrostatic Classifier) was used to make particle size distribution measurements in the range of 10-400 nanometers (nm) midpoint diameter. The Electrostatic Classifier separates particles by size for high-resolution measurements. Monodisperse aerosol exiting the Electrostatic Classifier passes to the Condensation Particle Counter, which measures particle number concentrations. By scanning quickly through the desired size range, the Scanning Mobility Particle Sizer measures the size distribution of the aerosol precisely, providing concentration and size-resolution measurements with a high degree of accuracy.

In operation, a polydisperse submicrometer aerosol passes through a radioactive bipolar charger, establishing a bipolar equilibrium charge level on the particles. Nearly all particles in the range scanned receive a single positive, single negative, or zero charge. The particles then enter the differential mobility analyzer and are separated according to their electrical mobility, which is inversely related to particle size.

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The pre-calibrated instrument was transported to the field and placed in the vicinity of the sampling array on a sturdy table. Thirty minutes prior to the start of the test run, the SMPS was turned on to warm up and equilibrate. The computer was turned on, and the sample acquisition program was initiated. On the SMPS, the sample flow and the sheath flow were manually adjusted to the manufacturer's specifications (sample flow equal to 0.6 Lpm; total flow 6 Lpm).

The Teflon® and quartz filters used in the dilution sampling system had a pore size of 2 µm. This filter pore size was selected for the dilution sampling system because the system pressure drop across the filter was too great with a filter pore size of 1 µm. The SMPS was set to monitor the range of 10-400 nm midpoint diameter to provide an indication of the particle size distribution in the range below 2 µm, as well as the concentration distribution of the particles within this size range. The data system was initially set up to collect data for particles ranging from 10 to 400 nm in size; particles larger in diameter than 400 nm were not collected. The particles were collected over multiple three-minute periods for the duration of the test with a filter in the inlet line to establish the absence of background contamination.

Shortly before the test run, the data system was programmed to collect particulate data that encompassed the expected duration of the test run. The instrument completed an upward/downward scan every three minutes, producing particle size and concentration data for the selected scan range. The particle size analyzer was the last piece of equipment connected to the Residence Chamber. When the test was started, the filter was removed from the inlet line of the particle sizer, the inlet line was attached to the port, and "Start Run" was initiated on the data system. Data were continually saved on the computer hard drive and a real-time display on the computer screen showed the particle distribution. Graphical presentations of the data were prepared off-line.

Operation of the Dilution Sampling System with Sample Collection Arrays

After completion of the pre-test run to establish experimental parameters for the test, the dilution sampling system was prepared for a full test run. Sampling probe temperature setpoints

were set equal to or slightly above the measured stack temperature. The system was equilibrated at temperature. Sampling arrays were loaded with appropriate media and flow/leak checks were performed with each array to ensure that the entire system would be leak-free in operation. Sampler flows were set just before initiation of the test to prevent heat loss from the heated probe. The blower and the ring compressor were started to achieve a slightly positive pressure, then the blower flow was adjusted to cause the stack gas to flow into the dilution sampling system after the probe was inserted in the stack. Sample collection array pumps were started and valves for the SUMMA® canisters were opened to initiate canister air sample collection. The sampling process was carefully monitored by the sampling team based on the pressure change in the canister to ensure that 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 Test #1 and Test #2 are shown in Tables 4-6 and 4-7; blower flow, dilution flow, and venturi flow for Tests #1 and #2 are shown graphically in Figures 4-10 through 4-15.

Dilution System Sample Collection Arrays: Train Recovery

When the sampling run was completed, 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. The SMPS was then connected to a small HEPA-filter unit and pulled ambient air through the filter and analyzer so that the unit could collect post-sampling blanks.

Table 4-6. Run Time Summary Information, Test Run #1 (August 8, 2000)

Test Run #1 (August 8, 2000)

Start Time	12:58:27 PM
End Time	5:16:21 PM
Run Time	257.90 min
Barometric Pressure	29.65 in. Hg
Nozzle Size	#8 (227 °C, 1905 ft/min)
Canister Flow	13.9 cm³/min

Parameter	Average
Venturi Flow	30.47 aLpm
	17.19 sLpm
PT-101	-2.96 in. WC
TE-104	239.86 °C
Dilution Flow	900.35 aLpm
	822.40 sLpm
PT-102	-3.06 in. WC
TE-108	40.95 °C
Blower Flow	909.56 aLpm
	809.53 sLpm
PT-103	-16.11 in. WC
TE-105	44.15 °C
Dilution Ratio	48.90
TE-101	240.25 °C
TE-102	238.98 °C
TE-103	NA

Sample Flow Rates

Actual Flow aLpm	Corrected Flow sLpm	Notes	Average Flow sLpm
16.09	17.20	PM2.5 Sample, Dilution Air: Start	17.28
16.24	17.36	PM2.5 Sample, Dilution Air: End	
16.53	17.67	PM2.5 Sample, Residence Chamber (Port 10): Start	17.59
16.39	17.51	PM2.5 Sample, Residence Chamber (Port 10): End	

(Continued)

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Table 4-6. (Continued)

Sample Flow Rates

Actual Flow aLpm	Corrected Flow sLpm	Notes	Average Flow sLpm
16.97	18.14	PM2.5 Sample, Residence Chamber (Port 8): Start	18.06
16.82	17.98	PM2.5 Sample, Residence Chamber (Port 8): End	
16.53	17.67	PM2.5 Sample, Residence Chamber (Port 6): Start	17.74
16.68	17.82	PM2.5 Sample, Residence Chamber (Port 6): End	
16.53	17.67	PM2.5 Sample, Residence Chamber (Port 4): Start	17.67
16.53	17.67	PM2.5 Sample, Residence Chamber (Port 4): End	
16.82	17.98	PM2.5 Sample, Residence Chamber (Port 2): Start	17.74
16.39	17.51	PM2.5 Sample, Residence Chamber (Port 2): End	
0.98	1.05	DNPH Sample, Residence Chamber (Port 3): Start	1.04
0.96	1.03	DNPH Sample, Residence Chamber (Port 3):End	

Canisters

	Start Pressure	End Pressure
#1473, Dilution	29.5 in. Hg	9.0 in. Hg
#4043, Source	29.0 in. Hg	7.0 in. Hg
#4031, Blank	29.5 in. Hg	29.5 in. Hg

NA = Not applicable; channel not connected.
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 (August 9, 2000)

Test Run #2 (August 9, 2000)

Start Time	9:07:38 AM
End Time	3:07:17 PM
Run Time	359.65 min
Barometric Pressure	29.62 in. Hg
Nozzle Size	#8 (227 °C, 1905 ft/min)
Canister Flow	13.9 cm³/min

Parameter	Average
Venturi Flow	30.05 aLpm
	17.06 sLpm
PT-101	-2.84 in. WC
TE-104	236.32 °C
Dilution Flow	898.27 aLpm
	823.46 sLpm
PT-102	-2.89 in. WC
TE-108	39.66 °C
Blower Flow	898.15 aLpm
	804.22 sLpm
PT-103	-15.58 in. WC
TE-105	42.44 °C
Dilution Ratio	49.33
TE-101	225.94 °C
TE-102	236.83 °C
TE-103	NA

Sample Flow Rates

Actual Flow aLpm	Corrected Flow sLpm	Notes	Average Flow sLpm
16.84	17.96	PM2.5 Sample, Dilution Air: Start	17.88
16.69	17.81	PM2.5 Sample, Dilution Air: End	
16.55	17.65	PM2.5 Sample, Residence Chamber (Port 10): Start	17.65
16.55	17.65	PM2.5 Sample, Residence Chamber (Port 10): End	

(Continued)

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Table 4-7. (Continued)

Sample Flow Rates

Actual Flow aLpm	Corrected Flow sLpm	Notes	Average Flow sLpm
16.69	17.81	PM2.5 Sample, Residence Chamber (Port 8): Start	17.88
16.84	17.96	PM2.5 Sample, Residence Chamber (Port 8): End	
16.55	17.65	PM2.5 Sample, Residence Chamber (Port 6): Start	17.65
16.55	17.65	PM2.5 Sample, Residence Chamber (Port 6): End	
16.55	17.65	PM2.5 Sample, Residence Chamber (Port 4): Start	17.73
16.69	17.81	PM2.5 Sample, Residence Chamber (Port 4): End	
16.84	17.96	PM2.5 Sample, Residence Chamber (Port 2): Start	17.96
16.84	17.96	PM2.5 Sample, Residence Chamber (Port 2): End	
0.96	1.02	DNPH Sample, Residence Chamber (Port 3): Start	1.02
0.96	1.02	DNPH Sample, Residence Chamber (Port 3):End	

Canisters

	Start Pressure	End Pressure
#1478, Dilution	29 in. Hg	4.0 in. Hg
#4040, Source	30 in. Hg	2.5 in. Hg
#3953, Blank	29 in. Hg	29 in. Hg

NA = Not applicable; channel not connected.
PT = pressure transducer
TE = thermocouple
aLpm = actual liters per minute
sLpm = standard liters per minute
WC = water column
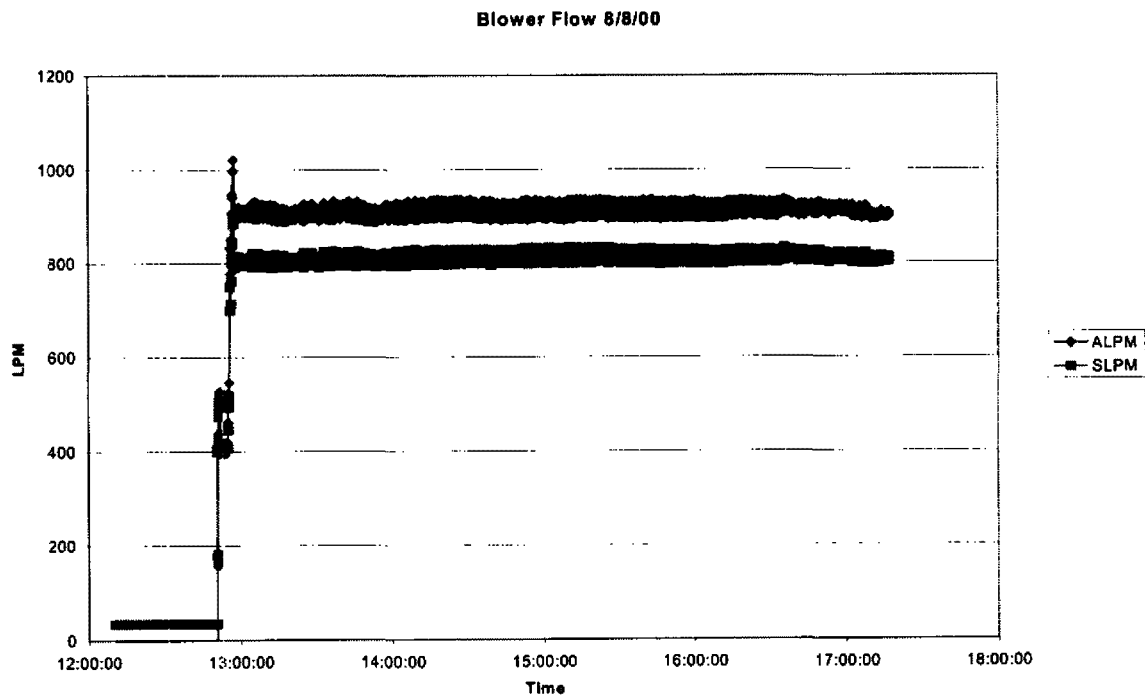
Figure 4-10. Blower flow, Test 1—Day 1, August 8, 2000.
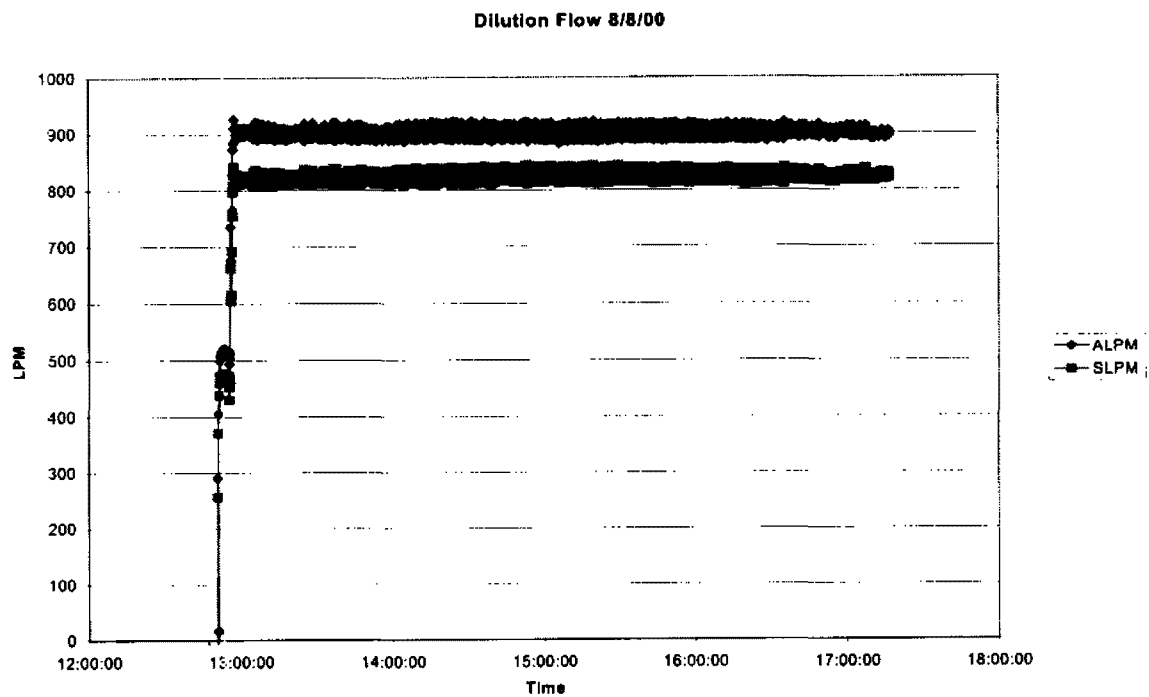
Figure 4-11. Dilution flow, Test 1—Day 1, August 8, 2000.

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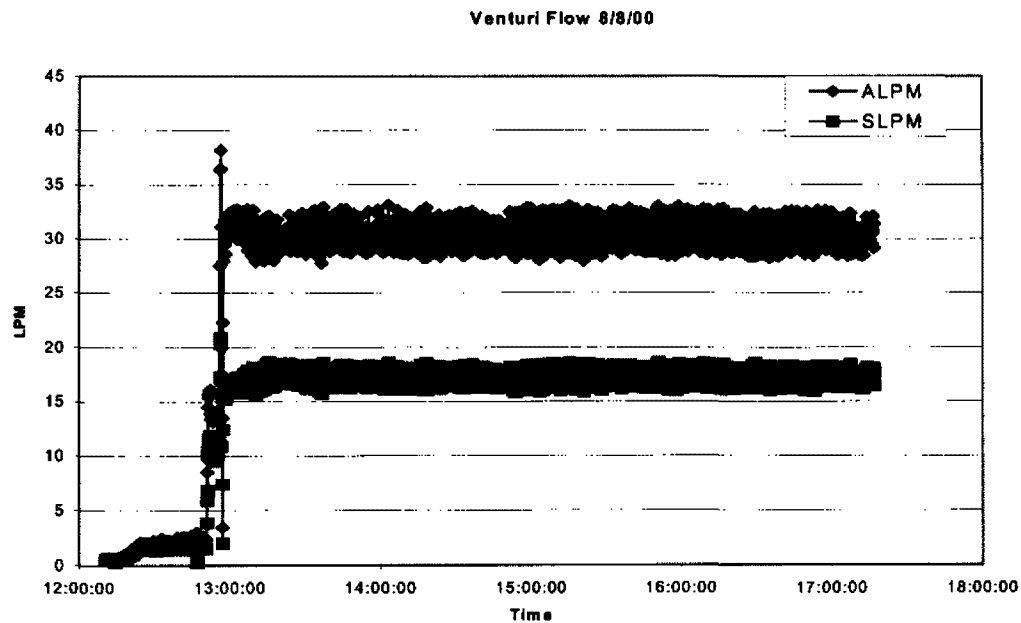
Figure 4-12. Venturi flow, Test 1—Day 1, August 8, 2000.
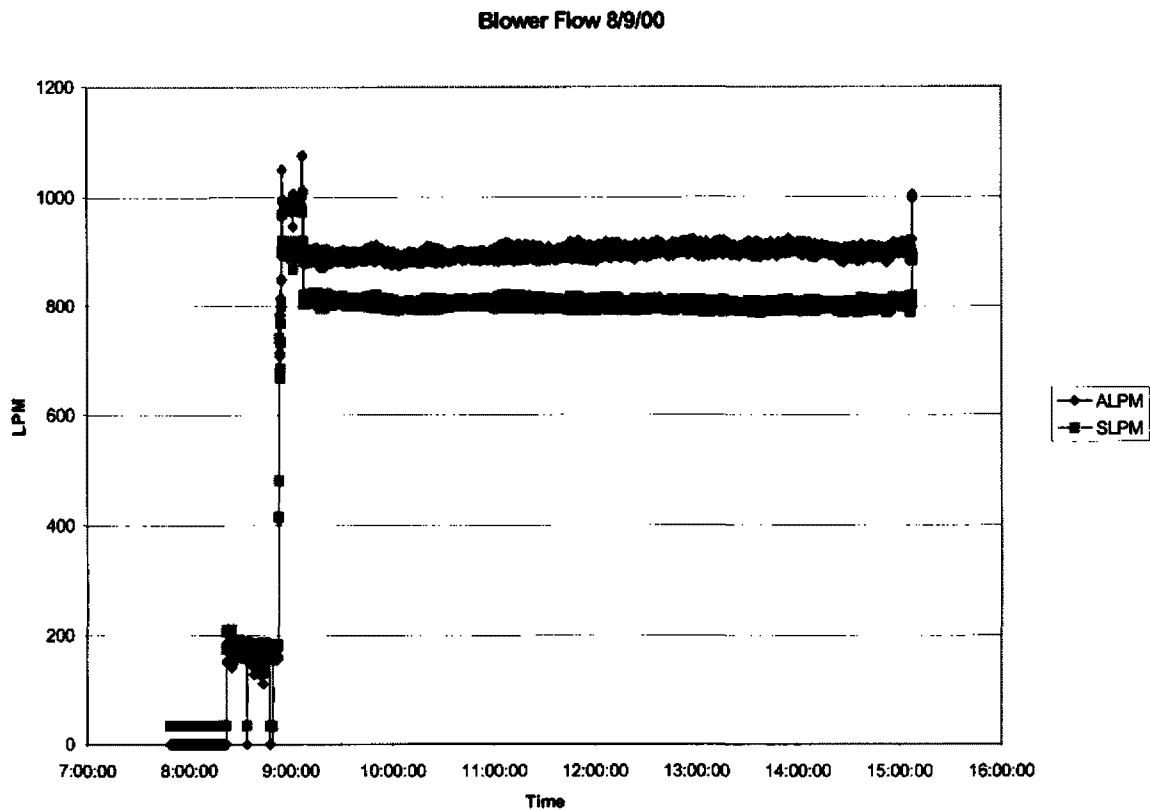
Blower Flow 8/9/00

Figure 4-13. Blower flow, Test 2—Day 2, August 9, 2000.
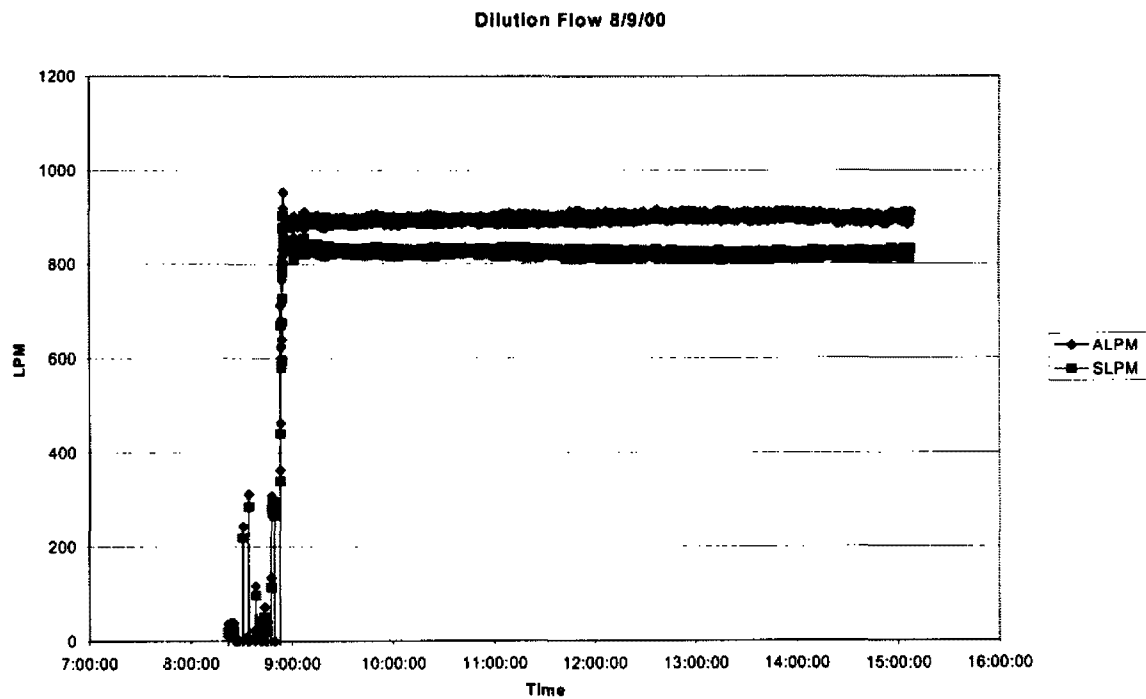
Dilution Flow 8/9/00

Figure 4-14. Dilution flow, Test 2—Day 2, August 9, 2000.
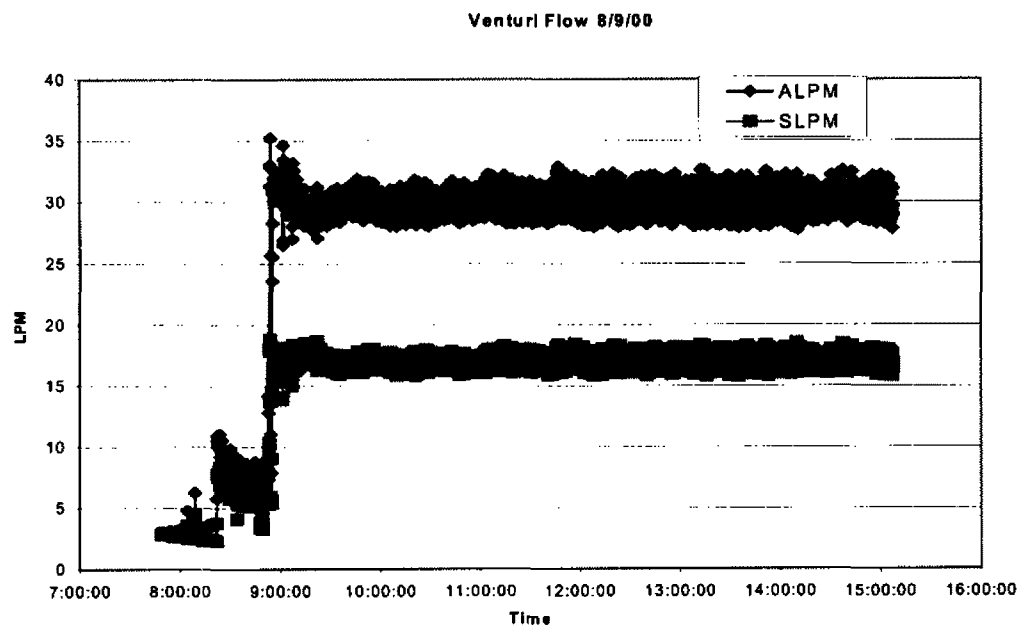
Venturi Flow 8/9/00

Figure 4-15. Venturi flow, Test 2—Day 2, August 9, 2000.

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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 upright in a secure container for transport to the sample recovery area.

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

- 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 (two carbonyl sampling tubes in series) were disassembled. The ends of the individual tubes were sealed with plastic caps and the sealed tubes placed in an aluminum foil packet, labeled to preserve the front/back order from the sample collection array, placed in a plastic bag, labeled, and chain of custody documentation initiated.

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

Denuders, PUF modules, and filters were all bagged and stored over ice.

At a later time, extraction on-site was performed for the denuders. The denuders were rinsed with a mixture of methylene chloride: acetone: hexane in a volume ratio of 2:3:5. The solvent mixture was added to the denuder and the denuder tube was capped and shaken (4 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.

Canisters and carbonyl tubes were transported to the ERG laboratory for analysis and the filters, PUF modules, and denuder extracts were transported to the EPA laboratory for analysis.

Laboratory Experimental Methodology

Components of the sample collection arrays, filters, DNPH-impregnated silica gel tubes used to sample carbonyl compounds, and canisters used to sample volatile organic compounds were returned for analysis to EPA and ERG laboratories, respectively (see Table 3-1 for responsible laboratory). The analyses described in the following sections were performed with the analytical methodology used by the respective laboratories summarized in Table 3-1.

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 gravimetric analysis before and after sample collection.

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Elemental Analysis

Individual elements above atomic number 9 (fluorine) were measured using a Philips Model 2404, wavelength-dispersive, X-ray fluorescence (XRF) spectrometer running the UniQuant™ program. This program gives qualitative and quantitative information on the elements present on a Teflon® membrane filter. The filter to be analyzed was covered with a 0.4 μm thick Prolene® film which was attached using glue. The glue was only on the outer rim of the filter and did not interfere with the analysis. Only elements which gave amounts greater than 1 standard error above the detection limit were reported.

Water-Soluble Inorganic Ions

Teflon® filter samples were analyzed for major inorganic anions and cations using a Dionex DX-120 ion chromatograph equipped with a 25 μL sample loop and a conductivity detector. Major ions determined were chloride, nitrate, sulfate, calcium, magnesium, potassium, and ammonium. Prior to extraction the filters were wetted with 350-500 μL of ethanol. Two sequential extractions with High Performance Liquid Chromatography (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 μm poly(ethylvinylbenzene-divinylbenzene) macroporous substrate resin functionalized with a relatively weak carboxylic acid stationary phase and a sulfuric acid mobile phase. Ion concentrations were determined from four-point calibration curves using an external standard method. All samples were extracted and analyzed in duplicate or triplicate.

Elemental Carbon/Organic Carbon

Elemental carbon (EC) and organic carbon (OC) content of PM samples collected on pre-fired quartz filters was determined by NIOSH Method 5040 (NIOSH, 1994) using a Sunset Laboratory thermal evolution instrument. 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 CO_2 in a bed of granular MnO_2, then reduced to methane in a methanator. Methane is subsequently quantified by a flame ionization detector (FID). In a second stage, the sample oven temperature is reduced, an oxygen-helium mixture is introduced, and the temperature is increased to 940 °C. With the introduction of oxygen, pyrolytically generated carbon is oxidized and the transmittance of a laser light beam through the filter increases. The point at which the filter transmittance reaches its initial value is defined as the split between OC and EC. Carbon evolved prior to the split is considered OC (including carbonate), and carbon volatilized after the split is considered elemental (EC). Elemental carbon evolved is similarly oxidized to CO_2 and subsequently reduced to methane to be measured by the FID.

Organic Compounds

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

An aliquot of the combined extract was derivatized with diazomethane to yield methyl esters of any fatty acids which might be present. After the methylation reaction was complete,

the methylated extract aliquot was reconcentrated by nitrogen blowdown. A separate portion of the methylated extract was derivatized a second time using bis (trimethylsilyl) trifluoroacetamide-N,O-bis (trimethylsilyl) acetamide (Sylon BFT®) reagent to convert compounds such as levoglucosan and cholesterol to their trimethylsilyl (TMS) derivatives. Both 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 μm film thickness) was employed along with an injector temperature of 65 °C and a GC/MS interface temperature of 300 °C. The initial GC oven temperature was set at 65 °C with an initial hold time of 10 minutes. The oven temperature was then ramped upward at 10 °C/min to 300 °C and held at the upper temperature for an additional 41.5 minutes. Helium was used as the carrier gas (1 mL/min) and the GC was operated in the split/splitless mode.

Positive identification of target compounds was obtained by comparing mass spectra of the analytes with those obtained from 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.

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Carbonyl Compounds

Sep-Pak® chromatographic-grade silica gel cartridges impregnated with DNPH were used in series for carbonyl sample collection. The tubes were used in series to check for compound breakthrough. Following sample collection in the field, the cartridges and accompanying chain of custody documentation were transported to the ERG laboratory, where they were logged into the laboratory sample tracking system. The cartridges were extracted and analyzed for the compounds listed in Table 4-8 using EPA Compendium Method TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)" (EPA, 1999). The analytical instrument was a Varian 5000 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 analytical column with a 5-μm particle size. An automatic sample injector was used to inject 25 μL aliquots into the HPLC.

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

Daily calibration checks were performed to ensure that the analytical procedures were in control. Daily quality control checks were performed after every 10 samples on the days that samples were analyzed, with compound responses within ±15% 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

Table 4-8. Carbonyl Compounds Analyzed by High Performance Liquid Chromatography: Method Detection Limits

Compound	CAS No.	Method Detection Limits µg
Formaldehyde	50-00-0	0.0838
Acetaldehyde	75-07-0	0.0916
Acetone	67-64-1	0.0428
Propionaldehyde	123-38-6	0.0934
Crotonaldehyde	4170-30-3	0.1283
Butyraldehyde	123-72-8	0.0956
Benzaldehyde	100-52-7	0.0959
Isovaleraldehyde	590-86-3	0.1076
Valeraldehyde	110-62-3	0.1758
o-Tolualdehyde	529-20-4	0.1439
m-Tolualdehyde	620-23-5	0.1439
p-Tolualdehyde	104-87-0	0.1439
Hexaldehyde	66-25-1	0.1377
2,5-Dimethylbenzaldehyde	5779-94-2	0.1337*
Diacetyl	432-03-8	0.0154*
Methacrolein	78-85-3	0.0125*
2-Butanone	78-93-3	0.0125*
Glyoxal	107-22-2	0.0412*
Acetophenone	98-86-2	0.0250*
Methylglyoxal	78-98-8	0.0244*
Octanal	124-13-0	0.0100*
Nonanal	124-19-6	0.0182*

*Estimated value.

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

The combined analysis for gas-phase air toxics and Speciated Nonmethane Organic Compounds was performed on a gas chromatograph(GC)/flame ionization detector(FID)/mass selective detector (MSD). A Hewlett-Packard 5971 MSD and a Hewlett-Packard 5890 Series II GC with a 60 m by 0.32 mm I.D. and a 1 µm film thickness J&W DB-1 capillary column followed by a 2:1 splitter was used to send the larger portion of the column effluent to the MSD and the smaller fraction to the FID. The chromatograph oven containing the DB-1 capillary column was cooled to -50 °C with liquid nitrogen at the beginning of the sample injection. This temperature was held for 5 minutes and then increased at the rate of 15 °C per minute to 0 °C. The oven temperature was then ramped at 6 °C/minute to 150 °C, then ramped at 20 °C/minute to 225 °C and held for 8 minutes. The gas eluting from the DB-1 capillary column passed through the 2:1 fixed splitter, to divide the flow between the MSD and the FID.

The air toxics analysis was performed according to the procedures of EPA Compendium Method TO-15, "Determination of Volatile Organic Compounds (VOCs) In Air Collected in Specially-Prepared Canister and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)" (U.S. EPA, 1999). The analysis of Speciated Nonmethane Organic Compounds was performed according to the procedures of "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (U.S. EPA, 1998). Detection limits for air toxics are shown in Table 4-9, and for the Speciated Nonmethane Organic Compounds in Table 4-10.

Particle Size Distribution Data

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

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Table 4-9. Detection Limits (ppbv) for Air Toxics Compounds (Analytical Method TO-15)

Target Compounds*	CAS No.	Method Detection Limit $\mu g/m^3$
Acetylene	74-86-2	0.24
Propylene	115-07-1	0.17
Dichlorodifluoromethane	75-71-8	0.40
Chloromethane	74-87-3	0.24
Dichlorotetrafluoroethane	1320-37-2	0.70
Vinyl chloride	75-01-4	0.31
1,3-Butadiene	106-99-0	0.31
Bromomethane	74-83-9	0.70
Chloroethane	75-00-3	0.42
Acetonitrile	75-05-8	0.84
Acetone	67-64-1	1.23
Trichlorofluoromethane	75-69-4	0.45
Acrylonitrile	107-13-1	0.91
1,1-Dichloroethene	75-35-4	0.79
Methylene chloride	75-09-2	0.42
Trichlorotrifluoroethane	26523-64-8	1.07
trans-1,2-Dichloroethylene	56-60-5	0.47
1,1-Dichloroethane	75-34-3	0.65
Methyl tert-butyl ether	1634-04-1	1.29
Methyl ethyl ketone	78-93-3	0.88
Chloroprene	126-99-8	0.73
cis-1,3-Dichloroethylene	156-59-2	0.79
Bromochloromethane	74-97-5	1.26
Chloroform	67-66-3	0.49
Ethyl tert-butyl ether	637-92-3	1.25
1,2-Dichloroethane	107-06-2	0.48
1,1,1-Trichloroethane	71-55-6	0.65
Benzene	71-43-2	0.25
Carbon tetrachloride	56-23-5	1.01
tert-Amyl methyl ether	994-05-8	1.00

(Continued)

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Table 4-9. (Continued)

Target Compounds*	CAS No.	Method Detection Limit $\mu g/m^3$
1,2-Dichloropropane	78-87-5	0.65
Ethyl acrylate	140-88-5	1.31
Bromodichloromethane	75-27-4	0.80
Trichloroethylene	79-01-6	0.75
Methyl methacrylate	80-62-6	1.47
cis-1,2-Dichloropropene	10061-01-5	0.82
Methyl isobutyl ketone	108-10-1	1.36
trans-1,2-Dichloropropene	10061-02-6	1.00
1,1,2-Trichloroethane	79-00-5	0.65
Toluene	108-88-3	0.45
Dibromochloromethane	124-48-1	1.36
1,2-Dibromoethane	106-93-4	1.23
n-Octane	111-65-9	0.56
Tetrachloroethylene	127-18-4	0.81
Chlorobenzene	108-90-7	0.55
Ethylbenzene	100-41-4	0.35
m-, p-Xylene	108-38-3/106-42-3	0.87
Bromoform	75-25-2	1.65
Styrene	100-42-5	0.59
1,1,2,2-Tetrachloroethane	79-34-5	0.82
o-Xylene	95-47-6	0.43
1,3,5-Trimethylbenzene	108-67-8	0.69
1,2,4-Trimethylbenzene	95-63-6	0.69
m-Dichlorobenzene	541-73-1	0.60
Chloromethylbenzene	100-44-7	0.72
p-Dichlorobenzene	106-46-7	1.08
o-Dichlorobenzene	95-50-1	0.72
1,2,4-Trichlorobenzene	120-82-1	0.89
Hexachloro-1,3-butadiene	87-68-3	1.28

*MDLs are instrument detection limits based on Fed. Reg., 1984. MDLs reported here are based on nominal injection volume of 200 mL of gas.

Table 4-10. Detection Limits (μg/m³) for Speciated Nonmethane Organic Compounds ("Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (U.S. EPA, 1998))

Compound	CAS No.	Method Detection Limits μg/m³
Ethylene	74-85-1	0.50
Acetylene	74-86-2	0.47
Ethane	74-84-0	0.54
Propylene	115-07-1	0.44
Propane	74-98-6	0.46
Propyne	74-99-7	0.42
Isobutane	75-28-5	0.43
Isobutene/1-butene	115-11-7/106-98-0	0.21
1,3-Butadiene	106-99-0	0.40
n-Butane	106-97-8	0.43
trans-2-Butene	624-64-6	0.42
cis-2-Butene	590-18-1	0.42
3-Methyl-1-butene	563-45-1	0.32
Isopentane	78-78-4	0.33
1-Pentene	109-67-1	0.32
2-Methyl-1-butene	563-46-2	0.45
n-Pentane	109-66-0	0.33
Isoprene	78-79-4	0.31
trans-2-Pentene	646-04-8	0.33
cis-2-Pentene	627-20-3	0.33
2-Methyl-2-butene	513-35-9	0.32
2,2-Dimethylbutane	75-83-2	0.46
Cyclopentene	142-29-0	0.31
4-Methyl-1-pentene	691-37-2	0.45
Cyclopentane	287-92-3	0.32
2,3-Dimethylbutane	79-29-8	0.46
2-Methylpentane	107-83-5	0.46
3-Methylpentane	96-14-0	0.46

(Continued)

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Table 4-10. (Continued)

Compound	CAS No.	Method Detection Limits $\mu g/m^3$
2-Methyl-1-pentene	763-29-1	0.46
1-Hexene	592-41-6	0.46
2-Ethyl-1-butene	760-21-4	0.45
n-Hexane	110-54-3	0.46
trans-2-Hexene	4050-45-7	0.46
cis-2-Hexene	7688-21-3	0.46
Methylcyclopentane	96-37-7	0.45
2,4-Dimethylpentane	108-08-7	0.35
Benzene	71-43-2	0.42
Cyclohexane	110-82-7	0.45
2-Methylhexane	591-76-4	0.40
2,3-Dimethylpentane	565-59-3	0.40
3-Methylhexane	589-34-4	0.40
1-Heptene	592-76-7	0.39
2,2,4-Trimethylpentane	540-84-1	0.51
n-Heptane	142-82-5	0.40
Methylcyclohexane	108-87-2	0.39
2,2,3-Trimethylpentane	564-02-3	0.51
2,3,4-Trimethylpentane	565-75-3	0.51
Toluene	108-88-3	0.37
2-Methylheptane	592-27-8	0.51
3-Methylheptane	589-81-1	0.51
1-Octene	111-66-0	0.50
n-Octane	111-65-9	0.51
Ethylbenzene	100-41-4	0.52
m-, p-Xylene	108-38-3/106-42-3	0.47
Styrene	100-42-5	0.46
o-Xylene	95-47-6	0.47
1-Nonene	124-11-8	0.40
n-Nonane	111-84-2	0.41

(Continued)

Table 4-10. (Continued)

Compound	CAS No.	Method Detection Limits $\mu g/m^3$
Isopropylbenzene	98-82-8	0.38
α-Pinene	80-56-8	0.39
n-Propylbenzene	103-65-1	0.38
m-Ethyltoluene	620-14-4	0.38
p-Ethyltoluene	622-96-8	0.38
1,3,5-Trimethylbenzene	108-67-8	0.38
o-Ethyltoluene	611-14-3	0.38
β-Pinene	127-91-3	0.39
1,2,4-Trimethylbenzene	95-63-6	0.38
1-Decene	872-05-9	0.33
n-Decane	124-18-5	0.33
1,2,3-Trimethylbenzene	526-73-8	0.38
m-Diethylbenzene	141-93-5	0.32
p-Diethylbenzene	105-05-5	0.32
1-Undecene	821-95-4	0.49
n-Undecane	1120-21-4	0.50
1-Dodecene	112-41-4	0.49
n-Dodecane	112-40-3	0.50
1-Tridecene	2437-56-1	0.49
n-Tridecane	629-50-5	0.50

Section 5
Results and Discussion

Analyses were performed in different laboratories according to the scheme shown in Table 3-1, with 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 elemental/organic carbon (EC/OC), major elements, and major inorganic ions as components of the fine particulate matter are reported in Table 5-1 as weight percent of measured PM-2.5 mass. Results tabulated in Table 5-1 also indicate a nearly three-fold range of PM-2.5 mass emission rates between the two days of testing. However, the absolute mass emission rates of PM-2.5 were quite low (3.54 and 1.23 mg/kg fuel) on both days.

EC/OC values for samples collected on quartz filters with and without an XAD-coated annular denuder fronting the filters exhibited a wide variance. Substantially lower OC values were found on the filters fronted with an organic denuder than on filters without a preceding denuder. It is likely that much of the OC collected on the quartz filters without a denuder in place represents adsorbed gas-phase semivolatile organic compounds.

Of the major water-soluble ions, only sulfate and potassium ions were above quantitation limits. Total potassium as measured by X-ray fluorescence spectrometry agreed well with water-soluble potassium determined by ion chromatography. Silicon was the element found in greatest concentration, perhaps originating from the firebrick lining of the boiler. Supporting data for the inorganic analyses are found in Appendices B through E.

Table 5-1. Fine Particle Emission Rate and Fine Particle Chemical Composition of Emissions from an Industrial Wood-Fired Boiler, Including Gas-Phase Volatile Organic and Carbonyl Compounds

PM-2.5 Emission Rate (mg/kg fuel burned)	1.23 - 3.54[a]	
Speciated Carbonyl Compounds Emission Rate (mg/kg fuel burned)	2.53 (Day 1)	
	0.80 (Day 2)	
Total Carbonyl Compound Emission Rate (mg/kg fuel burned)	2.74 (Day 1)	
	0.94 (Day 2)	
Speciated NMOC Emission Rate (mg/kg fuel burned)	4.83 (Day 1)	
	0.98 (Day 2)	
Total NMOC Emission Rate (mg/kg fuel burned)	7.50 (Day 1)	
	1.85 (Day 2)	
Elemental and Organic Carbon (Wt.% of Measured PM-2.5 Mass)	w/out denuder[b]	w/ denuder[c]
Elemental Carbon	3.0 ± 0.4	13.8 ± 3.1
Organic Carbon	84.6 ± 11.0	32.6 ± 8.0
Ionic Species (Wt.% of Measured PM-2.5 Mass)[d]		
Chloride	NQ	
Nitrate	NQ	
Sulfate	7.8 ± 0.6	
Potassium	6.6 ± 0.5	
Magnesium	ND	
Calcium	ND	
Elemental Composition (Wt.% of Measured PM-2.5 Mass)[e]		
Sodium	0.18 ± 0.04	
Magnesium	0.17 ± 0.01	
Silicon	16.2 ± 2.5	
Phosphorus	0.09 ± 0.03	
Sulfur	3.7 ± 0.4	
Chlorine	0.64 ± 0.04	
Potassium	10.6 ± 0.6	
Calcium	0.76 ± 0.06	

NQ-below quantitation limits
ND-below detection limits

a) range over two test days
b) average of two filters, one from each day of testing
c) average of two filters, one from each day of testing
d) average of two filters from each day of testing with the exception of sulfate, which was below
   quantitation limits on the second day
e) average of two filters from the first day of testing
Error shown is the standard deviation of the results from the individual filters.

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Speciated Particle-Phase (PM-2.5) Organic Compounds

Table 5-2(a, b) reports the emission rates (μg/kg of fuel) of individual organic compounds collected on the organic denuders, quartz filters, and PUF plugs in the sampling arrays. Compounds attributed to the particle-phase are also reported as weight percent of measured PM-2.5 mass. For the denuder/filter/PUF sampling arrays (Table 5-2a), organic compounds attributed to the particulate matter were those collected on the quartz filters and on the following PUF plugs. For the undenuded arrays (Table 5-2b), only the organic compounds found on the quartz filters were attributed to the particulate matter. Because of very low PM-2.5 mass loadings collected on individual filters, it was necessary to composite a number of quartz filters from different sampling arrays between the two test days to have sufficient material to quantify individual organic compounds. Organic compound speciation results reported in Table 5-2(a, b) therefore represent a composite over the two days. Minor variations in the stack gas and sampling flow rates which occurred between the two days have been factored into the calculations to determine the reported emission rates. Supporting data for these analyses are included in Appendix F.

Gas-Phase Carbonyl Compounds

Analytical results for the carbonyl field samples for each of the two test days are shown in Table 5-3(a, b). Results of the analysis are reported for the sum of the paired DNPH-impregnated silica gel tubes since the tubes were sampled as pairs, using the back tube as a check for breakthrough. At the bottom of the table, the entry reported as "Total Unspeciated" is the total mass (front plus back tube) of the compounds characterized as carbonyl compounds but not identified as a specific compound because no analytical standard was available. The entry reported as "Total Speciated + Unspeciated" includes the total mass (front and back tube) of both specifically identified carbonyl compounds and unspeciated carbonyl compounds. As Table 5-3 shows, the largest portion of the carbonyl compounds (>75%) consisted of speciated (i.e., specifically identified) carbonyl compounds. Supporting data showing results for each individual carbonyl sampling tube (front and back) are included in Appendix G.

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Table 5-2a. Gas- and Particle-Phase Organic Compounds as Measured by Denuder-Quartz Filter-PUF

Compound	Denuder (mg/kg of fuel)	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM$_{2.5}$ Mass
Naphthalene	0.30	ND	2.28	0.048 ± 0.006
Acenaphthylene	ND	ND	ND	ND
Acenaphthene	ND	ND	0.54	0.011 ± 0.003
Fluorene	ND	ND	2.01	0.042 ± 0.0003
Phenanthrene	0.24	ND	1.94	0.041 ± 0.009
Anthracene	ND	ND	ND	ND
Fluoranthene	ND	0.01	0.21	0.005 ± 0.0004
Pyrene	ND	ND	0.09	0.002 ± 0.00008
Benzo[a]anthracene	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND
Benzo[b]fluoranthene	ND	ND	ND	ND
Benzo[k]fluoranthene	ND	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND	ND
Benzo[ghi]perylene	ND	ND	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND
Indeno[1,2,3-cd]fluoranthene	ND	ND	ND	ND
Dibenzo[a,h]anthracene	ND	ND	ND	ND
Coronene	ND	ND	ND	ND
1-Methylnaphthalene	ND	ND	3.12	0.065 ± 0.010
2-Methylnaphthalene	ND	ND	4.24	0.089 ± 0.047
2,7-Dimethylnaphthalene	ND	ND	0.69	0.014 ± 0.002
1,3-Dimethylnaphthalene	ND	ND	2.40	0.050 ± 0.008
2,6-Dimethylnaphthalene	ND	ND	1.88	0.040 ± 0.006
9-Methylanthracene	ND	ND	ND	ND
Methylfluorene	ND	ND	1.35	0.028 ± 0.004
bis(2-Ethylhexyl)phthalate	1.59	0.19	4.09	0.090 ± 0.019
Butyl benzyl phthalate	8.04	ND	4.48	0.094 ± 0.052
Diethyl phthalate	1.45	ND	31.06	0.651 ± 0.221
Dimethyl phthalate	0.33	ND	20.80	0.436 ± 0.045
Di-n-butyl phthalate	0.63	ND	1.20	0.025 ± 0.014
Di-n-octyl phthalate	ND	ND	ND	ND
Octylcyclohexane	ND	ND	ND	ND
Decylcyclohexane	ND	ND	ND	ND

ND = Compound not detected. (Continued)

Table 5-2a. (Continued)

Compound	Denuder (mg/kg of fuel)	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM$_{2.5}$ Mass
Tridecylcyclohexane	ND	ND	ND	ND
Nonadecylcyclohexane	ND	ND	ND	ND
Norpristane	ND	ND	ND	ND
Pristane	ND	ND	ND	ND
Phytane	ND	ND	ND	ND
Squalane	ND	ND	ND	ND
ABB-20R-C27-Cholestane	ND	ND	ND	ND
BAA-20R-C27-Cholestane	ND	ND	ND	ND
AAA-20S-C27-Cholestane	ND	ND	ND	ND
AAA-20R-C27-Cholestane	ND	ND	ND	ND
ABB-20R-C28-Methylcholestane	ND	ND	ND	ND
ABB-20R-C29-Ethylcholestane	ND	ND	ND	ND
17A(H)-22, 29, 30-Trisnorhopane	ND	ND	ND	ND
17B(H)-21A(H)-30-Norhopane	ND	ND	ND	ND
17B(H)-21B(H)-Hopane	ND	ND	ND	ND
17B(H)-21A(H)-Hopane	ND	ND	ND	ND
17A(H)-21B(H)-Hopane	ND	ND	ND	ND
n-Decane (C10)	ND	ND	ND	ND
n-Undecane (C11)	ND	ND	ND	ND
n-Dodecane (C12)	3.94	ND	ND	ND
n-Tridecane (C13)	0.60	ND	ND	ND
n-Tetradecane (C14)	3.00	ND	ND	ND
n-Pentadecane (C15)	0.89	ND	1.80	0.038 ± 0.033
n-Hexadecane (C16)	2.06	ND	4.51	0.095 ± 0.057
n-Heptadecane (C17)	1.00	ND	2.98	0.062 ± 0.009
n-Octadecane (C18)	0.77	ND	4.47	0.094 ± 0.013
n-Nonadecane (C19)	1.77	ND	10.58	0.222 ± 0.028
n-Eicosane (C20)	5.60	ND	1.04	0.022 ± 0.003
n-Heneicosane (C21)	18.96	ND	2.74	0.057 ± 0.007
n-Docosane (C22)	160.29	ND	ND	ND
n-Tricosane (C23)	550.25	2.83	18.90	0.456 ± 0.086
n-Tetracosane (C24)	78.12	19.88	1.68	0.452 ± 0.085
n-Pentacosane (C25)	32.86	39.68	5.33	0.944 ± 0.178
n-Hexacosane (C26)	12.37	44.01	4.53	1.018 ± 0.192

ND = Compound not detected. (Continued)

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Table 5-2a. (Continued)

Compound	Denuder (mg/kg of fuel)	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% $PM_{2.5}$ Mass
n-Heptacosane (C27)	7.37	28.78	5.74	0.724 ± 0.137
n-Octacosane (C28)	6.29	17.00	2.45	0.408 ± 0.144
n-Nonacosane (C29)	3.38	7.62	3.58	0.235 ± 0.083
n-Triacontane (C30)	1.12	3.88	1.11	0.104 ± 0.032
n-Hentriacontane (C31)	0.67	2.26	1.51	0.079 ± 0.025
n-Dotriacontane (C32)	0.79	0.78	3.09	0.081 ± 0.020
n-Tritriacontane (C33)	0.46	0.27	1.28	0.033 ± 0.010
n-Tetratriacontane (C34)	0.30	0.11	2.77	0.060 ± 0.019
n-Pentatriacontane (C35)	0.94	0.24	2.79	0.064 ± 0.020
n-Hexatriacontane (C36)	ND	0.08	ND	0.002 ± 0.0006
n-Tetracontane (C40)	ND	ND	ND	ND
3-Methylnonadecane	0.33	ND	ND	ND
2-Methylnonadecane	1.70	ND	ND	ND
Cyclopenta[cd]pyrene	ND	ND	ND	ND
Dibenzo[a,e]pyrene	ND	ND	ND	ND
Pyrene	ND	ND	0.09	0.002 ± 0.0002
Benzo[a]pyrene	ND	ND	ND	ND
Methylfluoranthene	ND	ND	ND	ND
Methylchrysene	ND	ND	ND	ND
Retene	ND	ND	ND	ND
Anthroquinone	ND	ND	ND	ND
9-Fluorenone	ND	ND	1.34	0.028 ± 0.006
Benzo[a]anthracene-7,12-dione	ND	ND	ND	ND
1,8-Naphthalic anhydride	ND	ND	ND	ND
Squalene	2.65	ND	ND	ND
1-Octadecene	1.15	ND	ND	ND
Benzo[e]pyrene	ND	ND	ND	ND
Oxalic acid (C2)	ND	ND	ND	ND
Malonic acid (C3)	ND	ND	ND	ND
Maleic acid (C3=)	ND	ND	ND	ND
Fumaric acid (C4=)	ND	ND	ND	ND
Succininc acid (C4) Butanedioic acid	ND	ND	ND	ND
Glutaric acid (C5) Pentanedioic acid	ND	ND	ND	ND
Adipic acid (C6) Hexanedioic acid	ND	ND	ND	ND

ND = Compound not detected.   (Continued)

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Table 5-2a. (Continued)

Compound	Denuder (mg/kg of fuel)	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM$_{2.5}$ Mass
Pimelic acid (C7) Heptanedioic acid	ND	ND	ND	ND
Suberic acid (C8) Octanedioic acid	ND	ND	ND	ND
Azelaic acid (C9) Nonanedioic acid	ND	ND	ND	ND
Sebacic acid (C10) Decanedioic acid	ND	ND	ND	ND
Phthalic acid (1,2)	3.14	ND	ND	ND
Isophthalic acid (1,3)	5.39	ND	ND	ND
Terephthalic acid (1,4)	ND	ND	2.37	0.050 ± 0.015
1,2,4-Benzenetricarboxylic acid	ND	ND	ND	ND
1,2,4,5-Benzenetetracarboxylic acid	ND	ND	ND	ND
Methylphthalic acid	ND	ND	ND	ND
C6 Hexanoic acid	ND	ND	ND	ND
C8 Octanoic acid	0.29	ND	2.91	0.061 ± 0.014
C9 Nonanoic acid	0.63	ND	2.76	0.058 ± 0.013
C10 Decanoic acid	1.02	ND	ND	ND
C11 Undecanoic acid	0.69	ND	0.48	0.010 ± 0.005
C12 Dodecanoic acid	2.11	ND	1.20	0.025 ± 0.004
C13 Tridecanoic Acid	1.09	0.06	0.19	0.005 ± 0.0007
C14 Tetradecanoic acid	2.78	ND	1.08	0.023 ± 0.003
C15 Pentadecanoic Acid	0.95	ND	0.34	0.007 ± 0.001
C16 Hexadecanoic acid	16.34	1.73	2.03	0.079 ± 0.012
C17 Heptadecanoic Acid	ND	ND	0.26	0.005 ± 0.0007
C18 Octadecanoic acid	10.10	5.39	ND	0.113 ± 0.017
C19 Nonadecanoic Acid	ND	ND	0.01	0.000
C20 Eicosanoic acid	ND	0.21	ND	0.004 ± 0.0006
C21 Heneicosanoic Acid	ND	ND	ND	ND
C22 Docosanoic acid	ND	ND	0.07	0.001 ± 0.0001
C23 Tricosanoic Acid	ND	ND	ND	ND
C24 Tetracosanoic acid	0.25	ND	ND	ND
C25 Pentacosanoic Acid	ND	ND	ND	ND
C26 Hexacosanoic Acid	ND	ND	ND	ND
C27 Heptacosanoic Acid	ND	ND	ND	ND
Abietic acid	ND	ND	ND	ND
Octacosanoic acid	ND	ND	0.04	0.001 ± 0.0001
Nonacosanoic Acid	ND	ND	ND	ND

ND = Compound not detected.   (Continued)

Table 5-2a. (Continued)

Compound	Denuder (mg/kg of fuel)	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM$_{2.5}$ Mass
Triacontanoic acid	ND	ND	ND	ND
Pinonic acid	ND	ND	ND	ND
Palmitoleic acid (C16:1)	0.76	0.04	ND	0.001 ± 0.0001
Oleic acid (C18:1)	ND	0.21	ND	0.004 ± 0.0006
Linoleic acid (C18:2)	ND	0.11	ND	0.002 ± 0.0001
Linolenic acid	ND	ND	ND	ND
Pimaric acid	43.00	ND	ND	ND
Sandaracopimaric acid	ND	ND	ND	ND
Isopimaric acid	ND	ND	ND	ND
6,8,11,13-Abietatetraen-18-oic acid	ND	ND	ND	ND
Dehydroabietic acid	ND	ND	ND	ND
Levoglucosan (TMS derivative)	ND	0.88	ND	0.018 ± 0.011
Cholesterol (TMS derivative)	ND	2.09	ND	0.044 ± 0.004
Stigmasterol (TMS derivative)	ND	2.92	ND	0.061 ± 0.005
Monopalmitin (TMS derivative)	ND	0.33	ND	0.007 ± 0.001
Monoolein (TMS derivative)	ND	0.92	ND	0.019 ± 0.002
Monostearin (TMS derivative)	ND	1.47	ND	0.031 ± 0.002
Glycerine (TMS derivative)	ND	0.86	ND	0.018 ± 0.003
β-Sitosterol (TMS derivative)	ND	ND	ND	ND
Sitostenone (TMS derivative)	ND	ND	ND	ND
α-Amyrin	ND	ND	ND	ND
β-Amyrin	ND	ND	ND	ND
iso-Docosane	ND	ND	ND	ND
anteiso-Docosane	0.68	ND	ND	ND
iso-Tricosane	1.41	ND	ND	ND
anteiso-Tricosane	6.44	ND	ND	ND
iso-Tetracosane	0.83	1.01	ND	0.021 ± 0.004
anteiso-Tetracosane	0.74	0.43	ND	0.009 ± 0.002
iso-Pentacosane	0.56	2.49	ND	0.052 ± 0.010
anteiso-Pentacosane	0.77	1.51	ND	0.032 ± 0.006
iso-Hexacosane	0.44	2.34	ND	0.049 ± 0.009
anteiso-Hexacosane	0.56	1.91	ND	0.040 ± 0.008
iso-Heptacosane	0.10	1.73	ND	0.036 ± 0.007
anteiso-Heptacosane	0.18	1.41	ND	0.030 ± 0.006

ND = Compound not detected.   (Continued)

Table 5-2a. (Continued)

Compound	Denuder (mg/kg of fuel)	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM$_{2.5}$ Mass
iso-Octacosane	ND	0.77	ND	0.016 ± 0.003
anteiso-Octacosane	ND	0.80	ND	0.017 ± 0.003
iso-Nonacosane	0.38	0.43	ND	0.009 ± 0.003
anteiso-Nonacosane	0.54	0.31	ND	0.007 ± 0.002
iso-Triacontane	ND	0.28	ND	0.006 ± 0.002
anteiso-Triacontane	ND	0.22	ND	0.005 ± 0.002
iso-Hentriacontane	ND	0.10	ND	0.002 ± 0.0006
anteiso-Hentriacontane	ND	0.07	ND	0.001 ± 0.0003
iso-Dotriacontane	ND	0.06	ND	0.001 ± 0.0003
anteiso-Dotriacontane	ND	0.04	ND	0.001 ± 0.003
iso-Tritriacontane	ND	ND	ND	ND
anteiso-Tritriacontane	ND	ND	ND	ND

ND = Compound not detected.

Table 5-2b. Gas- and Particle-Phase Organic Compounds as Measured by Quartz Filter-PUF-PUF

Compound	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM$_{2.5}$ Mass
Naphthalene	ND	1.49	ND
Acenaphthylene	ND	ND	ND
Acenaphthene	ND	0.85	ND
Fluorene	ND	2.65	ND
Phenanthrene	ND	ND	ND
Anthracene	ND	ND	ND
Fluoranthene	0.01	ND	0.0002 ± 0.0001
Pyrene	ND	ND	ND
Benzo[a]anthracene	ND	ND	ND
Chrysene	ND	ND	ND
Benzo[b]fluoranthene	ND	ND	ND
Benzo[k]fluoranthene	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND
Benzo[ghi]perylene	ND	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	ND
Indeno[1,2,3-cd]fluoranthene	ND	ND	ND
Dibenzo[a,h]anthracene	ND	ND	ND
Coronene	ND	ND	ND
1-Methylnaphthalene	ND	2.81	ND
2-Methylnaphthalene	ND	3.49	ND
2,7-Dimethylnaphthalene	ND	1.67	ND
1,3-Dimethylnaphthalene	ND	2.39	ND
2,6-Dimethylnaphthalene	ND	2.37	ND
9-Methylanthracene	0.06	ND	0.0012 ± 0.00004
Methylfluorene	0.00	ND	0.0000
bis(2-Ethylhexyl)phthalate	0.57	3.75	0.0119 ± 0.0025
Butyl benzyl phthalate	ND	ND	ND
Diethyl phthalate	ND	19.10	ND
Dimethyl phthalate	ND	20.79	ND
Di-n-butyl phthalate	ND	ND	ND
Di-n-octyl phthalate	ND	0.29	ND
Octylcyclohexane	ND	ND	ND
Decylcyclohexane	ND	ND	ND
Tridecylcyclohexane	ND	ND	ND

ND = Compound not detected.   (Continued)

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Table 5-2b. (Continued)

Compound	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM$_{2.5}$ Mass
Nonadecylcyclohexane	ND	ND	ND
Norpristane	ND	ND	ND
Pristane	ND	ND	ND
Phytane	ND	ND	ND
Squalane	ND	ND	ND
ABB-20R-C27-Cholestane	ND	ND	ND
BAA-20R-C27-Cholestane	ND	ND	ND
AAA-20S-C27-Cholestane	ND	ND	ND
AAA-20R-C27-Cholestane	ND	ND	ND
ABB-20R-C28-Methylcholestane	ND	ND	ND
ABB-20R-C29-Ethylcholestane	ND	ND	ND
17A(H)-22, 29, 30-Trisnorhopane	ND	ND	ND
17B(H)-21A(H)-30-Norhopane	ND	ND	ND
17B(H)-21B(H)-Hopane	ND	ND	ND
17B(H)-21A(H)-Hopane	ND	ND	ND
17A(H)-21B(H)-Hopane	ND	ND	ND
n-Decane (C10)	ND	1.67	ND
n-Undecane (C11)	ND	3.30	ND
n-Dodecane (C12)	ND	ND	ND
n-Tridecane (C13)	ND	ND	ND
n-Tetradecane (C14)	ND	ND	ND
n-Pentadecane (C15)	ND	1.02	ND
n-Hexadecane (C16)	ND	2.66	ND
n-Heptadecane (C17)	ND	3.49	ND
n-Octadecane (C18)	ND	7.74	ND
n-Nonadecane (C19)	ND	14.24	ND
n-Eicosane (C20)	ND	9.83	ND
n-Heneicosane (C21)	ND	23.16	ND
n-Docosane (C22)	2.81	64.75	0.0588 ± 0.011
n-Tricosane (C23)	17.68	88.86	0.3707 ± 0.070
n-Tetracosane (C24)	47.75	16.15	1.0010 ± 0.189
n-Pentacosane (C25)	59.37	5.11	1.2446 ± 0.235
n-Hexacosane (C26)	57.32	6.17	1.2016 ± 0.227
n-Heptacosane (C27)	36.98	12.07	0.7752 ± 0.146
n-Octacosane (C28)	22.74	15.87	0.4767 ± 0.16

ND = Compound not detected. (Continued)

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Table 5-2b. (Continued)

Compound	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM₂.₅ Mass
n-Nonacosane (C29)	10.86	7.04	0.2276 ± 0.081
n-Triacontane (C30)	7.58	3.90	0.1590 ± 0.056
n-Hentriacontane (C31)	4.01	1.55	0.0841 ± 0.0212
n-Dotriacontane (C32)	1.55	0.50	0.0326 ± 0.0082
n-Tritriacontane (C33)	0.64	0.08	0.0134 ± 0.0034
n-Tetratriacontane (C34)	0.23	ND	0.0049 ± 0.0012
n-Pentatriacontane (C35)	0.33	ND	0.0068 ± 0.0017
n-Hexatriacontane (C36)	0.20	ND	0.0042 ± 0.0011
n-Tetracontane (C40)	ND	ND	ND
3-Methylnonadecane	ND	1.58	ND
2-Methylnonadecane	ND	1.51	ND
Cyclopenta[cd]pyrene	ND	ND	ND
Dibenzo[a,e]pyrene	ND	ND	ND
Pyrene	ND	0.05	ND
Benzo[a]pyrene	ND	ND	ND
Methylfluoranthene	ND	ND	ND
Methylchrysene	ND	ND	ND
Retene	ND	ND	ND
Anthroquinone	ND	ND	ND
9-Fluorenone	ND	ND	ND
Benzo[a]anthracene-7,12-dione	ND	ND	ND
1,8-Naphthalic anhydride	ND	ND	ND
Squalene	ND	ND	ND
1-Octadecene	ND	ND	ND
Benzo[e]pyrene	ND	ND	ND
Oxalic acid (C2)	0.06	ND	0.0012 ± 0.0005
Malonic acid (C3)	ND	ND	ND
Maleic acid (C3=)	ND	ND	ND
Fumaric acid (C4=)	ND	ND	ND
Succininc acid (C4) Butanedioic acid	ND	ND	ND
Glutaric acid (C5) Pentanedioic acid	ND	ND	ND
Adipic acid (C6) Hexanedioic acid	ND	ND	ND
Pimelic acid (C7) Heptanedioic acid	ND	ND	ND
Suberic acid (C8) Octanedioic acid	ND	ND	ND
Azelaic acid (C9) Nonanedioic acid	ND	ND	ND

ND = Compound not detected. (Continued)

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Table 5-2b. (Continued)

Compound	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM$_{2.5}$ Mass
Sebacic acid (C10) Decanedioic acid	ND	ND	ND
Phthalic acid (1,2)	ND	ND	ND
Isophthalic acid (1,3)	ND	ND	ND
Terephthalic acid (1,4)	ND	ND	ND
1,2,4-Benzenetricarboxylic acid	ND	ND	ND
1,2,4,5-Benzenetetracarboxylic acid	ND	ND	ND
Methylphthalic acid	ND	ND	ND
C6 Hexanoic acid	ND	ND	ND
C8 Octanoic acid	ND	3.21	ND
C9 Nonanoic acid	0.01	2.91	0.0003 ± 0.00007
C10 Decanoic acid	0.04	3.51	0.0009 ± 0.0005
C11 Undecanoic acid	0.00	0.85	0.0000
C12 Dodecanoic acid	ND	1.53	ND
C13 Tridecanoic Acid	0.06	0.27	0.0014 ± 0.0002
C14 Tetradecanoic acid	0.37	1.10	0.0078 ± 0.0012
C15 Pentadecanoic Acid	0.24	0.05	0.0051 ± 0.0008
C16 Hexadecanoic acid	11.09	2.15	0.2325 ± 0.0346
C17 Heptadecanoic Acid	ND	ND	ND
C18 Octadecanoic acid	10.66	0.68	0.2235 ± 0.0333
C19 Nonadecanoic Acid	ND	ND	ND
C20 Eicosanoic acid	0.38	0.03	0.0079 ± 0.0012
C21 Heneicosanoic Acid	ND	ND	ND
C22 Docosanoic acid	ND	0.18	ND
C23 Tricosanoic Acid	ND	0.00	ND
C24 Tetracosanoic acid	ND	0.02	ND
C25 Pentacosanoic Acid	ND	0.09	ND
C26 Hexacosanoic Acid	ND	0.04	ND
C27 Heptacosanoic Acid	ND	ND	ND
Abietic acid	ND	ND	ND
C28 Octacosanoic acid	ND	0.12	ND
C29 Nonacosanoic Acid	ND	ND	ND
C30 Triacontanoic acid	ND	ND	ND
Pinonic acid	2.57	ND	0.0538 ± 0.0169
Palmitoleic acid (C16:1)	0.08	0.29	0.0018 ± 0.0004
Oleic acid (C18:1)	0.90	ND	0.0189 ± 0.0029

ND = Compound not detected. (Continued)

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Table 5-2b. (Continued)

Compound	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% $PM_{2.5}$ Mass
Linoleic acid (C18:2)	0.44	ND	0.0092 ± 0.0012
Linolenic acid	ND	ND	ND
Pimaric acid	ND	ND	ND
Sandaracopimaric acid	ND	ND	ND
Isopimaric acid	ND	ND	ND
6,8,11,13-Abietatetraen-18-oic acid	ND	ND	ND
Dehydroabietic acid	ND	38.75	ND
Levoglucosan (TMS derivative)	0.06	ND	0.0013 ± 0.0008
Cholesterol (TMS derivative)	ND	ND	ND
Stigmasterol (TMS derivative)	ND	ND	ND
Monopalmitin (TMS derivative)	0.06	ND	0.0013 ± 0.0002
Monoolein (TMS derivative)	ND	ND	ND
Monostearin (TMS derivative)	1.08	ND	0.0226 ± 0.0018
Glycerine (TMS derivative)	ND	ND	ND
β-Sitosterol (TMS derivative)	ND	ND	ND
Sitostenone (TMS derivative)	ND	ND	ND
α-Amyrin	ND	ND	ND
β-Amyrin	ND	ND	ND
iso-Docosane	ND	ND	ND
anteiso-Docosane	ND	ND	ND
iso-Tricosane	ND	ND	ND
anteiso-Tricosane	ND	ND	ND
iso-Tetracosane	2.03	ND	0.0426 ± 0.0081
anteiso-Tetracosane	0.90	ND	0.0188 ± 0.0036
iso-Pentacosane	3.45	ND	0.0722 ± 0.0136
anteiso-Pentacosane	2.12	ND	0.0444 ± 0.0084
iso-Hexacosane	2.95	ND	0.0618 ± 0.0117
anteiso-Hexacosane	2.30	ND	0.0483 ± 0.0091
iso-Heptacosane	2.49	ND	0.0523 ± 0.0099
anteiso-Heptacosane	1.90	ND	0.0398 ± 0.0075
iso-Octacosane	1.34	ND	0.0282 ± 0.0053
anteiso-Octacosane	0.99	ND	0.0207 ± 0.0039
iso-Nonacosane	0.64	ND	0.0134 ± 0.0025
anteiso-Nonacosane	0.47	ND	0.0098 ± 0.0019
iso-Triacontane	0.43	ND	0.0089 ± 0.0017

ND = Compound not detected.

(Continued)

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Table 5-2b. (Continued)

Compound	Quartz filter (mg/kg of fuel)	PUFs 1 and 2 (mg/kg of fuel)	% PM$_{2.5}$ Mass
anteiso-Triacontane	0.27	ND	0.0058 ± 0.0011
iso-Hentriacontane	0.21	ND	0.0044 ± 0.0008
anteiso-Hentriacontane	0.14	ND	0.0030 ± 0.0006
iso-Dotriacontane	0.09	ND	0.0020 ± 0.0004
anteiso-Dotriacontane	0.08	ND	0.0017 ± 0.003
iso-Tritriacontane	ND	ND	ND
anteiso-Tritriacontane	ND	ND	ND

ND = Compound not detected.

Table 5-3a. Carbonyl Compounds Analyzed by High Performance Liquid Chromatography Field Samples, August 8, 2000

Compound	CAS No.	Res. Chamber Pair μ g	Blank μ g	Corrected Value	% Total[a]
formaldehyde	50-00-0	36.35	0.04	36.31 ± 4.00	63.051 ± 6.948
acetaldehyde	75-07-0	6.82	0.18	6.64 ± 0.08	11.532 ± 0.131
acetone	67-64-1	2.97	ND[b]	2.97 ± 0.13	5.164 ± 0.218
propionaldehyde	123-38-6	0.84	ND	0.84 ± 0.01	1.460 ± 0.010
crotonaldehyde	4170-30-0	0.12	0.03	0.09 ± 0.00	0.153 ± 0.004
butyraldehyde	123-72-8	0.80	ND	0.80 ± 0.05	1.394 ± 0.081
benzaldehyde	100-52-7	0.35	ND	0.35 ± 0.01	0.608 ± 0.019
isovaleraldehyde	590-86-3	ND	ND	ND	ND
valeraldehyde	110-62-3	0.17	ND	0.17 ± 0.02	0.298 ± 0.029
o-tolualdehyde	529-20-4	ND	ND	ND	ND
m-tolualdehyde	620-23-5	0.14	ND	0.14 ± 0.00	0.251 ± 0.003
p-tolualdehyde	104-87-0	ND	ND	ND	ND
hexaldehyde	66-25-1	0.13	0.02	0.11 ± 0.01	0.191 ± 0.018
2,5-dimethylbenzaldehyde	5779-94-2	ND	ND	ND	ND
diacetyl	431-03-8	ND	ND	ND	ND
methacrolein	78-85-3	0.36	ND	0.36 ± 0.02	0.627 ± 0.037
2-butanone	78-93-3	0.54	0.01	0.53 ± 0.04	0.917 ± 0.075
glyoxal	107-22-2	1.80	ND	1.80 ± 0.05	3.133 ± 0.086
acetophenone	98-86-2	0.91	ND	0.91 ± 0.04	1.572 ± 0.075
methylglyoxal	78-98-8	0.55	ND	0.55 ± 0.07	0.960 ± 0.118
octanal	124-13-0	ND	ND	ND	ND
nonanal	124-19-6	0.58	0.07	0.51 ± 0.04	0.891 ± 0.072
Total Speciated		53.45	0.36	53.09	
Total Unspeciated		6.90	2.33	4.57	
Total Speciated + Unspeciated		60.35	2.69	57.66	

Mass emission rate of Speciated Carbonyls = 2.53 mg/kg fuel

Mass emission rate of Total Carbonyls (Speciated + Unspeciated) = 2.74 mg/kg fuel

[a] Percent of each compound expressed as a percentage of Total Speciated + Unspeciated carbonyl compounds.
[b] ND = Compound not detected.

Table 5-3b. Carbonyl Compounds Analyzed by High Performance Liquid Chromatography Field Samples, August 9, 2000

Compound	CAS No.	Res. Chamber Pair μg	Blank μg	Corrected Value	% Total[a]
formaldehyde	50-00-0	12.29	0.04	12.26 ± 1.35	47.603 ± 5.246
acetaldehyde	75-07-0	2.64	0.08	2.56 ± 0.03	9.930 ± 0.113
acetone	67-64-1	0.77	0.22	0.55 ± 0.02	2.118 ± 0.090
propionaldehyde	123-38-6	0.43	ND[b]	0.43 ± 0.00	1.662 ± 0.011
crotonaldehyde	4170-30-0	0.07	ND	0.07 ± 0.00	0.264 ± 0.007
butyraldehyde	123-72-8	0.59	0.09	0.51 ± 0.03	1.961 ± 0.115
benzaldehyde	100-52-7	0.20	0.02	0.18 ± 0.01	0.705 ± 0.022
isovaleraldehyde	590-86-3	ND	ND	ND	ND
valeraldehyde	110-62-3	0.07	ND	0.07 ± 0.01	0.280 ± 0.27
o-tolualdehyde	529-20-4	ND	ND	ND	ND
m-tolualdehyde	620-23-5	0.10	0.03	0.07 ± 0.00	0.276 ± 0.004
p-tolualdehyde	104-87-0	0.04	ND	0.04 ± 0.00	0.157 ± 0.009
hexaldehyde	66-25-1	0.07	0.02	0.05 ± 0.00	0.198 ± 0.018
2,5-dimethylbenzaldehyde	5779-94-2	ND	ND	ND	ND
diacetyl	431-03-8	ND	ND	ND	ND
methacrolein	78-85-3	0.19	ND	0.19 ± 0.01	0.718 ± 0.042
2-butanone	78-93-3	0.21	0.03	0.18 ± 0.01	0.703 ± 0.057
glyoxal	107-22-2	2.06	ND	2.06 ± 0.06	8.000 ± 0.218
acetophenone	98-86-2	0.24	ND	0.24 ± 0.01	0.924 ± 0.044
methylglyoxal	78-98-8	0.55	ND	0.55 ± 0.07	2.120 ± 0.260
octanal	124-13-0	ND	ND	ND	ND
nonanal	124-19-6	0.48	ND	0.48 ± 0.04	1.868 ± 0.151
Total Speciated		21.99	0.52	21.47	
Total Unspeciated		6.13	1.48	4.65	
Total Speciated + Unspeciated		27.12	2.00	25.12	

Mass emission rate of Speciated Carbonyls = 0.80 mg/kg fuel

Mass emission rate of Total Carbonyls (Speciated + Unspeciated) = 0.94 mg/kg fuel

[a] Percent of each compound expressed as a percentage of Total Speciated + Unspeciated carbonyl compounds.
[b] ND = Compound not detected.

The mass emission rates of speciated plus unspeciated carbonyl compounds for the second testing day (8/9/2000) was approximately half the value observed on the first testing day. On a compound-by-compound basis, values for Day 1 are generally higher than values for Day 2, with the lighter carbonyl compounds (formaldehyde, acetaldehyde, and acetone) a factor of 2 to 3 higher on the first day than on the second day. There is no obvious explanation for these results based on the process information or testing conditions.

The values for total mass of carbonyl compounds (speciated and speciated + unspeciated corrected for the blank values) are shown in Table 5-4.

Table 5-4. Total Mass of Carbonyl Compounds for Each Test Day: Speciated and (Speciated + Unspeciated), Corrected for Blanks

Sample	Total Mass, μg	
	Speciated	Speciated + Unspeciated
Cartridge Pair (8/8/00)	53.45	60.35
Blank (8/8/00)	0.36	2.69
Corrected Value	53.09	57.66
Cartridge Pair (8/9/00)	21.99	27.12
Blank (8/9/00)	0.52	2.00
Corrected Value	21.47	25.12

These values were used in combination with the flow information and the mass of fuel consumed to calculate a mass emission rate of carbonyl compounds for each testing day; these calculations are shown in Tables G-3 through G-6.

The mass emission rates for speciated carbonyl compounds for the two test days were 2.53 mg/kg of fuel (Day #1) and 0.80 mg/kg of fuel (Day #2). The mass emission rates for all carbonyl compounds (speciated + unspeciated) for the two test days were 2.74 mg/kg of fuel (Day #1) and 0.94 mg/kg of fuel (Day #2). These mass emission rates reflect the difference in total mass of carbonyl compounds observed between the two days (a factor of more than two),

rather than a difference in the mass of fuel consumed (97,690 vs. 127,027 kg), since slightly more fuel was actually consumed on Testing Day 2.

Gas-Phase Air Toxics Whole Air Samples

Analytical results for the air toxics canister samples are shown in Table 5-5. The ERG concurrent analysis produces analytical results for both air toxics and nonmethane organic compound ozone precursors; these results are presented separately.

Method Detection Limits for the Air Toxics analysis are shown in Table 4-9, with values typically ranging to 1 $\mu g/m^3$ and lower. These values are at the lower end of the calibration curve for this analysis, and the typical ambient levels observed for these analytes show a maximum of 20 $\mu g/m^3$ where the compounds are observed at detectable levels. Relative to the analytical scale for ambient analysis, some very high values are observed for propylene, methylene chloride, and benzene. For propylene and methylene chloride, the concentrations obtained for the Dilution Air are approximately the same as the values obtained for the Residence Chamber Air, indicating that the compounds are present in the ambient air at the source. In the case of benzene, however, the concentration determined for the Residence Chamber Air is nearly three orders of magnitude higher than the concentration observed in the Dilution Air, indicating that the compound is present in the source at relatively high levels compared to ambient standards.

Gas-Phase Speciated Nonmethane Organic Compounds

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 5-6(a, b). Analytical results are presented in weight percent of total SNMOC (speciated + unspeciated). Mass emission rates of total SNMOC and total speciated plus unspeciated organic compounds are also provided. A Blank canister is a canister that has had no exposure to the stationary source matrix. Samples labeled "Dilution Air" reflect the

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Table 5-5. Analytical Results for Field Samples, Air Toxics Compounds (Analytical Method TO-15)

Compound	CAS No.	Blank 8/8/00	Dilution Air (µg/m³)	Residence Chamber Air	Blank 8/9/00	Dilution Air (µg/m³)	Residence Chamber Air
acetylene	74-86-2	ND	0.76	1.26	ND	0.68	7.19
propylene	115-07-1	ND	59.4	54.34	ND	7.2	10.4
dichlorodifluoromethane	75-71-8	ND	24.85	30.88	ND	128	130
chloromethane	74-87-3	ND	2.24	1.04	ND	1.39	1.33
dichlorotetrafluoroethane	1320-37-2	ND	ND	ND	ND	ND	ND
vinyl chloride	75-01-4	ND	ND	ND	ND	ND	ND
1,3-butadiene	106-99-0	ND	ND	ND	ND	ND	ND
bromomethane	74-83-9	ND	ND	ND	ND	ND	ND
chloroethane	75-00-3	ND	ND	ND	ND	ND	ND
acetonitrile	75-05-8	ND	ND	9.94	ND	10.50	15.55
acetone	67-64-1	ND	ND	ND	ND	ND	ND
trichlorofluoromethane	75-69-4	ND	ND	ND	ND	ND	ND
acrylonitrile	107-13-1	ND	ND	ND	ND	ND	ND
1,1-dichloroethene	75-35-4	ND	ND	ND	ND	ND	ND
methylene chloride	75-09-2	ND	77.87	47.99	ND	8.43	7.53
trichlorotrifluoroethane	26523-64-8	ND	ND	ND	ND	ND	ND
trans-1,2-dichloroethylene	56-60-5	ND	ND	ND	ND	ND	ND
1,1-dichloroethane	75-34-3	ND	ND	ND	ND	ND	ND
methyl tert-butyl ether	1634-04-1	ND	ND	ND	ND	ND	ND
methyl ethyl ketone	78-93-3	ND	ND	23.05	ND	3.62	16.43
chloroprene	126-99-8	ND	ND	ND	ND	ND	ND

(Continued)

Table 5-5. (Continued)

Compound	CAS No.	Blank 8/8/00	Dilution Air	Residence Chamber Air	Blank 8/9/00	Dilution Air	Residence Chamber Air
			μg/m³			μg/m³	
cis-1,3-dichloroethylene	156-59-2	ND	ND	ND	ND	ND	ND
bromochloromethane	74-97-5	ND	ND	ND	ND	ND	ND
chloroform	67-66-3	ND	ND	ND	ND	ND	ND
ethyl tert-butyl ether	637-92-3	ND	ND	ND	ND	ND	ND
1,2-dichloroethane	107-06-2	ND	ND	ND	ND	ND	ND
1,1,1-trichloroethane	71-55-6	ND	ND	ND	ND	ND	ND
benzene	71-43-2	ND	0.51	420	ND	0.45	108.50
carbon tetrachloride	56-23-5	ND	ND	ND	ND	ND	ND
tert-amyl methyl ether	994-05-8	ND	ND	ND	ND	ND	ND
1,2-dichloropropane	78-87-5	ND	ND	ND	ND	ND	ND
ethyl acrylate	140-88-5	ND	ND	ND	ND	ND	ND
bromodichloro-methane	75-27-4	ND	ND	ND	ND	ND	ND
trichloroethylene	79-01-6	ND	ND	10.70	ND	ND	ND
methyl methacrylate	80-62-6	ND	ND	ND	ND	ND	ND
cis-1,2-dichloropropene	10061-01-5	ND	ND	ND	ND	ND	ND
methyl isobutyl ketone	108-10-1	ND	9.56	ND	ND	ND	ND
trans-1,2-dichloropropene	10061-02-6	ND	ND	ND	ND	ND	ND
1,1,2-trichloroethane	79-00-5	ND	ND	ND	ND	ND	ND
toluene	108-88-3	ND	1.13	3.95	ND	0.68	1.88
dibromochloromethane	124-48-1	ND	ND	ND	ND	ND	ND
1,2-dibromoethane	106-93-4	ND	ND	ND	ND	ND	ND

(Continued)

Table 5-5. (Continued)

Compound	CAS No.	Blank 8/8/00	Dilution Air (μg/m³)	Residence Chamber Air	Blank 8/9/00	Dilution Air (μg/m³)	Residence Chamber Air
n-octane	111-65-9	ND	1.95	2.33	ND	0.65	ND
tetrachloroethylene	127-18-4	ND	ND	ND	ND	ND	1.40
chlorobenzene	108-90-7	ND	ND	ND	ND	ND	ND
ethylbenzene	100-41-4	ND	ND	1.13	ND	1.21	ND
m-, p-xylene	108-38-3/106-42-3	ND	0.52	2.94	ND	8.13	7.09
bromoform	75-25-2	ND	ND	ND	ND	ND	ND
styrene	100-42-5	ND	0.34	0.76	ND	0.72	0.76
1,1,2,2-tetrachloroethane	79-34-5	ND	ND	ND	ND	ND	ND
o-xylene	95-47-6	ND	ND	0.65	ND	0.91	0.91
1,3,5-trimethylbenzene	108-67-8	ND	ND	ND	ND	ND	ND
1,2,4-trimethylbenzene	95-63-6	ND	0.69	0.74	ND	0.64	0.64
m-dichlorobenzene	541-73-1	ND	ND	ND	ND	ND	ND
chloromethylbenzene	100-44-7	ND	ND	ND	ND	ND	ND
p-dichlorobenzene	106-46-7	ND	ND	ND	ND	ND	ND
o-dichlorobenzene	95-50-1	ND	ND	ND	ND	ND	ND
1,2,4-trichlorobenzene	120-82-1	ND	ND	ND	ND	ND	ND
hexachloro-1,3-butadiene	87-68-3	ND	ND	ND	ND	ND	ND

ND = Not detected; compound not observed in the performance of the analysis.

Table 5-6a. Speciated Nonmethane Organic Compound Data, August 8, 2000

Compound	CAS No.	Total μg Res. Cham.	Total μg Dilution	Total μg	% Total Speciated + Unspeciated
ethylene	4-84-0	3180.83	349.96	2830.87 ± 276.29	0.020 ± 0.200
acetylene	74-86-2	2035.38	184.52	1850.86 ± 180.64	0.013 ± 0.131
ethane	74-85-1	1507.05	585.39	921.66 ± 109.59	0.007 ± 0.079
propylene	115-07-01	11549.73	12140.43	*	0.00
propane	74-98-6	10482.23	11022.68	*	0.00
propyne	74-99-7	ND	ND	ND	0.00
isobutane	75-28-5	326.96	144.23	182.73 ± 6.7	0.001 ± 0.005
isobutene/1-butene	115-11-7/106-98-0	513.18	184.52	328.65 ± 10.94	0.002 ± 0.008
1,3-butadiene	106-99-0	67.12	ND	67.12 ± 2.3	0.000 ± 0.002
n-butane	106-97-8	337.79	180.28	157.50 ± 5.54	0.001 ± 0.004
trans-2-butene	624-64-6	121.26	48.78	72.47 ± 2.82	0.000 ± 0.002
cis-2-butene	590-18-1	145.08	91.20	53.87 ± 1.85	0.000 ± 0.001
3-methyl-1-butene	563-45-1	28.15	ND	28.15 ± 0.89	0.000 ± 0.001
isopentane	78-78-4	132.08	112.41	19.67 ± 0.57	0.000 ± 0.000
1-pentene	109-67-1	ND	ND	ND	0.00
2-methyl-1-butene	563-46-2	34.64	ND	34.64 ± 0.99	0.000 ± 0.001
n-pentane	109-66-0	181.89	53.02	128.86 ± 3.57	0.001 ± 0.003
isoprene	78-79-4	99.60	892.93	*	0.00
trans-2-pentene	646-04-8	132.08	63.63	68.45 ± 2.07	0.000 ± 0.002
cis-2-pentene	627-20-3	110.43	76.35	34.08 ± 1.07	0.000 ± 0.001
2-methyl-2-butene	513-35-9	ND	ND	ND	0.00
2,2-dimethylbutane	75-83-2	1180.09	2104.00	*	0.00

(Continued)

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Table 5-6a. (Continued)

Compound	CAS No.	Total μg Res. Cham.	Total μg Dilution	Total μg	% Total Speciated + Unspeciated
cyclopentene	142-29-0	49.80	46.66	3.14 ± 0.10	2.27E-05 ± 0.000
4-methyl-1-pentene	691-37-2	ND	ND	ND	0.00
cyclopentane	287-92-3	86.61	78.48	8.14 ± 0.27	5.89E-05 ± 0.000
2,3-dimethylbutane	79-29-8	129.72	125.14	4.78 ± 0.15	3.46E-05 ± 0.000
2-methylpentane	107-83-5	ND	114.53	*	0.00
3-methylpentane	96-14-0	108.27	114.53	*	0.00
2-methyl-1-pentene	763-29-1	ND	ND	ND	0.00
1-hexene	592-41-6	342.12	144.23	197.89 ± 6.47	0.001 ± 0.005
2-ethyl-1-butene	760-21-4	ND	ND	ND	0.00
n-hexane	110-54-3	472.04	1351.06	*	0.00
trans-2-hexene	4050-45-7	ND	ND	ND	0.00
cis-2-hexene	7688-21-3	ND	ND	ND	0.00
methylcyclopentane	96-37-7	140.74	184.52	*	0.00
2,4-dimethylpentane	108-08-7	88.78	78.48	10.30 ± 0.26	7.45E-05 ± 0.000
benzene	71-43-2	86655.43	74.23	86581.19 ± 2155.87	0.626 ± 1.560
cyclohexane	110-82-7	97.44	84.84	12.60 ± 0.33	9.12E-05 ± 0.000
2-methylhexne	591-76-4	47.64	195.13	*	0.00
2,3-dimethylpentane	565-59-3	99.60	112.41	*	0.00
3-methylhexane	589-34-4	207.87	241.79	*	0.00
1-heptene	592-76-7	ND	31.81	*	0.00
2,2,4-trimethylpentane	540-84-1	ND	129..38	*	0.00
n-heptane	142-82-5	326.96	142.11	184.86 ± 4.10	0.001 ± 0.003

(Continued)

Table 5-6a. (Continued)

Compound	CAS No.	Total µg Res. Cham.	Total µg Dilution	Total µg	% Total Speciated + Unspeciated
methylcyclohexane	108-87-2	173.22	1679.81	*	0.00
2,2,3-trimethylpentane	564-02-3	ND	ND	ND	0.00
2,3,4-trimethylpentane	565-75-3	108.27	76.35	31.91 ± 0.75	0.000 ± 0.001
toluene	108-88-3	844.47	277.85	566.62 ± 8.67	0.004 ± 0.006
2-methylheptane	592-27-8	90.94	93.32	*	0.00
3-methylheptane	589-81-1	140.74	118.77	21.97 ± 0.50	0.000 ± 0.000
1-octene	111-66-0	179.72	55.15	124.57 ± 3.38	0.001 ± 0.002
n-octane	111-65-9	588.96	506.91	82.05 ± 2.58	0.001 ± 0.002
ethylbenzene	100-41-4	294.48	214.22	80.26 ± 3.23	0.001 ± 0.002
m-xylene/p-xylene	108-38-3/106-42-3	368.10	256.64	111.46 ± 4.60	0.001 ± 0.003
styrene	100-42-5	162.40	142.11	20.29 ± 0.45	0.000 ± 0.000
o-xylene	95-47-6	ND	133.62	*	0.00
1-nonene	124-11-8	69.29	27.57	41.72 ± 1.83	0.000 ± 0.001
n-nonane	111-84-2	290.15	171.80	118.35 ± 5.24	0.001 ± 0.004
isopropylbenzene	98-82-8	90.94	69.99	20.95 ± 0.77	0.000 ± 0.001
alpha-pinene	80-56-8	621.44	1011.70	*	0.00
n-propylbenzene	103-65-1	99.60	74.23	25.37 ± 0.56	0.000 ± 0.000
m-ethyltoluene	620-14-4	309.64	322.39	*	0.00
p-ethyltoluene	622-96-8	225.19	218.46	6.73 ± 0.15	4.87E-05 ± 0.000
1,3,5-trimethylbenzene	108-67-8	242.51	214.22	28.30 ± 0.42	0.000 ± 0.000
o-ethyltoluene	611-14-3	558.65	545.09	13.56 ± 0.29	9.81E-05 ± 0.000
β-pinene	127-91-3	398.42	439.04	*	0.00

(Continued)

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Table 5-6a. (Continued)

Compound	CAS No.	Total μg Res. Cham.	Total μg Dilution	Total μg	% Total Speciated + Unspeciated
1,2,4-trimethylbenzene	95-63-6	389.75	305.42	84.33 ± 0.25	0.001 ± 0.000
1-decene	872-05-9	ND	ND	ND	0.00
n-decane	124-18-5	6225.25	6273.83	*	0.00
1,2,3-trimethylbenzene	526-73-8	110.43	84.84	25.59 ± 0.06	0.000 ± 0.000
m-diethylbenzene	141-93-5	123.42	142.11	*	0.00
p-diethylbenzene	105-05-5	43.31	50.90	*	0.00
1-undecene	821-95-4	ND	ND	ND	0.00
n-undecane	1120-21-4	961.39	950.19	11.20 ± 0.86	8.1E-05 ± 0.001
1-dodecene	112-41-4	207.87	178.16	29.71 ± 0.32	0.000 ± 0.000
n-dodecane	112-40-3	30838.25	30278.97	559.28 ± 30.82	0.004 ± 0.022
1-tridecene	2437-56-1	225.19	173.92	51.27 ± 2.83	0.000 ± 0.002
n-tridecane	629-50-5	194.88	178.16	16.72 ± 0.92	0.01 ± 0.001
Total speciated		166195.67	76749.42	89446.25	
Total unspeciated		65119.32	16335.71	48783.61	
Total speciated + unspeciated**		231314.99	93085.13	138229.9	

Mass emission rate of Total Speciated NMOC = 13.191 mg/kg fuel

Mass emission rate of Speciated + Unspeciated NMOC = 22.640 mg/kg fuel

ND = Compound not detected

*Concentration of analyte in Dilution Air is higher that concentration of analyte in Residence Chamber Air when dilution factor of 48.8 is considered.

**Total NMOC with unknowns in μg/m³ is an estimate based on propane only.

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Table 5-6b. Speciated Nonmethane Organic Compound Data, August 9, 2000

Compound	CAS No.	Total μg Res. Cham.	Total μg Dilution	Total μg	% Total Speciated + Unspeciated
ethylene	4-84-0	1466.12	379.08	1087.04 ± 106.10	1.386 ± 0.135
acetylene	74-86-2	2321.61	216.19	2105.42 ± 205.49	2.685 ± 0.262
ethane	74-85-1	1239.40	758.16	481.24 ± 57.22	0.614 ± 0.073
propylene	115-07-01	3028.98	2132.33	896.64 ± 27.35	1.143 ± 0.035
propane	74-98-6	7847.53	7703.05	144.47 ± 3.55	0.184 ± 0.005
propyne	74-99-7	ND	ND	ND	0.00
isobutane	75-28-5	250.90	177.69	73.21 ± 2.69	0.093 ± 0.003
isobutene/1-butene	115-11-7/106-98-0	314.38	154.00	160.38 ± 5.34	0.205 ± 0.007
1,3-butadiene	106-99-0	33.25	ND	33.25 ± 1.14	0.042 ± 0.002
n-butane	106-97-8	296.25	242.85	53.40 ± 1.88	0.068 ± 0.002
trans-2-butene	624-64-6	ND	79.96	*	0.00
cis-2-butene	590-18-1	145.10	115.50	29.60 ± 1.02	0.038 ± 0.001
3-methyl-1-butene	563-45-1	ND	ND	ND	0.00
isopentane	78-78-4	151.15	142.16	8.99 ± 0.26	0.011 ± 0.000
1-pentene	109-67-1	ND	ND	ND	0.00
2-methyl-1-butene	563-46-2	ND	ND	ND	0.00
n-pentane	109-66-0	284.16	148.08	136.08 ± 3.77	0.174 ± 0.005
isoprene	78-79-4	120.92	420.54	*	0.00
trans-2-pentene	646-04-8	105.80	77.00	28.80 ± 0.87	0.037 ± 0.001
cis-2-pentene	627-20-3	123.94	103.66	20.285 ± 0.64	0.026 ± 0.001
2-methyl-2-butene	513-35-9	ND	ND	ND	0.00
2,2-dimethylbutane	75-83-2	326.48	296.16	30.32 ± 0.98	0.039 ± 0.001

(Continued)

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Table 5-6b. (Continue)

Compound	CAS No.	Total μg Res. Cham.	Total μg Dilution	Total μg	% Total Speciated + Unspeciated
cyclopentene	142-29-0	48.37	26.65	21.71 ± 0.71	0.028 ± 0.001
4-methyl-1-pentene	691-37-2	ND	ND	ND	0.00
cyclopentane	287-92-3	120.92	100.69	20.22 ± 0.67	0.026 ± 0.001
2,3-dimethylbutane	79-29-8	163.24	156.96	6.27 ± 0.19	0.008 ± 0.000
2-methylpentane	107-83-5	ND	130.31	*	0.00
3-methylpentane	96-14-0	157.19	171.77	*	0.00
2-methyl-1-pentene	763-29-1	ND	ND	ND	0.00
1-hexene	592-41-6	256.95	192.50	64.45 ± 2.11	0.082 ± 0.003
2-ethyl-1-butene	760-21-4	ND	ND	ND	0.00
n-hexane	110-54-3	2224.88	2615.07	*	0.00
trans-2-hexene	4050-45-7	ND	ND	ND	0.00
cis-2-hexene	7688-21-3	ND	ND	ND	0.00
methylcyclopentane	96-37-7	308641.15	349.47	308291.7 ± 9002.12	393.143 ± 11.480
2,4-dimethylpentane	108-08-7	108.83	103.66	5.17 ± 0.13	0.007 ± 0.000
benzene	71-43-2	30365.33	142.16	30223.18 ± 752.56	38.541 ± 0.960
cyclohexane	110-82-7	126.96	133.27	*	0.00
2-methylhexane	591-76-4	169.28	195.46	*	0.00
2,3-dimethylpentane	565-59-3	157.19	156.96	0.23 ± 0.02	0.000 ± 0.000
3-methylhexane	589-34-4	154.17	142.16	12.01 ± 0.29	0.015 ± 0.000
1-heptene	592-76-7	ND	35.54	*	0.00
2,2,4-trimethylpentane	540-84-1	ND	112.54	*	0.00

(Continued)

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Table 5-6b. (Continue)

Compound	CAS No.	Total µg Res. Cham.	Total µg Dilution	Total µg	% Total Speciated + Unspeciated
n-heptane	142-82-5	136.03	103.66	32.38 ± 0.72	0.041 ± 0.001
methylcyclohexane	108-87-2	193.47	216.19	*	0.00
2,2,3-trimethylpentane	564-02-3	ND	35.54	*	0.00
2,3,4-trimethylpentane	565-75-3	102.78	91.81	10.97 ± 0.26	0.014 ± 0.000
toluene	108-88-3	580.40	308.00	272.40 ± 4.17	0.347 ± 0.005
2-methylheptane	592-27-8	139.05	130.31	8.75 ± 0.18	0.011 ± 0.000
3-methylheptane	589-81-1	108.83	94.77	14.06 ± 0.32	0.018 ± 0.000
1-octene	111-66-0	81.62	62.19	19.43 ± 0.53	0.025 ± 0.001
n-octane	111-65-9	396.00	432.39	*	0.00
ethylbenzene	100-41-4	414.14	414.62	*	0.00
m-xylene/p-xylene	108-38-3/106-42-3	997.57	1128.36	*	0.00
styrene	100-42-5	287.18	331.70	*	0.00
o-xylene	95-47-6	ND	358.35	*	0.00
1-nonene	124-11-8	ND	ND	ND	0.00
n-nonane	111-84-2	296.25	281.35	14.90 ± 0.66	0.019 ± 0.001
isopropylbenzene	98-82-8	99.76	94.77	4.99 ± 0.18	0.006 ± 0.000
alpha-pinene	80-56-8	302.29	121.42	180.87 ± 5.34	0.231 ± 0.007
n-propylbenzene	103-65-1	108.83	142.16	*	0.00
m-ethyltoluene	620-14-4	601.56	568.62	32.94 ± 0.51	0.042 ± 0.001
p-ethyltoluene	622-96-8	314.38	313.93	0.46 ± 0.01	0.001 ± 0.000
1,3,5-trimethylbenzene	108-67-8	256.95	299.12	*	0.00

(Continued)

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Table 5-6b. (Continue)

Compound	CAS No.	Total μg Res. Cham.	Total μg Dilution	Total μg	% Total Speciated + Unspeciated
o-ethyltoluene	611-14-3	556.22	518.28	37.94 ± 0.81	0.048 ± 0.001
β-pinene	127-91-3	332.52	319.85	12.67 ± 0.15	0.016 ± 0.000
1,2,4-trimethylbenzene	95-63-6	377.87	331.70	46.17 ± 0.14	0.059 ± 0.000
1-decene	872-05-9	ND	ND	ND	0.00
n-decane	124-18-5	7285.26	7842.25	*	0.00
1,2,3-trimethylbenzene	526-73-8	157.19	207.31	*	0.00
m-diethylbenzene	141-93-5	172.31	180.66	*	0.00
p-diethylbenzene	105-05-5	69.53	68.12	1.41 ± 0.05	0.002 ± 0.000
1-undecene	821-95-4	ND	ND	ND	0.00
n-undecane	1120-21-4	1091.28	1187.59	*	0.00
1-dodecene	112-41-4	287.18	284.31	2.87 ± 0.03	0.004 ± 0.000
n-dodecane	112-40-3	37647.57	42776.98	*	0.00
1-tridecene	2437-56-1	ND	233.96	*	0.00
n-tridecane	629-50-5	145.10	222.12	*	0.00
Total speciated		105995.22	55584.26	50410.96	
Total unspeciated		38326.93	10320.64	28006.29	
Total speciated + unspeciated**		144322.14	65904.90	78417.24	

ND = Compound not detected.

*Concentration of analyte in Dilution Air is higher than concentration of analyte in Residence Chamber Air when dilution factor of 49.3 is considered.

**Total NMOC with unknowns in μg/m³ is an estimate based on propane only.

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dilution air entering the sample dilution system; this dilution air has not been exposed to the stationary source matrix. The second canister sample on each test day is labeled "Residence Chamber Air" and reflects the diluted source matrix at the end of the residence chamber. Supporting data for the SNMOC analysis are found in Appendix H.

The Total Mass of Speciated Nonmethane Organic Compound results and the Total Speciated + Unspeciated results have been used to calculate the mass emission rates for Speciated Nonmethane Organic Compounds as well as Speciated + Unspeciated Nonmethane Organic Compounds (Table 5-7). 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 Speciated Nonmethane Organic Compounds for each test day; these calculations are shown in Tables H-3 through H-6 (Appendix H).

Table 5-7. Total Mass of Speciated as well as Speciated + Unspeciated Nonmethane Organic Compounds Collected, Test #1 and Test #2

	Total Mass (μg)	
Sample	Total Speciated NMOC	Total Speciated + Unspeciated NMOC
Residence Chamber Air (8/8/00)	3.52	4.60
Dilution Air (8/8/00)	1.66	1.79
Corrected Value (8/8/00)	1.86	2.82
Residence Chamber Air (8/9/00)	1.93	2.50
Dilution Air (8/9/00)	1.44	1.56
Corrected Value (8/9/00)	0.49	0.93

The mass emission rate for the SNMOC is consistent with the mass emission rate observed for the carbonyl compounds: Speciated, 13,190 μg/kg of fuel for Test Day #1 versus 50,411 μg/kg of fuel for Test Day #2; Speciated + Unspeciated, 22,640 μg/kg of fuel for Test

Day #1 versus 78,417 µg/kg of fuel for Test Day #2. There is no obvious explanation for a difference of approximately a factor of two between the two test days.

Particle Size Distribution Data

The TSI system was operated on both test days, collecting data on particle size distribution in the range below 2.5 µm (range monitored was 9 nm to approximately 400 nm). The analytical data 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 and 5-2). The supporting data for these plots are included in Appendix I.

The profiles for the two days are qualitatively different. Figure 5-2 shows an obvious deficit in particles in the range of 25 through 104 nm, with a slight shift of the particle size distribution for Day 2 toward larger diameter particles. Results for particles in this size range also reflect the general difference observed in carbonyls and SNMOC between Day 1 and Day 2: a maximum of ~6×10^4 particles/cm^3 for Day 1 versus ~0.8×10^4 particles/cm^3 for Day 2.

Figure 5-1. Particle size distribution (9 to 400 nanometers) for test day 1 (8/8/00).
(Figures shown are a composite of all three-minute scans collected for the duration of the test.)
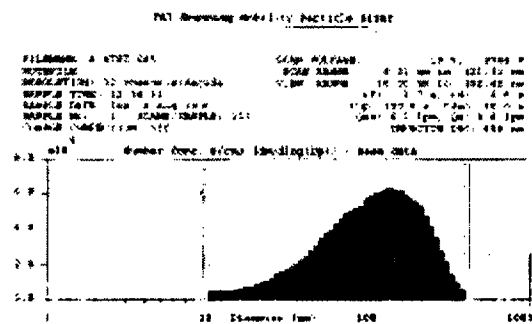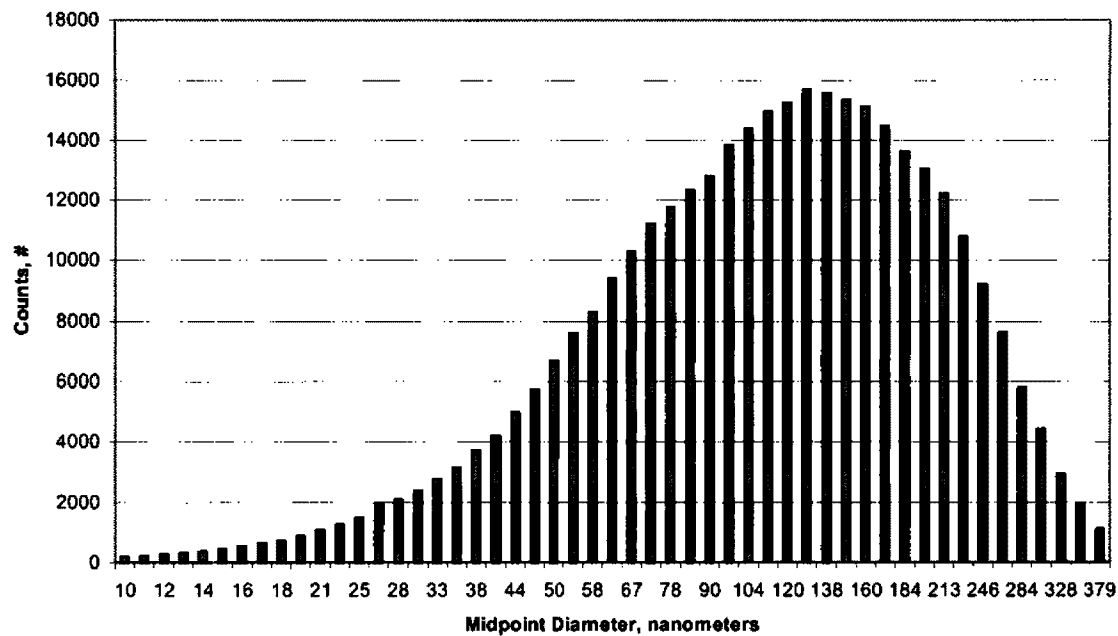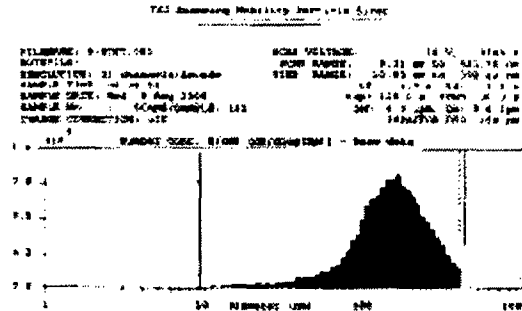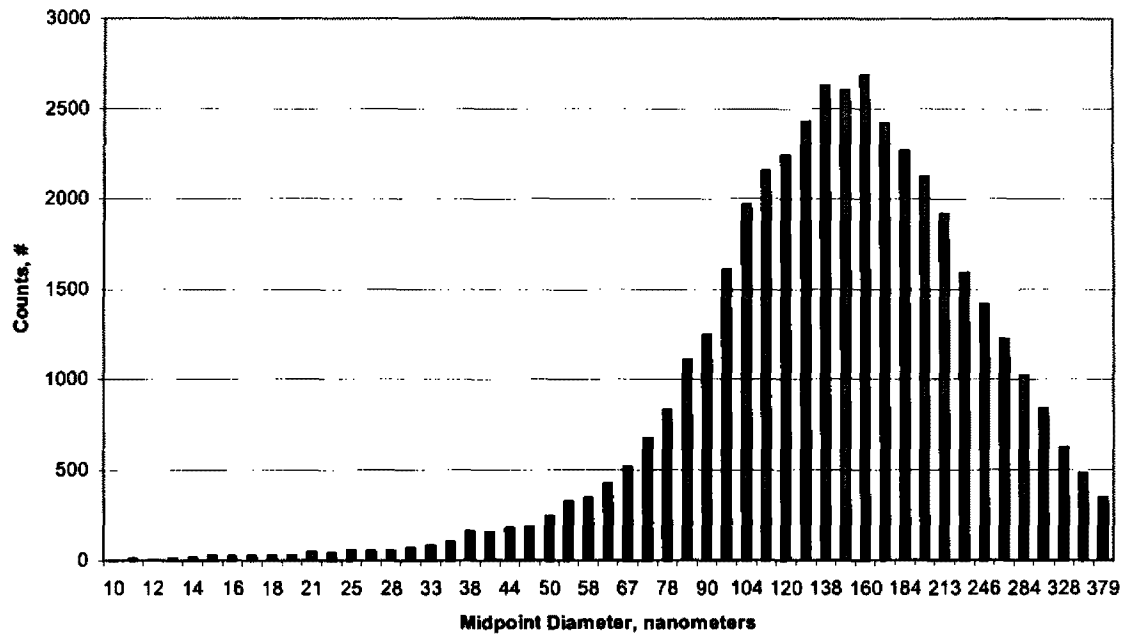
Figure 5-2. Particle size distribution (9 to 400 nanometers) for test day 2 (8/9/00).
(Figures shown are a composite of all three-minute scans collected for the duration of the test.)

Section 6

Quality Assurance/Quality Control

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.

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.

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

Table 6-1. Field Sampling Equipment Quality Control Measures

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

Reference. EPA Quality Assurance Project Plan - Source Sampling for Fine Particulate Matter (U.S. EPA, 2001).

Chain of Custody Record

ERG
EASTERN RESEARCH GROUP, INC.

PROJECT												
SITE												
COLLECTED BY (Signature)												

FIELD SAMPLE I.D.	SAMPLE MATRIX	DATE/TIME	NO. OF CONTAINERS	ANALYSES							REMARKS	SAM ID NO. (For lab use only)

REMARKS:

RELINQUISHED BY:	DATE	TIME	RECEIVED BY:	RELINQUISHED BY:	DATE	TIME
RELINQUISHED BY:	DATE	TIME	RECEIVED BY:	RELINQUISHED BY:	DATE	TIME

RECEIVED FOR LABORATORY BY: | DATE | TIME | AIRBILL NO. | OPENED BY | DATE | TIME | TEMP°C | SEAL # | CONDITION

LAB USE ONLY

REMARKS:

Figure 6-1. ERG chain of custody form.

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started when the sampling media were prepared; each sample substrate was assigned a unique identification number by the laboratory supplying the substrates.

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 data are a part of the project file at ERG.

Table 6-2. Carbonyl Analysis: Quality Control Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
HPLC Column Efficiency	Analyze second source QC sample (SSQC)	At setup and 1 per sample batch	Resolution between acetone and propionaldehyde ≥ 1.0 Column efficiency > 500 plates	Eliminate dead volume, backflush, or replace column; repeat analysis	Yes
Linearity Check	Analyze 5-point calibration curve and SSQC in triplicate	At setup or when calibration check does not meet acceptance criteria	Correlation coefficient ≥ 0.999, relative error for each level against calibration curve $\pm 20\%$ or less Relative Error	Check integration, re-integrate or re-calibrate	Yes
			Intercept acceptance should be $\geq 10,000$ area counts/compound; correlates to 0.06 mg/mL	Check integration, re-integrate or re-calibrate	Yes
Retention time	Analyze calibration midpoint	Once per 10 samples	Acetaldehyde, Benzaldehyde, Hexaldehyde within retention time window established by determining 3 σ or $\pm 2\%$ of the mean calibration and midpoint standards, whichever is greater	Check system for plug, regulate column temperature, check gradient and solvents	Yes
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

(Continued)

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Table 6-2. (Continued)

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
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 μg/mL standard	Once after calibration in triplicate	± 25% difference		
System Blank	Analyze acetonitrile	Bracket sample batch, 1 at beginning and 1 at end	Measured concentration ≤ 5 x MDL	Locate contamination and document levels of contamination in file	Yes
Duplicate Analyses	Duplicate Samples	As collected	± 20% difference	Check integration; check instrument function; re-analyze duplicate samples	Yes
Replicate Analyses	Replicate injections	Duplicate samples only	≤ 10% RPD for concentrations greater than 1.0 μg/mL	Check integration, check instrument function, re-analyze duplicate samples	Yes
Method Spike/Method Spike Duplicate (MS/MSD)	Analyze MS/MSD	One MS/MSD per 20 samples	80-120% recovery for all compounds	Check calibration, check extraction procedures	Yes

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Concurrent Air Toxics/Speciated Nonmethane Organic Compound 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.

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.

Table 6-3. Quality Control Procedures for the Concurrent Analysis for Air Toxics and SNMOC

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 ≤ 30% Relative Retention Times (RRTs) for target peaks ± 0.06 units from mean RRT	Repeat individual sample analysis; repeat linearity check; prepare new calibration standards and repeat analysis	Yes
Calibration check using mid-point of calibration range	Daily	Response factor ≤ 30% bias from calibration curve average response factor	Repeat calibration check; repeat calibration curve	Yes
System Blank	Daily following tune check and calibration check	0.2 ppbv/analyte or MDL, whichever is greater Internal Standard (IS) area response ± 40% and retention time ± 0.33 min of most recent calibration check	Repeat analysis with new blank; check system for leaks, contamination; re-analyze blank.	Yes
Laboratory Control Standard (LCS)	Daily	Recovery limits 70% - 130% IS Retention Time ± 0.33 min of most recent calibration	Repeat analysis; repeat calibration curve.	Yes
Replicate Analysis	All duplicate field samples	<30% RPD for compounds >5xMDL	Repeat sample analysis	Yes
Samples	All samples	IS RT ± 0.33 min of most recent calibration	Repeat analysis	Yes

(Continued)

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Table 6-3. (Continued)

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
SNMOC Analysis				
System Blank Analysis	Daily, following calibration check	20 ppbC total	Repeat analysis; check system for leaks; clean system with wet air	Yes
Multiple point calibration (minimum 5); propane bracketing the expected sample concentration range	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 ± 30% difference of calibration curve slope	Repeat calibration check; repeat calibration curve.	Yes
Replicate analysis	All duplicate field samples	Total NMOC within ± 30% RSD	Repeat sample analysis	Yes

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Table 6-4. PM Mass Measurements: Quality Control Criteria

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

Table 6-5. Elemental Analysis: Quality Control Criteria

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

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

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Linearity Check	Analyze 4-point calibration curve	At setup or when calibration check does not meet acceptance criteria	Correlation coefficient ≥0.999	Recalibrate	Yes
System Dead Volume	Analyze water	Bracket sample batch, 1 at beginning and 1 at end	Within 5% of previous analysis	Check system temperature, eluent, and columns	Yes
Retention Time	Analyze standard	At setup	Each ion within ± 5% of standard retention time	Check system temperature and eluent	Yes
Calibration check	Analyze 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, 1 at beginning and 1 at end	No quantifiable ions	Re-analyze	Yes
Replicate Analyses	Replicate Injections	Each sample	≤ 10% RPD for concentrations greater than 1.0mg/L	Check instrument function, re-analyze samples	Yes

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Table 6-7. Quality Control Procedures for Gas Chromatography-Mass Spectrometry Analysis of Semivolatile Organic Compounds.

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Mass spectrometer instrument tune check	Daily prior to calibration check	Mass assignments m/z = 69, 219, 502 (± 0.2) Peak widths = 0.59-0.65 Relative mass abundances = 100 % (69); ≥30 % (219); ≥ 1% (502).	Retune mass spectrometer; clean ion source	Yes
Five-point calibration bracketing the expected concentration range	Following maintenance or repair of either gas chromatograph or mass spectrometer or when daily quality control check is not acceptable	Correlation coefficient of either quadratic or linear regression ≥ 0.999	Check integration, 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

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Section 7
References

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Appendix A

Table of Unit Conversions

Unit Conversion Table

Multiply	By	To Obtain
atmospheres	101.3	kilopascals
atmospheres	29.92	inches of mercury
atmospheres	760	mm of mercury
atmospheres	33.94	feet of water
atmospheres	14.70	lb/in.^{2} (psi)
Btu	1054	joules
Btu	2.982×10^{-4}	kilowatt-hours
centimeters	0.3937	inches
cm/sec	1.969	ft/min
cm/sec	0.03281	ft/sec
cm/sec	0.036	km/hr
cm/sec	0.6	m/min
cm^3	3.53×10^{-2}	ft^3
cm^3	10^{-3}	liters
ft^3	0.02832	m^3
ft^3/min	0.4720	liters per second
in.^{3}	16.39	cm^3
m^3	35.31	ft^3
ft	12	in.
ft	0.3048	m
ft of water	0.8826	in. mercury
grams	0.03527	ounces
inches	2.540	cm
inches of water	0.07355	inches of mercury
kg	2.20462	lb
km	3280.84	ft

Multiply	By	To Obtain
km	0.6214	miles
kilowatts	56.92	Btu per min.
liters	0.03531	ft^3
liters	61.02	$in.^3$
liters	10^{-3}	m^3
liters per minute	5.855×10^{-4}	ft^3 per second
m	3.28084	ft
m	39.37	in.
m^3	0.02832	ft^3
miles	5280	feet
miles	1.6093	km
ounces	28.35	grams
pounds	453.6	grams
pounds per square inch	703.1	kg/m^2
cm^2	0.1550	$in.^2$
ft^2	929.0	cm^2
ft^2	0.09290	m^2
temperature ($^\circ C + 273$)	1	absolute temperature (K)
temperature ($^\circ C + 17.8$)	1.8	temperature ($^\circ F$)
temperature ($^\circ F + 460$)	1	temperature ($^\circ$Rankin)
temperature ($^\circ F-32$)	5/9	temperature ($^\circ C$)
watts	0.05692	Btu per min.
watts	44.26	foot-pounds per min.

Appendix B

Supporting Data for PM-2.5

**Table B-1. PM Masses from Wood-Fired Industrial Boiler,
August 8, 2000 and August 9, 2000**

Filter ID *	Tare Weight (g)	Final Weight (g)	PM mass (mg)	Comments
T053100A IB080800Hr2A1610	0.162028	0.162413	0.385	
T053100G IB080800Hr2B1622	0.161328	0.161712	0.384	
T053100H IB080800Hr6A1613	0.158369	0.158772	0.403	
T053100I IB080800Hr6B1614	0.166334	0.16673	0.396	
Z041200B IB080800Hr8A1564	0.26073	0.261214	0.484	
Z041200C IB080800Hr8B1642	0.256683	0.257115	0.432	
T061300A IB080800Hd1B1618	0.166579	0.166761	0.182	very high for a "blank"
T060800D IB080900Hr2A1610	0.168993	0.167522	-1.471	hole in filter
T063000C IB080900Hr2B1622	0.162283	0.162382	0.099	
T063000D IB080900Hr6A1613	0.167419	0.169122	1.703	
T060800E IB080900Hr6B1614	0.176678	0.176805	0.127	
Z031300C IB080900Hr8A1564	0.268824	0.268992	0.168	
Z031300B IB080900Hr8B1642	0.273316	0.273477	0.161	
T063000B IB080900Hd1B1618	0.166107	0.166169	0.062	

* ID Explanation:
      First 8 digits – clean filter ID
      IB – Name of test
      080800 – Date of test
      H – Hildemann sampler
      r – Residence chamber or d – Dilution chamber
      Next three digits (number, letter, number) – port, side, first filter
      Last three digits – array number

Appendix C

Elemental Analyses

Table C-1. Elemental Analysis

Element	Filter ID T053100A IB080800Hr2A1 wt% of PM mass	T053100G IB080800Hr2B1 wt% of PM mass
Sodium	0.15	0.21
Magnesium	0.18	0.16
Silicon	17.9	14.4
Phosphorus	0.11	0.07
Sulfur	4.0	3.4
Chloride	0.61	0.66
Potassium	11.1	10.2
Calcium	0.72	0.81

Analyzed for all elements with atomic number greater than 9. However, only elements with concentrations greater than one standard error above the detection limit are reported.

Appendix D

Major Ions

Table D-1. Ion Chromatographic Analysis. Data from Wood-Fired Boiler (wt% of PM mass)

Filter ID	Z041400B IB080800Hr8A1	Z041400C IB080800Hr8B1	Z033100C IB080900Hr8A1	Z033100B IB080900Hr8B1
Ion				
Chloride	NQ	NQ	NQ	NQ
Nitrate	NQ	NQ	NQ	NQ
Sulfate	7.4	8.3	NQ	NQ
Potassium	6.4	7.2	6.0	6.6
Magnesium	ND	ND	ND	ND
Calcium	ND	ND	ND	ND

NQ – Not Quantified
ND – Not Detected

Appendix E

Elemental Carbon / Organic Carbon

Table E-1. Elemental Carbon/Organic Carbon (wt% of PM Mass)

Filter ID	EC	OC
Q060200C IB080800Hr4A1	3.3	76.8
Q051200U IB080900Hr4A1	2.7	92.4

Appendix F

Semivolatile and Nonvolatile
Organic Species

Table F-1. Semivolatile and Nonvolatile Organic Compounds – Mass Emission Rates for Composite Wood-Fired Boiler Test #1 (T1) August 8, 2000, and Test #2 (T2) August 9, 2000

Mass of Fuel Consumed	=	224,717 kg
Total Volume of Combustion Air	=	(combustion air flow rate$_{T1}$ x time$_{T1}$) + (combustion air flow rate$_{T2}$ x time$_{T2}$)
	=	[(9851 scfm x 257.9 min) + (9851.6 scfm x 359.7 min)] x 28.32 sLpm/scfm
	=	172,290,407 liters
Volume of Combustion Air Sampled	=	(Venturi flow rate$_{T1}$ x time$_{T1}$) + (Venturi flow rate$_{T2}$ x time$_{T2}$)
	=	(17.19 sLpm x 257.9 min) + (17.06 sLpm x 359.7 min)
	=	10,569.8 liters
Volume of Dilution Air	=	(Critical Orifice flow rate$_{T1}$ x time$_{T1}$) + (Critical Orifice flow rate$_{T2}$
	=	x time$_{T2}$)
	=	(822.4 sLpm x 257.9 min) + (823.5 sLpm x 359.7 min)
		508,309 liters
Mass Flow Rate of Compound in Diluted Sample	=	(mass of compound collected) / [(sum of flow rates at sample collection units x (time$_{T1}$ + time$_{T2}$)]
	=	17.3 µg / [(8.835 sLpm + 8.865 sLpm) x (257.9 min + 359.7 min)]
	=	0.00158 µg/L
Mass Flow Rate of Compound in Dilution Air Sample	=	(mass of compound collected) / [(sum of flow rates at sample collection units x (time$_{T1}$ + time$_{T2}$)]
	=	0.24 µg / [(8.835 sLpm + 8.865 sLpm) x (257.9 min + 359.7 min)]
	=	0.0000219 µg/L
Mass Flow Rate Corrected for Compound in Dilution Air	=	(mass flow rate of compound in diluted sample) – (mass flow rate of compound in dilution air)
	=	(0.00158 µg/L) - (0.0000219 µg/L)
	=	0.00156 µg/L
Dilution Ratio	=	[(volume of dilution air$_{T1}$+volume of dilution air$_{T2}$) + (volume of combustion air sampled$_{T1}$ + volume of combustion air sampled$_{T2}$)] / (volume of combustion air sampled$_{T1}$ + volume of combustion air sampled$_{T2}$)
	=	[(212096.96 liters + 296157 liters) + (4433.3 liters + 6135 liters)] / (4433.3 liters + 6135 liters)
	=	49.09
Mass Flow Rate of Compound in Undiluted Sample	=	(mass flow rate of compound corrected for dilution air PM) x (dilution ratio)
	=	(0.00156 µg/L) x (49.09)
	=	0.076 µg/L
Mass of Compound in Sampled Air	=	(mass flow rate of compound in undiluted sample) x (volume of combustion air sampled$_{T1}$ + volume of combustion air sampled$_{T2}$)
	=	(0.076 µg/L) * (4433.3 liters + 6135 liters)
	=	803.19 µg
Mass of compound in total combustion air	=	[(mass of compound in sampled air) / (volume of combustion air sampled$_{T1}$ + volume of combustion air sampled$_{T2}$)] x (total volume of combustion air$_{T1}$+total volume of combustion air$_{T2}$)
	=	[(803.19 µg) / (4433.3 liters + 6135 liters)] x (172,290,407 liters)
	=	13,094,057.9 µg
Mass emission rate of compound	=	(mass of compound in total combustion air) / (mass of fuel
	=	consumed) 13,094,057.9 µg / 224,717 kg
	=	58.27 µg/kg fuel consumed

Table F-2. Calculated Gas- and Particle-Phase Emissions from the Wood-Fired Boiler, August 8, 2000 and August 9, 2000

Denuders

Mass of fuel (kg)		224717
Dilution ratio		49.05
Total air introduced (m³)		172275.6
Time (min)		617.55
Flow rate (L/min)		35.24
Extract Volume (µL)		210.00
Extract Volume (µL)		245.00

Compound	August 8 Extract Concentration D0619001&2 (ng/µL)	August 9 Extract Concentration D710001&2 (ng/µL)	Denuder (Composite of August 8 and August 9) Compound Emission Rate (µg/kg)
Naphthalene	0.15	0.58	0.30
Acenaphthylene	ND	ND	ND
Acenaphthene	ND	ND	ND
Fluorene	ND	ND	ND
Phenanthrene	ND	0.56	0.24
Anthracene	ND	ND	ND
Fluoranthene	ND	ND	ND
Pyrene	ND	ND	ND
Benzo[a]anthracene	ND	ND	ND
Chrysene	ND	ND	ND
Benzo[b]fluoranthene	ND	ND	ND
Benzo[k]fluoranthene	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND
Benzo[ghi]perylene	ND	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	ND
Indeno[1,2,3-cd]fluoranthene	ND	ND	ND
Dibenzo[a,h]anthracene	ND	ND	ND
Coronene	ND	ND	ND
1-Methylnaphthalene	ND	ND	ND
2-Methylnaphthalene	ND	ND	ND
2,7-Dimethylnaphthalene	ND	ND	ND
1,3-Dimethylnaphthalene	ND	ND	ND
2,6-Dimethylnaphthalene	ND	ND	ND
9-Methylanthracene	ND	ND	ND
Methylfluorene	ND	ND	ND
bis(2-Ethylhexyl)phthalate	2.42	1.69	1.59
Butyl benzyl phthalate	12.97	7.87	8.04
Diethyl phthalate	1.28	2.33	1.45
Dimethyl phthalate	0.38	0.45	0.33
Di-n-butyl phthalate	1.18	0.47	0.63
Di-n-octyl phthalate	ND	ND	ND

ND = Compound not detected. (Continued)

F-3

Table F-2. (Continued)

Compound	August 8 Extract Concentration D0619001&2 (ng/μL)	August 9 Extract Concentration D710001&2 (ng/μL)	Denuder (Composite of August 8 and August 9) Compound Emission Rate (μg/kg)
Octylcyclohexane	ND	ND	ND
Decylcyclohexane	ND	ND	ND
Tridecylcyclohexane	ND	ND	ND
Nonadecylcyclohexane	ND	ND	ND
Norpristane	ND	ND	ND
Pristane	ND	ND	ND
Phytane	ND	ND	ND
Squalane	ND	ND	ND
ABB-20R-C27-Cholestane	ND	ND	ND
BAA-20R-C27-Cholestane	ND	ND	ND
AAA-20S-C27-Cholestane	ND	ND	ND
AAA-20R-C27-Cholestane	ND	ND	ND
ABB-20R-C28-Methylcholestane	ND	ND	ND
ABB-20R-C29-Ethylcholestane	ND	ND	ND
17A(H)-22, 29, 30-Trisnorhopane	ND	ND	ND
17B(H)-21A(H)-30-Norhopane	ND	ND	ND
17B(H)-21B(H)-Hopane	ND	ND	ND
17B(H)-21A(H)-Hopane	ND	ND	ND
17A(H)-21B(H)-Hopane	ND	ND	ND
n-Decane (C10)	ND	ND	ND
n-Undecane (C11)	ND	ND	ND
n-Dodecane (C12)	3.12	6.63	3.94
n-Tridecane (C13)	ND	1.41	0.60
n-Tetradecane (C14)	2.68	4.80	3.00
n-Pentadecane (C15)	0.73	1.47	0.89
n-Hexadecane (C16)	2.13	3.05	2.06
n-Heptadecane (C17)	1.32	1.22	1.00
n-Octadecane (C18)	0.70	1.21	0.77
n-Nonadecane (C19)	2.90	1.69	1.77
n-Eicosane (C20)	15.42	ND	5.60
n-Heneicosane (C21)	28.04	20.75	18.96
n-Docosane (C22)	221.83	188.49	160.29
n-Tricosane (C23)	202.81	1125.95	550.25
n-Tetracosane (C24)	135.10	68.73	78.12
n-Pentacosane (C25)	49.27	35.38	32.86
n-Hexacosane (C26)	17.26	14.43	12.37
n-Heptacosane (C27)	9.81	8.99	7.37
n-Octacosane (C28)	8.03	7.97	6.29
n-Nonacosane (C29)	4.76	3.91	3.38
n-Triacontane (C30)	1.63	1.26	1.12

ND = Compound not detected. (Continued)

F-4

Table F-2. (Continued)

Compound	August 8 Extract Concentration D0619001&2 (ng/μL)	August 9 Extract Concentration D710001&2 (ng/μL)	Denuder (Composite of August 8 and August 9) Compound Emission Rate (μg/kg)
n-Hentriacontane (C31)	0.98	0.75	0.67
n-Dotriacontane (C32)	1.17	0.86	0.79
n-Tritriacontane (C33)	0.63	0.55	0.46
n-Tetratriacontane (C34)	0.49	0.28	0.30
n-Pentatriacontane (C35)	1.45	0.98	0.94
n-Hexatriacontane (C36)	ND	0.98	0.75
n-Tetracontane (C40)	ND	ND	ND
3-Methylnonadecane	ND	0.78	0.33
2-Methylnonadecane	2.91	1.53	1.70
Cyclopenta[cd]pyrene	ND	ND	ND
Dibenzo[a,e]pyrene	ND	ND	ND
Pyrene	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND
Methylfluoranthene	ND	ND	ND
Methylchrysene	ND	ND	ND
Retene	ND	ND	ND
Anthroquinone	ND	ND	ND
9-Fluorenone	ND	ND	ND
Benzo[a]anthracene-7,12-dione	ND	ND	ND
1,8 Naphthalic anhydride	ND	ND	ND
Squalene	2.71	3.93	2.65
1-Octadecene	3.17	ND	1.15
Benzo[e]pyrene	ND	ND	ND
Oxalic acid (C2)	ND	ND	ND
Malonic acid (C3)	ND	ND	ND
Maleic acid (C3=)	ND	ND	ND
Fumaric acid (C4=)	ND	ND	ND
Succininc acid (C4) Butanedioic acid	ND	ND	ND
Glutaric acid (C5) Pentanedioic acid	ND	ND	ND
Adipic acid (C6) Hexanedioic acid	ND	ND	ND
Pimelic acid (C7) Heptanedioic acid	ND	ND	ND
Suberic acid (C8) Octanedioic acid	ND	ND	ND
Azelaic acid (C9) Nonanedioic acid	ND	ND	ND
Sebacic acid (C10) Decanedioic acid	ND	ND	ND
Phthalic acid (1,2)	ND	7.16	3.14
Isophthalic acid (1,3)	ND	12.27	5.39
Terephthalic acid (1,4)	ND	ND	ND
1,2,4-Benzenetricarboxylic acid	ND	ND	ND
1,2,4,5-Benzenetetracarboxylic acid	ND	ND	ND
Methylphthalic acid	ND	ND	ND

ND = Compound not detected. (Continued)

Table F-2. (Continued)

Compound	August 8 Extract Concentration D0619001&2 (ng/µL)	August 9 Extract Concentration D710001&2 (ng/µL)	Denuder (Composite of August 8 and August 9) Compound Emission Rate (µg/kg)
C6 Hexanoic acid	ND	ND	ND
C8 Octanoic acid	0.27	0.36	0.29
C9 Nonanoic acid	0.74	0.64	0.63
C10 Decanoic acid	1.08	1.17	1.02
C11 Undecanoic acid	1.11	0.39	0.69
C12 Dodecanoic acid	2.78	1.82	2.11
C13 Tridecanoic acid	1.37	1.01	1.09
C14 Tetradecanoic acid	3.14	2.96	2.78
C15 Pentadecanoic acid	0.98	1.10	0.95
C16 Hexadecanoic acid	20.66	15.03	16.34
C17 Heptadecanoic acid	ND	ND	ND
C18 Octadecanoic acid	12.65	9.42	10.10
C19 Nonadecanoic acid	ND	ND	ND
C20 Eicosanoic acid	ND	ND	ND
C21 Heneicosanoic acid	ND	ND	ND
C22 Docosanoic acid	ND	ND	ND
C23 Tricosanoic acid	ND	ND	ND
C24 Tetracosanoic acid	0.22	0.33	0.25
C25 Pentacosanoic acid	ND	ND	ND
C26 Hexacosanoic acid	ND	ND	ND
C27 Heptacosanoic acid	ND	ND	ND
Abietic acid	ND	ND	ND
Octacosanoic acid	ND	ND	ND
Nonacosanoic acid	ND	ND	ND
Triacontanoic acid	ND	ND	ND
Pinonic acid	ND	ND	ND
Palmitoleic acid (C16:1)	ND	1.74	0.76
Oleic acid (C18:1)	ND	ND	ND
Linoleic acid (C18:2)	ND	ND	ND
Linolenic acid	ND	ND	ND
Pimaric acid	ND	73.01	43.00
Sandaracopimaric acid	ND	ND	ND
Isopimaric acid	ND	ND	ND
6,8,11,13-Abietatetraen-18-oic acid	ND	ND	ND
Dehydroabietic acid	ND	ND	ND
Levoglucosan (TMS derivative)	ND	ND	ND
Cholesterol (TMS derivative)	ND	ND	ND
Stigmasterol (TMS derivative)	ND	ND	ND
Monopalmitin (TMS derivative)	ND	ND	ND
Monoolein (TMS derivative)	ND	ND	ND

ND = Compound not detected.   (Continued)

Table F-2. (Continued)

Compound	August 8 Extract Concentration D0619001&2 (ng/μL)	August 9 Extract Concentration D710001&2 (ng/μL)	Denuder (Composite of August 8 and August 9) Compound Emission Rate (μg/kg)
Monostearin (TMS derivative)	ND	ND	ND
Glycerine (TMS derivative)	ND	ND	ND
β-Sitosterol (TMS derivative)	ND	ND	ND
Sitostenone (TMS derivative)	ND	ND	ND
α-Amyrin	ND	ND	ND
β-Amyrin	ND	ND	ND
Unresolved Complex Mixture (UCM)	ND	ND	ND
2-methylnonadecane	ND	ND	ND
3-methylnonadecane	ND	ND	ND
iso-docosane	ND	ND	ND
anteiso-docosane	1.88	ND	0.68
iso-tricosane	1.82	1.77	1.41
anteiso-tricosane	11.15	5.65	6.44
iso-tetracosane	1.26	0.88	0.83
anteiso-tetracosane	0.96	0.93	0.74
iso-pentacosane	0.82	0.61	0.56
anteiso-pentacosane	1.00	0.97	0.77
iso-hexacosane	0.61	0.52	0.44
anteiso-hexacosane	0.78	0.65	0.56
iso-heptacosane	0.28	ND	0.10
anteisoheptacosane	0.50	ND	0.18
iso-Octacosane	ND	ND	ND
anteiso-Octacosane	ND	ND	ND
iso-nonacosane	1.04	ND	0.38
anteiso-nonacosane	1.48	ND	0.54
iso-triacontane	ND	ND	ND
anteiso-triacontane	ND	ND	ND
iso-hentriacontane	ND	ND	ND
anteiso-hentriacontane	ND	ND	ND
iso-dotriacontane	ND	ND	ND
anteiso-dotriacontane	ND	ND	ND
iso-tritriacontane	ND	ND	ND
anteiso-tritriacontane	ND	ND	ND

ND = Compound not detected.   (Continued)

Table F-2. (Continued)

Quartz Filters (After Denuder)

Mass of fuel (kg)	224,717
Dilution ratio	49.05
Total air introduced (m^3)	172,275.6
Time (min)	617.55
Flow rate (L/min)	17.62
Extract Volume (μL)	2.50

Compounds	August 8 and August 9 Composite Extract Concentration (ng/μL)	Compound Emission Rate (μg/kg)
Naphthalene	0.31	0.26
Acenaphthylene	0.03	0.02
Acenaphthene	ND	ND
Fluorene	ND	ND
Phenanthrene	0.03	0.02
Anthracene	ND	ND
Fluoranthene	0.01	0.01
Pyrene	ND	ND
Benzo[a]anthracene	ND	ND
Chrysene	ND	ND
Benzo[b]fluoranthene	ND	ND
Benzo[k]fluoranthene	ND	ND
Benzo[a]pyrene	ND	ND
Benzo[ghi]perylene	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND
Indeno[1,2,3-cd]fluoranthene	ND	ND
Dibenzo[a,h]anthracene	ND	ND
Coronene	ND	ND
1-Methylnaphthalene	0.10	0.09
2-Methylnaphthalene	0.08	0.07
2,7-Dimethylnaphthalene	ND	ND
1,3-Dimethylnaphthalene	ND	ND
2,6-Dimethylnaphthalene	ND	ND
9-Methylanthracene	ND	ND
Methylfluorene	ND	ND
bis(2-Ethylhexyl)phthalate	2.88	2.48
Butyl benzyl phthalate	1.69	1.46
Diethyl phthalate	0.55	0.48
Dimethyl phthalate	ND	ND
Di-*n*-butyl phthalate	0.58	0.50
Di-*n*-octyl phthalate	ND	ND
Octylcyclohexane	ND	ND
Decylcyclohexane	ND	ND
Tridecylcyclohexane	ND	ND

ND = Compound not detected. (Continued)

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Table F-2. (Continued)

Compounds	August 8 and August 9 Composite Extract Concentration (ng/µL)	Compound Emission Rate (µg/kg)
Nonadecylcyclohexane	ND	ND
Norpristane	ND	ND
Pristane	ND	ND
Phytane	ND	ND
Squalane	ND	ND
ABB-20R-C27-Cholestane	ND	ND
BAA-20R-C27-Cholestane	ND	ND
AAA-20S-C27-Cholestane	ND	ND
AAA-20R-C27-Cholestane	ND	ND
ABB-20R-C28-Methylcholestane	ND	ND
ABB-20R-C29-Ethylcholestane	ND	ND
17A(H)-22, 29, 30-Trisnorhopane	ND	ND
17B(H)-21A(H)-30-Norhopane	ND	ND
17B(H)-21B(H)-Hopane	ND	ND
17B(H)-21A(H)-Hopane	ND	ND
17A(H)-21B(H)-Hopane	ND	ND
n-Decane (C10)	ND	ND
n-Undecane (C11)	ND	ND
n-Dodecane (C12)	ND	ND
n-Tridecane (C13)	ND	ND
n-Tetradecane (C14)	0.1	0.09
n-Pentadecane (C15)	0.135	0.12
n-Hexadecane (C16)	0.12	0.10
n-Heptadecane (C17)	0.1	0.09
n-Octadecane (C18)	0.09	0.08
n-Nonadecane (C19)	ND	ND
n-Eicosane (C20)	0.305	0.26
n-Heneicosane (C21)	0.32	0.28
n-Docosane (C22)	0.79	0.68
n-Tricosane (C23)	3.935	3.40
n-Tetracosane (C24)	23.8	20.56
n-Pentacosane (C25)	46.97	40.58
n-Hexacosane (C26)	52.335	45.21
n-Heptacosane (C27)	34.81	30.07
n-Octacosane (C28)	21.135	18.26
n-Nonacosane (C29)	10.045	8.68
n-Triacontane (C30)	5.21	4.50
n-Hentriacontane (C31)	3.405	2.94
n-Dotriacontane (C32)	1.255	1.08
n-Tritriacontane (C33)	0.485	0.42
n-Tetratriacontane (C34)	0.215	0.19
n-Pentatriacontane (C35)	0.28	0.24

ND = Compound not detected.   (Continued)

Table F-2. (Continued)

Compounds	August 8 and August 9 Composite Extract Concentration (ng/μL)	Compound Emission Rate (μg/kg)
n-Hexatriacontane (C36)	0.095	0.08
n-Tetracontane (C40)	ND	ND
3-Methylnonadecane	ND	ND
2-Methylnonadecane	ND	ND
Cyclopenta[cd]pyrene	ND	ND
Dibenzo[a,e]pyrene	ND	ND
Pyrene	ND	ND
Benzo[a]pyrene	ND	ND
Methylfluoranthene	ND	ND
Methylchrysene	ND	ND
Retene	ND	ND
Anthroquinone	ND	ND
9-Fluorenone	ND	ND
Benzo[a]anthracene-7,12-dione	ND	ND
1,8-Naphthalic anhydride	ND	ND
Squalene	ND	ND
1-Octadecene	ND	ND
Benzo[e]pyrene	ND	ND
Oxalic acid (C2)	ND	ND
Malonic acid (C3)	ND	ND
Maleic acid (C3=)	ND	ND
Fumaric acid (C4=)	ND	ND
Succininc acid (C4) Butanedioic acid	ND	ND
Glutaric acid (C5) Pentanedioic acid	ND	ND
Adipic acid (C6) Hexanedioic acid	ND	ND
Pimelic acid (C7) Heptanedioic acid	ND	ND
Suberic acid (C8) Octanedioic acid	ND	ND
Azelaic acid (C9) Nonanedioic acid	ND	ND
Sebacic acid (C10) Decanedioic acid	ND	ND
Phthalic acid (1,2)	ND	ND
Isophthalic acid (1,3)	ND	ND
Terephthalic acid (1,4)	ND	ND
1,2,4-Benzenetricarboxylic acid	ND	ND
1,2,4,5-Benzenetetracarboxylic acid	ND	ND
Methylphthalic acid	ND	ND
C6 Hexanoic acid	ND	ND
C8 Octanoic acid	ND	ND
C9 Nonanoic acid	ND	ND
C10 Decanoic acid	ND	ND
C11 Undecanoic acid	ND	ND
C12 Dodecanoic acid	0.15	0.15
C13 Tridecanoic acid	0.09	0.09

ND = Compound not detected. (Continued)

Table F-2. (Continued)

Compounds	August 8 and August 9 Composite Extract Concentration (ng/µL)	Compound Emission Rate (µg/kg)
C14 Tetradecanoic acid	0.17	0.16
C15 Pentadecanoic acid	0.11	0.11
C16 Hexadecanoic acid	3.19	3.09
C17 Heptadecanoic acid	ND	ND
C18 Octadecanoic acid	6.03	5.83
C19 Nonadecanoic acid	ND	ND
C20 Eicosanoic acid	0.24	0.23
C21 Heneicosanoic acid	ND	ND
C22 Docosanoic acid	ND	ND
C23 Tricosanoic acid	ND	ND
C24 Tetracosanoic acid	ND	ND
C25 Pentacosanoic acid	ND	ND
C26 Hexacosanoic acid	ND	ND
C27 Heptacosanoic acid	ND	ND
Abietic acid	ND	ND
Octacosanoic acid	ND	ND
Nonacosanoic acid	ND	ND
Triacontanoic acid	ND	ND
Pinonic acid	ND	ND
Palmitoleic acid (C16:1)	0.28	0.27
Oleic acid (C18:1)	0.5	0.48
Linoleic acid (C18:2)	0.28	0.27
Linolenic acid	ND	ND
Pimaric acid	ND	ND
Sandaracopimaric acid	ND	ND
Isopimaric acid	ND	ND
6,8,11,13-Abietatetraen-18-oic acid	ND	ND
Dehydroabietic acid	ND	ND
Levoglucosan (TMS derivative)	2.12	12.31
Cholesterol (TMS derivative)	3.96	22.99
Stigmasterol (TMS derivative)	3.63	21.07
Monopalmitin (TMS derivative)	0.53	3.08
Monoolein (TMS derivative)	0.58	3.37
Monostearin (TMS derivative)	0.79	4.59
Glycerine (TMS derivative)	1.18	6.85
β-Sitosterol (TMS derivative)	ND	ND
Sitostenone (TMS derivative)	ND	ND
α-Amyrin	ND	ND
β-Amyrin	ND	ND
Unresolved Complex Mixture (UCM)	ND	ND
2-methylnonadecane	ND	ND
3-methylnonadecane	ND	ND

ND = Compound not detected.   (Continued)

Table F-2. (Continued)

Compounds	August 8 and August 9 Composite Extract Concentration (ng/μL)	Compound Emission Rate (μg/kg)
iso-docosane	ND	ND
anteiso-docosane	ND	ND
iso-tricosane	ND	ND
anteiso-tricosane	ND	ND
iso-tetracosane	1.17	1.01
anteiso-tetracosane	0.495	0.43
iso-pentacosane	2.885	2.49
anteiso-pentacosane	1.745	1.51
iso-hexacosane	2.705	2.34
anteiso-hexacosane	2.205	1.91
iso-heptacosane	2.005	1.73
anteisoheptacosane	1.635	1.41
iso-Octacosane	0.89	0.77
anteiso-Octacosane	0.93	0.80
iso-nonacosane	0.555	0.48
anteiso-nonacosane	0.36	0.31
iso-triacontane	0.325	0.28
anteiso-triacontane	0.25	0.22
iso-hentriacontane	0.11	0.10
anteiso-hentriacontane	0.08	0.07
iso-dotriacontane	0.065	0.06
anteiso-dotriacontane	0.045	0.04
iso-tritriacontane	ND	ND
anteiso-tritriacontane	ND	ND

ND = Compound not detected.   (Continued)

Table F-2. (Continued)

Dilution Air Quartz Filters

Mass of fuel (kg)	224,717
Dilution ratio	48.05
Total air introduced (m³)	172,275.6
Time (min)	617.55
Flow rate (L/min)	17.585
Extract Volume (μL)	260

Compounds	August 8 and August 9 Composite Extract Concentration Q051200Q-Q051200T (ng/μL)	Compound Emission Rate (μg/kg)	Compound Emission Rate Corrected for Dilution Air (μg/kg)
Naphthalene	0.36	0.35	-0.09
Acenaphthylene	0.02	0.02	0.00
Acenaphthene	ND	ND	ND
Fluorene	ND	ND	ND
Phenanthrene	0.03	0.03	-0.01
Anthracene	ND	ND	ND
Fluoranthene	ND	ND	0.01
Pyrene	ND	ND	ND
Benzo[a]anthracene	ND	ND	ND
Chrysene	ND	ND	ND
Benzo[b]fluoranthene	ND	ND	ND
Benzo[k]fluoranthene	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND
Benzo[ghi]perylene	ND	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	ND
Indeno[1,2,3-cd]fluoranthene	ND	ND	ND
Dibenzo[a,h]anthracene	ND	ND	ND
Coronene	ND	ND	ND
1-Methylnaphthalene	0.06	0.06	0.03
2-Methylnaphthalene	0.10	0.10	-0.03
2,7-Dimethylnaphthalene	ND	ND	ND
1,3-Dimethylnaphthalene	ND	ND	ND
2,6-Dimethylnaphthalene	ND	ND	ND
9-Methylanthracene	ND	ND	ND
Methylfluorene	0.02	0.02	-0.02
bis(2-Ethylhexyl)phthalate	2.35	2.29	0.19
Butyl benzyl phthalate	0.73	0.71	0.74
Diethyl phthalate	0.88	0.86	-0.38
Dimethyl phthalate	0.05	0.05	-0.05
Di-*n*-butyl phthalate	0.72	0.70	-0.21
Di-*n*-octyl phthalate	ND	ND	ND
Octylcyclohexane	ND	ND	ND

ND = Compound not detected. (Continued)

Table F-2. (Continued)

Compounds	August 8 and August 9 Composite Extract Concentration Q051200Q-Q051200T (ng/μL)	Compound Emission Rate (μg/kg)	Compound Emission Rate Corrected for Dilution Air (μg/kg)
Decylcyclohexane	ND	ND	ND
Tridecylcyclohexane	ND	ND	ND
Nonadecylcyclohexane	ND	ND	ND
Norpristane	ND	ND	ND
Pristane	0.04	0.04	-0.04
Phytane	0.08	0.08	-0.08
Squalane	0.17	0.17	-0.17
ABB-20R-C27-Cholestane	ND	ND	ND
BAA-20R-C27-Cholestane	ND	ND	ND
AAA-20S-C27-Cholestane	ND	ND	ND
AAA-20R-C27-Cholestane	ND	ND	ND
ABB-20R-C28-Methylcholestane	ND	ND	ND
ABB-20R-C29-Ethylcholestane	ND	ND	ND
17A(H)-22, 29, 30-Trisnorhopane	ND	ND	ND
17B(H)-21A(H)-30-Norhopane	ND	ND	ND
17B(H)-21B(H)-Hopane	ND	ND	ND
17B(H)-21A(H)-Hopane	ND	ND	ND
17A(H)-21B(H)-Hopane	ND	ND	ND
n-Decane (C10)	ND	ND	ND
n-Undecane (C11)	ND	ND	ND
n-Dodecane (C12)	ND	ND	ND
n-Tridecane (C13)	ND	ND	ND
n-Tetradecane (C14)	0.15	0.15	-0.06
n-Pentadecane (C15)	0.13	0.13	-0.01
n-Hexadecane (C16)	0.11	0.11	0.00
n-Heptadecane (C17)	0.08	0.08	0.01
n-Octadecane (C18)	0.12	0.12	-0.04
n-Nonadecane (C19)	0.58	0.57	-0.57
n-Eicosane (C20)	1.73	1.69	-1.43
n-Heneicosane (C21)	1.89	1.85	-1.57
n-Docosane (C22)	0.98	0.96	-0.27
n-Tricosane (C23)	0.58	0.57	2.83
n-Tetracosane (C24)	0.7	0.68	19.88
n-Pentacosane (C25)	0.92	0.90	39.68
n-Hexacosane (C26)	1.23	1.20	44.01
n-Heptacosane (C27)	1.33	1.30	28.78
n-Octacosane (C28)	1.29	1.26	17.00
n-Nonacosane (C29)	1.08	1.05	7.62
n-Triacontane (C30)	0.64	0.62	3.88
n-Hentriacontane (C31)	0.7	0.68	2.26

ND = Compound not detected. (Continued)

Table F-2. (Continued)

Compounds	August 8 and August 9 Composite Extract Concentration Q051200Q-Q051200T (ng/μL)	Compound Emission Rate (μg/kg)	Compound Emission Rate Corrected for Dilution Air (μg/kg)
n-Dotriacontane (C32)	0.31	0.30	0.78
n-Tritriacontane (C33)	0.15	0.15	0.27
n-Tetratriacontane (C34)	0.08	0.08	0.11
n-Pentatriacontane (C35)	ND	ND	0.24
n-Hexatriacontane (C36)	ND	ND	0.08
n-Tetracontane (C40)	ND	ND	ND
3-Methylnonadecane	0.42	0.41	-0.41
2-Methylnonadecane	0.29	0.28	-0.28
Cyclopenta[cd]pyrene	ND	ND	ND
Dibenzo[a,e]pyrene	ND	ND	ND
Pyrene	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND
Methylfluoranthene	ND	ND	ND
Methylchrysene	ND	ND	ND
Retene	ND	ND	ND
Anthroquinone	ND	ND	ND
9-Fluorenone	ND	ND	ND
Benzo[a]anthracene-7,12-dione	ND	ND	ND
1,8-Naphthalic anhydride	ND	ND	ND
Squalene	0.71	0.69	-0.69
1-Octadecene	ND	ND	ND
Benzo[e]pyrene	ND	ND	ND
Oxalic acid (C2)	ND	ND	ND
Malonic acid (C3)	ND	ND	ND
Maleic acid (C3=)	ND	ND	ND
Fumaric acid (C4=)	ND	ND	ND
Succininc acid (C4) Butanedioic acid	ND	ND	ND
Glutaric acid (C5) Pentanedioic acid	ND	ND	ND
Adipic acid (C6) Hexanedioic acid	ND	ND	ND
Pimelic acid (C7) Heptanedioic acid	ND	ND	ND
Suberic acid (C8) Octanedioic acid	ND	ND	ND
Azelaic acid (C9) Nonanedioic acid	ND	ND	ND
Sebacic acid (C10) Decanedioic acid	ND	ND	ND
Phthalic acid (1,2)	1.06	1.08	-1.08
Isophthalic acid (1,3)	ND	ND	ND
Terephthalic acid (1,4)	ND	ND	ND
1,2,4-Benzenetricarboxylic acid	ND	ND	ND
1,2,4,5-Benzenetetracarboxylic acid	ND	ND	ND
Methylphthalic acid	ND	ND	ND
C6 Hexanoic acid	ND	ND	ND

ND = Compound not detected. (Continued)

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Table F-2. (Continued)

Compounds	August 8 and August 9 Composite Extract Concentration Q051200Q-Q051200T (ng/μL)	Compound Emission Rate (μg/kg)	Compound Emission Rate Corrected for Dilution Air (μg/kg)
C8 Octanoic acid	ND	ND	ND
C9 Nonanoic acid	0.08	0.08	-0.08
C10 Decanoic acid	0.09	0.09	-0.09
C11 Undecanoic acid	0.03	0.03	-0.03
C12 Dodecanoic acid	0.38	0.39	-0.24
C13 Tridecanoic acid	0.03	0.03	0.06
C14 Tetradecanoic acid	0.47	0.48	-0.31
C15 Pentadecanoic acid	0.12	0.12	-0.02
C16 Hexadecanoic acid	1.33	1.35	1.73
C17 Heptadecanoic acid	ND	ND	ND
C18 Octadecanoic acid	0.44	0.45	5.39
C19 Nonadecanoic acid	ND	ND	ND
C20 Eicosanoic acid	0.02	0.02	0.21
C21 Heneicosanoic acid	ND	ND	ND
C22 Docosanoic acid	ND	ND	ND
C23 Tricosanoic acid	ND	ND	ND
C24 Tetracosanoic acid	ND	ND	ND
C25 Pentacosanoic acid	ND	ND	ND
C26 Hexacosanoic acid	ND	ND	ND
C27 Heptacosanoic acid	ND	ND	ND
Abietic acid	ND	ND	ND
Octacosanoic acid	ND	ND	ND
Nonacosanoic acid	ND	ND	ND
Triacontanoic acid	ND	ND	ND
Pinonic acid	ND	ND	ND
Palmitoleic acid (C16:1)	0.23	0.23	0.04
Oleic acid (C18:1)	0.27	0.28	0.21
Linoleic acid (C18:2)	0.16	0.16	0.11
Linolenic acid	ND	ND	ND
Pimaric acid	ND	ND	ND
Sandaracopimaric acid	ND	ND	ND
Isopimaric acid	ND	ND	ND
6,8,11,13-Abietatetraen-18-oic acid	ND	ND	ND
Dehydroabietic acid	15.98	16.28	-16.28
Levoglucosan (TMS derivative)	1.87	11.43	0.88
Cholesterol (TMS derivative)	3.42	20.90	2.09
Stigmasterol (TMS derivative)	2.97	18.15	2.92
Monopalmitin (TMS derivative)	0.45	2.75	0.33
Monoolein (TMS derivative)	0.4	2.45	0.92
Monostearin (TMS derivative)	0.51	3.12	1.47

ND = Compound not detected.   (Continued)

Table F-2. (Continued)

Compounds	August 8 and August 9 Composite Extract Concentration Q051200Q-Q051200T (ng/μL)	Compound Emission Rate (μg/kg)	Compound Emission Rate Corrected for Dilution Air (μg/kg)
Glycerine (TMS derivative)	0.98	5.99	0.86
β-Sitosterol (TMS derivative)	ND	ND	ND
Sitostenone (TMS derivative)	ND	ND	ND
α-Amyrin	ND	ND	ND
β-Amyrin	ND	ND	ND
Unresolved Complex Mixture (UCM)	ND	ND	ND
2-methylnonadecane	0.29	0.28	-0.28
3-methylnonadecane	0.42	0.41	-0.41
iso-docosane	ND	ND	ND
anteiso-docosane	0.18	0.18	-0.18
iso-tricosane	ND	ND	ND
anteiso-tricosane	ND	ND	ND
iso-tetracosane	ND	ND	1.01
anteiso-tetracosane	ND	ND	0.43
iso-pentacosane	ND	ND	2.49
anteiso-pentacosane	ND	ND	1.51
iso-hexacosane	ND	ND	2.34
anteiso-hexacosane	ND	ND	1.91
iso-heptacosane	ND	ND	1.73
anteisoheptacosane	ND	ND	1.41
iso-Octacosane	ND	ND	0.77
anteiso-Octacosane	ND	ND	0.80
iso-nonacosane	0.05	0.05	0.43
anteiso-nonacosane	ND	ND	0.31
iso-triacontane	ND	ND	0.28
anteiso-triacontane	ND	ND	0.22
iso-hentriacontane	ND	ND	0.10
anteiso-hentriacontane	ND	ND	0.07
iso-dotriacontane	ND	ND	0.06
anteiso-dotriacontane	ND	ND	0.04
iso-tritriacontane	ND	ND	ND
anteiso-tritriacontane	ND	ND	ND

ND = Compound not detected. (Continued)

F-17

Table F-2. (Continued)

<u>PUF Plugs</u>

Mass of fuel (kg)	<u>August 8 Dilution Ratio</u>	Tot. Air Intro (m3)		<u>August 9 Dilution Ratio</u>
224717	49.05	172275.6		48.05
Time (min)	PUF Flow rate (L/min)		PUFs Flow rate - August 9 (L/min)	
617.55	17.62		17.585	
	Extract Volume 250.00 µL	Extract Volume 245.00 µL	Extract Volume 240 µL	Extract Volume 255 µL

Compound	August 8 Concentration P071900AB (ng/µL)	August 9 Concentration P073100AB (ng/µL)	Compound Emission Rate (µg/kg)	August 8 Concentration P073100GH (ng/µL)	August 9 Concentration P080100AB (ng/µL)	Compound Dilution Air Emission Rate (µg/kg)	Corrected Compound Emission Rate (µg/kg)
Naphthalene	2.65	1.49	3.55	0.56	0.94	1.27	2.28
Acenaphthylene	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	ND	0.64	0.54	ND	ND	ND	0.54
Fluorene	2.33	ND	2.01	ND	ND	ND	2.01
Phenanthrene	ND	3.46	2.93	0.62	0.56	0.99	1.94
Anthracene	ND	ND	ND	ND	0.06	0.05	ND
Fluoranthene	0.05	0.25	0.25	ND	0.05	0.04	0.21
Pyrene	0.03	0.12	0.13	ND	0.04	0.03	0.09
Benzo[a]anthracene	ND	ND	ND	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND	ND	ND	ND
Benzo[b]fluoranthene	ND	ND	ND	ND	ND	ND	ND
Benzo[k]fluoranthene	ND	ND	ND	ND	ND	ND	ND
Benzo[a]pyrene	ND	ND	ND	ND	ND	ND	ND
Benzo[ghi]perylene	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-cd]fluoranthene	ND	ND	ND	ND	ND	ND	ND
Dibenzo[a,h]anthracene	ND	ND	ND	ND	ND	ND	ND
Coronene	ND	ND	ND	ND	ND	ND	ND
1-Methylnaphthalene	3.27	0.92	3.60	0.26	0.32	0.49	3.12
2-Methylnaphthalene	4.60	1.53	5.27	0.49	0.73	1.03	4.24

ND = Compound not detected.

(Continued)

Table F-2. (Continued)

Compound	August 8 Concentration P071900AB (ng/µL)	August 9 Concentration P073100AB (ng/µL)	Compound Emission Rate (µg/kg)	August 8 Concentration P073100GH (ng/µL)	August 9 Concentration P080100AB (ng/µL)	Compound Dilution Air Emission Rate (µg/kg)	Corrected Compound Emission Rate (µg/kg)
2,7-Dimethylnaphthalene	1.50	ND	1.30	ND	0.7	0.61	0.69
1,3-Dimethylnaphthalene	2.13	0.83	2.54	ND	0.17	0.15	2.40
2,6-Dimethylnaphthalene	1.41	0.93	2.01	ND	0.14	0.12	1.88
9-Methylanthracene	ND	ND	ND	ND	ND	ND	ND
Methylfluorene	ND	2.23	1.89	0.21	0.43	0.54	1.35
bis(2-Ethylhexyl)phthalate	3.02	2.49	4.72	0.77	ND	0.63	4.09
Butyl benzyl phthalate	1.94	4.98	5.89	0.72	0.95	1.41	4.48
Diethyl phthalate	16.53	22.12	33.01	1.49	0.85	1.95	31.06
Dimethyl phthalate	24.07	ND	20.80	ND	ND	ND	20.80
Di-n-butyl phthalate	0.83	2.94	3.21	0.83	1.54	2.01	1.20
Di-n-octyl phthalate	ND	ND	ND	ND	ND	ND	ND
Octylcyclohexane	ND	ND	ND	ND	ND	ND	ND
Decylcyclohexane	ND	ND	ND	ND	ND	ND	ND
Tridecylcyclohexane	ND	ND	ND	ND	ND	ND	ND
Nonadecylcyclohexane	ND	ND	ND	ND	ND	ND	ND
Norpristane	ND	ND	ND	ND	ND	ND	ND
Pristane	1.28	ND	1.11	0.79	0.54	1.11	0.00
Phytane	ND	ND	ND	1.22	1.35	2.16	ND
Squalane	ND	ND	ND	ND	ND	ND	ND
ABB-20R-C27-Cholestane	ND	ND	ND	ND	ND	ND	ND
BAA-20R-C27-Cholestane	ND	ND	ND	ND	ND	ND	ND
AAA-20S-C27-Cholestane	ND	ND	ND	ND	ND	ND	ND
AAA-20R-C27-Cholestane	ND	ND	ND	ND	ND	ND	ND
ABB-20R-C28-Methylcholestane	ND	ND	ND	ND	ND	ND	ND
ABB-20R-C29-Ethylcholestane	ND	ND	ND	ND	ND	ND	ND
17A(H)-22, 29, 30-Trisnorhopane	ND	ND	ND	ND	ND	ND	ND
17B(H)-21 A(H)-30-Norhopane	ND	ND	ND	ND	ND	ND	ND
17B(H)-21 B(H)-Hopane	ND	ND	ND	ND	ND	ND	ND

ND = Compound not detected.

(Continued)

F-19

Table F-2. (Continued)

Compound	August 8 Concentration P071900AB (ng/μL)	August 9 Concentration P073100AB (ng/μL)	Compound Emission Rate (μg/kg)	August 8 Concentration P073100GH (ng/μL)	August 9 Concentration P080100AB (ng/μL)	Compound Dilution Air Emission Rate (μg/kg)	Corrected Compound Emission Rate (μg/kg)
17B(H)-21 A(H)-Hopane	ND	ND	ND	ND	ND	ND	ND
17A(H)-21 B(H)-Hopane	ND	ND	ND	ND	ND	ND	ND
n-Decane (C10)	ND	ND	ND	ND	ND	ND	ND
n-Undecane (C11)	ND	ND	ND	ND	ND	ND	ND
n-Dodecane (C12)	ND	ND	ND	ND	ND	ND	ND
n-Tridecane (C13)	2.77	ND	2.39	2.2	1.25	2.87	ND
n-Tetradecane (C14)	1.08	0.33	1.21	1.34	1.31	2.22	ND
n-Pentadecane (C15)	3.84	0.55	3.78	1.28	1.09	1.98	1.80
n-Hexadecane (C16)	6.02	2.56	7.37	1.51	1.88	2.86	4.51
n-Heptadecane (C17)	4.69	1.56	5.37	1.35	1.5	2.40	2.98
n-Octadecane (C18)	5.74	2.36	6.96	1.37	1.59	2.49	4.47
n-Nonadecane (C19)	11.02	6.23	14.80	2.01	2.98	4.21	10.58
n-Eicosane (C20)	3.26	1.47	4.06	1.28	2.29	3.02	1.04
n-Heneicosane (C21)	3.72	1.49	4.48	0.99	1.08	1.74	2.74
n-Docosane (C22)	7.01	2.83	8.45	0.74	ND	13.04	ND
n-Tricosane (C23)	17.98	5.55	20.23	1.64	1.34	1.34	18.90
n-Tetracosane (C24)	14.24	3.12	14.94	1.02	14.38	13.27	1.68
n-Pentacosane (C25)	6.42	3.65	8.64	1.91	2.03	3.31	5.33
n-Hexacosane (C26)	4.34	4.33	7.42	3.54	ND	2.88	4.53
n-Heptacosane (C27)	5.94	6.21	10.39	5.42	0.27	4.65	5.74
n-Octacosane (C28)	6.56	6.26	10.97	6.1	4.11	8.52	2.45
n-Nonacosane (C29)	7.96	6.25	12.17	5.84	4.43	8.59	3.58
n-Triacontane (C30)	2.87	1.86	4.05	2.06	1.47	2.95	1.11
n-Hentriacontane (C31)	2.65	1.42	3.49	1.2	1.16	1.98	1.51
n-Dotriacontane (C32)	3.37	1.43	4.12	1.27	ND	1.03	3.09
n-Tritriacontane (C33)	1.45	0.78	1.91	0.78	ND	0.63	1.28
n-Tetratriacontane (C34)	3.19	0.51	3.19	0.51	ND	0.42	2.77
n-Pentatriacontane (C35)	4.09	0.87	4.27	1.82	ND	1.48	2.79
n-Hexatriacontane (C36)	ND	ND	ND	1.37	ND	1.12	ND
n-Tetracontane (C40)	ND	ND	ND	ND	ND	ND	ND
3-Methylnonadecane	ND	ND	ND	ND	0.83	0.72	ND
2-Methylnonadecane	ND	ND	ND	ND	0.37	0.32	ND

ND = Compound not detected.

(Continued)

F-20

Table F-2. (Continued)

Compound	August 8 Concentration P071900AB (ng/μL)	August 9 Concentration P073100AB (ng/μL)	Compound Emission Rate (μg/kg)	August 8 Concentration P073100GH (ng/μL)	August 9 Concentration P080100AB (ng/μL)	Compound Dilution Air Emission Rate (μg/kg)	Corrected Compound Emission Rate (μg/kg)
Cyclopenta[cd]pyrene	ND	ND	ND	0.91	ND	0.74	ND
Dibenzo[a,e]pyrene	ND	ND	ND	ND	ND	ND	ND
Pyrene	ND	0.04	0.03	ND	ND	ND	0.03
Benzo[a]pyrene	ND	ND	ND	ND	ND	ND	ND
Methylfluoranthene	ND	ND	ND	ND	ND	ND	ND
Methylchrysene	ND	ND	ND	ND	ND	ND	ND
Retene	ND	ND	ND	ND	ND	ND	ND
Anthroquinone	ND	ND	ND	ND	ND	ND	ND
9-Fluorenone	1.55	ND	1.34	ND	ND	ND	1.34
Benzo[a]anthracene-7,12-dione	ND	ND	ND	ND	ND	ND	ND
1,8-Naphthalic anhydride	ND	ND	ND	ND	ND	ND	ND
Squalene	ND	4.44	3.76	ND	4.47	3.87	ND
1-Octadecene	ND	ND	ND	ND	ND	ND	ND
Benzo[e]pyrene	ND	ND	ND	ND	ND	ND	ND
Oxalic acid (C2)	ND	ND	ND	ND	ND	ND	ND
Malonic acid (C3)	ND	ND	ND	ND	ND	ND	ND
Maleic acid (C3=)	ND	ND	ND	ND	ND	ND	ND
Fumaric acid (C4=)	ND	ND	ND	ND	ND	ND	ND
Succininc acid (C4)	ND	ND	ND	ND	ND	ND	ND
Butanedioic acid	ND	ND	ND	ND	ND	ND	ND
Glutaric acid (C5)	ND	ND	ND	ND	ND	ND	ND
Pentanedioic acid	ND	ND	ND	ND	ND	ND	ND
Adipic acid (C6) Hexanedioic acid	ND	ND	ND	ND	ND	ND	ND
Pimelic acid (C7)	ND	ND	ND	ND	ND	ND	ND
Heptanedioic acid	ND	ND	ND	ND	ND	ND	ND
Suberic acid (C8) Octanedioic acid	ND	ND	ND	ND	ND	ND	ND
Azelaic acid (C9)	ND	ND	ND	ND	ND	ND	ND
Nonanedioic acid	ND	ND	ND	ND	ND	ND	ND

ND = Compound not detected.

(Continued)

F-21

Table F-2. (Continued)

Compound	August 8 Concentration P071900AB (ng/µL)	August 9 Concentration P073100AB (ng/µL)	Compound Emission Rate (µg/kg)	August 8 Concentration P073100GH (ng/µL)	August 9 Concentration P080100AB (ng/µL)	Compound Dilution Air Emission Rate (µg/kg)	Corrected Compound Emission Rate (µg/kg)
Sebacic acid (C10)							
Decanedioic acid	ND	ND	ND	ND	ND	ND	ND
Phthalic acid (1,2)	ND	ND	ND	ND	ND	ND	ND
Isophthalic acid (1,3)	ND	ND	ND	ND	ND	ND	ND
Terephthalic acid (1,4)	ND	3.78	2.37	ND	ND	ND	2.37
1,2,4-Benzenetricarboxylic acid	ND	ND	ND	ND	ND	ND	ND
1,2,4,5-Benzenetetracarboxylic acid	ND	ND	ND	ND	ND	ND	ND
Methylphthalic acid	ND	ND	ND	ND	ND	ND	ND
C6 Hexanoic acid	ND	ND	ND	ND	ND	ND	ND
C8 Octanoic acid	2.12	2.66	4.09	0.5	0.69	1.18	2.91
C9 Nonanoic acid	1.89	3.34	4.25	0.61	0.9	1.50	2.76
C10 Decanoic acid	ND	0.38	0.24	0.24	0.25	0.48	ND
C11 Undecanoic acid	0.28	0.51	0.64	0.07	0.09	0.16	0.48
C12 Dodecanoic acid	0.78	1.96	2.12	0.32	0.6	0.92	1.20
C13 Tridecanoic acid	ND	0.51	0.32	0.05	0.08	0.13	0.19
C14 Tetradecanoic acid	1.24	1.33	2.25	0.31	0.85	1.17	1.08
C15 Pentadecanoic acid	0.49	0.53	0.89	0.14	0.41	0.55	0.34
C16 Hexadecanoic acid	4.49	4.00	7.64	1.57	4.01	5.60	2.03
C17 Heptadecanoic acid	ND	0.51	0.32	0.07	ND	0.06	0.26
C18 Octadecanoic acid	2.08	2.36	3.86	1.41	3.2	4.62	ND
C19 Nomadecanoic acid	ND	0.04	0.03	0.02	ND	0.02	0.01
C20 Eicosanoic acid	0.09	0.13	0.18	0.14	0.15	0.28	ND
C21 Heneicosanoic acid	ND	ND	ND	ND	ND	ND	ND
C22 Docosanoic acid	0.06	ND	0.07	ND	ND	ND	0.07
C23 Tricosanoic acid	ND	ND	ND	ND	0.06	0.06	ND
C24 Tetracosanoic acid	0.14	0.18	0.27	0.08	0.24	0.32	ND
C25 Pentacosanoic acid	ND	0.04	0.03	ND	0.08	0.08	ND
C26 Hexacosanoic acid	ND	ND	ND	ND	ND	ND	ND
C27 Heptacosanoic acid	ND	ND	ND	ND	ND	ND	ND
Abietic acid	ND	ND	ND	ND	ND	ND	ND

ND = Compound not detected.

(Continued)

Table F-2. (Continued)

Compound	August 8 Concentration P071900AB (ng/μL)	August 9 Concentration P073100AB (ng/μL)	Compound Emission Rate (μg/kg)	August 8 Concentration P073100GH (ng/μL)	August 9 Concentration P080100AB (ng/μL)	Compound Dilution Air Emission Rate (μg/kg)	Corrected Compound Emission Rate (μg/kg)
Octacosanoic acid	ND	0.06	0.04	ND	ND	ND	0.04
Nonacosanoic acid	ND	ND	ND	ND	ND	ND	ND
Triacontanoic acid	ND	ND	ND	ND	ND	ND	ND
Pinonic acid	ND	ND	ND	ND	ND	ND	ND
Palmitoleic acid (C16:1)	ND	ND	ND	0.14	0.47	0.62	ND
Oleic acid (C18:1)	0.18	0.30	0.39	0.21	0.51	0.72	ND
Linoleic acid (C18:2)	ND	ND	ND	ND	ND	ND	ND
Linolenic acid	ND	ND	ND	ND	ND	ND	ND
Pimaric acid	ND	ND	ND	ND	ND	ND	ND
Sandaracopimaric acid	ND	ND	ND	ND	ND	ND	ND
Isopimaric acid	ND	ND	ND	ND	ND	ND	ND
6,8,11,13-Abietatetraen-18-oic acid	ND	ND	ND	ND	ND	ND	ND
Dehydroabietic acid	ND	ND	ND	6.93	ND	6.40	ND
Levoglucosan (TMS derivative)	ND	ND	ND	ND	ND	ND	ND
Cholesterol (TMS derivative)	ND	ND	ND	ND	ND	ND	ND
Stigmasterol (TMS derivative)	ND	ND	ND	ND	ND	ND	ND
Monopalmitin (TMS derivative)	ND	ND	ND	ND	ND	ND	ND
Monoolein (TMS derivative)	ND	ND	ND	ND	ND	ND	ND
Monostearin (TMS derivative)	ND	ND	ND	ND	ND	ND	ND
Glycerine (TMS derivative)	ND	ND	ND	ND	ND	ND	ND
β-Sitosterol (TMS derivative)	ND	ND	ND	ND	ND	ND	ND
Sitostenone (TMS derivative)	ND	ND	ND	ND	ND	ND	ND
α-Amyrin	ND	ND	ND	ND	ND	ND	ND
β-Amyrin	ND	ND	ND	ND	ND	ND	ND
Unresolved Complex Mixture (UCM)	ND	ND	ND	ND	ND	ND	ND
2-Methylnonadecane	ND	ND	ND	ND	ND	ND	ND
3-Methylnonadecane	ND	ND	ND	ND	ND	ND	ND
iso-Docosane	ND	ND	ND	ND	ND	ND	ND

ND = Compound not detected.

(Continued)

Table F-2. (Continued)

Compound	August 8 Concentration P071900AB (ng/µL)	August 9 Concentration P073100AB (ng/µL)	Compound Emission Rate (µg/kg)	August 8 Concentration P073100GH (ng/µL)	August 9 Concentration P080100AB (ng/µL)	Compound Dilution Air Emission Rate (µg/kg)	Corrected Compound Emission Rate (µg/kg)
anteiso-Docosane	ND	ND	ND	ND	ND	ND	ND
iso-Tricosane	ND	ND	ND	ND	ND	ND	ND
anteiso-Tricosane	ND	ND	ND	ND	ND	ND	ND
iso-Tetracosane	ND	ND	ND	ND	ND	ND	ND
anteiso-Tetracosane	ND	ND	ND	ND	ND	ND	ND
iso-Pentacosane	ND	ND	ND	ND	ND	ND	ND
anteiso-Pentacosane	ND	ND	ND	ND	ND	ND	ND
iso-Hexacosane	ND	ND	ND	ND	ND	ND	ND
anteiso-Hexacosane	ND	ND	ND	ND	ND	ND	ND
iso-Heptacosane	ND	ND	ND	ND	ND	ND	ND
anteisoHeptacosane	ND	ND	ND	ND	ND	ND	ND
iso-Octacosane	ND	ND	ND	ND	ND	ND	ND
anteiso-Dotriacontane	ND	ND	ND	ND	ND	ND	ND
iso-Tritriacontane	ND	ND	ND	ND	ND	ND	ND
anteiso-Tritriacontane	ND	ND	ND	ND	ND	ND	ND

ND = Compound not detected.

F-24

Appendix G

Supporting Data for Carbonyl Analysis

Table G-1. Carbonyl Compounds Analyzed by High Performance Liquid Chromatography
Field Samples, August 8-9, 2000
Results reported by individual carbonyl sampling tube.

Compound	CAS No.	Blank 8/8/00	Blank 8/9/00	Residence Chamber Front Tube	Residence Chamber Back Tube	Residence Chamber Front Tube	Residence Chamber Back Tube
				μg			
formaldehyde	50-00-0	0.0425	0.0365	36.28	0.07	12.8735	0.0505
acetaldehyde	75-07-0	0.079	0.083	6.6595	0.165	2.5435	0.0965
acetone	67-64-1	0.184	0.2235	0.804	2.1695	0.2155	0.5535
propionaldehyde	123-38-6	ND	ND	0.8405	ND	0.428	ND
crotonaldehyde	4170-30-3	ND	ND	0.122	ND	0.068	ND
butyraldehyde	123-72-8	0.034	0.0875	0.51	0.293	0.3455	0.247
benzaldehyde	100-52-7	ND	0.0205	0.35	ND	0.202	ND
isovaleraldehyde	590-86-3	ND	ND	ND	ND	ND	ND
valeraldehyde	110-62-3	ND	ND	0.1585	0.013	0.072	ND
o-tolualdehyde	529-20-4	ND	ND	ND	ND	ND	ND
m-tolualdehyde	620-23-5	ND	0.028	0.1125	0.032	0.099	ND
p-tolualdehyde	104-87-0	ND	ND	ND	ND	0.0405	ND
hexaldehyde	66-25-1	0.016	0.018	0.1075	0.0185	0.0485	0.0205
2,5-dimethylbenz-aldehyde	5779-94-2	ND	ND	ND	ND	ND	ND
diacetyl	431-03-8	ND	ND	ND	ND	ND	ND
methacrolein	78-85-3	ND	ND	0.361	ND	0.185	ND
2-butanone	78-93-3	0.013	0.026	0.221	0.320	0.026	0.181
glyoxal	107-22-2	ND	ND	1.579	0.225	2.060	ND
acetophenone	98-86-2	ND	ND	0.905	ND	0.238	ND
methylglyoxal	78-98-8	ND	ND	0.553	ND	0.546	ND
octanal	124-13-0	ND	ND	ND	ND	ND	ND
nonanal	124-19-6	0.070	ND	0.506	0.077	0.379	0.102

ND = Not detected; compound not observed at detectable levels.

Table G-2. Carbonyl Compounds Analyzed by High Performance Liquid Chromatography
Field Samples, Generated August 8-9, 2000

Compound	CAS No.	Blank 8/8/00 µg	Residence Chamber Paired Tubes 8/8/00 µg	Blank 8/9/00 µg	Residence Chamber Paired Tubes 8/9/00 µg
formaldehyde	50-00-0	0.0425	36.35	0.0365	12.924
acetaldehyde	75-07-0	0.079	6.8245	0.083	2.640
acetone	67-64-1	0.184	2.9735	0.2235	0.7690
propionaldehyde	123-38-6	ND	0.8405	ND	0.4280
crotonaldehyde	4170-30-3	ND	0.1220	ND	0.0680
butyraldehyde	123-72-8	0.034	0.8030	0.0875	0.5925
benzaldehyde	100-52-7	ND	0.3500	0.0205	0.2020
isovaleraldehyde	590-86-3	ND	ND	ND	ND
valeraldehyde	110-62-3	ND	0.1715	ND	0.0720
o-tolualdehyde	529-20-4	ND	ND	ND	ND
m-tolualdehyde	620-23-5	ND	0.1445	0.028	0.0990
p-tolualdehyde	104-87-0	ND	ND	ND	0.0405
hexaldehyde	66-25-1	0.016	0.1260	0.018	0.0690
2,5-dimethylbenz-aldehyde	5779-94-2	ND	ND	ND	ND
diacetyl	431-03-8	ND	ND	ND	ND
methacrolein	78-85-3	ND	0.3610	ND	0.1850
2-butanone	78-93-3	0.013	0.5410	0.026	0.2070
glyoxal	107-22-2	ND	1.8040	ND	2.0600
acetophenone	98-86-2	ND	0.9050	ND	0.2380
methylglyoxal	78-98-8	ND	0.5530	ND	0.5460
octanal	124-13-0	ND	ND	ND	ND
nonanal	124-19-6	0.070	0.5830	ND	0.4810
Total Speciated		0.3595	53.4525	0.5230	21.4680
Total Unspeciated		2.3270	6.8975	1.4755	4.6515
Total Speciated + Unspeciated		2.6865	60.3500	1.9985	25.1195

ND = Not detected; compound not observed in performance of the analysis.
Total Speciated = Total mass (front plus back tube) of identified carbonyl compounds.
Total Unspeciated = Total mass (front plus back tube) of compounds characterized as carbonyl compounds but not identified as a specific compound because no analytical reference standard was available.

Table G-3. Carbonyl Compounds (Speciated). Mass Emission Rates for Wood-Fired Boiler (SCC 10200902), Test #1 (August 8, 2000)

Mass Fuel Consumed	=	97,690 kg
Total Volume of Combustion Air	=	(combustion air flow rate) x (time)
	=	(3,263.6 scfm) x (28.31685 sLpm/scfm) x (257.90 min)
	=	23,833,795 liters
Volume of Combustion Air Sampled	=	(Venturi flow rate) x (time)
	=	(17.19 sLpm) x (257.90 min)
	=	4,433.301 liters
Volume of Dilution Air	=	(dilution air flow rate) x (time)
	=	(822.4 sLpm) x (257.90 min)
	=	212,096.96 liters
Dilution Ratio	=	(volume of dilution air + volume of combustion air)/volume of combustion air
	=	(212,096.96 liters + 4,433.301 liters)/4,433.301 liters
	=	48.8
Mass Flow Rate of Carbonyls in Diluted Sample	=	(mass carbonyls collected)/[(sample flow rate at cartridge) x (time)]
	=	(53.0930 µg)/[(0.970699 Lpm) x (257.90 min)]
	=	0.2120808 µg/liter
Mass Flow Rate of Carbonyls in Undiluted Sample	=	(mass flow rate carbonyls diluted) x dilution ratio
	=	(0.2120808 µg/liter) x 48.841768*
	=	10.358401 µg/liter
Total Mass of Carbonyls in Sampled Air	=	(mass flow rate of carbonyls in undiluted sample) x (volume of undiluted sample)
	=	10.358401 µg/liter x 4,433.301 liters
	=	45,921.91 µg
Total Carbonyls in Total Combustion Air	=	[(mass of carbonyls in sampled air)/(volume of sampled air)] x (total combustion air)
	=	[(45,853.58 µg)/(4,433.301 liters)] x (23,833,795 liters)
	=	246,880,011 µg
Mass Emission Rate of Speciated Carbonyls	=	(mass carbonyls in total combustion air)/(kg fuel burned)
	=	246,880,011 µg /97,690 kg
	=	2,527.2 µg/kg fuel
	=	2.53 mg/kg fuel

*Dilution factor is dimensionless

Table G-4. Carbonyl Compounds (Speciated). Mass Emission Rates for Wood-Fired Boiler (SCC 10200902), Test #2 (August 9, 2000)

Mass Fuel Consumed	=	127,027 kg
Total Volume of Combustion Air	=	(combustion air flow rate) x (time)
	=	(3,263.6 scfm) x (28.31685 sLpm/scfm) x (359.65 min)
	=	33,237,009 liters
Volume of Combustion Air Sampled	=	(Venturi flow rate) x (time)
	=	(17.06 sLpm) x (359.65 min)
	=	6,135.629 liters
Volume of Dilution Air	=	(dilution air flow rate) x (time)
	=	(823.46 sLpm) x (359.65 min)
	=	296,157.39 liters
Dilution Ratio	=	(volume of dilution air + volume of combustion air)/volume of combustion air
	=	(296,157.39 liters + 100,330,222 liters)/6,135.629 liters
	=	49.268464
Mass Flow Rate of Carbonyls in Diluted Sample	=	(mass carbonyls collected)/[(sample flow rate at cartridge) x (time)]
	=	(21.468 µg)/[(0.969695 Lpm) x (359.65 min)]
	=	0.0621336 µg/liter
Mass Flow Rate of Carbonyls in Undiluted Sample	=	(mass flow rate carbonyls diluted) x dilution ratio
	=	(0.0621336 µg/liter) x 49.268464*
	=	3.061223 µg/liter
Total Mass of Carbonyls in Sampled Air	=	(mass flow rate of carbonyls in undiluted sample) x (volume of undiluted sample)
	=	3.061223 µg/liter x 6,135.629 liters
	=	18,782.53 µg
Total Carbonyls in Total Combustion Air	=	[(mass of carbonyls in sampled air)/(volume of sampled air)] x (total combustion air)
	=	[(18,782.53 µg)/(6,135.629 liters)] x (33,237,009 liters)
	=	101,745,906 µg
Mass Emission Rate of Speciated Carbonyls	=	(mass carbonyls in total combustion air)/(kg fuel burned)
	=	101,745,906 µg /127,027 kg
	=	800.9786 µg/kg fuel
	=	0.801 mg/kg fuel

*Dilution factor is dimensionless

G-5

Table G-5. Carbonyl Compounds (Speciated + Unspeciated). Mass Emission Rates for Wood-Fired Boiler (SCC 10200902), Test #1 (August 8, 2000)

Mass Fuel Consumed	=	97,690 kg
Total Volume of Combustion Air	=	(combustion air flow rate) x (time)
	=	(3,263.6 scfm) x (28.31685 sLpm/scfm) x (257.90 min)
	=	23,833,795 liters
Volume of Combustion Air Sampled	=	(Venturi flow rate) x (time)
	=	(17.19 sLpm) x (257.90 min)
	=	4,433.3 liters
Volume of Dilution Air	=	(dilution air flow rate) x (time)
	=	(822.4 sLpm) x (257.90 min)
	=	212,097.0 liters
Dilution Ratio	=	(volume of dilution air + volume of combustion air)/volume of combustion air
	=	(212,097.0 liters + 4,433.3 liters)/4,433.3 liters
	=	48.8
Mass Flow Rate of Carbonyls in Diluted Sample	=	(mass carbonyls collected)/[(sample flow rate at cartridge) x (time)]
	=	(57.6635 μg)/[(0.970699 Lpm) x (257.90 min)]
	=	0.2303 μg/liter
Mass Flow Rate of Carbonyls in Undiluted Sample	=	(mass flow rate carbonyls diluted) x dilution ratio
	=	(0.2303 μg/liter) x 48.8*
	=	11.25 μg/liter
Total Mass of Carbonyls in Sampled Air	=	(mass flow rate of carbonyls in undiluted sample) x (volume of undiluted sample)
	=	11.25 μg/liter x 4,433.3 liters
	=	49,875.09 μg
Total Carbonyls in Total Combustion Air	=	[(mass of carbonyls in sampled air)/(volume of sampled air)] x (total combustion air)
	=	[(49,875.09 μg)/(4,433.3 liters)] x (23,833,795 liters)
	=	268,132,626 μg
Mass Emission Rate of Carbonyls (Speciated + Unspeciated)	=	(mass carbonyls in total combustion air)/(kg fuel burned)
	=	268,132,626 μg /97,690 kg
	=	2,744.7 μg/kg fuel
	=	2.74 mg/kg fuel

*Dilution factor is dimensionless

Table G-6. **Carbonyl Compounds (Speciated + Unspeciated). Mass Emission Rates for Wood-Fired Boiler (SCC 10200902), Test #2 (August 9, 2000)**

Mass Fuel Consumed	=	127,027 kg
Total Volume of Combustion Air	=	(combustion air flow rate) x (time)
	=	(3,263.6 scfm) x (28.31685 sLpm/scfm) x (359.65 min)
	=	33,237,008 liters
Volume of Combustion Air Sampled	=	(Venturi flow rate) x (time)
	=	(17.06 sLpm) x (359.65 min)
	=	6,135.6 liters
Volume of Dilution Air	=	(dilution air flow rate) x (time)
	=	(823.46 sLpm) x (359.65 min)
	=	296,157.4 liters
Dilution Ratio	=	(volume of dilution air + volume of combustion air)/volume of combustion air
	=	(296,157.4 liters + 6,135.6 liters)/6,135.6 liters
	=	49.3
Mass Flow Rate of Carbonyls in Diluted Sample	=	(mass carbonyls collected)/[(sample flow rate at cartridge) x (time)]
	=	(25.1195 µg)/[(0.960695 Lpm) x (359.65 min)]
	=	0.0727 µg/liter
Mass Flow Rate of Carbonyls in Undiluted Sample	=	(mass flow rate carbonyls diluted) x dilution ratio
	=	(0.0727 µg/liter) x 49.3*
	=	3.58 µg/liter
Total Mass of Carbonyls in Sampled Air	=	(mass flow rate of carbonyls in undiluted sample) x (volume of undiluted sample)
	=	3.58 µg/liter x 6,135.6 liters
	=	21,997.26 µg
Total Carbonyls in Total Combustion Air	=	[(mass of carbonyls in sampled air)/(volume of sampled air)] x (total combustion air)
	=	[(21,997.26 µg)/(6,135.6 liters)] x 33,237,008 liters
	=	119,051,905 µg
Mass Emission Rate of Carbonyls (Speciated + Unspeciated)	=	(mass carbonyls in total combustion air)/(kg fuel burned)
	=	119,051,905 µg /127,027 kg
	=	937.2 µg/kg fuel
	=	0.94 mg/kg fuel

*Dilution factor is dimensionless

Appendix H

**Supporting Data for
Speciated Nonmethane Organic Compound Analysis**

Table H-1. Analytical Results for Field Samples, Speciated Nonmethane Organic Compounds, Test #1, 8/8/00

Compound	CAS No.	Blank µg/m³	Dilution Air µg/m³	Dilution Air Total µg	Residence Chamber Air µg/m³	Residence Chamber Air Total µg
ethylene	74-85-1	0.15	1.65	350.0	14.69	3180.8
acetylene	74-86-2	ND	0.87	184.5	9.4	2035.4
ethane	74-84-0	0.17	2.76	585.4	6.96	1507.1
propylene	115-07-1	0.09	57.24	12140.4	53.34	11549.7
propane	74-98-6	0.18	51.97	11022.7	48.41	10482.2
propyne	74-99-7	ND	ND	ND	ND	ND
isobutane	75-28-5	0.09	0.68	144.2	1.51	327.0
isobutene/1-butene	115-11-7/106-98-0	0.07	0.87	184.5	2.37	513.2
1,3-butadiene	106-99-0	ND	ND	ND	0.31	67.1
n-butane	106-97-8	0.15	0.85	180.3	1.56	337.8
trans-2-butene	624-64-6	0.09	0.23	48.8	0.56	121.3
cis-2-butene	590-18-1	0.12	0.43	91.2	0.67	145.1
3-methyl-1-butene	563-45-1	ND	ND	ND	0.13	28.1
isopentane	78-78-4	0.14	0.53	112.4	0.61	132.1
1-pentene	109-67-1	ND	ND	ND	ND	ND
2-methyl-1-butene	563-46-2	ND	ND	ND	0.16	34.6
n-pentane	109-66-0	0.09	0.25	53.0	0.84	181.9
isoprene	78-79-4	0.09	4.21	892.9	0.46	99.6
trans-2-pentene	646-04-8	0.09	0.3	63.6	0.61	132.1
cis-2-pentene	627-20-3	0.13	0.36	76.4	0.51	110.4
2-methyl-2-butene	513-35-9	ND	ND	ND	ND	ND
2,2-dimethylbutane	75-83-2	0.16	9.92	2104.0	5.45	1180.1
cyclopentene	142-29-0	ND	0.22	46.7	0.23	49.8
4-methyl-1-pentene	691-37-2	ND	ND	ND	ND	ND
cyclopentane	287-92-3	0.09	0.37	78.5	0.4	86.6

ND = Compound not detected.

(Continued)

Table H-1. (Continued)

Compound	CAS No.	Blank µg/m³	Dilution Air µg/m³	Dilution Air Total µg	Residence Chamber Air µg/m³	Residence Chamber Air Total µg
2,3-dimethylbutane	79-29-8	0.19	0.59	125.1	0.6	129.9
2-methylpentane	107-83-5	0.08	0.54	114.5	ND	ND
3-methylpentane	96-14-0	0.16	0.54	114.5	0.5	108.3
2-methyl-1-pentene	763-29-1	ND	ND	ND	ND	ND
1-hexene	592-41-6	0.21	0.68	144.2	1.58	342.1
2-ethyl-1-butene	760-21-4	ND	ND	ND	ND	ND
n-hexane	110-54-3	0.12	6.37	1351.1	2.18	472.0
trans-2-hexene	4050-45-7	ND	ND	ND	ND	ND
cis-2-hexene	7688-21-3	ND	ND	ND	ND	ND
methylcyclopentane	96-37-7	0.11	0.87	184.5	0.65	140.7
2,4-dimethylpentane	108-08-7	0.15	0.37	78.5	0.41	88.8
benzene	71-43-2	0.12	0.35	74.2	400.2	86655.4
cyclohexane	110-82-7	0.15	0.4	84.8	0.45	97.4
2-methylhexane	591-76-4	0.07	0.92	195.1	0.22	47.6
2,3-dimethylpentane	565-59-3	0.19	0.53	112.4	0.46	99.6
3-methylhexane	589-34-4	0.12	1.14	241.8	0.96	207.9
1-heptene	592-76-7	ND	0.15	31.8	ND	ND
2,2,4-trimethylpentane	540-84-1	0.14	0.61	129.4	ND	ND
n-heptane	142-82-5	0.12	0.67	142.1	1.51	327.0
methylcyclohexane	108-87-2	0.14	7.92	1679.8	0.8	173.2
2,2,3-trimethylpentane	564-02-3	ND	ND	ND	ND	ND
2,3,4-trimethylpentane	565-75-3	0.1	0.36	76.4	0.5	108.3
toluene	108-88-3	0.18	1.31	277.8	3.9	844.5
2-methylheptane	592-27-8	0.1	0.44	93.3	0.42	90.9
3-methylheptane	589-81-1	0.11	0.56	118.8	0.65	140.7

ND = Compound not detected.

(Continued)

Table H-1. (Continued)

Compound	CAS No.	Blank µg/m³	Dilution Air µg/m³	Dilution Air Total µg	Residence Chamber Air µg/m³	Residence Chamber Air Total µg
1-octene	111-66-0	ND	0.26	55.1	0.83	179.7
n-octane	111-65-9	0.12	2.39	506.9	2.72	589.0
ethylbenzene	100-41-4	0.1	1.01	214.2	1.36	294.5
m-, p-xylene	108-38-3/106-42-3	0.15	1.21	256.6	1.7	368.1
styrene	100-42-5	0.06	0.67	142.1	0.75	162.4
o-xylene	95-47-6	0.1	0.63	133.6	ND	ND
1-nonene	124-11-8	0.1	0.13	27.6	0.32	69.3
n-nonane	111-84-2	0.15	0.81	171.8	1.34	290.2
isopropylbenzene	98-82-8	0.3	0.33	70.0	0.42	90.9
α-pinene	80-56-8	ND	4.77	1011.7	2.87	621.4
n-propylbenzene	103-65-1	0.1	0.35	74.2	0.46	99.6
m-ethyltoluene	620-14-4	0.18	1.52	322.4	1.43	309.6
p-ethyltoluene	622-96-8	0.14	1.03	218.5	1.04	225.2
1,3,5-trimethylbenzene	108-67-8	0.09	1.01	214.2	1.12	242.5
o-ethyltoluene	611-14-3	0.1	2.57	545.1	2.58	558.6
β-pinene	127-91-3	ND	2.07	439.0	1.84	398.4
1,2,4-trimethylbenzene	95-63-6	0.15	1.44	305.4	1.8	389.9
1-decene	872-05-9	ND	ND	ND	ND	ND
n-decane	124-18-5	0.13	29.58	6273.8	28.75	6225.2
1,2,3-trimethylbenzene	526-73-8	ND	0.4	84.8	0.51	110.4
m-diethylbenzene	141-93-5	0.11	0.67	142.1	0.57	123.4
p-diethylbenzene	105-05-5	0.1	0.24	50.9	0.2	43.3
1-undecene	821-95-4	ND	ND	ND	ND	ND
n-undecane	1120-21-4	0.14	4.48	950.2	4.44	961.4
1-dodecene	112-41-4	ND	0.84	178.2	0.96	207.9

ND = Compound not detected.

(Continued)

Table H-1. (Continued)

Compound	CAS No.	Blank µg/m³	Dilution Air µg/m³	Dilution Air Total µg	Residence Chamber Air µg/m³	Residence Chamber Air Total µg
n-dodecane	112-40-3	0.07	142.76	30279.0	142.42	30838.2
1-tridecene	2437-56-1	ND	0.82	173.9	1.04	225.2
n-tridecane	629-50-5	ND	0.84	178.2	0.9	194.9
Total Speciated		6.55	361.86	76749.4	767.54	166195.7
Total Unspeciated		6.37	77.02	16335.7	300.74	65119.3
Total Speciated + Unspeciated*		12.92	438.88	93085.1	1068.28	231315.0

* Total NMOC with unknowns in µg/m³ is an estimate based on propane only.

ND = Not detected; compound not observed in the performance of the analysis.
NR = Not reported because of compound co-elution
Total Speciated = Sum of concentrations for all identified peaks.
Total Unspeciated = Concentration obtained by taking the difference between (Total Speciated + Unspeciated) and Total Speciated.
Total Speciated + Unspeciated = Concentration obtained from the integration of all of the peaks in the chromatogram

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Table H-2. Analytical Results for Field Samples, Speciated Nonmethane Organic Compounds, Test #2, 8/9/00

Compound	CAS No.	Blank		Dilution Air		Residence Chamber Air	
		µg/m³	Total µg	µg/m³	Total µg	µg/m³	Total µg
ethylene	74-85-1	0.15	1.25	379.1	4.85	1466.1
acetylene	74-86-2	ND	0.73	216.2	7.68	2321.6
ethane	74-84-0	0.16	2.56	758.2	4.1	1239.4
propylene	115-07-1	0.11	7.2	2132.3	10.02	3029.0
propane	74-98-6	0.17	26.01	7703.1	25.96	7847.5
propyne	74-99-7	ND	ND	ND	ND	ND
isobutane	75-28-5	0.08	0.6	177.7	0.83	250.9
isobutene/1-butene	115-11-7/106-98-0	0.07	0.52	154.0	1.04	314.4
1,3-butadiene	106-99-0	ND	ND	ND	0.11	33.3
n-butane	106-97-8	0.14	0.82	242.8	0.98	296.2
trans-2-butene	624-64-6	0.08	0.27	80.0	ND	ND
cis-2-butene	590-18-1	0.13	0.39	115.5	0.48	145.1
3-methyl-1-butene	563-45-1	ND	ND	ND	ND	ND
isopentane	78-78-4	0.14	0.48	142.2	0.5	151.1
1-pentene	109-67-1	ND	ND	ND	ND	ND
2-methyl-1-butene	563-46-2	ND	ND	ND	ND	ND
n-pentane	109-66-0	0.09	0.5	148.1	0.94	284.2
isoprene	78-79-4	0.12	1.42	420.5	0.4	120.9
trans-2-pentene	646-04-8	0.10	0.26	77.0	0.35	105.8
cis-2-pentene	627-20-3	0.13	0.35	103.7	0.41	123.9
2-methyl-2-butene	513-35-9	ND	ND	ND	ND	ND
2,2-dimethylbutane	75-83-2	0.16	1	296.2	1.08	326.5
cyclopentene	142-29-0	ND	0.09	26.7	0.16	48.4
4-methyl-1-pentene	691-37-2	ND	ND	ND	ND	ND
cyclopentane	287-92-3	0.09	0.34	100.7	0.4	120.9

(Continued)

ND = Compound not detected.

Table H-2. (Continued)

Compound	CAS No.	Blank μg/m³	Dilution Air μg/m³	Dilution Air Total μg	Residence Chamber Air μg/m³	Residence Chamber Air Total μg
2,3-dimethylbutane	79-29-8	0.2	0.53	157.0	0.54	163.2
2-methylpentane	107-83-5	0.06	0.44	130.3	ND	ND
3-methylpentane	96-14-0	0.17	0.58	171.8	0.52	157.2
2-methyl-1-pentene	763-29-1	ND	ND	ND	ND	ND
1-hexene	592-41-6	0.20	0.65	192.5	0.85	256.9
2-ethyl-1-butene	760-21-4	ND	ND	ND	ND	ND
n-hexane	110-54-3	0.12	8.83	2615.1	7.36	2224.9
trans-2-hexene	4050-45-7	ND	ND	ND	ND	ND
cis-2-hexene	7688-21-3	ND	ND	ND	ND	ND
methylcyclopentane	96-37-7	0.10	1.18	349.5	1021	308641.2
2,4-dimethylpentane	108-08-7	0.14	0.35	103.7	0.36	108.8
benzene	71-43-2	0.12	0.48	142.2	100.45	30365.3
cyclohexane	110-82-7	0.14	0.45	133.3	0.42	127.0
2-methylhexane	591-76-4	0.07	0.66	195.5	0.56	169.3
2,3-dimethylpentane	565-59-3	0.19	0.53	157.0	0.52	157.2
3-methylhexane	589-34-4	0.14	0.48	142.2	0.51	154.2
1-heptene	592-76-7	ND	0.12	35.5	ND	ND
2,2,4-trimethylpentane	540-84-1	0.14	0.38	112.5	ND	ND
n-heptane	142-82-5	0.11	0.35	103.7	0.45	136.0
methylcyclohexane	108-87-2	0.14	0.73	216.2	0.64	193.5
2,2,3-trimethylpentane	564-02-3	ND	0.12	35.5	ND	ND
2,3,4-trimethylpentane	565-75-3	0.11	0.31	91.8	0.34	102.8
toluene	108-88-3	0.20	1.04	308.0	1.92	580.4
2-methylheptane	592-27-8	0.09	0.44	130.3	0.46	139.1
3-methylheptane	589-81-1	0.11	0.32	94.8	0.36	108.8

(Continued)

ND = Compound not detected.

H-7

Table H-2. (Continued)

Compound	CAS No.	Blank	Dilution Air		Residence Chamber Air	
		µg/m³	µg/m³	Total µg	µg/m³	Total µg
1-octene	111-66-0	ND	0.21	62.2	0.27	81.6
n-octane	111-65-9	0.14	1.46	432.4	1.31	396.0
ethylbenzene	100-41-4	0.12	1.4	414.6	1.37	414.1
m-, p-xylene	108-38-3/106-42-3	0.17	3.81	1128.4	3.3	997.6
styrene	100-42-5	0.08	1.12	331.7	0.95	287.2
o-xylene	95-47-6	0.09	1.21	358.4	ND	ND
1-nonene	124-11-8	ND	ND	ND	ND	ND
n-nonane	111-84-2	0.10	0.95	281.4	0.98	296.2
isopropylbenzene	98-82-8	0.16	0.32	94.8	0.33	99.8
α-pinene	80-56-8	ND	0.41	121.4	1	302.3
n-propylbenzene	103-65-1	0.10	0.48	142.2	0.36	108.8
m-ethyltoluene	620-14-4	0.16	1.92	568.6	1.99	601.6
p-ethyltoluene	622-96-8	0.13	1.06	313.9	1.04	314.4
1,3,5-trimethylbenzene	108-67-8	0.10	1.01	299.1	0.85	256.9
o-ethyltoluene	611-14-3	0.09	1.75	518.3	1.84	556.2
β-pinene	127-91-3	ND	1.08	319.9	1.1	332.5
1,2,4-trimethylbenzene	95-63-6	0.14	1.12	331.7	1.25	377.9
1-decene	872-05-9	ND	ND	ND	ND	ND
n-decane	124-18-5	0.15	26.48	7842.2	24.1	7285.3
1,2,3-trimethylbenzene	526-73-8	ND	0.7	207.3	0.52	157.2
m-diethylbenzene	141-93-5	0.13	0.61	180.7	0.57	172.3
p-diethylbenzene	105-05-5	0.08	0.23	68.1	0.23	69.5
1-undecene	821-95-4	ND	ND	ND	ND	ND
n-undecane	1120-21-4	0.13	4.01	1187.6	3.61	1091.3
1-dodecene	112-41-4	ND	0.96	284.3	0.95	287.2

ND = Compound not detected.

(Continued)

H-8

Table H-2. (Continued)

Compound	CAS No.	Blank μg/m³	Dilution Air μg/m³	Dilution Air Total μg	Residence Chamber Air μg/m³	Residence Chamber Air Total μg
n-dodecane	112-40-3	0.06	144.44	42777.0	124.54	37647.6
1-tridecene	2437-56-1	ND	0.79	234.0	ND	ND
n-tridecane	629-50-5	ND	0.75	222.1	0.48	145.1
Total Speciated		6.60	262.07	77614.0	350.7	75937.2
Total Unspeciated		6.46	48.66	14411.0	126.81	27458.2
Total Speciated + Unspeciated*		13.06	310.73	92025.0	477.51	103395.4

*Total NMOC with unknowns in μg/m³ is an estimate based on propane only.

ND = Not detected; compound not observed in the performance of the analysis.
NR = Not reported because of compound co-elution.
Total Speciated = Sum of concentrations for all identified peaks.
Total Unspeciated = Concentration obtained by taking the difference between (Total Speciated + Unspeciated) and Total Speciated.
Total Speciated + Unspeciated = Concentration obtained from the integration of all of the peaks in the chromatogram.

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Table H-3. **Speciated Nonmethane Organic Compounds. Mass Emission Rates for Wood-Fired Boiler (SCC 10200902), Test #1 (August 8, 2000)**

Mass Fuel Consumed	=	97,690 kg
Total Volume of Combustion Air	=	(combustion air flow rate) x (time)
	=	(3,263.6 scfm) x (28.31685 sLpm/scfm) x (257.9 min)
	=	23,833,795 liters
Volume of Combustion Air Sampled	=	(Venturi flow rate) x (time)
	=	(17.19 sLpm) x (257.9 min)
	=	4,433.301 liters
Volume of Dilution Air	=	(dilution air flow rate) x (time)
	=	(822.4 sLpm) x (257.9 min)
	=	212,096.96 liters
Dilution Ratio	=	(volume of dilution air + volume of combustion air)/volume of combustion air
	=	(212,096.96 liters + 4,433.301 liters) / 4,433.301 liters
	=	48.8
Mass Flow Rate of SNMOC in Diluted Sample	=	(mass SNMOC collected)/[(sample flow rate at canister) x (time)]
	=	$(1.862 \mu g)/[(0.0178 \text{ Lpm}) \times (257.9 \text{ min})]$
	=	0.4056097 µg/liter
Mass Flow Rate of SNMOC in Undiluted Sample	=	(mass flow rate SNMOC diluted) x dilution ratio
	=	(0.4056097 µg/liter) x 48.8*
	=	19.810695 µg/liter
Total Mass of SNMOC in Sampled Air	=	(mass flow rate of SNMOC in undiluted sample) x (volume of undiluted sample)
	=	19.810695 µg/liter x 4,433.301 liters
	=	87826.774 µg
Total SNMOC in Total Combustion Air	=	[(mass of SNMOC in sampled air)/(volume of sampled air)] x (total combustion air)
	=	[(87826.774 µg)/(4,433.301 liters)] x 23,833,795 liters
	=	472,245,958 µg
Mass Emission Rate of Speciated SNMOC	=	(mass SNMOC in total combustion air)/(kg fuel burned)
	=	472,245,958 µg /97,690 kg
	=	4,834.1369 µg/kg fuel
	=	4.834 mg/kg fuel

*Dilution factor is dimensionless.

Table H-4. Speciated Nonmethane Organic Compounds. Mass Emission Rates for Wood-Fired Boiler (SCC 10200902), Test #2 (August 9, 2000)

Mass Fuel Consumed	=	127,027 kg
Total Volume of Combustion Air	=	(combustion air flow rate) x (time)
	=	(3,263.6 scfm) x (28.31685 sLpm/scfm) x (359.65 min)
	=	33,237,009 liters
Volume of Combustion Air Sampled	=	(Venturi flow rate) x (time)
	=	(17.06 sLpm) x (359.65 min)
	=	6,135.629 liters
Volume of Dilution Air	=	(dilution air flow rate) x (time)
	=	(823.46 sLpm) x (359.65 min)
	=	296,157.39 liters
Dilution Ratio	=	(volume of dilution air + volume of combustion air)/volume of combustion air
	=	(296,157.39 liters + 6,135.629 liters) / 6,135.629 liters
	=	49.3
Mass Flow Rate of SNMOC in Diluted Sample	=	(mass SNMOC collected)/[(sample flow rate at canister) x (time)]
	=	(0.918 µg)/[(0.0153 Lpm) x (359.65 min)]
	=	0.0761819 µg/liter
Mass Flow Rate of SNMOC in Undiluted Sample	=	(mass flow rate SNMOC diluted) x dilution ratio
	=	(0.0761819 µg/liter) x 49.3*
	=	3.753 µg/liter
Total Mass of SNMOC in Sampled Air	=	(mass flow rate of SNMOC in undiluted sample) x (volume of undiluted sample)
	=	3.753 µg/liter x 6,135.629 liters
	=	23,029.26 µg
Total SNMOC in Total Combustion Air	=	[(mass of SNMOC in sampled air)/(volume of sampled air)] x (total combustion air)
	=	[(23,029.26 µg)/(6,135.629 liters)] x 33,237,009 liters
	=	124,750,631 µg
Mass Emission Rate of Speciated SNMOC	=	(mass SNMOC in total combustion air)/(kg fuel burned)
	=	124,750,631 µg /127,027 kg
	=	982.080 µg/kg fuel
	=	0.982 mg/kg fuel

*Dilution factor is dimensionless.

Table H-5. Calculation of Mass Emission Rate for Speciated + Unspeciated Nonmethane Organic Compounds for a Wood-Fired Boiler (SCC 10200902), Test #1

Mass Fuel Consumed	=	97,690 kg
Total Volume of Combustion Air	=	(combustion air flow rate) x (time)
	=	(3,263.6 scfm) x (28.31685 sLpm/scfm) x (257.90 min)
	=	23,833,795 liters
Volume of Combustion Air Sampled	=	(Venturi flow rate) x (time)
	=	(17.19 sLpm) x (257.90 min)
	=	4,433.3 liters
Volume of Dilution Air	=	(dilution air flow rate) x (time)
	=	(822.4 sLpm) x (257.90 min)
	=	212,097.0 liters
Dilution Ratio	=	(volume of dilution air + volume of combustion air)/volume of combustion air
	=	(212,097.0 liters + 4,433.3 liters)/4,433.3 liters
	=	48.8
Mass Flow Rate of SNMOC in Diluted Sample	=	(mass SNMOC collected)/[(sample flow rate at canister) x (time)]
	=	(2.889336 µg)/[(0.0178 Lpm) x (257.90 min)]
	=	0.6294 µg/liter
Mass Flow Rate of SNMOC in Undiluted Sample	=	(mass flow rate SNMOC diluted) x dilution ratio
	=	(0.6294 µg/liter) x 48.8*
	=	30.7410 µg/liter
Total Mass of SNMOC in Sampled Air	=	(mass flow rate of SNMOC in undiluted sample) x (volume of undiluted sample)
	=	30.7410 µg/liter x 4,433.3 liters
	=	136,284.15 µg
Total SNMOC in Total Combustion Air	=	[(mass of SNMOC in sampled air)/(volume of sampled air)] x (total combustion air)
	=	[(136,284.15 µg)/4,433.3 liters)] x (23,833,795 liters)
	=	732,674,863 µg
Mass Emission Rate of SNMOC (Speciated + Unspeciated)	=	(mass SNMOC in total combustion air)/(kg fuel burned)
	=	732,674,863 µg /97,690 kg
	=	7500.0125 µg/kg fuel
	=	7.500 mg/kg fuel

*Dilution factor is dimensionless.

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Table H-6. Calculation of Mass Emission Rate for Speciated + Unspeciated Nonmethane Organic Compounds for a Wood-Fired Boiler (SCC 10200902), Test #2

Mass Fuel Consumed	=	127,027 kg
Total Volume of Combustion Air	=	(combustion air flow rate) x (time)
	=	(3,263.6 scfm) x (28.31685 sLpm/scfm) x (359.65 min)
	=	33,237,009 liters
Volume of Combustion Air Sampled	=	(Venturi flow rate) x (time)
	=	(17.06 sLpm) x (359.65 min)
	=	6,135.6 liters
Volume of Dilution Air	=	(dilution air flow rate) x (time)
	=	(823.46 sLpm) x (359.65 min)
	=	296,157.4 liters
Dilution Ratio	=	(volume of dilution air + volume of combustion air)/volume of combustion air
	=	(296,157.4 liters + 6,135.6 liters)/6,135.6 liters
	=	49.3
Mass Flow Rate of SNMOC in Diluted Sample	=	(mass SNMOC collected)/[(sample flow rate at canister) x (time)]
	=	(0.917731 µg)/[(0.0153 Lpm) x (359.65 min)]
	=	0.14336 µg/liter
Mass Flow Rate of SNMOC in Undiluted Sample	=	(mass flow rate SNMOC diluted) x dilution ratio
	=	(0.14336 µg/liter) x 49.3*
	=	7.06292 µg/liter
Total Mass of SNMOC in Sampled Air	=	(mass flow rate of SNMOC in undiluted sample) x (volume of undiluted sample)
	=	7.06292 µg/liter x 6,135.6 liters
	=	43,335.46 µg
Total SNMOC in Total Combustion Air	=	[(mass of SNMOC in sampled air)/(volume of sampled air)] x (total combustion air)
	=	[(43,335.46 µg)/(6,135.6 liters)] x 33,237,009 liters
	=	234,750,372 µg
Mass Emission Rate of SNMOC (Speciated + Unspeciated)	=	(mass SNMOC in total combustion air)/(kg fuel burned)
	=	234,750,372 µg /127,027 kg
	=	1848.035 µg/kg fuel
	=	1.848 mg/kg fuel

*Dilution factor is dimensionless.

Appendix I

Data from the Scanning Mobility Particle Sizer

TSI Scanning Mobility Particle Sizer

FILENAME: 8-8TST.005
NOTEFILE:
RESOLUTION: 32 channels/decade
SAMPLE TIME: 12:58:31
SAMPLE DATE: Tue 8 Aug 2000
SAMPLE No: 1, SCANS/SAMPLE: 107
CHARGE CORRECTION: off

SCAN VOLTAGE: 10 V, 9748 V
SCAN RANGE: 9.31 nm to 421.70 nm
VIEW RANGE: 10.00 nm to 392.42 nm
tf: 3.7 s, td: 0.6 s
tup: 120.0 s, tdwn: 30.0 s
Qsh: 6.0 lpm, Qa: 0.6 lpm
IMPACTOR D50: 458 nm

Particle Size Statistics:	No Assumption(1)	Lognormal Assumption(2)
Number Count:		
median (nm)	106.616	106.616
mean (nm)	122.413	141.164
geometric mean (nm)	96.366	
mode (nm)	128.640	60.816
standard deviation	78.125	
geo. standard deviation	2.115	2.115
skewness	-0.080	
coeff. of variation (%)	63.821	
Total Concentration (#/cm3)	5.1057E+04	
Surface Area:		
median (nm)	210.401	327.667
mean (nm)	211.591	
geometric mean (nm)	194.017	433.846
mode (nm)	245.824	
standard deviation	79.670	
geo. standard deviation	1.565	
dia. of average surface (nm)		186.908
Total Concentration (nm2/cm3)	3.3826E+09	
Volume:		
median	242.954	574.432
mean	241.589	
geometric mean	228.085	760.574
mode	264.165	
standard deviation	74.778	
geo. standard deviation	1.434	
dia. of average volume (nm)		247.474
Total Concentration (nm3/cm3)	1.1929E+11	

1 The statistics in 'No Assumptions' column are calculated based on the number size distribution. The validity of the statistics depends on the completeness of the distribution as well as the appropriateness of the calculation. For example: standard deviation and geometric standard deviation cannot both be valid since they are appropriate only for normal and lognormal distributions, respectively.

2 The statistics in the 'Lognormal Assumption' are calculated based on the number median and geometric standard deviation of the sampled data. The remaining values are derived from the Hatch-Choate conversion equations for lognormal distributions.

TSI Scanning Mobility Particle Sizer

Conc. [d(N,S,V)/dlog(Dp) - Base data

Channel number	Midpoint diameter (nanometers)	CONCENTRATION		
		Number (# /cm3)	Surface (nm2 / cm3)	Volume (nm3 / cm3)
32	10.37	4.5569E+03	1.5384E+06	2.6579E+06
33	11.14	4.5236E+03	1.7635E+06	3.2742E+06
34	11.97	5.1825E+03	2.3331E+06	4.6549E+06
35	12.86	5.1946E+03	2.7006E+06	5.7900E+06
36	13.82	5.6878E+03	3.4146E+06	7.8671E+06
37	14.86	6.1452E+03	4.2602E+06	1.0548E+07
38	15.96	6.8709E+03	5.5006E+06	1.4635E+07
39	17.15	7.7160E+03	7.1333E+06	2.0395E+07
40	18.43	8.1688E+03	8.7208E+06	2.6794E+07
41	19.81	9.4522E+03	1.1653E+07	3.8473E+07
42	21.29	1.0769E+04	1.5331E+07	5.4394E+07
43	22.88	1.1672E+04	1.9188E+07	7.3158E+07
44	24.58	1.2838E+04	2.4371E+07	9.9852E+07
45	26.42	1.5840E+04	3.4726E+07	1.5289E+08
46	28.39	1.6109E+04	4.0782E+07	1.9295E+08
47	30.51	1.7367E+04	5.0773E+07	2.5814E+08
48	32.78	1.9013E+04	6.4189E+07	3.5070E+08
49	35.23	2.0555E+04	8.0133E+07	4.7048E+08
50	37.86	2.3000E+04	1.0354E+08	6.5328E+08
51	40.68	2.4900E+04	1.2945E+08	8.7766E+08
52	43.71	2.8154E+04	1.6902E+08	1.2314E+09
53	46.98	3.0985E+04	2.1481E+08	1.6818E+09
54	50.48	3.4716E+04	2.7793E+08	2.3383E+09
55	54.25	3.8191E+04	3.5307E+08	3.1922E+09
56	58.29	4.0189E+04	4.2905E+08	4.1686E+09
57	62.64	4.4154E+04	5.4434E+08	5.6832E+09
58	67.32	4.6956E+04	6.6849E+08	7.5001E+09
59	72.34	4.9890E+04	8.2019E+08	9.8886E+09
60	77.74	5.1283E+04	9.7358E+08	1.2614E+10
61	83.54	5.2677E+04	1.1548E+09	1.6078E+10
62	89.77	5.3890E+04	1.3643E+09	2.0412E+10
63	96.47	5.7513E+04	1.6814E+09	2.7033E+10
64	103.66	5.9258E+04	2.0005E+09	3.4564E+10
65	111.40	6.1053E+04	2.3801E+09	4.4190E+10
66	119.71	6.1970E+04	2.7898E+09	5.5661E+10
67	128.64	6.3754E+04	3.3144E+09	7.1061E+10
68	138.24	6.3446E+04	3.8089E+09	8.7756E+10
69	148.55	6.2819E+04	4.3557E+09	1.0784E+11
70	159.63	6.2378E+04	4.9938E+09	1.3286E+11
71	171.54	6.0367E+04	5.5808E+09	1.5956E+11

TSI Scanning Mobility Particle Sizer

FILENAME: 8-8TST.005
NOTEFILE:
RESOLUTION: 32 channels/decade
SAMPLE TIME: 12:58:31
SAMPLE DATE: Tue 8 Aug 2000
SAMPLE No: 1, SCANS/SAMPLE: 107
CHARGE CORRECTION: off

SCAN VOLTAGE: 10 V, 9748 V
SCAN RANGE: 9.31 nm to 421.70 nm
VIEW RANGE: 10.00 nm to 392.42 nm
tf: 3.7 s, td: 0.6 s
tup: 120.0 s, tdwn: 30.0 s
Qsh: 6.0 lpm, Qa: 0.6 lpm
IMPACTOR D50: 458 nm

Conc. [d(N,S,V)/dlog(Dp)] - Base data

Channel number	Midpoint diameter (nanometers)	CONCENTRATION		
		Number (# /cm3)	Surface (nm2 / cm3)	Volume (nm3 / cm3)
71	171.54	6.0367E+04	5.5808E+09	1.5956E+11
72	184.34	5.7673E+04	6.1570E+09	1.8917E+11
73	198.10	5.6045E+04	6.9094E+09	2.2812E+11
74	212.88	5.3459E+04	7.6106E+09	2.7002E+11
75	228.76	4.8207E+04	7.9251E+09	3.0216E+11
76	245.82	4.2193E+04	8.0101E+09	3.2818E+11
77	264.16	3.5734E+04	7.8339E+09	3.4491E+11
78	283.87	2.7981E+04	7.0837E+09	3.3515E+11
79	305.05	2.2023E+04	6.4385E+09	3.2735E+11
80	327.81	1.4979E+04	5.0570E+09	2.7629E+11
81	352.27	1.0229E+04	3.9878E+09	2.3413E+11
82	378.55	6.0963E+03	2.7445E+09	1.7316E+11
		5.1057E+04	3.3826E+09	1.1929E+11

TSI Scanning Mobility Particle Sizer

FILENAME: 8-9TST.002
NOTEFILE:
RESOLUTION: 32 channels/decade
SAMPLE TIME: 09:08:54
SAMPLE DATE: Wed 9 Aug 2000
SAMPLE No: 1, SCANS/SAMPLE: 145
CHARGE CORRECTION: off

SCAN VOLTAGE: 10 V,   9748 V
SCAN RANGE: 9.31 nm to 421.70 nm
VIEW RANGE: 10.00 nm to 392.42 nm
            tf: 3.7 s, td: 0.6 s
        tup: 120.0 s, tdwn: 30.0 s
        Qsh: 6.0 lpm, Qa: 0.6 lpm
            IMPACTOR D50: 458 nm

Particle Size Statistics:	No Assumption(1)	Lognormal Assumption(2)
Number Count:		
median (nm)	146.075	146.075
mean (nm)	157.554	173.687
geometric mean (nm)	136.453	
mode (nm)	159.634	103.322
standard deviation	77.155	
geo. standard deviation	1.801	1.801
skewness	-0.027	
coeff. of variation (%)	48.970	
Total Concentration (#/cm3)	4.2470E+03	
Surface Area:		
median (nm)	222.565	291.971
mean (nm)	227.765	
geometric mean (nm)	212.504	347.161
mode (nm)	264.165	
standard deviation	79.502	
geo. standard deviation	1.477	
dia. of average surface (nm)		206.518
Total Concentration (nm2/cm3)	4.1063E+08	
Volume:		
median	257.948	412.784
mean	255.516	
geometric mean	242.590	490.811
mode	305.053	
standard deviation	76.281	
geo. standard deviation	1.402	
dia. of average volume (nm)		245.555
Total Concentration (nm3/cm3)	1.5588E+10	

1 The statistics in 'No Assumptions' column are calculated based on the
number size distribution. The validity of the statistics depends on the
completeness of the distribution as well as the appropriateness of the
calculation. For example: standard deviation and geometric standard
deviation cannot both be valid since they are appropriate only for normal
and lognormal distributions, respectively.

2 The statistics in the 'Lognormal Assumption' are calculated based on the
number median and geometric standard deviation of the sampled data. The
remaining values are derived from the Hatch-Choate conversion equations
for lognormal distributions.

TSI Scanning Mobility Particle Sizer

Conc. [d(N,S,V)/dlog(Dp)] - Base data

Channel number	Midpoint diameter (nanometers)	CONCENTRATION Number (# /cm3)	Surface (nm2 / cm3)	Volume (nm3 / cm3)
3 !	10.37	6.1826E+01	2.0872E+04	3.6061E+04
3 l	11.14	1.4589E+02	5.6874E+04	1.0559E+05
3 l	11.97	8.8804E+01	3.9979E+04	7.9764E+04
3 ;	12.86	1.4405E+02	7.4887E+04	1.6056E+05
3 ;	13.82	1.8591E+02	1.1161E+05	2.5715E+05
3 l	14.86	2.9475E+02	2.0434E+05	5.0591E+05
3 l	15.96	2.2742E+02	1.8206E+05	4.8439E+05
3)	17.15	2.6769E+02	2.4748E+05	7.0756E+05
4)	18.43	2.1454E+02	2.2904E+05	7.0369E+05
4 .	19.81	2.1332E+02	2.6298E+05	8.6826E+05
4 !	21.29	3.3789E+02	4.8103E+05	1.7067E+06
4 l	22.88	3.0047E+02	4.9398E+05	1.8834E+06
4 l	24.58	3.8752E+02	7.3570E+05	3.0142E+06
4 ;	26.42	3.1271E+02	6.8556E+05	3.0184E+06
4 ;	28.39	3.1644E+02	8.0111E+05	3.7902E+06
4 l	30.51	3.7706E+02	1.1023E+06	5.6044E+06
4 l	32.78	4.2752E+02	1.4433E+06	7.8855E+06
4)	35.23	5.0509E+02	1.9691E+06	1.1561E+07
5)	37.86	7.3758E+02	3.3205E+06	2.0950E+07
5 .	40.68	6.8136E+02	3.5422E+06	2.4016E+07
5 !	43.71	7.5086E+02	4.5078E+06	3.2842E+07
5 l	46.98	7.4023E+02	5.1318E+06	4.0178E+07
5 l	50.48	9.4686E+02	7.5803E+06	6.3776E+07
5 ;	54.25	1.2043E+03	1.1133E+07	1.0066E+08
5 ;	58.29	1.2382E+03	1.3219E+07	1.2843E+08
5 l	62.64	1.4787E+03	1.8230E+07	1.9033E+08
5 l	67.32	1.7411E+03	2.4787E+07	2.7810E+08
5)	72.34	2.2113E+03	3.6354E+07	4.3830E+08
6)	77.74	2.6765E+03	5.0813E+07	6.5833E+08
6 .	83.54	3.4839E+03	7.6378E+07	1.0634E+09
6 l	89.77	3.8691E+03	9.7951E+07	1.4655E+09
6 l	96.47	4.9400E+03	1.4442E+08	2.3219E+09
6 l	103.66	5.9773E+03	2.0179E+08	3.4864E+09
6 ;	111.40	6.4918E+03	2.5309E+08	4.6988E+09
6 ;	119.71	6.7091E+03	3.0204E+08	6.0261E+09
6 l	128.64	7.2795E+03	3.7844E+08	8.1138E+09
6 l	138.24	7.8915E+03	4.7376E+08	1.0915E+10
6 l	148.55	7.8599E+03	5.4490E+08	1.3491E+10
7)	159.63	8.1725E+03	6.5427E+08	1.7407E+10
7 ;	171.54	7.4512E+03	6.8885E+08	1.9695E+10

TSI Scanning Mobility Particle Sizer

FILENAME: 8-9TST.002
NOTEFILE:
RESOLUTION: 32 channels/decade
SAMPLE TIME: 09:08:54
SAMPLE DATE: Wed 9 Aug 2000
SAMPLE No: 1, SCANS/SAMPLE: 145
CHARGE CORRECTION: off

SCAN VOLTAGE: 10 V, 9748 V
SCAN RANGE: 9.31 nm to 421.70 nm
VIEW RANGE: 10.00 nm to 392.42 nm
tf: 3.7 s, td: 0.6 s
tup: 120.0 s, tdwn: 30.0 s
Qsh: 6.0 lpm, Qa: 0.6 lpm
IMPACTOR D50: 458 nm

Conc. [d(N,S,V)/dlog(Dp)] - Base data

Channel number	Midpoint diameter (nanometers)	CONCENTRATION		
		Number (# /cm3)	Surface (nm2 / cm3)	Volume (nm3 / cm3)
71	171.5i	7.4512E+03	6.8885E+08	1.9695E+10
72	184.3i	7.0760E+03	7.5542E+08	2.3209E+10
73	198.1)	6.7181E+03	8.2823E+08	2.7345E+10
74	212.8i	6.1852E+03	8.8055E+08	3.1241E+10
75	228.7i	5.2374E+03	8.6102E+08	3.2828E+10
76	245.8i	4.7803E+03	9.0752E+08	3.7182E+10
77	264.1i	4.2269E+03	9.2666E+08	4.0799E+10
78	283.8i	3.6308E+03	9.1920E+08	4.3489E+10
79	305.0i	3.0688E+03	8.9716E+08	4.5614E+10
80	327.8.	2.3582E+03	7.9611E+08	4.3496E+10
81	352.2i	1.8652E+03	7.2715E+08	4.2692E+10
82	378.5i	1.4157E+03	6.3732E+08	4.0210E+10
Totals		4.2470E+03	4.1063E+08	1.5588E+10

16. ABSTRACT The report provides a profile for a wood-fired industrial boiler equipped with a multistage electrostatic precipitator control device. Along with the profile of emissions of fine particulate matter of aerodynamic diameter of 2.5 micrometers or less (PM-2.5), data are also provided for gas-phase emissions of several organic compounds. Data are provided in a format suitable for inclusion in the EPA source profile database SPECIATE. A source-receptor model is a tool often used by states in apportioning ambient PM-2.5 to the sources. Such a model requires a knowledge of the PM-2.5 chemical composition of PM-2.5 collected at the receptor (ambient monitoring) sites. PM-2.5 has been implicated in adverse health effects, and a National Ambient Air Quality Standard for PM-2.5 was promulgated in July 1997 by the EPA. A national network of ambient monitoring stations has been established to assist states in determining areas that do not meet the ambient standard for PM-2.5. For such areas, it is important to determine the major sources of PM-2.5 so the states can devise and institute a control strategy to attain the ambient concentrations set by the standard.

17.	KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Gases Particles Organic Compounds Wood Standards Combustion Boilers Chemical Composition Electrostatic Precipitators		Pollution Control Stationary Sources	13B 14G 07C 11L 21B 13A 07D 13I
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CONTROL OF MERCURY EMISSIONS
FROM COAL-FIRED ELECTRIC
UTILITY BOILERS:
INTERIM REPORT
INCLUDING ERRATA DATED 3-21-02

Prepared for

Office of Air Quality Planning and Standards

Prepared by

National Risk Management
Research Laboratory
Research Triangle Park, NC 27711

Foreword

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

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

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

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

EPA REVIEW NOTICE

Control of Mercury Emissions from Coal-Fired Electric Utility Boilers: Interim Report

James D. Kilgroe, Charles B. Sedman, Ravi K. Srivastava, Jeffrey V. Ryan, C. W. Lee, and Susan A. Thorneloe

Errata Pages
for
EPA-600/R-01-109

Control of Mercury Emissions from Coal-Fired Electric Utility Boilers: Interim Report
December 2001

Errata Pages

March 21, 2002

Abstract

In December 2000, the U.S. Environmental Protection Agency (USEPA) announced its intent to regulate mercury emissions from coal-fired electric utility steam generating plants. This report, produced by EPA's Office of Research and Development (ORD), National Risk Management Research Laboratory (NRMRL), provides additional information on mercury emissions control, following the release of " Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Plants - Final Report to Congress," in February 1998. The first three chapters describe EPA's December 2000 decision to regulate mercury under the National Emission Standards for Hazardous Air Pollutants (NESHAP) provisions of the Clean Air Act, coal use in electric power generation, and mercury behavior in coal combustion. Chapters 4-9 report: new information on current electric utility fuels, boilers, and emission control technologies; mercury emissions associated with these diverse technology combinations; results and implications of tests to evaluate the performance of mercury control technologies and strategies; retrofit control cost modeling; and mercury behavior in solid residues from coal combustion. The final chapter summarizes current research and identifies future efforts needed to ensure cost-effective control of mercury emissions. References are provided at the conclusion of each chapter.

Preface

This is an interim report, based on data available as of mid-2001, which in some cases are limited. As more data are collected and evaluated, some of the conclusions reached in this report may be modified.

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Acronyms

ADP	Acid Dew Point
AES	Atomic Emission Spectrometry
AHC	Advanced Hybrid Collector
ASTM	American Society for Testing and Materials
CAA	Clean Air Act
CCR	Coal Combustion Residues
CEM	Continuous Emission Monitors
CFBA	Circulating Fluidized-bed Adsorber
COHPAC	Compact Hybrid Particulate Collector
CS-ESP	Cold-side Electrostatic Precipitator
CuCl	Cuprous Chloride
CVAAS	Cold-vapor Atomic Absorption Spectrometry
CVAFS	Cold-vapor Atomic Fluorescence Spectrometry
DI	Dry Injection
DOE	United States Department of Energy
EPA	United States Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	Electrostatic Precipitator
ETV	Environmental Technology Verification
FBC	Fluidized-bed Combustion
FF	Fabric Filter
FGD	Flue Gas Desulfurization
HAP	Hazardous Air Pollutant
Hg	Mercury
Hg^0	Elemental Mercury
HgO	Mercuric Oxide
Hg^{2+}	Oxidized or Ionic Mercury
Hg_p	Particle-bound Mercury
Hg_T	Total Mercury
$HgCl_2$	Mercuric Chloride
$HgSO_4$	Mercuric Sulfate
HS-ESP	Hot-side Electrostatic Precipitator

Acronyms (continued)

IGCC	Integrated Gasification Combined Cycle
ICR	Information Collection Request
kWh	Kilowatt Hour
LNB	Low NO_x Burner
MC	Mechanical Collector
MESA	Mercury Speciation Adsorption
MWC	Municipal Waste Combustor
MWe	Megawatt Electric
MWFA	Mixed Waste Focus Area
NESCAUM	Northeast States for Coordinated Air Use Management
NETL	National Energy Technology Laboratory (DOE)
NO_x	Nitrogen Oxides
OAR	EPA's Office of Air and Radiation
OH Method	Ontario-Hydro Method
O&M	Operation and Maintenance
PAC	Powdered Activated Carbon
PFF	Polishing Fabric Filter
PM	Particulate Matter
PRB	Powder River Basin
PS	Particle Scrubber
PTFE	Polytetrafluoroethylene
QA/QC	Quality Assurance/Quality Control
R_fD	Reference Dose
SC	Spray Cooling
SCR	Selective Catalytic Reduction
SDA	Spray Dryer Adsorber
SEM	Scanning Electron Microscope
SNCR	Selective Noncatalytic Reduction

Acronyms (concluded)

TGM	Total Gaseous Mercury
UND/EERC	University of North Dakota/Energy and Environmental Research Center
UVDOAS	Ultraviolet Differential Optical Absorption Spectroscopy
Wet FGD	Flue Gas Desulfurization by Liquid Scrubbing

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Acknowledgements

Executive Summary

Overview

This report documents current knowledge on the emission and control of mercury (Hg) from coal-fired electric utility plants. The purpose of the report is to provide information on the status of government and industry efforts in developing improved technologies for the control of Hg emissions.

This is an interim report, which contains information available in the public domain prior to June 2001. Since then, the results of additional research have been published. This additional information can be found in DOE, EPA, and EPRI reports, in journal articles, and in the proceedings of conferences. Two recent conferences provided significant new information on the control of Hg emissions -- the A&WMA 2001 Annual Conference (Orlando, FL, June 2001), and the A&WMA Specialty Conference on Mercury (Chicago, IL, August 2001).

The first part of the report (Chapters 1 through 3) is directed to readers outside the research community who are interested in Hg emission and Hg control issues. Information is provided on:

- Legislative and regulatory background of EPA's December 2000 decision to regulate Hg emissions from coal-fired electric utility generating stations,

- Studies made in support of EPA's regulatory determination,

- Fuels, combustion technologies, and pollution control technologies used for coal-fired steam electric generating units, and

- Research results from an official Information Collection Request (ICR) on the fuels and technologies used by the utility industry in 1999 at coal-fired steam electric generating stations.

The second part of the report (Chapters 4 through 10) is directed to all readers. It focuses on the review and evaluation of information that has been gathered since the publication of: EPA's Mercury Study Report to Congress; EPA's Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units--Final Report to Congress; and the A&WMA

<u>Critical Review: Mercury Measurement and Its Control</u>. The second part of the report contains information on:

- Hg measurement methods,

- Forms of Hg (speciation) and the capture of Hg in flue gas from combustion of coal,

- Evaluation of the ICR flue gas data on Hg concentrations upstream and downstream of air pollution control devices (APCDs),

- Summary of retrofit control technologies that can be used to limit Hg emissions at coal-fired plants currently equipped with particulate matter (PM) control devices, and dry or wet flue gas desulfurization (FGD) scrubbing systems,

- Estimates of the costs of controlling Hg emissions by the use of powdered activated carbon (PAC),

- Overview of the current coal combustion residue (CCR) management practices and the identification of environmental issues requiring additional research, and

- Conclusions, overview of current research, and research recommendations.

Detailed supporting information is provided in Appendices.

Background

The 1990 Clean Air Act Amendments required EPA to study the health and environmental impacts of hazardous air pollutants (HAPs) emitted from electric utility boilers. The Agency was also required to conduct a study of the potential health and environmental impacts of Hg emitted from anthropogenic sources in the United States. The EPA subsequently published an 8-volume <u>Mercury Study Report to Congress</u> in December 1997 and a <u>Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units--Final Report to Congress</u> in February 1998. The Hg report to Congress identified coal-fired utility boilers as the largest single anthropogenic source of Hg emissions in the United States. The utility HAP report indicated that there was a plausible link between Hg emissions from coal-fired boilers and health risks posed by indirect exposure to methylmercury.

In December 2000, EPA announced its intent to regulate HAP emissions from coal- and oil-fired electrical generating stations. The decision to regulate HAP emissions from coal-fired units was based on:

- A National Academy of Science study on the health effects of methylmercury,

- The collection and analysis of coal- and flue-gas Hg data under an official Information Collection Request (ICR), and

- Studies concerning the status of Hg emission control technologies.

Three important milestones are incorporated in EPA's decision to regulate HAP emissions from coal-fired electric generating units:

- The proposal of regulations by December 2003,

- The promulgation of regulations by December 2004, and

- Compliance with the regulations by December 2007.

Electric Utility Coal Combustion and Air Pollution Control Technologies

The EPA ICR data collection effort was conducted in three phases. In Phase I, information was collected on the fuels, boiler types, and air pollution control devices (APCDs) used at all coal-fired utility boilers in the United States. In Phase II, coal data were collected and analyzed by the utility industry for 1,140 coal-fired and three integrated gasification, combined cycle (IGCC) electric power generating units. Each coal sample was analyzed for Hg content, chlorine (Cl) content, sulfur content, moisture content, ash content, and calorific value. In Phase III, flue gas Hg measurements were made using the modified Ontario-Hydro (OH) Method for total and speciated Hg. Additional coal samples were collected and analyzed in conjunction with the OH Method measurements.

The EPA ICR data indicated that, in 1999, coal-fired steam electric generating units in the U.S. burned 786 million tons of coal of which about 52 percent was bituminous and 37 percent was subbituminous. Other fuels included lignite, anthracite coal, reclaimed waste coal, mixtures of coal and petroleum coke (pet-coke), and mixtures of coal and tire-derived fuel (TDF). Pulverized coal-fired (PC) boilers represent approximately 86 percent of the total number and 90 percent of total utility boiler capacity. Based on capacity, other types of boilers include cyclone-fired boilers (7.6 percent), fluidized-bed combustors (1.3 percent), and stoker-fired boilers (1.0 percent).

The 1999 EPA ICR responses indicate that a variety of emission control technologies are employed to meet requirements for sulfur dioxide (SO_2), nitrogen oxides (NO_x), and particulate matter (PM). Most utilities control NO_x by combustion modification techniques and SO_2 by the use of compliance coal. For post-combustion controls, 77.4 percent of the units have PM control only, 18.6 percent have both PM and SO_2 controls, 2.5 percent have PM and NO_x controls, and 1.3 percent have three post-combustion control devices.

The different types of post-combustion control devices are listed below:

Particulate matter (PM) control technologies include electrostatic precipitators (ESPs), fabric filters (FFs) (also called "baghouses"), and particulate scrubbers (PS). ESPs and FFs may be classified as either cold-side (CS) devices [installed upstream of the air heater where flue gas temperatures range from 284 to 320 °F (140 to 160 °C)] or hot-side [installed downstream of the air heater and operate at temperatures ranging from 662 to 842 °F (350 to 450 °C)]. Based on current information, it appears that little Hg can be captured in HS-ESPs.

SO_2 post-combustion control technologies are systems that are classified as wet flue gas desulfurization (FGD) scrubbers, semi-dry scrubbers, or dry injection. Wet FGD scrubber controls remove SO_2 by dissolving it in a solution. A PM control device is always located upstream of a wet scrubber. PM devices that may be used with wet FGD scrubbers include a PS, CS-ESP, HS-ESP, or FF baghouse. Semi-dry scrubbers include spray dryer absorption (SDA). Dry injection involves injecting dry powdered lime or other suitable sorbent directly into the flue gas. A PM control device (ESP or FF) is always installed downstream of a semi-dry scrubber or dry injection point to remove the sorbent from the flue gas.

NO_x post-combustion control technologies include selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) processes. With both of these methods, a reducing agent such as ammonia or urea is injected into the duct to reduce NO_x to N_2. SCR operates at lower temperatures than SNCR and is more effective at reducing NO_x, but it is more expensive.

For PM control, ESPs are used on 84 percent of the existing electric utility coal-fired boiler units, and FF baghouses are used on 14 percent of the utility units. Post-combustion SO_2 controls are less common. Wet flue gas desulfurization (FGD) systems are used on 15.1 percent of the units; and, dry scrubbers, predominantly spray dryer absorbers (SDA), are used on 4.6 percent of units that were surveyed. While the application of post-combustion NO_x controls is becoming more prevalent, only 3.8 percent of units used either selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) systems in 1999.

Mercury Measurement Methods

When the coal is burned in an electric utility boiler, the resulting high combustion temperatures vaporize the Hg in the coal to form gaseous elemental mercury (Hg^0). Subsequent cooling of the combustion gases and interaction of the gaseous Hg^0 with other combustion products result in a portion of the Hg being converted to gaseous oxidized forms of mercury (Hg^{2+}) and particle-bound mercury (Hg_p). The term *speciation* is used to denote the relative

amounts of these three forms of Hg in the flue gas. The total Hg in flue gas (Hg_T) is the sum of Hg_p, Hg^{2+}, and Hg^0. It is the ability to measure these forms of Hg, either collectively or individually, which distinguishes the capabilities of available measurement methodologies.

The Hg in flue gas can be measured by either manual sampling methods or by the use of a continuous emission monitor (CEM). Manual methods are available for the measurement of Hg_T and the speciation of Hg, including Hg_p. CEMs are now available to measure gas-phase Hg_T.

Manual Test Methods

Manual sampling methods for measuring Hg_T from combustion processes are well established. EPA Methods 101A and 29 are routinely used to measure Hg_T in flue gas from incineration and coal combustion. While a validated reference method for the measurement of the speciated forms of Hg does not exist, the Ontario-Hydro (OH) method is the *de facto* method of choice.

Generally, sampling trains used to collect flue gas samples for Hg analysis consist of the same components: a nozzle and probe operated to extract a representative sample from a duct or stack; a filter to collect PM; and a series of impingers with liquid reagents to capture gas-phase Hg. Sampling trains used for speciation measurements sequentially capture Hg^{2+} and Hg^0 in different impingers. After sampling, the filter and sorption media are prepared and analyzed for Hg in a laboratory.

While several research methods exist for performing speciated Hg measurements, the OH Method is presently the method of choice for measuring Hg species in the flue gas from coal-fired utility plants. The OH method has been shown to provide valid Hg speciation measurements when samples are taken downstream of an efficient PM control device. However, the OH Method can give erroneous speciation measurements for locations upstream of PM control devices because of sampling artifacts.

Fly ash captured by the sampling train filter can absorb Hg^{2+} and Hg^0. Catalytic properties of the fly ash can also oxidize Hg^0, resulting in physical and chemical transformations within the sampling train. Transformations caused by the sampling process are called artifacts, and the resulting measurements do not accurately reflect critical properties of Hg at the locations where the samples were taken. Sampling methods have not yet been developed to overcome measurement artifacts associated with high flue gas concentrations of fly ash.

Continuous Emission Monitors (CEMs)

Continuous emission monitors (CEMs) are in some respects superior to manual measurement methods. CEMs provide a rapid real-time or near real-time response, which can be used to characterize temporal process variations that cannot be measured with manual measurement methodologies. Mercury CEMs are similar to most combustion process CEMs in that a flue gas sample must be extracted from the stack and then transferred to the analyzer for

detection. However, Hg monitoring is complicated by the fact that Hg exists in different forms and that quantitative transport of all forms is difficult.

The CEMs designed to measure total gas-phase Hg (Hg^{2+} and Hg^0) are now routinely used in Europe and Japan to measure Hg emissions from incinerators. The Hg concentrations in the stack gas from well-controlled emission sources contain negligible amounts of Hg_p, and the measurement of gas-phase Hg downstream of the emission control devices can be considered to be equivalent to the measurement of Hg_T.

The detectors in Hg CEMs typically measure Hg^0 by the use of cold vapor atomic absorption spectroscopy (CVAAS) or cold vapor atomic fluorescence spectroscopy (CVAFS). Hg_T concentrations are measured by converting (reducing) all of the Hg^{2+} in the sample to Hg^0 before it enters the detector. Various conversion techniques exist, including thermal, catalytic, and wet chemical methods. The wet chemical technique is currently used in commercial monitors that are capable of speciation measurement. The use of wet chemical reagents results in high operating costs, which are the primary limitation to the Hg CEM's use as a compliance tool.

Speciating Hg CEMs are highly valuable as research tools. Several commercially available Hg_T CEMs have been modified to indirectly measure Hg^{2+} by determining the difference between gas-phase Hg_T and Hg^0. Hg CEMs are susceptible to the same PM-related measurement artifacts associated with manual measurements, and users of Hg CEMs in high dust conditions must consider this problem.

Regardless of the sampling method, the key to reliable and accurate Hg sampling and continuous monitoring is maintaining sample integrity. Flue gases may contain particles that change the species of Hg within the sampling train or CEM system. While this does not change the total Hg measurement, it may bias the determination of Hg vapor species, which may be used to estimate the potential for Hg capture, as well as to assess the performance of control devices. Similarly, common flue gas constituents, such as SO_2, HCl and NO_x, may affect quantitative measurement performance.

Additional research is needed to investigate and overcome measurement obstacles so that speciating CEMs can serve as process monitors and as a research tool for evaluating the effectiveness of emission controls. Such research can also provide a better understanding of the factors that affect Hg speciation.

Speciation and Capture of Mercury

Mercury Speciation

The capture of Hg by flue gas cleaning devices is dependent on Hg speciation. Both Hg^0 and Hg^{2+} are in vapor-phase at flue gas cleaning temperatures. Hg^0 is insoluble in water and cannot be captured in wet scrubbers. The predominant Hg^{2+} compounds in coal flue gas are weakly to strongly soluble, and the more-soluble species can be generally captured in wet FGD

scrubbers. Both Hg^0 and Hg^{2+} are adsorbed onto porous solids such as fly ash, powdered activated carbons (PAC), or calcium-based acid gas sorbents for subsequent collection in a PM control device. Hg^{2+} is generally easier to capture by adsorption than Hg^0. Hg_p is attached to solids that can be readily captured in ESPs and FFs.

Flue gas cleaning technologies that are applied on combustion sources employ three basic methods to capture Hg:

- Capture of Hg_p in PM control devices;
- Adsorption of Hg^0 and Hg^{2+} onto entrained sorbents for subsequent capture in PM control devices; and
- Solvation of Hg^{2+} in wet scrubbers.

The factors that affect the speciation and capture of Hg in coal-fired combustion systems include the type and properties of coal, the combustion conditions, the types of flue gas cleaning technologies employed, and the temperatures at which the flue gas cleaning systems operate.

Oxidation reactions that affect the speciation of Hg include homogeneous, gas-phase reactions and heterogeneous gas-solid reactions associated with entrained particles and surface deposits. Suspected flue gas oxidants involved in Hg^0 oxidation include oxygen (O_2), ozone (O_3), hydrochloric acid (HCl), chlorine (Cl), nitrogen dioxide (NO_2) and sulfur trioxide (SO_3). Many of these oxidants are also acid species, which may be significantly impaired by the presence of alkaline species in fly ash, such as sodium, calcium and potassium. Heterogeneous oxidation reactions may be catalyzed by metals such as iron, copper, nickel, vanadium, and cobalt. Conversion of Hg^0 to Hg^{2+} may be followed by adsorption to form Hg_p.

The determination of which mechanisms, oxidants, and catalysts are dominant is crucial in developing and implementing Hg control strategies. For example, the impaired oxidation of Hg in subbituminous coals and lignites is probably related to lower concentrations of HCl in flue gas and high alkalinity of the fly ash. PM collectors and scrubbers reflect this in the low removals of Hg in the ICR database.

Fundamentals of Sorption

Sorbents used for the capture of Hg can be classified as Hg sorbents or multipollutant sorbents. Sorbents evaluated for Hg capture have been manufactured from a number of different materials such as lignite, bituminous coal, zeolites, waste biomass, and waste tires. The manufacturing process typically involves some type of thermal treatment. Additives are often used to produce impregnated sorbents.

For coal-fired electric utility boiler applications, the use of sorbents to capture gas-phase Hg (or gas-phase Hg and acid gases) is limited to the use of finely ground powdered sorbents. These sorbents can be injected upstream of PM control devices to collect the sorbent and adsorbed Hg. The development of improved sorbents is needed because of poor sorbent

utilization that results from low flue gas concentrations of Hg and short sorbent exposure times in units equipped with CS-ESPs. The performance of a sorbent is related to its physical and chemical characteristics. The best performing sorbents must be carefully matched to performance requirements as defined by the application for which it is to be used. For example, properties and performance requirements of sorbents used for capture of SO_2 and Hg^0 are quite different. In a similar fashion, the performance criteria for sorbents used with flue gas from bituminous coal will probably be different from the sorbents used with sub-bituminous coals.

Sorbents are porous materials. The most common physical properties related to sorbent performance are surface area, pore size distribution, and particle size distribution. The capacity for Hg capture generally increases with increasing surface area and pore volume. The ability of Hg and other sorbates to penetrate into the interior of a particle is related to pore size distribution. The pores of the sorbent must be large enough to provide free access to internal surface area by Hg^0 and Hg^{2+} while avoiding excessive blockage by previously adsorbed reactants. As particle size decreases, access to the internal surface area of the particle increases, along with potential adsorption rates. Powdered activated carbons used for Hg control typically have diameters of 44 μm or smaller.

Mercury can be either physically or chemically adsorbed. Physical adsorption (physisorption) typically results from van der Waals and Coulombic (electrostatic) interactions between the sorbent and the sorbate. The resulting bonds are weak (typically < 10-15 kcal/mole) and are easily reversed.

Chemical adsorption (chemisorption) involves the establishment of a chemical bond (as the result of a chemical reaction, electron transfer). Chemisorption results in stronger bonds than physisorption and is not necessarily reversible. Chemical adsorption is also dependent on the presence of chemically active sites where the sorbate is chemically bound. Some of the chemical constituents of activated carbons influencing Hg capture include: sulfur content, iodine content, and chlorine content. Impregnation of carbons with sulfur, iodine, or chlorine can increase the reactivity and capacity of sorbents. Hg^0 is likely oxidized and sorbed in a rapid two step reaction, either chemically by reaction with strong ionic groups such as Cl^-, I^-, or $S^=$ or physically through interaction with functional groups in sorbent pores.

The $HgCl_2$ is readily adsorbed onto both carbon and calcium based sorbents, probably by acid-base reactions. Section 5.5 details the fundamental research to develop carbon and calcium sorbents for Hg vapor capture.

Evaluation of Sorbents

Sorbents may be evaluated by bench-, pilot-scale, or full-scale experiments. The initial screening of sorbents has typically been conducted using bench-scale, packed-bed experimental reactors. These reactors are used to evaluate the adsorption capacity of sorbents exposed to Hg in a synthetic flue gas made from compressed bottled gases. The reactor is held at a predetermined temperature, and either Hg^0 or $HgCl_2$ is fed into the synthetic flue gas upstream of

the reactor. An on-line Hg analyzer is used to continuously monitor the Hg content of the inlet flue gas and of that after exposure to the sorbent fixed bed. These reactors are used to determine the effects of temperature and flue gas composition on the performance of sorbents. These reactors provide results that are primarily applicable to the capture of Hg in FF baghouses.

Flow reactors that expose sorbents to flue gas during short residence experiments can be used to simulate conditions associated with ESPs. These reactors can be used to explore the rates of Hg adsorption and determine the effects of temperature and flue gas composition. The most effective screening tests are conducted with reactors that are installed on a slip stream from a pilot- or full-scale coal combustion system. Large pilot- or full-scale tests must be used to assess the effects of mass transfer limitations (i.e., mixing and diffusion of flue gas constituents) and long-term equipment operability.

Wet FGD Scrubbers

Oxidized mercury compounds such as $HgCl_2$ are soluble in water and alkaline scrubbing solutions. Thus, the oxidized fraction of Hg vapors in flue gas is effectively captured when a power plant is operated with wet or semi-dry scrubbers for removing SO_2. The elemental fraction, on the other hand, is insoluble and is not removed to any significant degree. The challenge to Hg removal in wet FGD scrubbers, then, is to find some way to oxidize the elemental Hg vapor before it reaches the scrubber or to modify the liquid phase of the scrubber to cause oxidation to occur.

Evaluation of EPA ICR Mercury Emissions Data

The methods used to evaluate the ICR data were based on two interrelated objectives. The first method was to estimate the speciated amount and the geographical distribution of national Hg emissions from coal-fired power plants in 1999. The second method was to characterize the effects of coal properties, combustion conditions, and flue gas cleaning methods on the speciation and capture of Hg.

Mercury Capture by Existing Air Pollution Control Devices

The air pollution control technologies now used on pulverized-coal-fired utility boilers exhibit average levels of Hg control that range from 0 to 98 percent, as shown in Table ES-1. The best levels of control are generally obtained by emission control systems that use FFs. The amount of Hg captured by a given control technology is better for bituminous coal than for either subbituminous coal or lignite.

The lower levels of Hg capture in plants firing subbituminous coal and lignite are attributed to low fly ash carbon content and the higher relative amounts of Hg^0 in the flue gas from combustion of these fuels. The average capture of Hg based on OH Method inlet measurements in PC fired plants equipped with a cold-side ESP is 35 percent for bituminous coal, 3 percent for sub-bituminous coal and near zero for lignite.

Table ES-1. Mean mercury emission reduction for pulverized-coal-fired boilers.

Post-combustion Emission Controls Used for PC Boiler		Average Mercury Emission Reduction (%) [a]		
		Bituminous-coal-fired	Subbituminous-coal-fired	Lignite-fired
PM Control Only	CS-ESP	36 %	3 %	-4 %
	HS-ESP	9 %	6 %	not tested
	FF	90 %	72 %	not tested
	PS	not tested	9 %	not tested
PM Control and Spray Dryer Adsorber	SDA + ESP	not tested	35 %	not tested
	SDA + FF	98 %	24 %	0 %
	SDA + FF + SCR	98 %	not tested	not tested
PM Control and Wet FGD System	PS + FGD	12 %	-8 %	33 %
	CS-ESP + FGD	75 %	29 %	44 %
	HS-ESP + FGD	49 %	29 %	not tested
	FF + FGD	98 %	not tested	not tested

a) Mean reduction from test 3-run averages for each PC boiler unit in Phase III EPA ICR data base.

Plants that employ only post-combustion PM controls display average Hg emission reductions ranging from 0 to 89 percent. The highest levels of control were observed for units with FFs. Decreasing levels of control were shown for units with ESPs, PS, and mechanical collectors.

Units equipped with lime spray dryer absorber scrubbers (SDA/ESP or SDA/FF systems) exhibited average Hg captures ranging from 98 percent for units burning bituminous coals to 3 percent for units burning subbituminous coal. The predominance of Hg^0 in stack gas units that are fired with subbituminous coal and lignite results from low levels of Hg^0 oxidization.

The capture of Hg in units equipped with wet FGD scrubbers is dependent on the relative amount of Hg^{2+} in the inlet flue gas and on the PM control technology used. Average Hg captures in wet FGD scrubbers ranged from 23 percent for one PC-fired HS-ESP + FGD unit burning subbituminous coal to 97 percent in a PC-fired FF + FGD unit burning bituminous coal. The high Hg capture in the FF + FGD unit is attributed to increased oxidization and capture of Hg in the FF.

Mercury captures in PC-fired units equipped with spray dry scrubbers and wet limestone scrubbers appear to provide similar levels of control on a percentage reduction basis. However, this observation is based on a small number of short-term tests at a limited number of facilities.

Additional testing will be required to characterize the effects of fuel, combustion conditions, and APCD conditions on the speciation and capture of Hg.

National Emission Estimates

The data used for estimating the national Hg emissions were: (1) the mean Hg content of coal burned in any given unit during 1999, (2) the amount of coal burned in that unit during 1999, and (3) best match coal-boiler-control device emission factor for the unit. The results of these estimates indicated that:

- Coal and related fuels burned in coal-fired utility boilers in 1999 contained 75 tons of Hg, and

- Forty-eight tons of Hg was emitted to the atmosphere in 1999 from coal-fired utility power plants.

Multipollutant Controls

The EPA ICR data indicate that technologies currently in place for control of criteria pollutants achieve reductions in Hg emissions that range from 0 to > 90 percent. Current levels of Hg control can be increased by application of retrofit technologies or methods designed to increase capture of more than one pollutant. This multipollutant approach can utilize the synergisms that accrue through the simultaneous application of technologies for NO_x and Hg control, SO_2 and Hg control, or SO_2, NO_x, and Hg control.

Bench- and pilot-scale tests have shown that Hg capture in PM control devices generally increases as the carbon content of fly ash increases. Increased use of combustion modification techniques that increase ash carbon content will generally increase the amount and capture of Hg_p.

The EPA ICR data indicate that SCR systems may enhance the oxidation and capture of Hg. Recent pilot- and full-scale tests on bituminous coal-fired units equipped with SNCR + CS-ESP and SCR + SDA/FF systems have confirmed these results. However, improvement in Hg capture appears to be highly dependent on the type of coal burned and the design and operating conditions of SCR systems. The potential in increased Hg capture associated with the NO_x control system cannot now be quantified. It is believed, however, that the use of combustion modification techniques and post combustion NO_x control technologies on NO_x state implementation plan (SIP) units will also increase the capture of Hg in these units.

The retrofit of coal-fired electric utility boiler units to control emission of SO_2 and fine PM is also expected to provide co-benefits in the control of Hg. This is apparent from the increased control of Hg on units equipped with FFs, dry FGD scrubbers, and wet FGD scrubbers. Mercury or multipollutant sorbents will add minimal capital costs to units that are retrofitted with FFs or SDA/FF for control of other pollutants. The use of multipollutant sorbents would be more

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costly, but the incremental costs of Hg control would be modest. Technologies designed for use on existing wet FGD units could also be used for new scrubbers that are intended to control SO_2 and the precursors to secondary fine PM.

Generally, the control of Hg emissions via multipollutant control technologies can provide a cost-effective method for collectively controlling the various pollutants of concern.

Potential Retrofit Mercury Control Technologies

A practical approach to controlling Hg emissions at existing utility plants is to minimize capital costs by adapting or retrofitting the existing equipment to capture Hg. Potential retrofit options for control of Hg were investigated for units that currently use any of the following post combustion emission control methods: (1) ESPs or FFs for control of PM, (2) dry FGD scrubbers for control of PM and SO_2, and (3) wet FGD scrubbers for the control of PM and SO_2.

ESP and FF Systems

Least costly retrofit options for the control of Hg emissions from units with ESP or FF are believed to include:

- Injection of a sorbent upstream of the ESP or FF. Cooling of the stack gas or modifications to the ducting may be needed to keep sorbent requirements at acceptable levels.

- Injection of a sorbent between the ESP and a pulsejet FF retrofitted downstream of the ESP. This approach will increase capital costs but reduce sorbent costs.

- Installation of a semi-dry circulating fluidized-bed absorber (CFA) upstream of an existing ESP used in conjunction with sorbent injection. The CFA recirculates both fly ash and sorbent to create an entrained bed with a large number of reaction sites. This leads to higher sorbent utilization and enhanced fly ash capture of Hg and other pollutants.

Units equipped with a FF require less sorbent than units equipped with an ESP. ESP systems depend on in-flight adsorption of Hg by entrained fly ash or sorbent particles. FFs obtain the same in-flight Hg adsorption as ESPs and additional adsorption as the flue gas passes through the FF cake.

In general, the successful application of cost-effective sorbent injection technologies for ESP and FF units will depend on: (1) the development of lower cost and/or higher performing sorbents, and (2) appropriate modifications to the operating conditions of equipment being currently used to control emission of PM, NO_x, and SO_2.

Semi-Dry FGD Systems

SDA systems that use calcium-based sorbents are the most common dry FGD systems used in the electric utility industry. An aqueous slurry containing the sorbent is sprayed into an absorber vessel where the flue gas reacts with the drying slurry droplets. The resulting, particle-laden, dry flue gas then flows to an ESP or a FF where fly ash and SO_2 reaction products are collected.

CFAs are "vertical duct absorbers" that allow simultaneous gas cooling, sorbent injection and recycle, and gas absorption by flash drying of wet lime reagents. It is believed that CFAs can potentially control Hg emissions at costs lower than those associated with use of spray dryers.

Dry FGD systems are already equipped to control emissions of SO_2 and PM. The modification of these units by the use of appropriate sorbents for the capture of Hg and other air toxics is considered to be the easiest retrofit problem to solve.

Wet FGD Systems

Wet FGD systems are typically installed downstream of an ESP or FF. Wet limestone FGD scrubbers are the most commonly used scrubbers on coal-fired utility boilers. These FGD units are expected to capture more than 90 percent of the Hg^{2+} in the flue gas entering the scrubber. Consequently, existing wet FGD scrubbers may lower Hg emissions between 20 and 80 percent, depending on the speciation of Hg in the inlet flue gas.

Improvements in wet scrubber performance in capturing Hg depend primarily on the oxidation of Hg^0 to Hg^{2+}. This may be accomplished by (1) the injection of appropriate oxidizing agents or (2) the installation of fixed oxidizing catalysts upstream of the scrubber to promote oxidization of Hg^0 to soluble species.

An alternative strategy for controlling Hg emissions from wet FGD scrubbing systems is to inject sorbents upstream of the PM control device. In wet FGD systems equipped with ESPs, performance gains are limited by the in-flight oxidization of Hg^0 and the in-flight capture of Hg^{2+} and Hg^0. In systems equipped with FFs, increased oxidization and capture of Hg can be achieved as the flue gas flows through the FF. Increased oxidization of Hg^0 in the FF will result in increased Hg removal in the downstream scrubber.

Multipollutant Control Methods

From a long-term perspective, the most cost-effective Hg controls will be those implemented with a multipollutant emission control scheme, wherein Hg sorbents also remove other pollutants, and catalysts and absorbers are employed to remove bulk contaminants such as NO and SO_2. Mercury is also removed as a consequence of using particular bulk gas sorbents, catalysts, particle collectors, and absorbers. Therefore, while sorbents injected upstream of PM collectors may be readily employed for Hg control, the best long-term schemes will result from

modifying or adding control systems for other pollutants that also control Hg emissions. Chapter 9 discusses several applications under development.

Costs of Retrofit Mercury Control Technologies

Preliminary annualized costs of Hg controls using powdered activated carbon (PAC) injection have been estimated based on recent pilot-scale evaluations with commercially available adsorbents (see Table ES-2). These control costs range from 0.305 to 3.783 mills/kWh, with the highest costs associated with plants having hot-side electrostatic precipitators (HS-ESPs). For plants representing 89 percent of current capacity and using controls other than HS-ESPs, the costs range from 0.305 to 1.915 mills/kWh. Assuming a 40 percent reduction in sorbent costs by use of a composite lime-PAC sorbent for Hg removal, cost projections range from 0.18 to 2.27 mills/kWh with higher costs again being associated with plants using HS-ESPs.

Table ES-2. Estimates of current and projected annualized operating costs for retrofit mercury emission control technologies.

Coal Type (sulfur content)	Existing APCD [a]	Retrofit Mercury Control [b]	Current Cost (mills/kWh)	Projected Cost (mills/kWh)
Bituminous (3% S)	CS-ESP+FGD	PAC	0.727 – 1.197	0.436 – 0.718
	FF+FGD	PAC	0.305 – 0.502	0.183 – 0.301
	HS-ESP+FGD	PAC+PFF	1.501 – NA[c]	0.901 – NA[c]
Bituminous (0.6% S)	CS-ESP	SC+PAC	1.017 – 1.793	0.610 – 1.076
	FF	SC+PAC	0.427 – 0.753	0.256 – 0.452
	HESP	SC+ PAC+PFF	1.817 – 3.783	1.090 – 2.270
Subbituminous (0.5% S)	CS-ESP	SC+PAC	1.150 – 1.915	0.69 – 1.149
	FF	SC+PAC	0.423 – 1.120	0.254 – 0.672
	HESP	SC+PAC+PFF	1.419 – 2.723	0.851 – 1.634

a) CS-ESP = cold-side electrostatic precipitator; HS-ESP = hot-side electrostatic precipitator; FF= fabric filter; FGD = flue gas desulfurization

b) PAC=powdered activated carbon; SC=spray cooling; PFF=polishing fabric filter

c) NA = not available

In comparison, the estimated annual costs of Hg controls, as a function of plant size, lie mostly between the costs for low-NO_x burners (LNBs) and selective catalytic reduction (SCR) systems. The costs of Hg control will dramatically diminish if retrofit hardware and sorbents are employed for control of other pollutants such as NO_x, SO_2, or fine PM.

The performance and cost estimates of PAC injection-based Hg control technologies presented in this document are based on relatively few data points from pilot-scale tests and are considered to be preliminary. However, based on pilot-scale tests and the results of ICR data

evaluations, better sorbents and technologies now being developed will reduce the costs of Hg controls beyond current estimates.

Within the next 2 to 3 years, the evaluation of retrofit technologies at plants where co-control is being practiced will lead to a more thorough characterization of the performance and costs of Hg control. Future cost studies will focus on the development of performance and cost information needed to refine cost estimates for sorbent injection based controls, will develop cost estimates for wet scrubbing systems that employ methods for oxidizing Hg^0, and will determine the costs of various multipollutant control options.

The issue of Hg in residues will also be examined to address concerns related to the release of captured Hg species into the environment. These evaluations will be conducted in conjunction with the development and evaluation of air pollution emission control technologies.

Coal Combustion Residues and Mercury Control

Operation of power plants results in solid discharges including fly ash, bottom ash, boiler slag, and FGD residues. These residues already contain Hg, presumably bound Hg that is relatively insoluble and non-leachable. In 1998, approximately 108 million tons of coal combustion residues (CCRs) were generated. Of this amount, about 77 million tons were landfilled and about 31 million tons were utilized for beneficial uses.

Increased control of Hg emissions from coal-fired power plants may change the amount and composition of CCRs. Such changes may increase the potential for release of Hg to the environment from either landfilling or uses of CCRs. Mercury volatilization from CCRs in landfills and/or surface impoundments is expected to be low due to the low temperatures involved and the existence of relatively small surface area per unit volume of residue. For Hg control retrofits involving dry or wet FGD scrubbers, the residues are typically alkaline and the acid leaching potential of Hg from these residues is expected to be minimal.

There are several commercial uses of CCR where available data on which to characterize the Hg emission potential are lacking. The following CCR uses are given a priority for developing additional data in order to characterize the ultimate fate of Hg:

- The use of fly ash in cement production,
- The volatilization and leaching of residues used for structural fills,
- Leaching of residues exposed to the acidic conditions during mining applications,
- Volatilization of Hg during the production of wallboard from gypsum in wet scrubber residues,
- Mercury volatilization during the production and application of asphalt with fly ash fillers, and
- Leaching or plant uptake of Hg from fly ash, bottom ash, and FGD sludge that are used as soil amendments.

Current and Planned Research

DOE, EPA, EPRI, the utility industry, and the control technology industry are funding research on the control of Hg emissions from coal-fired boilers. A major portion of this research is being funded under cooperative agreements with DOE. These agreements include cost sharing by EPRI and other industrial partners. Research on these projects is being jointly coordinated under DOE's, EPA's, and EPRI's Hg control technology programs. These research efforts will be used to:

- Develop hazardous air pollution Maximum Achievable Control Technology (MACT) requirements for electric utility generating units,

- Optimize control of Hg emissions from units that must comply with more stringent NO_x emission requirements under the NO_x SIP, and

- Develop technologies that can be used to control emissions under multipollutant control legislation options that are currently being considered.

Current research efforts include three full-scale test projects, six pilot-scale test projects on coal-fired units, the evaluation of Hg CEMs, supporting research on the speciation and capture of Hg, and research on CCRs and CCBs. This research includes:

- One full-scale ESP sorbent injection project with tests at four sites,

- One full-scale wet FGD scrubber project at two sites,

- One full-scale project on the effects of SNRC, SCR, and SO_3 conditioning systems at five sites,

- On-going research on the development and use of Hg CEMs,

- On-going speciation, capture, and sorbent development research, and

- Small Business Administration projects on development of sorbents, and measurement methods.

Six new pilot-scale DOE projects have been announced in FY2001. These are:
- Advance particulate collector with sorbent injection (North Dakota-EERC)
- Evaluation of Hg^0 oxidization catalysts (URS Radian Group)
- Spray cooling and multipollutant sorbents (CONSOL)
- Evaluation of multipollutant sorbents and CFBA (SRI)
- Electrical discharge multi-pollution control system (Power Span)
- Evaluation of advanced sorbents (Apogee Scientific)

Conclusions and Recommendations

Additional efforts are planned to characterize the behavior of Hg in coal combustion systems. Further research is needed on the speciation and capture of Hg and on the stability of Hg in CCRs and residue by-products. Studies on the control capabilities and costs of potential Hg retrofit technologies currently under pilot-scale development are being continued and appropriate control technologies are to be evaluated on full-scale units. Additionally, an evaluation of the co-control of Hg with available PM, SO_2, and NO_x controls is needed.

Mercury measurement and monitoring capabilities must be consistent with the regulatory approaches being considered; e.g., speciated vs. total Hg emissions. Field activities need to be coordinated to (1) improve the emissions data base, (2) develop the technologies most appropriate for Agency goals (e.g., Hg-specific vs. multipollutant), and (3) refine cost data and cost-performance models based on actual field experience.

Finally, EPA must continue to work closely with DOE, EPRI and the utility industry to develop Hg and multipollutant control technologies. Collaboration will help ensure that all of the scientific knowledge, engineering skills, and financial resources needed to develop control technologies and establish the most cost-effective regulatory requirements are available.

Current and future research should focus on:

- Control of emissions for units with ESPs,

- Control of Hg emissions from subbituminous coals and lignite,

- Evaluation of CFA systems,

- Demonstration of Hg control for units with SDA/ESP and SDA/FF systems,

- Development of Hg^0 oxidizing methods for wet FGD systems,

- Evaluation additives for the oxidization of Hg^0 and the sequestration of Hg^{2+} in wet scrubbers,

- Enhancement of fly ash capture by combustion modification techniques,

- Optimization of NO_x controls for Hg control,

- Control of Hg and other air toxic emissions from units equipped with SCR and wet FGD scrubbers,

- Use and evaluation of Hg CEMs,

- Tests with CEMs to study the variability of Hg emissions,

- Effects of coal blending on Hg capture, and

- Effects of cyclone-, stoker-, and fluidized-bed combustion on Hg control.

Chapter 1
Report Background

1.1 Introduction

Mercury (Hg) is a metallic element that can be released into the atmosphere from both anthropogenic (i.e., made by humans) and natural sources. Ambient Hg concentrations in the air are typically very low. Human exposure by direct inhalation of Hg in the air is not the predominant public health concern for this metal. However, the Hg in ambient air eventually can be re-deposited on land surfaces or directly into rivers, lakes, and oceans. Mercury that enters bodies of water by direct deposition from the air or runoff from land surfaces ultimately is transformed by biological processes into a highly toxic form of Hg (methylmercury [MeHg]) that concentrates in fish and other organisms living in these waters. A study by the National Academy of Sciences (NAS) concluded that human exposure to MeHg from eating contaminated fish and seafood is associated with adverse health effects related to neurological and developmental damage varying in severity depending on the Hg concentrations in the ingested food.[1] An extreme example of these health effects cited by this study is the high-dosage exposure from the consumption of MeHg-contaminated fish by the residents living near Minamata Bay in Japan in the 1950s that resulted in fatalities and severe neurological damage.[2]

The largest anthropogenic source of Hg emissions in the United States is the Hg released from burning coal to produce steam for generating electricity. Mercury naturally occurs in trace amounts in all coal deposits. When coal is burned in a steam boiler or a furnace, most of the Hg bound in the coal is released during the combustion process as gaseous elemental mercury (Hg^0). Subsequent cooling of the combustion gases and interaction of the gaseous Hg^0 with other combustion products result in a portion of the Hg being converted to gaseous oxidized forms of mercury (Hg^{2+}) and particle-bound mercury (Hg_p).

Coal-fired electric utility power plants currently do not use air pollution controls specifically designed to reduce Hg emissions to the atmosphere. However, certain control technologies now used at coal-fired electric utility power plants to reduce other air pollutant emissions (particulate matter [PM], sulfur dioxide [SO_2], nitrogen oxides [NO_x]) also reduce Hg emissions with varying levels of effectiveness. Methods for enhancing Hg removal by these existing controls are being studied. New control technologies to specifically control Hg emissions from coal combustion are being developed. Multipollutant control technologies that will achieve both high Hg removal and effective control of PM, SO_2, and NO_x are being investigated.

The Clean Air Act (CAA) directs the U.S. Environmental Protection Agency (EPA) to regulate emissions of air toxics from stationary sources by establishing national air emission standards for hazardous air pollutants (NESHAP). Mercury is one of the compounds listed under CAA Section 112 as a hazardous air pollutant (HAP). The EPA Administrator has found that it is appropriate and necessary to establish a NESHAP regulating HAP emissions, including Hg, from coal-fired electric utility power plants.

1.2 Report Purpose

The EPA Office of Research and Development (ORD) National Risk Management Research Laboratory (NRMRL) has prepared this Hg emission control technology report. The overall purpose of the report is to review and evaluate recent scientific data and new knowledge about control technologies that potentially can be used to reduce Hg emissions from coal-fired electric utility power plants. The first part of the report is directed to readers outside the research community involved in Hg emission control issues by providing background information regarding EPA's NESHAP decision, the use of coal for electrical power generation, and Hg behavior in coal combustion gases. The second part of the report is directed to all readers and focuses on a review and evaluation of new information that has been gathered by the EPA since the Agency's reports to Congress related to the control of Hg emissions from electric utility power plants. Also included in this report are summaries of the results to date from companion NRMRL studies investigating the costs of retrofitting potential Hg control technologies to existing coal-fired electric utility power plants in the United States and Hg behavior in the ash and other solid residues from coal combustion.

The remainder of Chapter 1 provides a summary of the statutory authority and past major studies completed by the EPA that led to the Agency's regulatory finding on the HAP emissions from electric utility power plants. Background on major research programs investigating Hg emissions from coal combustion is presented. This chapter concludes with a description of topics presented in Chapters 2 through 10 of this report.

1.3 NESHAP Statutory Background

Title III of the CAA regulates stationary sources that emit HAPs. Section 112 in Title III was comprehensively amended in 1990. Under the amended CAA Section 112(b), Congress listed specific chemicals, compounds, and groups of chemicals as HAPs. Mercury is one of the chemicals included on this HAP list. The EPA is directed by Section 112 to regulate the HAP emissions from stationary sources by establishing "national emission standards for hazardous air pollutants" or "NESHAP." The EPA develops and promulgates individual NESHAPs for specific categories of stationary sources. The NESHAP for a given source category is codified under its own subpart in the Code of Federal Regulations under part 63 to title 40.

Section 112 of the CAA established specific directives as to how the EPA must develop NESHAPs. The statute requires that each NESHAP must require the maximum degree of HAP emission reduction that is achievable, taking into consideration the cost of achieving such an emission reduction and any non-air quality health and environmental impacts and energy requirements. The control technology that achieves this level of HAP emission control is called "maximum achievable control technology" or "MACT."

The 1990 CAA Amendments include several provisions in Section 112 that specifically address the regulation of HAP emissions from electric utility steam generating units. First, CAA Section 112(a) defines the term "electric utility steam generating unit" to mean

". . . any fossil fuel fired combustion unit of more than 25 megawatts that serves a generator that produces electricity for sale. A unit that cogenerates steam and electricity and supplies more than one-third of its potential electric output capacity and more than 25 megawatts electrical output to any utility power distribution system for sale shall be considered an electric utility steam generating unit."

Section 112(n)(1)(A) directs the EPA to perform a study and report to Congress about the hazards to public heath reasonably anticipated to occur as result of exposure to HAP emissions from electric utility steam generating units. After considering the result of this study, the EPA must determine whether regulation of electric utility steam generating units under Section 112 is appropriate and necessary. In July 1995, the EPA submitted its draft version of the report for peer review and, concurrently, released that version of the report for public review and comment. The EPA completed the final report and submitted to it Congress in February 1998.[3]

A related directive in Section 112(n)(1)(B) requires the EPA to perform a second study and report to Congress about Hg emissions from electric utility steam generating units, municipal waste combustion units, and other sources including area sources. This section directs the EPA's study to consider the rate and mass of the Hg emissions from these sources, the health and environmental effects of such emissions, the technologies that are available to control such emissions, and the cost of these technologies. The EPA completed this study and submitted its final report to Congress in December 1997.[4]

The 1990 CAA amendments to Section 112 also direct the EPA to perform additional studies that include analyses of Hg emissions from electric utility steam generating units. Included among these studies is the requirement under CAA Section 112(m) for the EPA to study the atmospheric deposition of HAPs to the Great Lakes, Chesapeake Bay, Lake Champlain, and coastal waters. This group of surface water bodies collectively is referred to as the "Great Waters." Section 112(m) directs the EPA to investigate the contribution of atmospheric deposition to pollutant loadings in the Great Waters; environmental and public health effects of atmospheric pollution deposited to these waters; and the sources of the pollutants deposited to these waters. Three reports to Congress on the atmospheric deposition of pollutants to the Great Waters have been prepared to date (May 1994, June 1997, and June 2000).[5,6,7]

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In addition to requiring the EPA to prepare the above cited reports, Congress directed the EPA to fund an independent evaluation conducted by the NAS of the available data related to the health impacts of MeHg and provide recommendations for the reference dose (RfD) to be used for health impact analyses. The RfD is the amount of a chemical which, when ingested daily over a lifetime, is anticipated to be without adverse health effects to humans, including sensitive subpopulations. The NAS conducted an 18-month study of the available data on the health effects of MeHg and published a report of its findings in 2000.[1] On the basis of its evaluation, the NAS committee's consensus is that the value of EPA's current RfD for MeHg is a scientifically appropriate level for the protection of public health.

1.4 Major Findings of EPA Reports to Congress

1.4.1 Study of HAP Emissions from Electric Utility Steam Generating Units

The findings of the EPA's study of the hazards to public heath reasonably anticipated to occur as result of exposure to HAP emissions from electric utility steam generating units are presented in the two-volume report titled *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units--Final Report to Congress*.[3] The assessment for Hg in the report includes a description of Hg emissions, deposition estimates, control technologies, and a dispersion and fate modeling assessment that includes predicted levels of Hg in various media (including soil, water, and freshwater fish) based on modeling from four representative utility plants using hypothetical scenarios. The EPA did not evaluate human or wildlife exposures to Hg emissions from utilities in that report. With regard to non-inhalation exposures (e.g., ingestion) to other HAPs, the report presents a limited qualitative discussion of arsenic, cadmium, dioxins, and lead.

Based on information and analyses available at the time the report was prepared, electric utility steam generating units can emit a significant number of the HAPs listed in CAA Section 112(b). However, except for Hg, electric utility steam generating units are responsible for a very small percentage of the total nationwide emissions of these particular HAPs. The EPA concluded that Hg emitted from coal-fired steam generating units is the HAP of greatest potential concern for electric utility steam generating units. For two other HAPs (arsenic and dioxin), the EPA's analysis concluded that further evaluations and review are needed to better characterize the impacts of these HAP emissions from coal-fired steam generating units.

Nickel emissions are the only HAP emissions of potential concern from oil-fired electric utility steam generating units. The EPA acknowledged that there are significant uncertainties concerning the chemical forms of nickel emitted from these units and the health effects of those various nickel compounds. At the time the study was prepared, the EPA projected that future nationwide nickel emissions from oil-fired steam generating units would decrease because of anticipated declining use of oil by utilities for electric power generation.

The impacts due to HAP emissions from natural-gas-fired steam generating units are negligible based on the results of the study. The EPA concluded that no further evaluation is needed of HAP emissions from natural-gas-fired electric utility steam generating units.

The EPA identified uncertainties that make it difficult to quantify the magnitude of the risks due to Hg emissions from coal-fired electric utility steam generating units, and identified the research areas where more information is needed to gain a better understanding of the risks and impacts of these Hg emissions. Included among the research areas that the EPA recommended for further evaluation were: 1) collection and assessment of additional data on the Hg content of various types of coals; 2) collection and assessment of additional data on Hg emissions from coal-fired steam generating units; 3) collection and assessment of additional information on control technologies or pollution prevention options; and 4) further review of the available data on the health impacts associated with exposure to Hg. Following completion of the report, the EPA initiated studies addressing the identified research needs.

1.4.2 Mercury Study Report

The findings of the EPA's assessment of the magnitude of Hg emissions from sources in the United States, the health and environmental implication of those emissions, and the availability and costs of control technologies are presented in the eight-volume report titled *Mercury Study Report to Congress.*[4] The report provides an extensive analysis of the public health impacts and environmental impacts resulting from Hg emissions to the atmosphere and deposition on surface waters and land. The findings of the report related to Hg emissions from electric utility steam generating units and other anthropogenic sources in the United States (as discussed in Volume II of the report) are summarized below.

Mercury cycles in the environment occur as a result of both natural processes and human activities (anthropogenic sources). The EPA prepared a nationwide inventory of annual Hg emissions from anthropogenic sources in the United States. This inventory was based on the period 1994-1995 and estimated the total annual nationwide emissions of Hg to be 144 megagrams (158 tons). Most of these emissions (approximately 87 percent) are produced when waste or fuels containing Hg are burned. Four specific source categories account for approximately 80 percent of the total nationwide anthropogenic emissions: coal-fired electric utility boilers (33 percent), municipal waste combustors (19 percent), industrial and commercial boilers (18 percent), and medical waste incinerators (10 percent). Another 10 percent of the Hg emissions were estimated to be from manufacturing sources that use Hg as a processing agent, product ingredient, or where Hg is present as a trace constituent in a process raw material. The largest manufacturing sources are chloro-alkali plants and Portland cement manufacturing plants. The remaining 3 percent of the emissions were estimated to be released from area and miscellaneous sources.

In the report, the EPA also assessed future trends in Hg emissions. Emissions from two of the significant combustion sources identified in the 1994-95 nationwide inventory are predicted to decline significantly when the national emission standards for municipal waste combustors

(MWCs) and medical waste incinerators are fully implemented. Industrial use of Hg was found to be declining in those manufacturing sectors where acceptable substitute materials can be used (e.g., use of electronic thermometers in place of Hg thermometers, elimination of Hg additives in paints and pesticides, reduced use of Hg in batteries).

1.4.3 Great Waters Reports

The findings of the EPA's study of the atmospheric HAP deposition to the Great Waters are presented in a series of three reports to Congress; the first report dated May 1994, the second report dated June 1997, and the third report dated June 2000. The HAPs of concern emitted from electric utilities addressed by the Great Waters study include lead, cadmium, dioxins, and, in particular, Hg.

The first Great Waters report to Congress noted that the water bodies are polluted by HAPs that originate from both local and distant sources; however, more data are needed to identify the specific sources of the pollutants. The report recommendations were the following: 1) the EPA should strive to reduce emissions of the pollutants of concern through implementation of the CAA; 2) a comprehensive approach should be taken, both within the EPA and with other agencies, to reduce and preferably prevent pollution in air, water, and soil; and 3) the EPA should continue to support research for emissions inventories, risk assessment, and regulatory benefits assessment.

The second Great Waters report to Congress confirmed, and provided additional support for, the findings of the first report that persistent and bioaccumulative toxic pollutants and excessive nitrogen can adversely affect the environmental conditions of the Great Waters. Electric utilities and mobile sources are identified by the report based on air modeling studies and emissions data as major contributors of nitrogen oxides to the Chesapeake Bay and its watershed.

The most recent Great Waters report to Congress presents updated scientific and programmatic information to support and build upon the broad conclusions presented in the first two reports. Specific to Hg, fate and transport modeling and exposure assessments presented in the report predict that the anthropogenic contribution of the total amount of MeHg in fish is, in part, the result of Hg releases from combustion and industrial sources. Furthermore, consumption of fish is the dominant pathway of exposure to MeHg for fish-consuming humans and wildlife.

1.5 Information Collection Request to Electric Utility Industry

The EPA's 1998 report to Congress on HAP emissions from electric utility steam generating units identified additional information needed to gain a better understanding of the risks, impacts, and control of Hg emissions from coal-fired steam generating units. As part of the Agency's effort to gather this information, the EPA conducted an information collection project beginning in late 1998 to survey all coal-fired steam generating units meeting the CAA Section

112(a) definition that were operating in the United States.[8] This information collection provided the EPA with data on the Hg content and amount of coal burned by these units during the 1999 calendar year. As part of the information request, the EPA also selected a subset of the coal-fired electric utility steam generating units at which field-source testing was performed to obtain Hg emission data for the air pollutant control devices now being used for these units.

There were three parts to the EPA information collection effort. Part I of this effort consisted of gathering the information to first identify the location of each coal-fired steam generating unit meeting the CAA Section 112(a) definition that was operating in the United States. The EPA sent information collection requests (ICRs) to the owners and operators of approximately 1,100 facilities that potentially could be operating coal-fired steam generating units. Information requested in the Part I questionnaire sent to each of these facilities included the type of coal burned, the method of firing the coal, and the methods used for control of air pollutants. Based on the ICR responses, 1,143 coal-fired steam generating units that meet the CAA Section 112(a) definition were identified at 461 facilities. These coal-fired steam generating units were located across the entire nation in 47 of the 50 states, with the exceptions being Idaho, Rhode Island, and Vermont.

Part II of the information collection effort, during calendar year 1999, consisted of gathering information on the quantities, Hg content, and other selected properties of coal burned by each of the 1,143 coal-fired steam generating units. The owner or operator of each coal-fired steam generating unit provided to the EPA, on a quarterly basis, analysis results for samples of the coal fired in the steam generating unit. These analyses were performed according to a demonstrably acceptable protocol and reported the Hg content of the coal burned and other important coal properties (e.g., coal heating value and the sulfur, ash, moisture, and chlorine contents). Each owner or operator also reported data on the total amount of coal burned on a monthly basis during 1999.

Part III of the information collection effort consisted of conducting Hg emission source testing at selected electric utility power plants operating coal-fired steam generating units. The test locations were selected by the EPA to approximate the nationwide distribution of coal-fired steam generating units by type of boiler, coal burned, and air emission controls used. The testing at each location was performed by the facility owner or operator (or a source testing contractor hired by the facility). At each of the selected test locations, measurements were made of the Hg content in the inlet and outlet gas stream for the farthest downstream control device used on the unit. The testing followed an EPA-approved sampling protocol and included three sample runs at each sampling location. Samples of the coal burned during the source test were also collected. Each test was completed and a final test report was provided to the EPA. The EPA review of the test reports ultimately found acceptable test results for 80 coal-fired steam generating units.

All of the nationwide industry survey data (information collected for Part I of the survey), coal analysis data (information collected for Part II of the survey), and Hg emission testing (data collected for Part III of the survey) are available to the public on the EPA web site, <http://www.epa.gov/ttn/atw/combust/utiltox/utoxpg.html>. Selected information from the ICR

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data base are also summarized in chapters of this report as related to characterizing the coal properties, control configurations, and Hg emissions from existing coal-fired electric utility steam generating units. In this report, the term "EPA ICR data" is used to refer to the compilation of coal-fired electric utility power plant, coal property, and Hg emissions data gathered by this nationwide information collection project.

1.6 Regulatory Finding on HAP Emissions from Electric Utility Steam Generating Units

On December 20, 2000, the EPA published in the Federal Register a notice (65 FR 79825) presenting the EPA Administrator's finding as to whether regulation of emissions of HAP from fossil-fuel-fired electric utility steam generating units is appropriate and necessary. This finding is based on the results of EPA's reports to Congress, the EPA's analysis of the ICR responses, and other information the Agency subsequently collected concerning HAP emissions from electric utility steam generating units.

Based on the available information, the Administrator concluded that Hg is both a public health concern and a concern in the environment. The EPA's analysis shows that coal-fired electric utility steam generating units are the largest source of Hg emissions to the atmosphere in the United States. Further, the Administrator concluded that there is a plausible link between MeHg concentrations in fish and Hg emissions from these coal-fired steam generating units. Therefore, the Administrator found that it is appropriate and necessary to regulate HAP emissions, including Hg, from coal-fired electric utility steam generating units under CAA Section 112 (i.e., establish a NESHAP), because the implementation of other requirements under the CAA will not adequately address the serious public health and environmental hazards arising from these emissions. As a result, the EPA added coal-fired electric utility steam generating units to the list of source categories under CAA Section 112(c).

In its 1998 report to Congress, the EPA found that nickel emissions are the only HAP of potential concern from oil-fired electric utility steam generating units. The Administrator found that there remained uncertainties regarding the extent of the public health impact from nickel emissions from oil-fired electric utility steam generating units. Therefore, the EPA also added oil-fired electric utility steam generating units to the CAA Section 112(c) source category list.

The Administrator found that regulation of HAP emissions from natural-gas-fired electric utility steam generating units is not appropriate or necessary. Because the EPA believes that the CAA Section 112(a)(8) definition of electric utility steam generating units excludes stationary combustion turbines, the Administrator's finding for natural-gas-fired electric utility steam generating units does not apply to stationary combustion turbines.

In response to the regulatory finding, the EPA has begun development of a NESHAP to specifically control HAP emissions from coal-fired electric utility steam generating units. The current schedule for this rule is to propose a NESHAP for the source category by December 15, 2003, and take final action on the rule by December 15, 2004.

1.7 Mercury Emissions Research Programs

Mercury emissions from combustion sources including coal-fired electric utility power plants have been the subject of extensive research and study throughout the 1990s by government agencies, the electric utility industry, and university researchers. Researchers at the U.S. Department of Energy's (DOE) National Energy Technology Laboratory (NETL) (previously known as the Federal Energy Technology Center) have prepared a comprehensive literature search and review summarizing the data and findings of many of these studies published in 1999.[9]

Currently, the EPA, the DOE/NETL, and the Electric Power Research Institute (EPRI) are funding major on-going research work on Hg emissions from coal combustion. Each organization conducts these projects "in-house" as well as through contracts with university researchers and private companies. In addition, the EPA, the DOE/NETL, and EPRI are collaborating on a number of joint projects. The on-going projects range from fundamental studies based on bench-scale laboratory experiments and computer modeling to field test programs at coal-fired electric utility power plants. Table 1-1 presents a summary overview of the research topics being investigated. Major objectives of these research efforts include:

- Improving the test methods for measuring Hg emissions from coal-fired electric utility boilers and other coal combustion systems. The current focus of this effort is development of continuous emission monitors (CEMs) to measure Hg.

- Understanding the chemical, physical, and operating factors that affect Hg behavior in combustion gases and residues from burning coal.

- Developing cost-effective techniques for controlling Hg that can be readily retrofitted to existing coal-fired electric utility power plants.

- Developing Hg control technologies for application to new coal-fired electric utility power plants.

- Developing multipollutant control technologies that will control Hg emissions together with SO_2 or NO_x emissions.

1.8 Relationship to Mercury Emission Control Research for Municipal Waste Combustors

The EPA has identified MWCs as the second largest source category of Hg emissions in the United States after coal-fired electric utility steam generating units.[4] The control of Hg emissions from MWCs has been, and continues to be, the subject of research in both the United States and Europe.

Table 1-1. Current research areas related to controlling Hg emissions from coal-fired electric utility power plants.

Research Area	Major Research Sponsor			
	DOE	EPA	EPRI	USGS
Hg content of coals		✓		✓
Coal cleaning methods for Hg removal	✓		✓	✓
Hg behavior and speciation in coal combustion gases	✓	✓	✓	
Hg measurement and monitoring in coal combustion gases	✓	✓	✓	
Hg adsorption on fly ash in coal combustion gases	✓			
Improving Hg capture by conventional wet scrubber systems	✓	✓	✓	
Improving Hg capture by conventional particulate control devices	✓			
Hg capture using activated carbon sorbent injection	✓	✓	✓	
Hg capture using other Hg-specific sorbents	✓			
Hg capture using multipollutant sorbents		✓		
Hg behavior in solid residues from Hg control systems	✓	✓	✓	
Hg control costs and economics	✓	✓	✓	

An MWC is an enclosed combustion unit used to burn municipal solid waste for the purpose of reducing the volume of waste that must be disposed in a landfill. Many people also refer to these combustion units as waste incinerators. Although an MWC may function as a simple incinerator, more commonly these combustion units are equipped with heat recovery equipment that is used for producing steam. The steam is used in a variety of different ways depending on the facility location including generating electrical power, industrial process steam, or district heating systems. Other terms sometimes used to refer to this type of MWC facility include "resource recovery facility" and "waste-to-energy plant."

The EPA and some states have established regulations to reduce the level of Hg emissions from MWC facilities operating in the United States. To comply with these regulations, a combination of control strategies, including the application of add-on control devices, are now in use for new and existing MWC facilities. Direct transfer to coal-fired electric utility steam generating units of all of the specific control strategies that are used to meet the Hg emission regulations for MWC facilities is not feasible, effective, or practical because of the distinct differences between the two categories of combustion sources (e.g., properties of the fuel burned; the design, operation, and scale of the combustion unit; and the characteristics of the post-combustion gases). Nevertheless, understanding how Hg emissions are controlled in an MWC does provide useful information to help identify potential Hg control technologies for coal-fired electric utility steam generating units and to assess the performance and costs of using these controls.

In the United States, the municipal solid waste that can be burned in MWCs is primarily composed of household, commercial, and institutional refuse. These wastes cannot include any hazardous wastes regulated under subtitle C of the Resource Conservation and Recovery Act (RCRA). However, small amounts of Hg may be in certain discarded consumer products that are not RCRA hazardous wastes and are burned in MWCs (e.g., batteries, some fluorescent bulbs, electrical switches, thermometers). Most of this Hg is released during the combustion process and remains in combustion gases vented from the MWCs.

Mercury emissions from MWC facilities in the United States are decreasing for three major reasons. First, Section 129 of the CAA requires the EPA to develop national emission standards for Hg (and a number of other pollutants) being emitted from MWC facilities. The EPA finalized the standards as new source performance standards (NSPS) and Emission Guidelines (EG) under 40 CFR part 60 in October 1995. The NSPS (subpart Eb) applies to those MWCs constructed after September 20, 1994 (i.e., "new sources"); the EG (subpart Cb) applies to those MWCs built before this date (i.e., "existing sources"). For Hg, the same emission limit of 0.08 milligram per dry standard cubic meter (mg/dscm) applies to both new and existing MWC facilities.

In addition to the Federal standards and emission guidelines, individual states with significant numbers of MWC facilities operating within their jurisdiction have enacted legislation controlling Hg emissions from these MWC facilities. Several states (e.g., Florida and New Jersey) have established Hg emission limits for MWCs, effectively requiring these units to use a

specific control technology. Some states have enacted regulations limiting or banning the sale of certain Hg-containing products that, when discarded, would have been mixed in refuse burned in an MWC. These regulations differ from state to state, with Minnesota having the most extensive set of restrictions on the disposal of Hg-containing products.

The third reason for the decline in Hg emissions from MWC facilities is the trend by manufacturers to limit or discontinue the use of Hg in many products that ultimately are mixed in the waste burned in MWCs. These products include household alkaline batteries and interior and exterior paints. Other products that traditionally have used Hg (e.g., Hg thermometers and thermostats) are increasingly being replaced by digital, electronic versions that do not require Hg components.

Despite the reductions in the Hg content of the waste burned, MWCs still need to use add-on emission controls to capture Hg in the combustion gases exhausted from the combustor. Mercury removal from the combustion gases using these control systems can vary depending on the combination of controls used and the site-specific conditions. The injection of powdered activated carbon into the gas upstream of a particulate matter control device is a common method currently used in the United States to control Hg emissions from MWCs. In Europe, wet scrubbing systems are commonly used to control MWC Hg emissions. Because of factors such as the differences in flue gas characteristics and duct configurations (discussed further in Chapter 7), the Hg control technologies now used for MWCs cannot be directly transferred to coal-fired utility boilers. However, the commercial experience with MWC Hg emission controls does point to potential control technologies that should be investigated further for application to coal-fired electric utility power plants.

1.9 Report Organization

The remainder of this report consists of nine chapters (Chapters 2 through 10) presenting background information, recent research findings, and the current status of research studies related to Hg emission behavior and control in coal-fired electric utility power plants. Each chapter addresses specific topics related to the application of Hg emission control technologies to coal-fired steam generating units. Appendices are presented at the end of the report to support and supplement information presented in the chapters.

Chapter 2
Coal-fired Electric Utility Boilers

Chapter 2 presents an overview of the coals burned and combustion technologies used for electric power generation. The design and operating characteristics of the different types of coal-fired boilers used by electric utilities in the United States are presented. The properties of the coal burned by electric utilities in the year 1999 are summarized using information compiled from the EPA ICR database.

Chapter 3
Criteria Air Pollutant Emission Controls for
Coal-fired Electric Utility Boilers

Chapter 3 presents a summary review of the different air pollution control devices (APCDs) currently used at coal-fired electric utility power plants to meet criteria air pollutant emissions standards. The nationwide distribution of APCD configurations used at these power plants to comply with the air standards is presented using information from the EPA ICR database.

Chapter 4
Measurement of Mercury

Chapter 4 discusses the principles, applications, and limitations of Hg measurement methodologies, particularly with respect to understanding and interpreting the ICR data. The chapter discusses the Ontario-Hydro method and other manual test methods available for measuring Hg in coal combustion flue gas. This chapter introduces the principles and issues related to Hg continuous emission monitors (CEMs) and their use as a valuable research tool.

Chapter 5
Mercury Speciation and Capture

Chapter 5 provides an introduction to Hg chemistry and behavior of Hg as it leaves the combustion zone of the furnace and passes in the flue gas through the downstream boiler sections, air heater, and air pollution control devices. Recent laboratory research on Hg chemistry in coal combustion flue gas is summarized. Mercury speciation is discussed as related to coal properties, combustion conditions, flue gas composition, fly ash properties, time/temperature profile between the boiler and air pollution control devices, and post-combustion flue gas cleaning methods. Results from recent studies on the mechanisms for capturing Hg by adsorption of gaseous Hg, by solid particles in the flue gas, and by absorption capture of Hg by alkaline solutes/slurries are analyzed.

Chapter 6
Mercury Capture by Existing Control Systems Used by
Coal-fired Electric Utility boilers

Chapter 6 discusses the level of Hg capture achieved by the air emission control devices now in use at coal-fired electric utility power plants to meet Federal and state air emission standards for particulate matter, sulfur oxides, and nitrogen oxides. The results of the Hg emission source testing compiled in the Part III EPA ICR data are presented and analyzed. The methods used to evaluate these

Hg emissions data are described to meet two interrelated objectives. First, an analysis of the EPA ICR data is presented as used for EPA's estimate of nationwide Hg emissions from coal-fired electric utility power plants in 1999. Second, the EPA ICR data are analyzed to characterize the effects of coal properties, combustion conditions, and flue gas cleaning methods on the speciation and capture of Hg.

Chapter 7
Research and Development Status of
Potential Retrofit Mercury Control Technologies

Chapter 7 discusses potential retrofit control technologies for increasing Hg emission capture levels in the air pollutant control systems now in use at existing coal-fired electric utility power plants. The use of activated carbon and other dry sorbents for Hg emission control is discussed. Current knowledge is summarized regarding the enhancement of Hg capture by existing particulate matter control devices and wet scrubbing systems. Recent pilot-scale and full-scale test data for Hg capture by potential retrofit control technologies are presented. This chapter also summarizes the status of emerging Hg and multipollutant control technologies that are being developed for the control of Hg emissions from coal combustion.

Chapter 8
Cost Evaluation of Retrofit Mercury Controls for
Coal-fired Electric Utility Boilers

Chapter 8 presents a preliminary evaluation of total annual costs to apply potential activated carbon injection-based control technologies to existing coal-fired electric utility power plants. The evaluation is based on estimating the control costs using a computer model for a series of model plant scenarios. The cost estimate methodology and assumptions are described. The cost estimates are presented and discussed.

Chapter 9
Coal Combustion Residues and Mercury Control

The EPA/NRMRL presently is conducting a life-cycle analysis project to help evaluate any potential environmental trade-offs and to ensure that there is not an increased environmental risk from the management of coal combustion residues (CCRs) resulting from the implementation of Hg control technologies at coal-fired electric utility power plants. In support of this evaluation, the NRMRL is gathering data and information to assess future increases in Hg concentrations in

CCRs resulting from application of Hg emissions control requirements to coal-fired electric utility boilers. Chapter 9 summarizes some of the CCR information gathered by NRMRL to date and identifies the major data gaps and priorities of EPA's research to ensure that Hg controlled at the coal-fired electric utility power plant stack is not later released from CCRs in an amount that is problematic for the environment.

Chapter 10
Conclusions and Recommendations

Chapter 10 summarizes the major findings of this report and presents recommendations for further work, which would benefit the understanding of Hg behavior in the coal combustion processes at electric utility power plants.

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Chapter 2
Coal-fired Electric Utility Boilers

2.1 Introduction

The steam produced in a boiler can be used to drive a steam turbine that, in turn, spins an electric generator. In a conventional steam boiler used for electrical power generation, water is heated under pressure to form high-temperature, high-pressure steam. The heat required to produce steam can be supplied by burning a fossil fuel inside an enclosed space in the boiler. Electricity generation in the Unities States relies extensively on burning coal in steam boilers.

This chapter presents an overview of the use of coal by electric utilities for power generation. An introduction to the properties of coal and coal resources in the United States is presented. The major components and general operation of a conventional coal-fired electric utility boiler are described. A profile of the different coal-firing configurations used by electric utility power plants in the United States is presented based on analysis of the Part II EPA ICR data. Ash produced by coal combustion is described. The chapter concludes with a summary of the Part II EPA ICR data for the mercury content of the coals burned by electric utility power plants in 1999. Air pollutant emissions and the control strategies currently used for these coal-fired electric utility power plants are discussed in Chapter 3.

2.2 Coal

Coal is a combustible "rock" composed of organic and mineral materials that have formed over time by vegetative decay and mineral deposition. The principal chemical constituents of coal are carbon, hydrogen, oxygen, nitrogen, and sulfur. Coal also contains incombustible mineral matter and trace amounts of metallic elements, oxides, and rare gases. The properties of a given coal deposit vary depending on a variety of site-specific factors including the type of vegetative matter from which the coal formed, the age of the deposit, and the conditions under which the coal formed.

2.2.1 Coal Property Tests

Standardized tests for determining the properties of coal have been adopted by the American Society for Testing and Materials (ASTM).[1] These ASTM methods are widely used in

the United States by coal producers, electric utility companies, and government agencies to obtain coal property data for many purposes including classifying coal resources, designing coal combustion equipment, pricing coal, and monitoring coal shipment quality. Standardized procedures for collecting coal samples for analysis also have been established by ASTM methods.

2.2.1.1 Coal Heating Value

One of the key properties of coal is the quantity of heat that can be released when the coal is burned. The heating value of coal is determined using one of several ASTM test methods (e.g., ASTM D2015 or D3286). These tests involve burning a coal sample in a bomb calorimeter and measuring the temperature rise following the procedure specified in the method. As used in the United States, heating value is most commonly expressed in units of British thermal units per pound of coal (Btu/lb). Heating value can also be expressed in units of joules per kilogram, kilojoules or kilocalories per kilogram, or calories per gram. Also, heating value may be reported as higher heating value (HHV) or lower heating value (LHV). The HHV is the value measured by the actual test. The LHV is calculated by subtracting the heat of water vaporization from the value measured in the bomb calorimeter.

2.2.1.2 Coal Proximate Analysis

The proximate analysis is a widely used test procedure for determining for a given coal the total moisture, volatile matter, fixed carbon, and ash contents expressed on a weight-percent basis. The protocol for performing a proximate analysis for coal is established by ASTM D3172 that specifies the overall procedure to be followed and the other specific ASTM test methods to be used. The analysis involves performing a series of tests in a specific order on a given coal sample. First, the total moisture of the coal is determined by drying the sample in an oven according to ASTM test method 3173. The difference in weight before and after drying is the amount of moisture in the coal.

Volatile matter is not naturally present in coal. However, combustible gases (e.g., hydrogen, methane, and other hydrocarbons) are formed by thermal decomposition when the coal sample is heated under controlled temperature and time conditions. The conditions are specified in ASTM test method 3175. The difference in weight before and after heating the coal sample for a second time in a furnace is the amount of volatile matter contained in the coal. The coal sample is then completely burned under conditions specified in ASTM test method 3174. The weight of the noncombustible matter remaining after combustion is the ash content in the coal. The percentage of fixed carbon is obtained by subtracting from 100 percent the sum of the percentages of total moisture, volatile matter, and ash.

2.2.1.3 Coal Ultimate Analysis

The second analysis procedure commonly performed is the ultimate analysis. This analysis determines the composition of the coal based on elemental constituents. The protocol

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for performing a coal ultimate analysis is established by ASTM D3176 which specifies the overall procedure to be followed and the specific ASTM test methods to be used. As defined in ASTM D3176, the elements determined are total carbon, total hydrogen, total sulfur, total nitrogen, and total oxygen. Determination of ash is included in the analysis. The quantity of chlorine present in the coal is also commonly included as part of the ultimate analysis. However, the contents of mercury and other trace constituents in the coal are not included in the results from a coal ultimate analysis.

2.2.1.4 Coal Mercury Analysis

A separate analysis must be conducted to determine the Hg content of coal. Several ASTM test methods are available for measuring the total Hg concentration in a coal sample. Two methods are established by ASTM D6414 "Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption." The lower quantitative limits for these methods are, respectively, 0.02 ppm and 0.03 ppm. A third, commonly used method is ASTM D3684 "Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method" with a lower quantitative limit of 0.06 ppm. An interlaboratory study conducted by EPRI evaluated the use of these three analytical methods to measure coal Hg content for submitting data to the EPA ICR.[2] The study indicated that all three methods had certain limitations, especially when used to analyze very low Hg content coals and coal ashes. However, the study concluded that the uncertainty in these methods should not have a significant impact on the use of the data collected by the EPA ICR for nationwide Hg emission estimates.

2.2.2 Coal Classification

Over the years, a number of coal classification systems have been developed by the United States Geological Survey (USGS) and others. These coal classification systems allow assessments of coal resources and provide data for designing coal combustion equipment.[3] In the United States, coals are classified using a hierarchy ranking coals relative to other coals based on the degree of metamorphism (effectively, the geological age of the coal and the conditions under which the coal formed). These classification criteria have been standardized by ASTM method D-388. Under the ASTM method, coals are divided into four major categories called "ranks." Each rank is further subdivided into groups. The basic ranking criteria are coal heating value, volatile matter content, fixed carbon content, and agglomerating behavior. The coal ranks are summarized below.

> *Anthracite coal.* The highest rank class of coal that is defined to be a nonagglomerating coal having more than 86 percent fixed carbon and less than 14 percent volatile matter on a dry, mineral-matter-free basis. This coal rank is subdivided into three groups based on decreasing fixed carbon and increasing volatile matter content: meta-anthracite, anthracite, and semianthracite.

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Bituminous coal. The second highest rank of coal defined to be high in carbonaceous matter, having less than 86 percent fixed carbon, and a 14 percent volatile matter on a dry, mineral-matter-free basis, and a heating value of more than 10,500 Btu/lb on a moist, mineral-matter-free basis. This coal can be either agglomerating or nonagglomerating. The rank is subdivided into five bituminous coal groups on the basis of decreasing heat content and fixed carbon and increasing volatile matter: low-volatile bituminous coal, medium-volatile bituminous coal, and high-volatile bituminous coals A, B, and C.

Subbituminous coal. The third-highest rank of coal defined to be nonagglomerating coals having a heating value of more than 8,300 Btu/lb but less than 11,500 Btu/lb on a moist, mineral-matter-free basis. This rank of coal is subdivided on the basis of decreasing heat value into three groups: subbituminous A coal (10,500 to 11,500 Btu/lb), subbituminous B coal (9,500 to 10,500 Btu/lb), and subbituminous C coal (8,300 to 9,500 Btu/lb). Note that the heating value range for the upper-end subbituminous A coals overlaps with the heating value range for the lower-end high-volatile bituminous C coals.

Lignite. The lowest rank of coal defined to consist of brownish-black coal having heating values less than 8,300 Btu/lb on a moist, mineral-matter-free basis. This rank of coal is subdivided into two groups: lignite A (6,300 to 8,300 Btu/lb) and lignite B (less than 6,300 Btu/lb).

2.2.3 United States Coal Resources

Coal is the most abundant fossil fuel in the United States. The DOE Energy Information Administration (EIA), the Federal government agency responsible for estimating coal resources in the United States, estimates that the demonstrated reserve base of coal in the United States is approximately 508 billion tons.[4] The distribution of this coal by major coal rank is presented in Table 2-1. Over half of the coal reserve base is classified as bituminous coal. Another third of the reserves are classified as subbituminous coal.

Not all of the coal identified in the demonstrated reserve base can be extracted from the ground for a variety of reasons. Of the estimated 508 billion tons of demonstrated coal reserves, the DOE EIA estimates that approximately 275 billion tons of coal can be recovered by standard mining technologies, assuming that a market and an adequate selling price exist for this coal.

In the United States, coal deposits have been found in 36 states. Figure 2-1 shows the distribution of coal resources in the United States by coal region as designated by the USGS. Coal resources in the Eastern United States are concentrated primarily along the Appalachian Mountains and are estimated by the DOE EIA to contain 108 billion tons. The major deposits of bituminous coals are concentrated in the Central Appalachian region comprised of eastern Kentucky, western Virginia, and southern West Virginia. Most of the anthracite coal resources in the United States are located in eastern Pennsylvania (Pennsylvania Anthracite and Northern Appalachian regions).

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Table 2-1. Demonstrated reserve base of major coal ranks in the United States estimated by DOE/EIA (source: Reference 4).

Coal Rank	Estimated U.S. Demonstrated Coal Reserves (billion tons)	Percentage of U.S Demonstrated Coal Reserves
Anthracite	8	2 %
Bituminous	271	53 %
Subbituminous	185	36 %
Lignite	44	9 %
Total	508	100 %
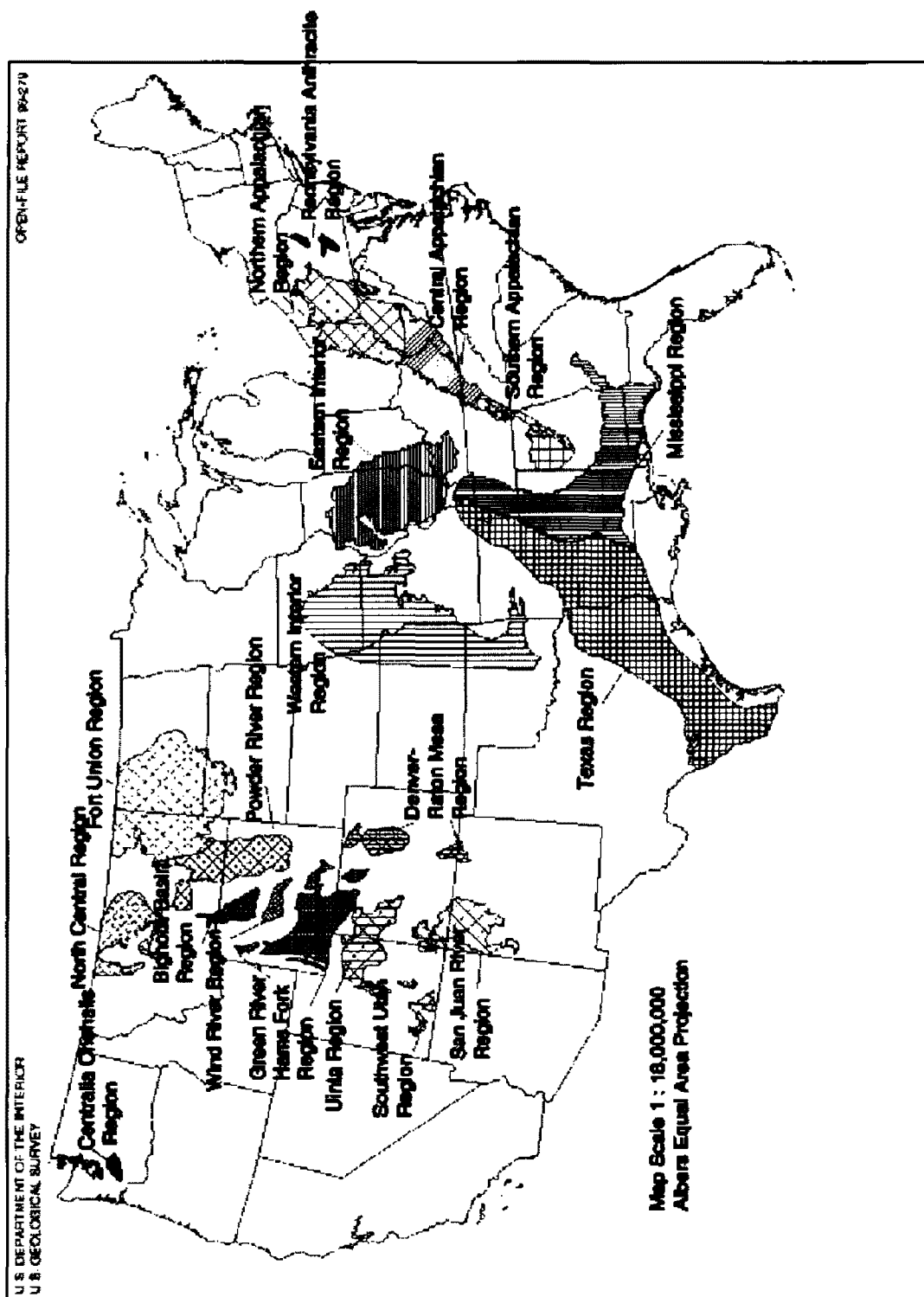
Figure 2-1. Distribution of coal deposits in the continental United States by USGS coal resource region (source: Reference 5).

The coal regions in the Central United States (Eastern Interior, Western Interior, Texas, and Mississippi regions) are estimated by the DOE EIA to contain 160 billion tons of coal. Most of the coal deposits in these regions are bituminous coal (largest deposits in the Eastern Interior region). A band of lignite deposits occur along the Gulf Coast (Texas and Mississippi regions) with the largest deposits in eastern Texas.

The coal reserves in the Western United States coal regions are estimated by the DOE EIA to be 240 billion tons. Subbituminous coal is the most prevalent coal type with the major deposits located throughout Montana and Wyoming (Powder River, Bighorn Basin, Wind River, and Green River – Hams Fork regions) and in northwestern New Mexico (San Juan River region). Large deposits of lignite are found in eastern Montana and North Dakota (Fort Union region). Bituminous coal is found mostly in the coal regions in Colorado and Utah (Uinta, Raton Mesa, and Southwest Utah regions).

2.2.4 Mercury Content in Coals

Mercury is a naturally occurring impurity contained in coal in trace amounts. It can occur in coal in several forms. Most of the Hg is believed to be present in combination with sulfide minerals, particularly pyrite. The mercury-pyrite association accounts for as much as 65 to 70 percent of the Hg in some coals. Mercury is also associated with other ash-forming minerals and with the organic fraction in coal. On the order of 25 to 35 percent of the Hg in coal is typically associated with the organic material.

Data on the Hg content of "in-the-ground" coals are available in the USGS COALQUAL database.[6] One study evaluated the Hg content of coals using this database and selecting coal types representing major coal producing regions in the United States.[7] The data from the study are summarized in Table 2-2. The average concentration of Hg in the coal samples ranged from 0.08 to 0.22 $\mu g/g$. These data show that the Hg content of coals is not constant but varies depending on the coal deposit. The data also show that Hg content is not a function of coal rank (i.e., one coal type does not have inherently lower Hg concentrations than another coal type).

A comparison of the Hg concentrations in the different coals cannot be directly related to the amount of Hg emissions emitted from boilers burning these coals. Other coal properties and how the coal is prepared prior to firing in a boiler affect the theoretical potential level of Hg emissions that would occur in the absence of applying any Hg emissions controls. In other words, one cannot conclude that burning a coal with higher as-mined Hg concentration will necessarily result in higher Hg emissions from a coal-fired electric utility boiler.

Coals with higher heating values require less coal to be burned in a boiler on a mass basis to produce a given electricity output. For two coals with the same Hg content but different heating values, burning the coal with the higher heating value in a given boiler will result in less Hg being emitted in boiler combustion gases per unit of electricity output. On an equal energy basis, the Hg content of the bituminous and subbituminous coals listed in Table 2-2 span the

Table 2-2. Mercury content of selected as-mined coal samples by coal rank and USGS coal resource region (source: table prepared by summarizing and interpreting coal data presented in Reference 7).

Coal Rank	USGS Coal Resource Region	Hg Concentration (ppm)	Heating Value (Btu/lb)	Hg Content By Heating Value (lb Hg per 10^{12} Btu)
Anthracite	Pennsylvania Anthracite	0.18	12,440	15.4
Bituminous	Uinta	0.08	10,800	7.3
	Raton Mesa	0.09	12,320	6.6
	Eastern Interior	0.10	11,400	8.2
	Western Interior	0.18	10,970	16.1
	Appalachian	0.20	12,790	15.4
Subbituminous	San Juan River	0.08	9,610	7.7
	Hams River	0.09	10,570	4.8
	Green River	0.09	9,580	6.6
	Powder River	0.10	8,090	12.6
	Southwest Utah	0.10	9,290	11.0
	Wind River	0.19	9,560	18.7
Lignite	Fort Union	0.13	6,360	21.8
	Texas and Mississippi	0.22	6,490	36.4

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same general range of values. No trend is apparent from these data; both bituminous and subbituminous coals are found at the lower and upper ends of the range. For example, a bituminous coal from the Raton Mesa region and a subbituminous coal from the Green River region each have an average Hg content of 6.6 lb per 10^{12} Btu. At the other end of the range, a bituminous coal from the Western Interior region has an average Hg content of 16.1 lb per 10^{12} Btu and a subbituminous coal from the Wind River region has an average Hg content of 18.7 lb per 10^{12} Btu. On the other hand, the Hg contents reported for the two lignite coals listed in Table 2-2 are significantly higher than any of the bituminous and subbituminous coals (an average of 21.8 lb per 10^{12} Btu for Fort Union lignite and 36.4 lb per 10^{12} Btu for Gulf Coast lignite).

Another key reason why the Hg content of as-mined coals cannot be related to Hg emissions is the as-mined coal frequently is not burned in an electric utility boiler as it comes directly from the mine. The as-mined, or raw, coal often is first processed at a coal preparation plant to remove non-coal impurities in order to provide the coal purchaser with a uniform coal that meets a predetermined, contractual set of specifications. These processes commonly are collectively referred to as "coal cleaning." Depending on the properties of the coal and the type of process used, coal cleaning can reduce the Hg content of the coal that is ultimately fired in the electric utility boiler.

2.3 Coal Cleaning

2.3.1 Coal Cleaning Processes

Raw coal from a mine contains separate rock, clay, and other minerals. After the coal is mined, it may first pass through a series of processes known as coal preparation or coal cleaning before it is shipped to an electric utility power plant. The coal is processed for three main reasons: 1) to reduce the ash content; 2) to increase the heating value; and 3) to reduce the sulfur content to ultimately lower emissions of sulfur dioxide when the coal is burned in the utility boiler. The removal of impurities from the coal also helps to reduce power plant maintenance costs and to extend the service life of the boiler system.

Coal cleaning processes currently in use separate the organic fraction of the as-mined coal from the mineral materials according to the differences in either the density-based or surface-based characteristics of the different materials. Physical coal cleaning typically involves a series of process steps including: 1) size reduction and screening, 2) gravity separation of coal from sulfur-bearing mineral impurities, and 3) dewatering and drying.

Bituminous coals from mines in the Eastern and Midwestern United States frequently are cleaned to meet the electric utility customer's specifications for heating value, ash content, and sulfur. It is estimated that about three-fourths (77 percent) of these coals are cleaned prior to shipment to an electric utility power plant.[8] The subbituminous and lignite coals from mines in the Western United States routinely are not cleaned before shipment to an electric utility power

plant, but in special cases these types of coals can be cleaned. For example, some of subbituminous coal from mines in the Powder River coal region (a major source of coal for many electric utilities) is cleaned for shipment to electric utility customers.

2.3.2 Mercury Removal by Coal Cleaning

Conventional coal cleaning methods will also remove a portion of the Hg associated with the incombustible mineral materials but not the Hg associated with the organic carbon structure of the coal. Any reduction in Hg content of the coal shipped to an electric utility power plant obtained from the Hg removed by coal cleaning processes transfers the removed Hg to the coal cleaning wastes. Limited data have been gathered on the level of Hg removed by conventional coal cleaning methods.

A review of test data for 26 bituminous coal samples from coal seams in four states (Illinois, Pennsylvania, Kentucky, and Alabama) prepared for EPA's *Mercury Study Report to Congress* indicates a wide range in the amount of Hg removed by coal cleaning.[8] In some cases, analysis of coal samples from the same coal seam also showed considerable variability. Analysis of five of the coal samples showed no Hg removal associated with conventional coal cleaning while the remaining 21 coal samples had Hg reductions ranging from approximately 3 to 64 percent. The average Hg reduction for all of the data was approximately 21 percent.

Other studies have reported higher average Hg reductions for Eastern and Midwestern bituminous coals. One study tested 24 samples of cleaned coal.[7] These data also showed a wide range in Hg reduction rates. The average decrease in Hg reduction on an energy basis was 37 percent, with values ranging from 12 to 78 percent. On a mass basis, the average Hg reduction from coal cleaning was 30 percent. A higher Hg reduction was reported on an energy basis than on a mass basis because the coal cleaning raises the heating value per unit mass of the coal, as well as removing Hg. A second study of the effects of coal cleaning on Hg content for three Ohio coals reported reductions in Hg content of the coals ranging from 36 to 47 percent.[9]

The variation in Hg reductions observed from the test data might be a function of the type of process used to clean a given coal and the proportion of Hg in the coal that is present in combination with pyrite (iron disulfide). Coal-cleaning processes that make separations according to the density differential of particles are generally more effective in removing Hg associated with pyrite than are surface-based processes. The heavier pyrite is easily removed by density-based processes, but not by surface-based processes where the similar surface characteristics of pyrite and the organic matter make separation of the two components difficult. For coals that have larger portions of Hg associated with pyrite, density-based cleaning processes are expected to have higher Hg removals. However, some coals may contain large portions of Hg associated with the organic fraction of the coal; Hg removal in these cases would be expected to be substantially lower since the organic fraction of coal is not removed during cleaning. Additional reductions in Hg can probably be achieved by using more intensive coal cleaning methods. Several advanced coal cleaning techniques being investigated to improve Hg removal are discussed in Chapter 7.

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2.4 Coal-fired Electric Utility Boilers

The large steam boilers used by electric utilities are also referred to as "steam generators," "steam generating units," or simply "boilers." As discussed in Chapter 1, CAA Section 112(a) defines the term "electric utility steam generating unit" to include those units that cogenerate steam and electricity and supply more than one-third of its potential electric output capacity and more than 25 megawatts electrical output to any utility power distribution system for sale. For simplicity in the remainder of this report, the term "electric utility boiler" is used to mean "electric utility steam generating unit" as defined in CAA Section 112(a)(8).

A total of 1,143 coal-fired units meeting the CAA definition of an "electric utility steam-generating unit" were reported in the Part II EPA ICR data to be in the United States in 1999.[10] More than one boiler unit is often operated at an electric utility power plant. The 1,143 units were located at a total of 461 facilities. These facilities can be categorized in three facility types: conventional coal-fired electric utility power plants, coal-fired cogeneration facilities, and integrated coal gasification and combined cycle (IGCC) power plants.

2.4.1 Conventional Coal-fired Electric Utility Power Plants [11,12]

A conventional electric utility power plant burns coal in a boiler unit solely for the purpose of generating steam for electrical power production. A total of 1,122 coal-fired electric utility boilers were reported in the Part II EPA ICR data to be operating at conventional electric utility power plants. Each of these boilers was designed to meet plant load and performance specifications by burning coals within a specific range of coal properties (e.g., heating value, ash content and characteristics, and sulfur content). While the specific equipment and design of a coal-fired electric utility boiler will vary from plant to plant, the same basic process is used to generate electricity. Figure 2-2 presents a simplified schematic of the major components of a coal-fired electric utility boiler operated at a conventional electric utility power plant.

Coal typically is delivered to a power plant by railcars, trucks, or barges. At some power plants located near the mine supplying the coal, coal is delivered by a slurry pipeline or an extended conveyor system. Also, a few power plants burn imported coal that is delivered to the facility by ship. The delivered coal is unloaded and stored in outdoor storage piles or covered storage structures such as silos or bins. Depending on how the coal is burned in the boiler (e.g., in a bed or burned in suspension), the coal is crushed or pulverized before being fed to the boiler.

A conventional coal-fired electric utility boiler consists of multiple sections, each of which serves a specific purpose. The coal is ignited and burned in the section of the boiler called the "furnace chamber." Blowing ambient air into the furnace chamber provides the oxygen required for combustion. The carbon and hydrogen comprising the coal are oxidized at the high temperatures produced by combustion to form the primary combustion products of carbon dioxide (CO_2) and water (H_2O). Sulfur in the coal is oxidized to form SO_2. Molecular nitrogen in the combustion air and nitrogen bound in the coal react with oxygen in certain sections of the combustion zone in the furnace chamber to form NO_x. Small amounts of other gaseous
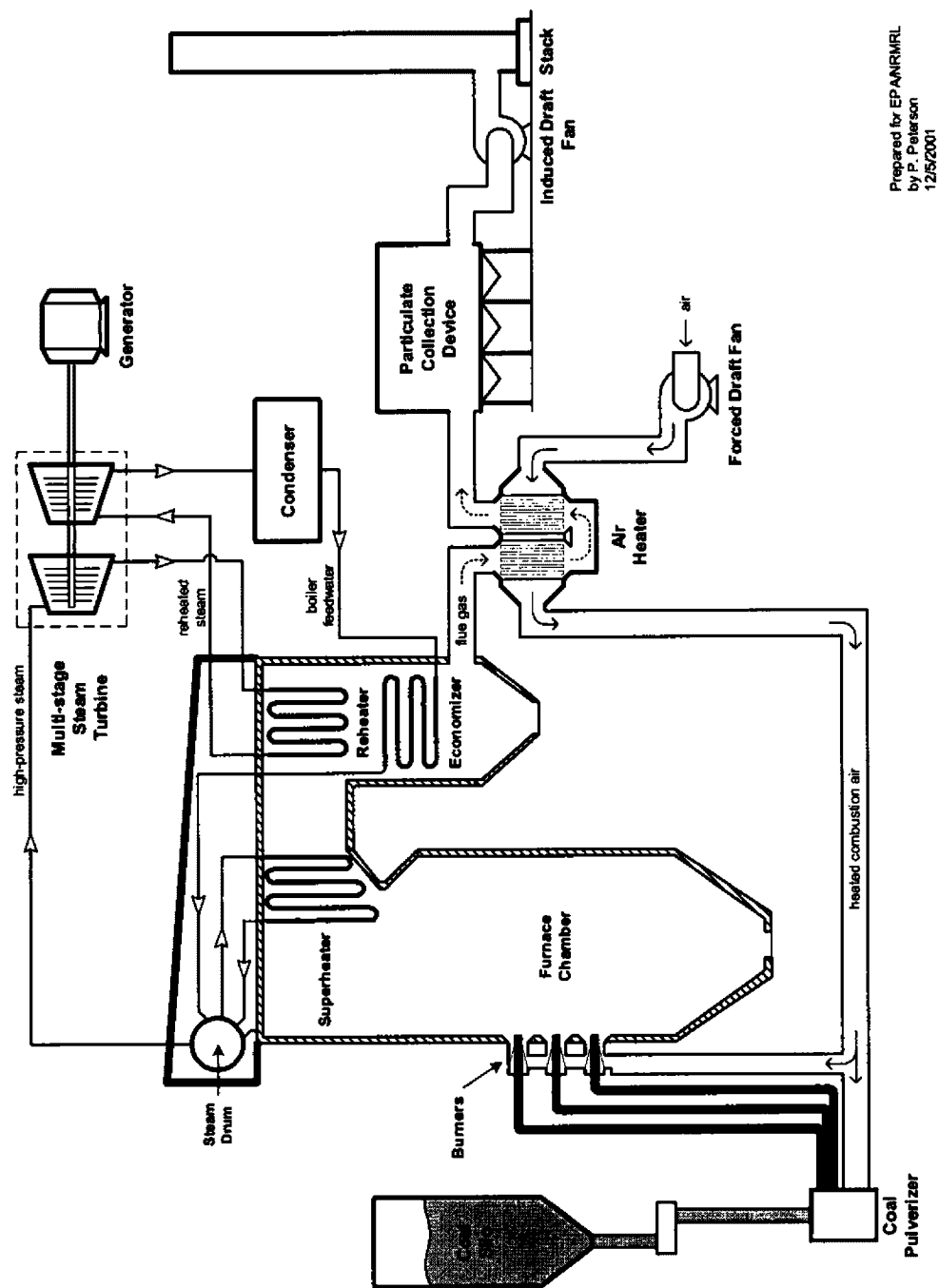
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Figure 2-2. Simplified schematic of coal-fired electric utility boiler burning pulverized, low-sulfur coal.

combustion products form from other impurities in the coal. These hot combustion products are vented from the furnace in a gas stream called collectively "flue gas." Additionally, most but not all the carbon in the coal is burned in the furnace. Unburned or partially burned solid carbon particles are entrained and vented from the furnace in the flue gas.

The walls of the furnace chamber are lined with vertical tubes containing water. Heat transfer from the hot combustion gases in the furnace boils the water in the tubes to produce high-temperature, high-pressure steam. This steam flows from the boiler to a steam turbine. In the turbine, the thermal energy in the steam is converted to mechanical energy to drive a shaft that spins a generator, which produces electricity. After the steam exits the turbine, it is condensed and the water is pumped back to the boiler.

To improve overall energy conversion efficiency, modern coal-fired electric utility boilers contain a series of heat recovery sections. These heat recovery sections are located downstream of the furnace chamber and are used to extract additional heat from the flue gas. The first heat recovery section contains a "superheater," which is used to increase the steam temperature. The second heat recovery section contains a "reheater," which reheats the steam exhausted from the first stage of the turbine. This steam is then returned for another pass thorough a second stage of the turbine. The reheater is followed by an "economizer," which preheats feed water to the boiler tubes in the furnace. The final heat recovery section is the "air heater," which preheats ambient air used for combustion of the coal.

A portion of all coals is composed of mineral matter that is noncombustible. This matter forms the ash that continuously must be removed from the operating utility boiler. The ash collection points and removal systems used for a given boiler unit are dependent on the ash properties and content in the coal-fired, the boiler design, and the air pollution control devices used. The removal and handling of the coal ash is discussed further in Section 2.6.

The flue gas exhausted from the boiler passes through air pollution control equipment and is vented to the atmosphere through a tall stack. The types and configurations of air pollution controls currently used for coal-fired electric utility boilers are discussed in Chapter 3.

2.4.2 Coal-fired Cogeneration Facilities

Approximately six percent of the boiler units are at cogeneration facilities, which are owned and operated by independent power producers or industrial companies. Of the 1,143 total coal-fired electric utility boilers reported in the EPA Part II ICR data, 68 are classified as cogeneration units. The total generating capacity of these cogeneration units is 867 MWe. There are more coal-fired boilers in the United States operating as cogeneration units; however, these units do not meet the criteria specified in the CAA definition of a steam-generating unit (i.e., the cogeneration unit is rated below 25 MWe or less than one-third of the unit's electrical output is sold). These units were not surveyed for the EPA ICR database.

Operation of a cogeneration facility differs from the operating configuration of the conventional electric utility power plant shown in Figure 2-2. Two basic cogeneration unit configurations are used: the "topping" mode or the "bottoming" mode. In the topping cogeneration configuration, steam produced by the coal-fired electric utility boiler is used first to generate electricity and then all or part of the exhaust heat is subsequently used for an industrial process. The bottoming cogeneration configuration reverses this sequence using waste heat generated by an industrial process to produce steam in a heat recovery boiler for driving a steam turbine and generating electricity. All of the cogeneration boiler units listed in the EPA ICR data operate using the topping mode configuration.

2.4.3 *Integrated Coal Gasification Combined Cycle Power Plants*

The IGCC power plants represent a new technology and are different from conventional electric utility power plants in two major characteristics. First, the IGCC power plants do not burn the coal in its solid form. Instead, the coal is first converted to a combustible gas using a coal gasification process at the facility site. Second, the IGCC power plants generate electricity using two separate thermal cycles and associated turbines referred to as a "combined cycle" operation. The coal-derived gas from the gasification process is first burned in a gas turbine that drives an electrical generator. The exhaust gases from this gas turbine pass through a heat recovery boiler to generate steam to power a steam turbine that drives a second electrical generator. Three IGCC power plants have been built in the United States. The operation of these power plants is discussed further in Section 2.5.5.

2.5 Coal-firing Configurations for Electric Utility Boilers

Coal can be burned in a boiler using one of three basic techniques: burning coal particles in suspension, burning large coal chunks in a fuel bed, or in a two-step process in which the coal is first converted to a synthetic gas which is then fired in the boiler. Five basic firing configurations are used to burn coal for electric power generation: pulverized-coal-fired furnace, cyclone furnace, fluidized-bed combustor, stoker-fired furnace, and gasified-coal-fired combustor. A general comparison of the different coal-firing configurations used for electric utility power plants is presented in Table 2-3.

Table 2-4 shows the distribution of the 1,143 coal-fired electric utility boilers listed in the EPA ICR data by coal-firing configuration. Pulverized-coal-fired designs account for the vast majority of the coal-fired electric utility boilers both in terms of total number of units (approximately 86 percent) and nationwide generating capacity. Cyclone furnaces are used to burn coal in approximately eight percent of the units. Fluidized-bed combustors are used for about four percent of the coal-fired electric utility boilers. Stoker-fired furnaces account for about three percent of the total number of coal-fired electric utility boilers but provide less than one percent of the total coal-fired megawatts. Only three IGCC units have been built in the United States.

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Table 2-3. Characteristics of coal-firing configurations used for electric utility power plants.

Coal-firing Configuration	Coal Combustion Process Description	Distinctive Design/Operating Characteristics	
Pulverized-coal-fired furnace	Coal is ground to a fine powder that is pneumatically fed to a burner where it is mixed with combustion air and then blown into the furnace. The pulverized-coal particles burn in suspension in the furnace. Unburned and partially burned coal particles are carried off with the flue gas.	Wall-fired	An array of burners fire into the furnace horizontally, and can be positioned on one wall or opposing walls depending on the furnace design.
		Tangential-fired (Corner-fired)	Multiple burners are positioned in opposite corners of the furnace producing a fireball that moves in a cyclonic motion and expands to fill the furnace.
Cyclone furnace	Coal is crushed into small pieces and fed through a burner into the cyclone furnace. A portion of the combustion air enters the burner tangentially creating a whirling motion to the incoming coal.	Designed to burn low-ash fusion coals and retain most of the ash in the form of a molten slag.	
Fluidized-bed combustor	Coal is crushed to fine particles. The coal particles are suspended in a fluidized bed by upward-blowing jets of air. The result is a turbulent mixing of combustion air with the coal particles. Typically, the coal is mixed with an inert material (e.g., sand, silica, alumina) and a sorbent such as limestone (for SO_2 emission control). The unit can be designed for combustion within the bed to occur at atmospheric or elevated pressures. Operating temperatures for FBC are in the range of 850 to 900 °C.	Bubbling fluidized bed (BFB)	Operates at relatively low gas stream velocities and with coarse-bed size particles. Air in excess of that required to fluidize the bed passes through the bed in the form of bubbles.
		Circulating fluidized bed (CFB)	Operates at higher gas stream velocities and with finer-bed size particles. No defined bed surface. Must use high-volume, hot cyclone separators to recirculate entrained solid particles in flue gas to maintain the bed and achieve high combustion efficiency.

(continued)

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Table 2-3. (continued).

Coal-firing Configuration	Coal Combustion Process Description	Distinctive Design/Operating Characteristics	
Stoker-fired furnace	Coal is crushed into large lumps and burned in a fuel bed on a moving, vibrating, or stationary grate. Coal is pushed, dropped, or thrown onto the grate by a mechanical device called a "stoker."	Spreader-stoker	A flipping mechanism throws the coal into the furnace above the grate. The fine coal particles burn in suspension while heavier coal lumps fall to the grate and burn in a fuel bed.
		Underfeed	Coal fed by pushing coal lumps along in a feed through underneath the grate.
		Traveling grate	Coal is fed by gravity onto a moving grate and leveled by a stationary bar at the furnace entrance.
Gasified-coal-fired combustor	Synthetic combustible gas derived from an on-site coal gasification process is burned in a gas turbine combustor. The hot combustion gases turn the gas turbine blades mounted on a shaft that drives an electric generator. The hot exhaust gases from the gas turbine pass through a waste heat boiler to produce steam for driving a steam turbine/generator unit.	Gasified-coal-fired combustors are unique from the other coal-firing configurations because a gaseous fuel is burned instead of solid coal.	

Table 2-4. Nationwide distribution of electric utility units by coal-firing configuration for the year 1999 as reported in the Part II EPA ICR data (source: Reference 10).

Coal-firing Configuration	Nationwide Total Number of Units	Percent of Nationwide Total	Percent of Nationwide Electricity Generating Capacity
Pulverized-coal-fired furnace	979	85.6 %	90.1 %
Cyclone furnace	87	7.6 %	7.6 %
Fluidized-bed combustor	42	3.7 %	1.3 %
Stoker-fired furnace	32	2.8 %	1.0 %
Gasified-coal-fired combustor	3	0.3 %	< 0.1 %
Nationwide Total	1,143	100 %	100 %

2.5.1 Pulverized-coal-fired Furnace

To burn in a pulverized-coal-fired furnace, the coal must first be pulverized in a mill to the consistency of talcum powder (i.e.; at least 70 percent of the particles will pass through a 200-mesh sieve). The pulverized coal is generally entrained in primary air before being fed through the burners to the combustion chamber, where it is fired in suspension. Pulverized-coal furnaces are classified as either dry or wet bottom, depending on the ash removal technique. Dry bottom furnaces fire coals with high ash fusion temperatures, and dry ash removal techniques are used. In wet bottom (slag tap) furnaces, coal with a low ash fusion temperature is fired, and molten ash is drained from the bottom of the furnace.

Pulverized-coal-fired furnaces are further classified by the firing position of the burners. Wall-fired boilers are characterized by rows of burners on one or more walls of the furnace. The two basic forms of wall-fired furnaces are single-wall (having burners on one wall) or opposed (having burners on walls that face each other). Circular register burners and cell burners are types of burner configurations used in both single-wall and opposed-wall-fired units. A circular register burner is a single burner mounted in the furnace wall, separated from other burners so that it has a separate, distinct flame zone. Cell burners are several circular register burners grouped closely together to concentrate their distinct flame zones.

Tangential-fired boilers are based on the concept of a single flame envelope and project both fuel and combustion air from the corners of the furnace. The flames are directed on a line tangent to a small circle lying in a horizontal plane at the center of the furnace. This action produces a fireball that moves in a cyclonic motion and expands to fill the furnace.

2.5.2 Cyclone Furnace

Cyclone furnaces use burner design and placement (i.e., several water-cooled horizontal burners) to produce high-temperature flames that circulate in a cyclonic pattern. The coal is not pulverized but instead crushed to a 4-mesh size. The crushed coal is fed tangentially, with primary air, to a horizontal cylindrical combustion chamber. In this chamber, small coal particles are burned in suspension, while the larger particles are forced against the outer wall. The high temperatures developed in the relatively small furnace volume, combined with the low fusion temperature of the coal ash, causes the ash to form a molten slag, which is drained from the bottom of the furnace through a slag tap opening.

2.5.3 Fluidized-bed Combustor

Fluidized-bed combustion increasingly is being used for coal-fired electric utility power plants. A variety of coals, including those with high concentrations of ash, sulfur, and nitrogen, can be burned in a fluidized-bed combustor (FBC). The term "fluidized" refers to the state of the bed materials (fuel or fuel and inert material [or sorbent]) as gas passes through the bed. In a typical FBC, combustion occurs when coal, with inert material (e.g., sand, silica, alumina, or ash) and a sorbent such as limestone, is suspended through the action of primary combustion air

which is distributed below the combustor floor. The gas cushion between the solids allows the particles to move freely, giving the bed a liquid-like characteristic (i.e., fluidized). In an FBC, crushed coal (between ¼ and 3/8 inches in diameter) is injected into a bed above a grate-like air distributor. Air is injected upward through the grate, lifting and suspending the solid particles. Inert materials such as sand or alumina are often mixed with the coal to maintain the bed in a fluidized state. Limestone particles can also be added to the bed to adsorb sulfur dioxide produced during combustion (discussed in Chapter 3).

2.5.4 Stoker-fired Furnace

Stoker-firing of coal is used for the oldest furnace designs in the electric utility industry, being first introduced to the industry in the late 1800s. Today, this design is used by only a few of the operating power plants. New power plants are not expected to adopt this design. In stoker furnaces, coal is burned on a bed at the bottom of the furnace. The bed of coal burns on a grate. Heated air passes upward through openings in the grate. Stokers are classified according to the way coal is fed to the grate; the three general classes in use today are underfeed stokers, overfeed stokers, and spreader stokers. Underfeed stokers feed coal by pushing it upward through the bottom of the grate. In overfeed stokers, the coal is deposited directly on the grate from a gravity-fed bin. In spreader stokers, a flipping mechanism throws the coal into the furnace above the grate; in this method, fine coal particles burn in suspension while heavier particles fall to the grate and burn. Additional combustion air is added above the grate to support suspension burning. Overfeed stokers can burn every type of coal except caking bituminous coal; spreader stokers can burn all types of coal except anthracite.

2.5.5 Gasified-coal-fired Combustor

Unlike the four coal-firing configurations discussed above, IGCC power plants do not burn solid coal. In place of the coal-fired boiler used at a conventional coal-fired electric utility power plant, at an IGCC power plant a coal gasification unit is used coupled with a gas turbine combustor and heat recovery boiler. The solid coal is gasified by a process in which a coal/water slurry is reacted at high temperature and pressure with oxygen (or air) and steam in a vessel (the gasifier) to produce a combustible gas. This combustible gas is composed of a mixture of carbon dioxide and hydrogen and is often referred to as a synthetic gas or "syngas." Molten ash flows out of the bottom of the gasifier into a water-filled sump where it forms a solid slag. The syngas is cleaned and conditioned before being burned in a gas turbine that drives an electrical generator. The hot combustion gases from the gas turbine are exhausted directly through a heat recovery boiler (i.e., no combustion takes place in the boiler) to produce steam that is then expanded through a steam turbine that drives a second generator to produce more electrical power.

The generation of electricity using the IGCC process offers a number of advantages compared to using conventional coal-fired boilers including higher thermal conversion efficiencies (e.g., more kilowatt-hours of electricity generated per kilogram of coal burned), greater fuel flexibility (e.g., capability to use a wider variety of coal grades), and improved

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control of particulate matter and SO_2 emissions without the need for post-combustion control devices (e.g., almost all of the sulfur and ash in the coal is removed during the gasification process). Three IGCC power plant projects have been constructed in the United States as part of the DOE's Clean Coal Technology Program, a joint government-industry cost-share technology development program. These facilities are the 250 MWe Tampa Electric Company Polk Power Project, the 307 MWe Wabash River Coal Gasification Repowering Project, and the 107 MWe Sierra Pacific Pinon Pine IGCC Power Project. Two of the facilities currently are operating (the Polk and Wabash River IGCC facilities). The Pinon Pine IGCC facility presently is shut down because of recurring problems with particulate matter in the syngas causing premature gas turbine blade erosion.[13]

In IGCC applications, the syngas from the gasifier is cleaned and conditioned before it is burned in the gas turbine using several different techniques. For example, at the Wabash River IGCC facility, the syngas from the coal gasifier passes through a series of gas cleaning and conditioning steps including a barrier filter for particulate removal, a water scrubber for gas cooling, and an amine scrubber for removal of reduced-sulfur species. In contrast, at the Polk IGCC facility, a hot-gas cleaning process is used and the syngas from the coal gasifier is not cooled before it is burned in the gas turbine.

2.6 Ash from Coal Combustion

Coal contains inorganic matter that does not burn including oxides of silicon, aluminum, iron, and calcium. This noncombustible matter forms ash when the coal is burned. Burning of coal in electric utility boilers generates large quantities of ash that must be removed and disposed of. The finer, lighter ash particles are entrained in the combustion gases and vented from the furnace section with the flue gas. This portion of the coal ash is referred to as "fly ash." The coarser, heavier ash particles fall to the bottom of the furnace section in the boiler unit. This portion of the coal ash is referred to as "bottom ash." The proportion of fly ash to bottom ash generated in a coal combustion unit varies depending on how the coal is burned.

In general, the fly ash is collected as a dry material at several points downstream of the furnace section. These points include collection hoppers beneath the boiler economizer, air heater, and the particulate matter control devices (other than wet scrubbers). From the collection hopper, the fly ash is conveyed using a mechanical system, vacuum system, pneumatic system, or combination of these systems to a storage silo. If a wet scrubbing system is used for air pollutant control, fly ash is captured and removed in the scrubber wastewaters.

For most boiler designs, the bottom ash is collected in a pit or hopper at the bottom of the boiler furnace. The ash is collected in the form of either a dry material or a molten slag depending on whether the furnace operating temperature is above the ash fusion temperature (i.e., the temperature at which the mineral compounds composing the ash melt). The ash is continuously removed from the ash pit using a mechanical, pneumatic, or hydraulic conveyance system.

When coal is burned in a pulverized-coal furnace, on the order of 60 to 80 percent of the total ash generated is fly ash. The high amount of fly ash results because the coal enters the furnace in a fine powder form that burns rapidly in suspension resulting in many tiny, lightweight ash particles that can easily be carried out of the furnace section with the flue gas. The heavier ash particles fall to the bottom of the furnace where they are removed. Two pulverized-coal boiler design approaches are used to collect bottom ash. The more frequently used design approach, commonly referred to as a "dry-bottom" furnace, collects the ash as essentially a dry material. For the typical dry-bottom furnace, the ash and slag particles fall into a water-filled hopper. The water serves several purposes including providing an air seal to prevent the infiltration of ambient air into the furnace, solidifying molten slag particles, and facilitating ash handling. The ash is then continuously removed from the ash pit using either a mechanical or an hydraulic conveyance system. The other design approach, referred to as a "wet-bottom" furnace, positions the coal burners on the furnace wall to maintain the ash that collects on the furnace floor in a molten state. The slag is drained through a slag tap opening into a slag tank.

The cyclone furnace is specifically designed to burn low-ash fusion coals and retains most of the ash in the form of a molten slag. The molten slag collects in a trough on the bottom of furnace and is continually drained through a slag tap opening into a slag tank. Water in the slag tank solidifies the ash for disposal. Only 20 to 30 percent of the ash produced by burning coal in a cyclone furnace is entrained as fly ash.

By nature of the fluidized-bed combustion process, most of the ash in the coal leaves the fluidized-bed combustor as fly ash. Because the temperatures in the FBC remain below the ash fusion temperature, formation of slag is avoided. Bottom ash is removed as a dry material to maintain the fluidized bed at a constant level. The ash removal system can be either a mechanical or pneumatic system.

In stoker-fired furnaces where the coal is burned in a fuel bed, most of the ash remains on the grate and is removed as bottom ash. Some smaller ash particles are entrained in the upward flow of combustion air through the grate and exit the furnace section as fly ash. The spreader stoker has a greater proportion of the ash entrained as fly ash (up to 50 percent of the ash) than the other stoker types (on the order of 20 percent fly ash). This occurs because the spreader stoker mechanically throws the crushed coal across the top of the grate. This allows the smaller coal fines in the incoming coal to burn in suspension before falling to the grate. This produces the small, lightweight ash particles that are carried out of the furnace section with the flue gas.

No ash is produced when burning syngas derived from coal in an IGCC power plant. The ash contained in the coal is removed by the gasification process that is used to produce the syngas. Before the syngas can be burned in the gas turbine, the gas must be precleaned to remove all types of particulate matter in order to prevent premature wear and destruction of the turbine blades.

2.7 Coals Burned by Electric Utilities In 1999

The EPA ICR Part II survey collected data on the coal, coal wastes, and some supplemental fuels burned in each coal-fired electric utility boiler operating in the United States during the entire calendar year 1999. Coal samples were analyzed for, at a minimum, the higher heating value (HHV) and the coal sulfur, ash, Hg, moisture, and chlorine content. Samples were collected every third to twelfth fuel shipment in each month of 1999, depending on the statistical characteristics of initial analysis results for each boiler unit. Either the coal shipper or the power plant operator could take the sample if the samples were collected at a point after any coal cleaning had been completed. Thus, "as-shipped" or "as-received" coals are considered to be equivalent to "as-fired" coals, and Hg analyses from such samples are assumed to represent the quantity of Hg entering the boiler.

In 1999, a nationwide total of approximately 786 million tons of coal and supplemental fuels were burned in coal-fired electric utility boilers that met the CAA Section 112(a) definition of an electric utility steam generating unit (i.e., boiler units of more than 25 megawatts that serve a generator that produces electricity for sale). Table 2-5 shows the nationwide distribution of the coal burned by rank as reported by the respondents to the EPA ICR (i.e., the power plant owners and operators).

Most electric utility power plants burn either bituminous or subbituminous coals. Half of the coals burned by the electric utility industry in 1999 were bituminous coal (52 percent of the total nationwide tonnage). Approximately one-third of the coals burned were subbituminous coals (36.5 percent of the total nationwide tonnage). Some power plants reported burning both bituminous and subbituminous coals. At most of these facilities, the two coal types are blended together before firing in the boiler unit. A few of the facilities switch between the two coal types for firing in the boiler unit to address site-specific circumstances. The vast majority of the bituminous or subbituminous coals were supplied from mines in the United States. However, imported coals were burned in 1999 at a few power plant locations. Ten plants, located near Gulf of Mexico or Atlantic Ocean seaports, imported bituminous coal from South America and three plants located in Hawaii and Florida imported subbituminous coal from Indonesia.

In general, the burning of lignite or anthracite coals by electric utilities is limited to those power plants that are located near the mines supplying the coal. Lignite accounted for approximately 6.5 percent of the total coal tonnage burned at electric utility power plants in 1999. A total of 17 electric utility power plants reported burning lignite. All of these facilities are located near the coal deposits from which the lignite is mined in Texas, Louisiana, Montana, or North Dakota. Similarly, burning of anthracite coal in 1999 was limited to a few power plants located close to the anthracite coal mines in eastern Pennsylvania. The coal-fired electric utility boilers at these facilities burned either newly mined anthracite coal or waste anthracite coal reclaimed from mine waste piles.

Table 2-5 also shows that small amounts of supplemental fuels (e.g., petroleum coke or tire derived fuel [TDF] chips) also were co-fired with coal in some coal-fired electric utility

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Table 2-5. Nationwide quantities of coals and supplemental fuels burned in coal-fired electric utility boilers for the year 1999 as reported in the Part II EPA ICR data (source: Reference 10).

Fuel Type	Total Tonnage Burned (million tons)	Percentage by Weight
Bituminous coal	406	51.7%
Subbituminous coal	287	36.5%
Lignite	51	6.5%
Bituminous/subbituminous coal mixture	24	3.0%
Bituminous coal/petroleum coke mixture	6	0.7%
Waste anthracite coal	5	0.6%
Waste bituminous coal	4	0.5%
Petroleum coke	2	0.3%
Other (a)	1	< 0.2%
Total	786	100%

(a) Mixes of anthracite, bituminous, and waste bituminous fuel, tires, subbituminous coal and petroleum coke, or waste subbituminous coal.

boilers. At these facilities, the supplemental fuels are mixed with coal before firing in the boiler unit. These supplemental fuels typically have heating values higher than that of coal and serve to boost the overall heating value of the fuel mix burned in the boiler unit. Less than 0.5 percent of the total fuel tonnage burned in 1999 consisted of supplemental fuels.

Selected properties of the coal and supplemental fuel burned nationwide in coal-fired electric utility boilers in 1999, as reported in the EPA ICR Part II data, are summarized by fuel type in Appendix A. Table 2-6 presents a summary of the Hg content data reported for the coals and supplemental fuels as fired in the boiler units. The EPA ICR data do not identify the coal resource regions from which the coal burned in a given boiler unit was mined. However, consistent with the Hg content data for as-mined coals presented in Table 2-2, the data presented in Table 2-6 indicate that there is no general relationship between coal rank and Hg content of the coal. For bituminous, subbituminous, and lignite coals, the Hg concentrations reported in the EPA ICR data ranged from trace amounts to upper levels of approximately 1 ppm.

A review of the EPA ICR data suggests that there is no direct correlation between the sulfur content of a coal and its Hg content. In other words, "high" sulfur coals are not necessarily "high" Hg coals. Trace concentrations of Hg were reported for coals with high-sulfur contents. Conversely, Hg concentrations at the upper end of the concentration ranges also were reported for high sulfur-content coals. This observation is consistent with previous studies of the Hg content in coal based on a much smaller database. For example, an earlier study comparing the sulfur and Hg concentrations in 153 samples of coal shipments found no relationship between the sulfur and Hg concentrations in these coals.[14]

Table 2-6. Mercury content of as-fired coals and supplemental fuels burned in coal-fired electric utility boilers for the year 1999 as reported in the Part II EPA ICR data (source: Reference 10).

Fuel Type	Number of Samples Analyzed	Hg Concentration (ppm dry)		Hg Content by Fuel Heating Value (lb Hg per 10^12 Btu)	
		Range	Mean	Range	Mean
Bituminous coal	27,793	0.0 - 1.3	0.11	0.07 - 103.81	8.61
South American bituminous coal (a)	270	0.01 - 0.42	0.08	0.70 - 31.06	5.52
Subbituminous coal	8,180	0.008 - 0.9	0.07	0.66 - 71.02	5.75
Indonesian subbituminous coal (b)	78	0.02 - 0.1	0.03	1.54 - 9.23	2.70
Lignite coal	1,047	0.02 - 0.75	0.11	1.84 - 75.06	10.80
Anthracite coal	65	0.06 - 0.23	0.14	5.02 - 17.49	11.36
Waste anthracite coal	426	0.04 - 0.54	0.19	8.39 - 4.73	28.55
Waste bituminous coal	572	0.03 - 1.18	0.46	2.47 - 172.92	60.79
Waste subbituminous coal	53	0.07 - 0.35	0.12	5.81 - 30.35	11.42
Petroleum coke	1,150	0.0009 - 0.5	0.05	0.06 - 32.16	3.30
Tire-derived fuel	149	0.01 - 0.33	0.056	0.60 - 19.89	3.72

(a) Bituminous coal imported from South America and burned at 10 power plants.
(b) Subbituminous coal imported from Indonesia and burned at three power plants in Hawaii and Florida.

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Chapter 3
Criteria Air Pollutant Emission Controls for
Coal-fired Electric Utility Boilers

3.1 Introduction

The EPA uses "criteria pollutants" as indicators of ambient air quality. For each criteria air pollutant, the EPA has established maximum concentrations for specific exposure periods above which adverse effects on human health may occur. Under authority of the CAA, these threshold concentrations for the criteria air pollutants are codified as the national ambient air quality standards (NAAQS). The EPA has set NAAQS for six criteria air pollutants: carbon monoxide (CO), lead (Pb), nitrogen dioxide (NO_2), ozone (O_3), particulate matter (PM), and sulfur dioxide (SO_2).

Estimates of national emissions for criteria air pollutants prepared by the EPA show that electric utility power plants that burn coal are significant emission sources of SO_2, nitrogen oxides (NO_x), and PM.[1] Electric utility power plants are the Nation's largest source of SO_2 emissions, contributing approximately 68 percent of the estimated total national SO_2 emissions in 1998 (most recent year for which national estimates are available). Over 90 percent of these SO_2 emissions are coal-fired electric utility boilers. Electric utilities contributed 25 percent of total national NO_x emissions in 1998. Again coal combustion is the predominant source of NO_x emissions from the electric utilities (almost 90 percent of the estimated NO_x emissions). Coal-fired electric utility power plants also are one of the largest industrial sources of PM emissions. In general, the high combustion efficiencies achieved by coal-fired electric utility boilers result in low emissions of CO and volatile organic compounds (a precursor for the photochemical formation of ozone in the atmosphere). Lead is listed as a HAP in addition to being listed as a criteria air pollutant. Lead emissions from electric utility boilers were evaluated as part of EPA's report to Congress on HAP emissions from electric utility power plants (discussed in Section 1.4.1).[2] The EPA found that electric utility boilers contribute a very small percentage of the nationwide Pb emissions.

All coal-fired electric utility power plants in the United States use control devices to reduce PM emissions. Many coal-fired electric utility boilers also are required to use controls for SO_2 and NO_x emissions depending on site-specific factors such as the properties of the coal burned, when the power plant was built, and the area where the power plant is located. As discussed in Chapter 6, certain control technologies used to reduce criteria air pollutant

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emissions from coal-fired electric utility boilers also remove some of the mercury (Hg) from the flue gas. In addition, the existing control configuration used for a given coal-fired electric utility boiler to meet criteria air pollutant emissions standards directly can affect the applicability, performance, and costs of retrofitting additional Hg controls to the unit.

The purpose of this chapter is to present a summary review of the different control technologies currently used by coal-fired electric utility boilers to meet the applicable criteria air pollutant emissions standards. The nationwide distribution of control configurations used at coal-fired electric utility power plants to comply with these standards is presented using information from the EPA ICR database. The impact or influence of these control configurations on control of Hg emissions is discussed in the Chapter 6.

3.2 Criteria Air Pollutants of Concern from Coal Combustion

3.2.1 Particulate Matter[3,4]

Dust, dirt, soot, smoke, and liquid droplets are directly emitted into the air from anthropogenic sources as well as natural sources such as forest fires and windblown dust. This type of PM sometimes is called "primary particulate matter." In addition, gaseous air pollutants (e.g., sulfur dioxide, nitrogen oxides, and volatile organic compounds) are considered to be PM precursors causing "secondary particulate matter" through complex transformations that occur in the ambient environment. Human exposure to concentrations of PM at various levels results in effects on breathing and respiratory symptoms, aggravation of existing respiratory and cardiovascular disease, alterations in the body's defense systems against foreign materials, damage to lung tissue, carcinogenesis, and premature death. The people most sensitive to the effects of PM include individuals with chronic obstructive pulmonary or cardiovascular disease or influenza, asthmatics, the elderly, and children. Particulate matter also contributes to visibility impairment in the United States.

Primary PM emissions from coal-fired electric utility boilers consist primarily of fly ash. Ash is the unburned carbon char and the mineral portion of combusted coal. The amount of ash in the coal, which ultimately exits the boiler unit as fly ash, is a complex function of the coal properties, furnace-firing configuration, and boiler operation. For the dry-bottom, pulverized-coal-fired boilers, approximately 80 percent of the total ash in the as-fired coal will exit the boiler as fly ash. Wet-bottom, pulverized-coal-fired boilers emit significantly less fly ash: on the order of 50 percent of the total ash exits the boiler as fly ash. In a cyclone furnace boiler, most of the ash is retained as liquid slag; thus, the quantity of fly ash exiting the boiler is typically 20 to 30 percent of the total ash. However, the high operating temperatures unique to these designs may also promote ash vaporization and larger fractions of submicron fly ash compared to dry bottom designs. Fluidized-bed combustors emit high levels of fly ash since the coal is fired in suspension and the ash is present in dry form. Spreader-stoker-fired boilers can also emit high levels of fly ash. However, overfeed and underfeed stokers emit less fly ash than spreader stokers, since combustion takes place in a relatively quiescent fuel bed.

In addition to the fly ash, PM emissions from a coal-fired electric utility power plant result from reactions of the SO_2 and NO_x compounds as well as unburned carbon particles carried in the flue gas from the boiler. The SO_2 and NO_x compounds are initially in the vapor phase following coal combustion in the furnace chamber but can partially chemically transform in the stack, or near plume, to form fine PM in the form of nitrates, sulfur trioxide (SO_3), and sulfates. Firing configuration and boiler operation can affect the fraction of carbon (from unburned coal) contained in the fly ash. In general, the high combustion efficiencies achieved by pulverized-coal-fired boilers and cyclone-fired boilers result in relatively small amounts of unburned carbon particles in the exiting combustion gases. Those pulverized-coal-fired electric utility boilers that use special burners for NO_x control (discussed in Section 3.7) tend to burn coal less completely; consequently, these furnaces tend to emit a higher fraction of unburned carbon in the combustion gases exiting the furnace.

Another potential source of PM in the flue gas from a coal-fired electric utility boiler is the use of a dry sorbent-based control technology. Solid sorbent particles are injected into the combustion gases to react with the air pollutants and then recaptured by a downstream control device. Sorbent particles that escape capture by the control device are emitted as PM to the atmosphere. Control technologies using sorbent injection are discussed in Chapter 7.

3.2.2 Sulfur Dioxide [3,4]

Exposure of people to SO_2 concentrations above threshold levels affects their breathing and may aggravate existing respiratory and cardiovascular disease. Sensitive populations include asthmatics, individuals with bronchitis or emphysema, children, and the elderly. Sulfur dioxide is also a primary contributor to acid deposition, or acid rain, which causes acidification of lakes and streams and can damage trees, crops, historic buildings, and statues. In addition, SO_x compounds in the air contribute to visibility impairment. In the United States, SO_2 is primarily emitted from the combustion of fossil fuels and by metallurgical processes.

Coal deposits contain sulfur in amounts ranging from trace quantities to as high as eight percent or more. Most of this sulfur is present as either pyritic sulfur (sulfur combined with iron in the form of a mineral that occurs in the coal deposit) or organic sulfur (sulfur combined directly in the coal structure). During combustion, sulfur compounds in coal are oxidized to gaseous SO_2 or SO_3. When firing bituminous coal, almost all of the sulfur present in coal will be emitted as gaseous sulfur oxides (on average 98 percent). The more alkaline nature of ash in some subbituminous coals causes a portion of the sulfur in the coal to react to form various sulfate salts; these salts are emitted as fly ash or retained in the boiler bottom ash. Generally, the percentage of sulfur in the as-fired coal that is converted to sulfur oxides during combustion does not vary with the utility boiler design or operation.

3.2.3 Nitrogen Oxides [4,5]

Nitrogen dioxide (NO_2) is a highly reactive gas. The major mechanism for the formation of NO_2 in the atmosphere is the oxidation of nitric oxide (NO) when exposed to solar radiation.

These two chemical species are collectively referred to as nitrogen oxides (NO_x). Exposure of people to NO_2 can irritate the lungs, cause bronchitis and pneumonia, and lower resistance to respiratory infections. Nitrogen oxides are an important precursor together with volatile organic compounds in the photochemical formation of ozone in the atmosphere. Ozone is a criteria pollutant and the major component of smog. Nitrogen dioxide is also a primary contributor to acid rain. The major NO_x emissions sources are transportation vehicles and stationary combustion units.

Both NO and NO_2 are formed during coal combustion by oxidation of molecular nitrogen that is present in the combustion air or nitrogen compounds contained in the coal. Overall, total NO_x formed during combustion is composed predominantly of NO mixed with small quantities of NO_2 (typically less than 10 percent of the total NO_x formed). However, once NO formed during coal combustion is emitted to the atmosphere, the NO is oxidized to NO_2.

The NO_x formed during coal combustion by oxidation of molecular nitrogen (N_2) in the combustion air is referred to as "thermal NO_x." The oxidation reactions converting N_2 to NO and NO_2 become very rapid once gas temperatures rise above 1,700 °C (3,100 °F). Formation of thermal NO_x in a coal-fired electric utility boiler is dependent on two conditions occurring simultaneously in the combustion zone: high temperature and an excess of combustion air. A boiler design feature or operating practice that increases the gas temperature above 1,700 °C, the gas residence time at these temperatures, and the quantity of excess combustion air will affect thermal NO_x formation. The formation of NO_x by oxidation of nitrogen compounds contained in the coal is referred to as "fuel NO_x." The nitrogen content in most coals ranges from approximately 0.5 to 2 percent. The amount of nitrogen available in the coal is relatively small compared with the amount of nitrogen available in the combustion air. However, depending on the combustion conditions, significant quantities of fuel NO_x can be formed during coal combustion.

3.3 Existing Control Strategies Used for Coal-fired Electric Utility Boilers

Electric utilities must comply with applicable Federal standards and programs that specifically regulate criteria air emissions from coal-fired electric utility boilers. These regulations and programs include New Source Performance Standards (NSPS), the CAA Title IV Acid Rain Program, and the CAA Title V Operating Permits Program. The EPA has delegated authority to individual state and local agencies for implementing many of these regulatory requirements. In addition, individual states have established their own standards and requirements for those power plants that operate within their jurisdictions. Electric utility companies use one or a combination of the following three control strategies to comply with the specific set of requirements applicable to a given coal-fired boiler.

Pre-combustion Controls. Control measures in which fuel substitutions are made or fuel pre-processing is performed to reduce pollutant formation in the combustion unit.

Combustion Controls. Control measures in which operating and equipment modifications are made to reduce the amount of pollutants formed during the combustion process; or in which a material is introduced into the combustion unit along with the fuel to capture the pollutants formed before the combustion gases exit the unit.

Post-combustion Controls: Control measures in which one or more air pollution control devices are used at a point downstream of the furnace combustion zone to remove the pollutants from the post-combustion gases.

Table 3-1 shows the distribution of emissions control strategies for PM, SO_2, and NO_x used for coal-fired electric utility boilers in 1999 as reported in the Part II EPA ICR data.[6] All coal-fired electric utility boilers in the United States are controlled for PM emissions by using some type of post-combustion controls. These particulate emission control types are discussed in Section 3.4. Approximately two-thirds of the total coal-fired electric utility boilers use add-on controls for SO_2 emissions. Most of these controlled units use either a pre-combustion or a post-combustion control strategy for SO_2 emissions. The methods used for controlling SO_2 emissions from coal-fired electric utility boilers are discussed in Section 3.5. Although approximately two-thirds of the coal-fired electric utility boilers are controlled for NO_x emissions, these units are not necessarily the same units controlled for SO_2 emissions. The predominant strategy for controlling NO_x emissions is to use combustion controls. Section 3.6 discusses the application of NO_x emission controls to coal-fired electric utility boilers.

3.4 Particulate Matter Emission Controls

Four types of control devices are used to collect PM emissions from coal-fired electric utility boilers: electrostatic precipitators, fabric filters, mechanical collectors, and particle scrubbers. Table 3-2 presents the 1999 nationwide distribution of PM controls on coal-fired electric utility boilers by total number of units and by percentage of nationwide electricity generating capacity. Electrostatic precipitators are the predominant control type used on coal-fired electric utility boilers both in terms of number of units (84 percent) and total generating capacity (87 percent). The second most common control device type used is a fabric filter. Fabric filters are used on about 14 percent of the coal-fired electric utility boilers. Particle scrubbers are used on approximately three percent of the boilers. The least used control device type is a mechanical collector. Less than one percent of the coal-fired electric utility boilers use this type of control device as the sole PM control. Other boilers equipped with a mechanical collector use this control device in combination with one of the other PM control device types.

3.4.1 Electrostatic Precipitators [4,7]

Electrostatic precipitator (ESP) control devices have been used to control PM emissions for over 80 years. These devices can be designed to achieve high PM collection efficiencies (greater than 99 percent), but at the cost of increased unit size. An ESP operates by imparting an electrical charge to incoming particles, and then attracting the particles to oppositely charged

Table 3-1. Criteria air pollutant emission control strategies as applied to coal-fired electric utility boilers in the United States for the year 1999 as reported in the Part II EPA ICR data (source: Reference 6).

Criteria Air Pollutant	Percentage of Coal-fired Electric Utility Boilers Using Control Strategy as Reported in Phase II EPA ICR Data [a,b]			
	Meet Applicable Standards Without Additional Controls	Pre-combustion Controls	Combustion Controls	Post-combustion Controls
Particulate matter	0 %	0 %	0 %	100 %
Sulfur dioxide	37 %	40 %	3 %	20 %
Nitrogen oxides	40 %	0 %	57 %	3 %

(a) Approximately 1.5 % of the boilers use a combination of pre-combustion and post-combustion SO_2 controls.

(b) Approximately 1% of the boilers using post-combustion NO_x controls also use some type of combustion controls.

Table 3-2. Nationwide distribution of existing PM emission controls used for coal-fired electric utility boilers for the year 1999 as reported in the Part II EPA ICR data (source: Reference 6).

PM Control Type	Abbreviation Code	Phase II EPA ICR Data		
		Number of Boilers	Percent of Nationwide Total Number of Units	Percent of Nationwide Electricity Generating Capacity
Electrostatic precipitator (Cold-side)	CS- ESP	822 (a)	72.1 %	74.7 %
Electrostatic precipitator (Hot-side)	HS-ESP	122	10.8 %	11.3 %
Fabric filter	FF	155 (b)	13.6 %	9.4 %
Particle scrubber	PS	23 (c)	2.0%	3.0 %
Mechanical collector (d)	MC	5	0.4 %	0.2 %
Multiple control device combinations (e)		13	1.1 %	1.4 %
Nationwide Total		1,140 (f)	100 %	100 %

(a) Includes 10 boilers with cold-side ESP in combination with upstream mechanical collector.
(b) Includes eight boilers with baghouse in combination with upstream mechanical collector.
(c) Includes two boilers with particle scrubber in combination with upstream mechanical collector.
(d) Boilers using mechanical collector as only PM control device.
(e) Boilers using a combination of two or more different control device types other than mechanical collectors. Includes two boilers that use a hot-side ESP in series with a cold-side ESP.
(f) Does not include the three IGCC units.

metal plates for collection. Periodically, the particles collected on the plates are dislodged in sheets or agglomerates (by rapping the plates) and fall into a collection hopper. The dust collected in the ESP hopper is a solid waste that must be disposed of.

The effectiveness of particle capture in an ESP depends largely on the electrical resistivity of the particles being collected. An optimum value exists for a given ash. Above and below this value, particles become less effectively charged and collected. Table 3-3 presents the PM collection efficiency of an ESP compared with the other control device types. Coal that contains a moderate to high amount of sulfur (more than approximately three percent) produces an easily collected fly ash. Low-sulfur coal produces a high-resistivity fly ash that is more difficult to collect. Resistivity of the fly ash can be changed by operating the boiler at a different temperature or by conditioning the particles upstream of the ESP with sulfur trioxide, sulfuric acid, water, sodium, or ammonia. In addition, collection efficiency is not uniform for all particle sizes. For coal fly ash, particles larger than about 1 to 8 μm and smaller than about 0.3 μm (as opposed to total PM) are typically collected with efficiencies from 95 to 99.9 percent. Particles near the 0.3 μm size are in a poor charging region that reduces collection efficiency to 80 to 95 percent.

An ESP can be used at one of two locations in a coal-fired electric utility boiler system. For many years, every ESP was installed downstream of the air heater where the temperature of the flue gas is between 130 and 180 °C (270 and 350 °F). An ESP installed at this location is referred is as a "cold-side" ESP. However, to meet SO_2 emission requirements, many electric utilities switched to burning low-sulfur coal (discussed in the Section 3.5.1). These coals have higher electrical ash resistivities, making the fly ash more difficult to capture downstream of the air heater. Therefore, to take advantage of the lower fly-ash resistivities at higher temperatures, some ESPs are installed upstream of the air heater, where the temperature of the flue gas is in the range of 315 to 400 °C (600 to 750 °F). An ESP installed upstream of the air heater is referred to as a "hot-side" ESP.

3.4.2 Fabric Filters[4,8]

Fabric filters (FF) have been used for fly ash control from coal-fired electric utility boilers for about 30 years. This type of control device collects fly ash in the combustion gas stream by passing the gases through a porous fabric material. The buildup of solid particles on the fabric surface forms a thin, porous layer of solids or a filter, which further acts as a filtration medium. Gases pass through this cake/fabric filter, but the fly ash is trapped on the cake surface. The fabric material used is typically fabricated in the shape of long, cylindrical bags. Hence, fabric filters also are frequently referred to as "baghouses."

Gas flow through a FF becomes excessively restricted if the filter cake on the bags becomes too thick. Therefore, the dust collected on the bags must be removed periodically. The type of mechanism used to remove the filter cake classifies FF design types. Depending on the FF design type, the dust particles will be collected either on the inside or outside of the bag. For designs in which the dust is collected on the inside of the bags, the dust is removed by either

Table 3-3. Comparison of PM collection efficiencies for different PM control device types (source: Reference 4)

PM Control Type	Representative PM Mass Collection Efficiency Range	
	Total PM	PM less than 0.3 μm
Electrostatic precipitator (Cold-side)	99 to 99.7 %	80 to 95 %
Electrostatic precipitator (Hot-side)	99 to 99.7 %	80 to 95 %
Fabric filter	99 to 99.9 %	99 to 99.8%
Particle scrubber	95 to 99 %	30 to 85 %
Mechanical collector	70 to 90 %	0 to 15 %

mechanically shaking the bag (called a "shaker type" FF) or by blowing air through the bag from the opposite side (called a "reverse-air" FF). An alternate design mounts the bags over internal frame structures, called "cages" to allow collection of the dust on the outside of the bags. A pulsed jet of compressed air is used to cause a sudden stretching then contraction of the bag fabric dislodging the filter cake from the bag. This design is referred to as a "pulse-jet" FF. The dislodged dust particles fall into a hopper at the bottom of the baghouse. The dust collected in the hopper is a solid waste that must be disposed of.

An FF must be designed and operated carefully to ensure that the bags inside the collector are not damaged or destroyed by adverse operating conditions. The fabric material must be compatible with the gas stream temperatures and chemical composition. Because of the temperature limitations of the available bag fabrics, location of an FF for use in a coal-fired electric utility boiler is restricted to downstream of the air heater. In general, fabric filtration is the best commercially available PM control technology for high-efficiency collection of small particles (see Table 3-3).

Electrostatic stimulation of fabric filtration (ESFF) involves a modified fabric filter that uses electrostatic charging of incoming dust particles to increase collection efficiency and reduce pressure drop compared to fabric filters without charging. Filter bags are specially made to include wires or conductive threads, which produce an electrical field parallel to the fabric surface. Conductors can also be placed as a single wire in the center of the bag. When the bags are mounted in the baghouse, the conductors are attached to a wiring harness that supplies electricity. As particles enter the field and are charged, they form a porous mass or cake of agglomerates at the fabric surface. Greater porosity of the cake reduces pressure drop, while the agglomeration increases efficiency of small particle collection. Cleaning is required less frequently, resulting in longer bag life. For felted or nonwoven bags, the field promotes collection on the outer surface of the fabric, which also promotes longer bag life. Filtration velocity can be increased so that less fabric area is required in the baghouse. The amount of reduction is based on an economic balance among desired performance, capital cost, and operating costs. A number of variations exist on the ESFF idea of combining particle charging with fabric filtration.

The University of North Dakota, Energy and Environmental Research Center (UND/EERC) has developed another type of combined control device called the Advanced Hybrid Collector (AHC).[9] A charging (and collection) section can also be placed ahead of the bags in a fabric filter. This approach is used in the AHC along with the use of membrane fabrics (woven or felted fabrics having a membrane laminated to the filtration surface of the fabric). The membrane is typically polytetrafluoroethylene (PTFE). With about 90 percent of the mass of particles collected in the electrostatic charging and collection section of the AHC, the load on the fabric filter part of the system is much reduced. With a membrane fabric for the bags, it is likely that filtration velocity can be increased significantly.

3.4.3 Particle Scrubbers[4]

Particle scrubbers operate by shattering streams of water into small droplets that collide with and trap solid particles contained in the flue gas or by forcing the gases into intimate contact with water films. The particle-laden droplets or water films coalesce and are collected in a sump at the bottom of the scrubber. The three basic types of particle scrubbers are venturi scrubbers, preformed spray scrubbers, and moving-bed scrubbers. Venturi scrubbers are the type most commonly used for coal-fired electric utility boilers. This scrubber design transports the particle-laden flue gas through a constriction where violent mixing takes place. Water is introduced either at or upstream of the constriction. Preformed spray scrubbers are usually vertical cylinders with flue gas passing upward through droplets sprayed from nozzles near the top of the unit. Moving-bed scrubbers have an upper chamber in which a bed of low-density spheres (often plastic) is irrigated by streams of water from above. Gas passing upward through the bed agitates the wetted spheres, which continually expose fresh liquid surfaces for particle transfer. Regardless of the scrubber design, all particle scrubber systems generate wastewaters from the scrubber blowdown that must be treated and discharged.

Particle scrubbers are more sensitive to particle size distribution in the flue gas than either an ESP or an FF. In general, particle scrubbers are not as effective as these other control devices at collecting small particles (see Table 3-3). Also, while a venturi particle scrubber will have a lower initial cost for a given boiler unit application than either an ESP or an FF, the high pressure drop required for the scrubber to achieve a high collection efficiency results in high operating costs. These factors, in large part, account for the low use of particle scrubbers at coal-fired utilities.

3.4.4 Mechanical Collectors[4]

Mechanical collectors are the oldest, simplest, and least efficient of the four types of PM control devices. The collectors used for utility boilers are generally in the form of groups of cylinders with conical bottoms (multicyclones). Flue gas entering the cylinder tangentially to the wall is imparted with a circular motion around the cylinder's axis. Particles in the gas stream are forced toward the wall by centrifugal force, then downward through a discharge at the bottom of the cone. Collection efficiency for a typical multicyclone can be about 70 to 75 percent for 10-μm particles, but can drop to less than 20 percent for smaller 1-μm particles. Mechanical collectors can be efficient for relatively large particles because their settling velocity is high compared to fine particles. In a cyclone, larger particles are forced through the gas stream towards the outer wall because of their mass and inertia, while small particles have insufficient mass to be much affected. Electrically charging particles tends to agglomerate them, especially small particles, with the resulting larger agglomerates having increased mass over the individual small particles. In charged mechanical collectors, a charging section is placed ahead of a mechanical collector, and collection efficiency for smaller particles is significantly increased.

3.5 SO₂ Emission Controls

Sulfur dioxide emissions from most coal-fired electric utility boilers are controlled using either of two basic approaches. The first approach is to use pre-combustion measures, namely, the firing coal that contains lower amounts of sulfur. The low-sulfur coal may be naturally occurring or the result of coal cleaning. The other approach is to remove the sulfur compounds from the flue gas before the gas is discharged to the atmosphere. These post-combustion processes are collectively called "flue gas desulfurization" or "FGD" systems. All FGD systems can be further classified as wet or dry flue gas scrubbing systems. A third control approach available for those coal-fired electric utility boilers using a fluidized-bed combustor is to burn the coal together with limestone. An FBC can be characterized as a boiler type with inherently lower SO_2 emissions. In this report, however, combustion of coal in fluidized-bed with limestone is also considered to be an SO_2 combustion control method. The SO_2 control approaches include a number of different technology subcategories that are now commercially used in the United States, Europe, or Pacific Rim countries.

Table 3-4 presents the 1999 nationwide distribution of SO_2 controls used for coal-fired electric utility boilers by total number of units and by percentage of nationwide electricity generating capacity. For approximately one-third of the boilers, no SO_2 controls were reported in the Part II EPA ICR data. The other two-thirds of the units reported using some type of control to meet the SO_2 emission standards applicable to the unit. Pre-combustion control by burning a low-sulfur content coal was reported for approximately 40 percent of the boilers. Post-combustion control devices for SO_2 removal are used for approximately 20 percent of the boilers. Wet FGD systems are the most commonly used post-combustion control technique. The newer technologies of spray dryer systems or dry injection are limited in their application to existing units. The remaining 3 percent of the boilers use fluidized-bed combustion with limestone.

3.5.1 Low-sulfur Coal

A coal with sufficiently low sulfur content that when burned in the boiler meets the applicable SO_2 emission standards without the use of additional controls is sometimes referred to as "compliance coal." Coals naturally low in sulfur content may be mined directly from the ground. Alternatively, the sulfur content of coal fired in the boiler may be lowered first by cleaning the coal or blending coals obtained from several sources. However, burning low-sulfur coal may not be a technically feasible or economically practical SO_2 control alternative for all boilers. In some cases, a coal with the required sulfur content to meet the applicable standard may not be available or cannot be fired satisfactorily in a given boiler unit design. Even if such a coal is available, use of the low-sulfur coal that must be transported long distances from the mine may not be cost-competitive with burning higher sulfur coal supplied by closer mines and using a post-combustion control device.

Various coal cleaning processes may be used to reduce the sulfur content of the coal. A significant portion of the pyritic sulfur minerals mixed with the mined coal can usually be

Table 3-4. Nationwide distribution of existing SO$_2$ emissions controls used for coal-fired electric utility boilers for the year 1999 as reported in the Part II EPA ICR data (source: Reference 6).

SO$_2$ Control Type	Abbreviation Code	Phase II EPA ICR Data		
		Number of Boilers	Percent of Nationwide Total Number of Units	Percent of Nationwide Electricity Generating Capacity
Burn low-sulfur coal ("compliance coal")	LSC	455	39.9 %	38.2 %
Wet FGD system	FGD	173 (a)	15.2 %	23.8 %
Spray dryer system	SDA	52 (b)	4.6%	3.4 %
Fluidized-bed coal combustion with limestone (a)	FBC	37 (c)	3.2%	1.1 %
Dry injection	DI	2	0.2 %	< 0.1 %
No controls reported (d)		421	36.9 %	33.5 %
Nationwide Total		1,140 (e)	100 %	100 %

(a) Includes one FBC boiler unit using a wet FGD system.
(b) Includes three FBC boilers using spray dryer systems.
(c) FBC boilers using no downstream post-combustion SO$_2$ controls.
(d) Entry in ICR response indicated none or was left blank.
(e) Does not include the three IGCC units.

removed by physical gravity separation or surface property (flotation) methods. However, physical coal cleaning methods are not effective for removing the organic sulfur bound in coal. Another method of reducing the overall sulfur content of the coal burned in a given boiler unit is to blend coals with different sulfur contents to meet a desired or target sulfur level.

3.5.2 Fluidized-bed Combustion with Limestone

One of the features of FBC boilers is the capability to control SO_2 emissions during the combustion process. This is accomplished by adding finely crushed limestone to the fluidized bed. During combustion, calcination of the limestone (reduction to lime by subjecting to heat) occurs simultaneously with the oxidation of sulfur in the coal to form SO_2. The SO_2, in the presence of excess oxygen, reacts with the lime particles to form calcium sulfate. The sulfated lime particles are removed with the bottom ash or collected with the fly ash by a downstream PM control device. Fresh limestone is continuously fed to the bed to replace the reacted limestone.

3.5.3 Wet FGD Systems

The SO_2 in flue gas can be removed by reacting the sulfur compounds with a solution of water and an alkaline chemical to form insoluble salts that are removed in the scrubber effluent. These processes are called "wet FGD systems" in this report. Most wet FGD systems for control of SO_2 emissions from coal-fired electric utility boilers are based on using either limestone or lime as the alkaline source. At some of these facilities, fly ash is mixed with the limestone or lime. Several other scrubber system designs (e.g., sodium carbonate, magnesium oxide, dual alkali) are also used by a small percentage of the total number of boilers.

The basic wet limestone scrubbing process is simple and is the type most widely used for control of SO_2 emissions from coal-fired electric utility boilers. Limestone sorbent is inexpensive and generally locally available throughout the United States. In a wet limestone scrubber, the flue gas containing SO_2 is brought into contact with a limestone/water slurry. The SO_2 is absorbed into the slurry and reacts with limestone to form an insoluble sludge. The sludge, mostly calcium sulfite hemihydrate and gypsum, is disposed of in a pond specifically constructed for the purpose or is recovered as a salable byproduct.

The wet lime scrubber operates in a similar manner to the wet limestone scrubber. In a wet lime scrubber, flue gas containing SO_2 is contacted with a hydrated lime/water slurry; the SO_2 is absorbed into the slurry and reacts with hydrated lime to form an insoluble sludge. The hydrated lime provides greater alkalinity (higher pH) and reactivity than limestone. However, lime-scrubbing processes require appropriate disposal of large quantities of waste sludge.

The SO_2 removal efficiencies of existing wet limestone scrubbers range from 31 to 97 percent, with an average of 78 percent. The SO_2 removal efficiencies of existing wet lime scrubbers range from 30 to 95 percent. For both types of wet scrubbers, operating parameters affecting SO_2 removal efficiency include liquid-to-gas ratio, pH of the scrubbing medium, and the ratio of calcium sorbent to SO_2. Periodic maintenance is needed because of scaling, erosion,

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and plugging problems. Recent advancements include the use of additives or design changes to promote SO_2 absorption or to reduce scaling and precipitation problems.

3.5.4 Spray Dryer Adsorber

A spray dryer adsorber (sometimes referred to as wet-dry or semi-dry scrubbers) operates by the same principle as wet lime scrubbing, except that the flue gas is contacted with a fine mist of lime slurry instead of a bulk liquid (as in wet scrubbing). For the spray dryer absorber process, the combustion gas containing SO_2 is contacted with fine spray droplets of hydrated lime slurry in a spray dryer vessel. This vessel is located downstream of the air heater outlet where the gas temperatures are in the range of 120 to 180 °C (250 to 350 °F). The SO_2 is absorbed in the slurry and reacts with the hydrated lime reagent to form solid calcium sulfite and calcium sulfate as in a wet lime scrubber. The water is evaporated by the hot flue gas and forms dry, solid particles containing the reacted sulfur. These particles are entrained in the flue gas, along with fly ash, and are collected in a PM collection device. Most of the SO_2 removal occurs in the spray dryer vessel itself, although some additional SO_2 capture has also been observed in downstream particulate collection devices, especially fabric filters. This process produces dry reaction waste products for easy disposal.

The primary operating parameters affecting SO_2 removal are the calcium-reagent-to-sulfur stoichiometric ratio and the approach to saturation in the spray dryer. To increase overall sorbent use, the solids collected in the spray dryer and the PM collection device may be recycled. The SO_2 removal efficiencies of existing lime spray dryer systems range from 60 to 95 percent.

3.5.5 Dry Injection

For the dry injection process, dry powdered lime (or another suitable sorbent) is directly injected into the ductwork upstream of a PM control device. Some systems use spray humidification followed by dry injection. This dry process eliminates the slurry production and handling equipment required for wet scrubbers and spray dryers, and produces dry reaction waste products for easier disposal. The SO_2 is adsorbed and reacts with the powdered sorbent. The dry solids are entrained in the combustion gas stream, along with fly ash, and then collected by the PM control device. The SO_2 removal efficiencies of existing dry injection systems range from 40 to 60 percent.

3.5.6 Circulating Fluidized-bed Adsorber

In the circulating fluidized-bed adsorber (CFBA), the flue gas flows upward through a bed of sorbent particles to produce a fluid-like condition in the bed. This condition is obtained by adjusting gas flow rate sufficiently to support the particles, but not carry them out of the system. Characteristics of the bed are high heat and mass transfer, because of high mixing rates, and particle-to-gas contact. These conditions allow the CFBA's bed of sorbent particles to remove a sorbate from the gas stream with high effectiveness. In a CFBA, material is withdrawn from the bed for treatment (such as desorption) then re-injected into the bed. Currently, CFBAs

are used with limestone and ash as sorbents for SO_2 control, but they also have the capability to remove Hg from the flue gas. The SO_2 removal ranges for CFBAs from 80 to 98 percent.

3.6 NO$_x$ Emission Controls

Control techniques used to reduce NO_x formation include combustion and post-combustion control measures. Combustion measures consist of operating and equipment modifications that reduce the peak temperature and excess air in the furnace. Post-combustion control involves converting the NO_x in the flue gas to molecular nitrogen and water using either a process that requires a catalyst (selective catalytic reduction) or a process that does not use a catalyst (selective noncatalytic reduction).

Table 3-5 presents the 1999 nationwide distribution of NO_x controls used for coal-fired electric utility boilers by total number of units and by percentage of nationwide electricity generating capacity. Approximately one-third of the boilers do not use additional NO_x controls. The other two-thirds of the units use additional controls to meet the applicable NO_x standards. The predominant control NO_x strategy is to use one or more combustion control techniques. Post-combustion NO_x reduction technologies (both catalytic and noncatalytic) accounted for only a small percentage of the NO_x emission controls used in 1999 (approximately three percent of the total units). However, a number of electric utilities are considering the addition of these types of controls to their coal-fired boilers to comply with new NO_x emission control requirements.

3.6.1 Combustion Controls

A variety of combustion control practices can be used including low NO_x burners, overfire air, off-stoichiometric firing, selective or biased burner firing, reburning, and burners-out-of-service. Control of NO_X also can be achieved through staged combustion (also called air staging). With staged combustion, the primary combustion zone is fired with most of the air needed for complete combustion of the coal. The remaining air needed is introduced into the products of the partial combustion in a second combustion zone. Air staging lowers the peak flame temperature, thereby reducing thermal NO_x, and reduces the production of fuel NO_x by reducing the oxygen available for combination with the fuel nitrogen. Staged combustion may be achieved through methods that require modifying equipment or operating conditions so that a fuel-rich condition exists near the burners (e.g., using specially designed low-NO_x burners, selectively removing burners from service, or diverting a portion of the combustion air). In cyclone boilers and some other wet bottom designs, combustion occurs with a molten ash layer and the combustion gases flow to the main furnace; this design precludes the use of low NO_x burners and air staging. Low-NO_x burners may be used to lower NO_x emissions by about 25 to 55 percent. Use of overfire air (OFA) as a single NO_x control technique reduces NO_x by 15 to 50 percent. When OFA is combined with low-NO_x burners, reductions of up to 60 percent may result. The actual NO_x reduction achieved with a given combustion control technique may vary from boiler to boiler.

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Table 3-5. Nationwide distribution of existing NO$_x$ emissions controls used for coal-fired electric utility boilers for the year 1999 as reported in the Part II EPA ICR data (source: Reference 6).

NO$_x$ Control Type	Abbreviation Code	Phase II EPA ICR Data		
		Nationwide Number of Boilers	Nationwide Percentage of Boilers	Percent of Nationwide Electricity Generating Capacity
Combustion controls - low-NO$_x$ burners	CC-LNB	404	35.4 %	43.0 %
Combustion controls - low-NO$_x$ burners + overfire air	CC-LNB/OFA	84	7.4 %	10.4 %
Combustion controls - overfire air	CC-OFA	79	6.9 %	10.6 %
Other combustion controls (a)	CC	83	7.3 %	5.6 %
Selective noncatalytic reduction	SNCR	32	2.8 %	0.6 %
Selective catalytic reduction	SCR	6	0.5 %	1.3 %
No controls reported (b)		452	39.7%	28.5 %
Nationwide Total		1,140 (c)	100 %	100 %

(a) Combustion controls other than low-NO$_x$ burners or overfire air. The controls include burners-out-of service, flue gas recirculation, off-stoichiometric firing, and fluidized-bed combustion.
(b) Entry in ICR response indicated "none," "not applicable," or was left blank.
(c) Does not include the three IGCC units.

Just as the combustion air to the primary combustion zone can be reduced, part of the fuel may be diverted to create a secondary flame with fuel-rich conditions downstream of the primary combustion zone. This combustion technique is termed reburning and involves injecting 10 to 20 percent of the fuel after the primary combustion zone and completing the combustion with overfire air. The fuel injected downstream may not necessarily be the same as that used in the primary combustion zone. In most applications of reburning, the primary fuel is coal and the reburn fuel is natural gas (methane).

Other ways to reduce NO_x formation by reducing peak flame temperature include using flue gas recirculation (FGR), reducing boiler load, injecting steam or water into the primary combustion zone, and increasing spacing between burners. By using FGR to return part of the flue gas to the primary combustion zone, the flame temperature and the concentration of oxygen in the primary combustion zone are reduced.

Temperatures can also be reduced in the primary combustion zone by increasing the space between burners for greater heat transfer to heat-absorbing surfaces. Another combustion control technique involves reducing the boiler load. In this case, the formation of thermal NO_x generally decreases directly with decreases in heat release rate; however, reducing the load may cause poor air and fuel mixing and increase CO and soot emissions.

3.6.2 Selective Catalytic Reduction

The selective catalytic reduction (SCR) process uses a catalyst with ammonia gas (NH_3) to reduce the NO and NO_2 in the flue gas to molecular nitrogen and water. The ammonia gas is diluted with air or steam, and this mixture is injected into the flue gas upstream of a metal catalyst bed (composed of vanadium, titanium, platinum, or zeolite). In the reactor, the reduction reactions occur at the catalyst surface. The SCR catalyst bed reactor is usually located between the economizer outlet and air heater inlet, where temperatures range from 230 to 400 °C (450 to 750 °F).

3.6.3 Selective Noncatalytic Reduction

The selective noncatalytic reduction (SNCR) process is based on the same basic chemistry of reducing the NO and NO_2 in the flue gas to molecular nitrogen and water but does not require the use of a catalyst to prompt these reactions. Instead, the reducing agent is injected into the flue gas stream at a point where the flue gas temperature is within a very specific temperature range. Currently, two SNCR processes are commercially available: the THERMAL DeNO$_x$[7] and the NO$_x$OUT[7]. The THERMAL DeNO$_x$[7] uses ammonia gas as the reagent and requires the gas be injected where the flue gas temperature is in the range of 870 to 1090 °C (1,600 to 2,000 °F). Consequently, the ammonia gas is injected at a location upstream of the economizer. However, if the ammonia is injected above 1,090 °C (2,000 °F), the ammonia will oxidize and form more NO_x. Once the flue gas temperature drops below the optimum temperature range, the effectiveness of the process drops significantly. By adding hydrogen gas or other chemical enhancers, the reduction reactions can be sustained to temperatures down to

approximately 700 °C (1,300 °F). The NO_xOUT^7 is a similar process but uses an aqueous urea solution as the reagent in place of ammonia.

Using nitrogen-based reagents requires operators of SNCR systems to closely monitor and control the rate of reagent injection. If injection rates are too high, NO_x emissions may increase, and stack emissions of ammonia in the range of 10 to 50 ppm may also result. A portion (usually around 5 percent) of the NO reduction by SNCR systems results from transformation of NO to N_2O, which is a global warming gas.

3.7 Emission Control Configurations for Coal-fired Electric Utility Boilers

Mercury can exist in several forms in the flue gas from a coal-fired electric utility boiler (discussed in Chapter 5). The distribution of these Hg forms in the flue gas stream can be altered when reagents for post-combustion pollutant control processes are introduced into the flue gas. Also, as will be discussed in Chapter 6, some of the existing post-combustion control devices already in use at coal-fired electric utility power plants to meet PM and SO_2 emission standards also control Hg emissions with varying levels of effectiveness. Control measures can be implemented that may enhance the capture of Hg by these control devices. Other Hg control measures can be implemented in conjunction with control devices already in place at a given facility. Therefore, understanding which types of post-combustion control devices how electric utilities currently are implementing at their coal-fired power plants is useful when investigating potential Hg control measures for these facilities.

Table 3-6 presents the 1999 nationwide distribution of post-combustion control device configurations used for coal-fired electric utility boilers. For approximately 70 percent of the boilers, the only control device used downstream of the furnace is an ESP. If the unit is subject to SO_2 and/or NO_x emission limit standards, these units do burn low-sulfur coals to meet the SO_2 emission limit and use some type of NO_x combustion controls to meet the NO_x emission limit. Approximately 25 percent of the boilers use some combination of post-combustion control devices. The most common configuration used is an ESP with a downstream wet scrubber for SO_2 control. Less than 2 percent of the units use a combination of PM, SO_2, and NO_x post-combustion control devices.

Table 3-6. Nationwide distribution of post-combustion emission control configurations used for coal-fired electric utility boilers for the year 1999 as reported in the Part II EPA ICR data (source: Reference 6).

Post-combustion Control Strategy	ESP	FF	PS	MC	WS	SDA	DI	SCR	SNCR	Number of boilers	Percent of nationwide total number
Post-combustion PM controls only	✓									791	69.4%
		✓								80	7.0%
	✓	✓								6	0.5%
			✓							5	0.4%
	✓		✓							4	0.4%
				✓						2	0.2%
	✓									2 (a)	0.2%
Post-combustion PM controls and SO₂ controls	✓				✓					133	11.7%
		✓				✓				38	3.3%
			✓		✓					18	1.6%
		✓			✓					13	1.1%
	✓					✓				4	0.4%
				✓	✓					3	0.2%
	✓						✓			2	0.2%
	✓	✓			✓					1	0.1%
Post-combustion PM controls and NOₓ controls		✓							✓	12	1.0%
	✓								✓	11	0.9%
	✓							✓		1	0.1%
Post-combustion PM controls, SO₂ controls, and NOₓ controls		✓				✓			✓	6	0.5%
		✓				✓		✓		4	0.4%
		✓			✓				✓	2	0.2%
	✓				✓			✓		1	0.1%
	✓				✓				✓	1	0.1%
Total										1,140 (b)	100 %

(a) Units using hot-side ESP in series with a cold-side ESP. Counted as "multiple control device combination" in Table 3-2.
(b) Does not include the three IGCC units.

3.8 References

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Chapter 4
Measurement of Mercury

4.1 Introduction

Accurate measurements of the various forms of Hg present in flue gas from a coal-fired electric utility boiler are important: to characterize and determine facility and/or fuel-type absolute emissions, for understanding the behavior of Hg in combustion processes and combustion configurations, and to evaluate the removal efficiency of control technologies for Hg. A variety of measurement techniques, both manual and continuous monitoring, are available for measuring total Hg and select, speciated forms. It is the latter need and ability that is most critical to supporting the understanding of Hg behavior and its control.

Because of the importance of these measurements, particularly speciated Hg measurements, research on Hg measurement techniques and performance is an integral component of the overall Hg control research strategy. The science of speciated Hg measurements from coal-fired electric utility boilers has only recently been investigated, with the majority of research on the subject occurring within the last 5 years. This research has examined the development and performance of both manual and continuous emission monitor measurements. Much of this work began with examining and understanding measurement performance under very controlled and simplistic conditions, primarily through the use of blended gases in a laboratory setting. This afforded the ability to investigate specific measurement variables and issues individually. Based on this knowledge, experimentation expanded to pilot-scale combustion systems where gases/Hg species of interest could be doped into the combustion system, and measurement performance characterized. Though still simplistic, this approach results in a measurement environment that more closely represents real-world measurement scenarios. Ultimately, investigations moved to pilot-scale coal combustion test units, and finally to full-scale, field applications. At each step, the measurement complexity increases. The complexities associated with the combustion of different coal types, relative amounts of coal combustion emissions (e.g., SO_x, NO_x, HCl, Cl_2, PM), and pollution control device availability and configuration all have an impact on the ability to perform quality Hg measurements.[1]

The purpose of this chapter is to provide an understanding of the principles, applications, and limitations of Hg measurement methodologies, particularly with respect to understanding and interpreting the Part III EPA ICR data. This chapter also serves to introduce principles and

issues related to Hg CEMs and their use as a valuable research tool. The following sections provide a summary of the approaches and state-of-the art of manual and continuous emission measurement methods and issues associated with performing Hg measurements from coal-fired electric utility boilers.

4.2 Manual Methods for Hg Measurements

Manual methods are well established for measuring total Hg emissions from a variety of combustion sources. The EPA Method 101A[2] and Method 29[3] were developed to measure total Hg emissions (particulate phase and gas phase) from combustion sources such as sewage sludge incinerators and municipal waste combustors. These reference methods were developed and used to support total Hg regulatory needs. A reference method for speciated Hg measurement does not exist, essentially because there are no regulations requiring speciated Hg emissions measurements. However, a valid, accepted methodology was needed to characterize the emissions from coal-fired electric utility power plants to better assess the contribution from this category as well as potential risk. The Ontario-Hydro Method[4] (called the OH Method in this report) presently is the method of choice for measuring Hg species in the flue gas from coal-fired electric utility plants. This method has been submitted to the American Society for Testing and Materials (ASTM) for acceptance as a standard reference method.[1] The Hg emission data collected for the Part III EPA ICR were measured using the OH Method.

Generally, all sampling trains consist of the same sampling components: a nozzle and probe operated isokinetically for extracting a representative sample from the stack or duct, a filter to collect particulate matter, and a liquid solution and/or reagent to capture gas-phase Hg. After sampling, the filter and sorption media are prepared and analyzed for Hg in a laboratory. Figure 4-1 shows a diagram of the sampling train used for the OH Method.

Several of the manual methods, including the OH Method, being developed for speciated Hg measurements from combustion sources have been adapted/modified from accepted test methods for measuring total Hg. Measurement of total Hg is based on the concept that all forms of gaseous Hg can be captured with a strong oxidizing solution such as potassium permanganate. The speciation is accomplished relying on the solubility and insolubility of the gaseous Hg species. To speciate gaseous Hg into the oxidized Hg (Hg^{2+}) and elemental Hg (Hg^0) forms, multiple solutions/reagents are used. The Hg^{2+} form is considered to be readily soluble in aqueous solutions, while Hg^0 is essentially insoluble.[1] When the aqueous solutions are positioned immediately after the filter, the Hg^{2+} is captured and the Hg^0 passes through to the oxidizing solution where it is then captured. These solutions are analyzed separately to determine the distribution of oxidized and Hg^0 within the sampling train. Table 4-1 presents a comparison of the different manual test methods, their configuration, and the solutions used that have been investigated for measuring speciated Hg.

The OH Method, along with the other test methods listed in Table 4-1, were thoroughly evaluated to determine their appropriateness for performing speciated Hg measurements from
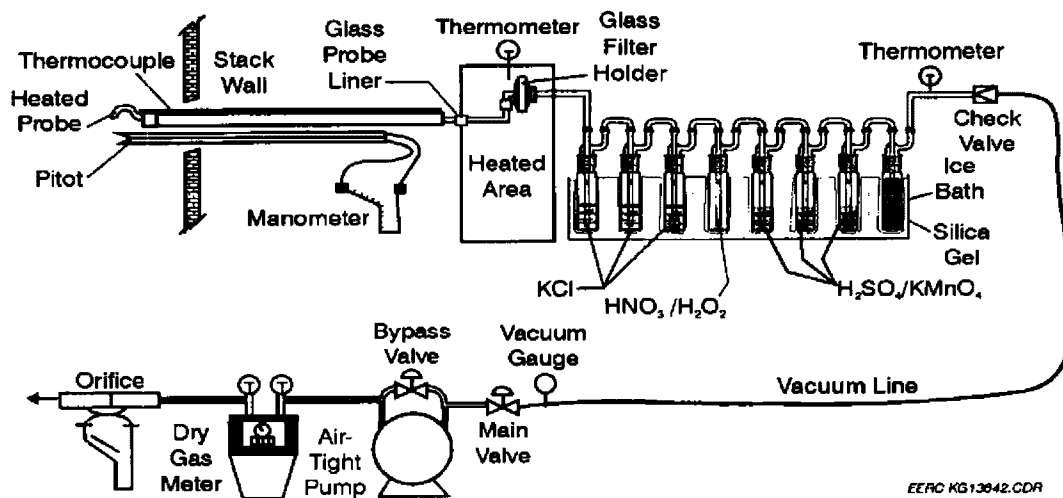
Figure 4-1. Diagram of sampling train for Ontario-Hydro Method (source: Reference 4).

Table 4-1. Summary of selected manual test methods evaluated for measurement of Hg in combustion gases.

Manual Test Method	Sampling Train Configuration		Impinger Configuration (number of impingers - impinger set solution)			Analytical Method
	Front-half collection (PM and Hg$_p$)	Back-half collection (gaseous Hg)	First Set	Second Set	Third Set	
EPA Method 29	glass fiber filter	impinger solutions	2 HNO$_3$-H$_2$O$_2$	1 dry	2 H$_2$SO$_4$-KMnO$_4$	CVAA[b]
EPA Method 101A[a]	glass fiber filter	impinger solutions	3 H$_2$SO$_4$-KMnO$_4$	none used	none used	CVAA
EPA Method 101B (draft)	glass fiber filter	impinger solutions	2 deionized water	1 HNO$_3$-H$_2$O$_2$	2 H$_2$SO$_4$-KMnO$_4$	CVAA
Ontario-Hydro Method	glass fiber filter	impinger solutions	3 KCl	1 HNO$_3$-H$_2$O$_2$	3 H$_2$SO$_4$-KMnO$_4$	CVAA
Tris-Buffer Method	glass fiber filter	impinger solutions	2 tris solution[c]	2 H$_2$SO$_4$-KMnO$_4$	none used	CVAA
MESA Method	glass wool[d]	sorbent beds	2 KCl-soda lime	2 iodated carbon	none used	CVAFS[e]

a. Test method developed and validated by EPA for measuring Hg emissions from chlor-alkali plants.
b. CVAA = Cold-vapor atomic absorption.
c. Tris solution is tris(hydroxymethyl) aminomethane in a solution of ethylenediaminetetraacetic acid in water.
d. Glass wool is only used to trap particulate matter and prevent its carry-over to the sorbent beds. The glass fiber filter in the other test methods is used to collect and quantitate particulate matter.
e. CVAFS = Cold-vapor atomic fluorescence spectrometry.

coal-fired combustion sources.[1] The University of North Dakota, Energy and Environmental Research Center (UND/EERC) performed a thorough, parametric evaluation of these methods under a variety of laboratory and pilot-scale test conditions, including the combustion of multiple, representative coal varieties. A detailed presentation of these tests and their results are contained in two comprehensive reports.[1,5]

Initial experimental work focused on EPA Method 29. These results indicated that Method 29 exhibited speciation measurement biases under some conditions.[1] The testing expanded to include the Mercury Speciation Adsorption (MESA) Method, Tris-Buffer Method, draft EPA Method 101B, and OH Method.[1] Pilot-scale coal combustion experiments were then performed in conjunction with the dynamic spiking of Hg^0 or mercuric chloride into the duct at various locations within the post-combustion facility. Samples by the respective methods were collected at sampling locations both upstream and downstream of particulate control systems. These tests were used to isolate the most appropriate methods for further, more definitive testing.

It was during the initial dynamic Hg spiking tests that effects from fly ash on the quality of speciated measurements were observed. Speciated Hg measurements using the OH Method and Tris-Buffer Method where the gas sampling and dynamic spiking of Hg^0 took place at the inlet and outlet of the PM control device indicated that significant oxidation of the Hg^0 occurred as a result of reactivity with the coal fly ash (see Figures 4-2 and 4-3).

The effects of PM on Hg speciation can be significant, particularly at sampling locations upstream of PM control devices. The flue gas upstream of a PM control device contains a high concentration of PM (relative to flue gas downstream of a PM control device). When sampling takes place upstream of a PM control device, the sampling train filter has the potential to collect a high loading of fly ash (due to the high concentration of PM in the flue gas). The speciated Hg measurement can be biased in two ways. The fly ash on the filter can adsorb gaseous Hg from the flue gas as it passes through the filter. Reactive fly ashes can also oxidize gaseous Hg^0 entering the filter. When adsorption and/or oxidation occur across the filter, they alter the distribution of total Hg and/or gaseous Hg measured. For example, if particles on the filter adsorb gaseous Hg, the filter will contain a greater amount of Hg_p than if no adsorption had taken place; in this case, the sampling-train method will overestimate the amount of Hg_p in the flue gas and underestimate the gaseous Hg, thus, the total distribution of Hg will be altered. Alternatively, fly ash on the filter can oxidize gaseous Hg^0 to Hg^{2+} (without adsorption) overestimating the amount of Hg^{2+} in the flue gas. Thus, the distribution of gaseous Hg will be altered. The rates of these transformations are dependent on the properties of the coal and resulting fly ash, the amount of fly ash, the temperature, the flue gas composition, and the sampling duration. As a result, the magnitude of these biases varies significantly and cannot be uniformly assessed. It is for this reason, that ICR measurements performed at the inlet of PM control systems possess a large degree of uncertainty. A more detailed discussion of the implications of fly ash speciation biases on the ICR data is presented in Chapter 6.

A final series of pilot-scale tests were conducted to more definitively evaluate the two most promising methods identified as a result of the initial dynamic spiking experiments
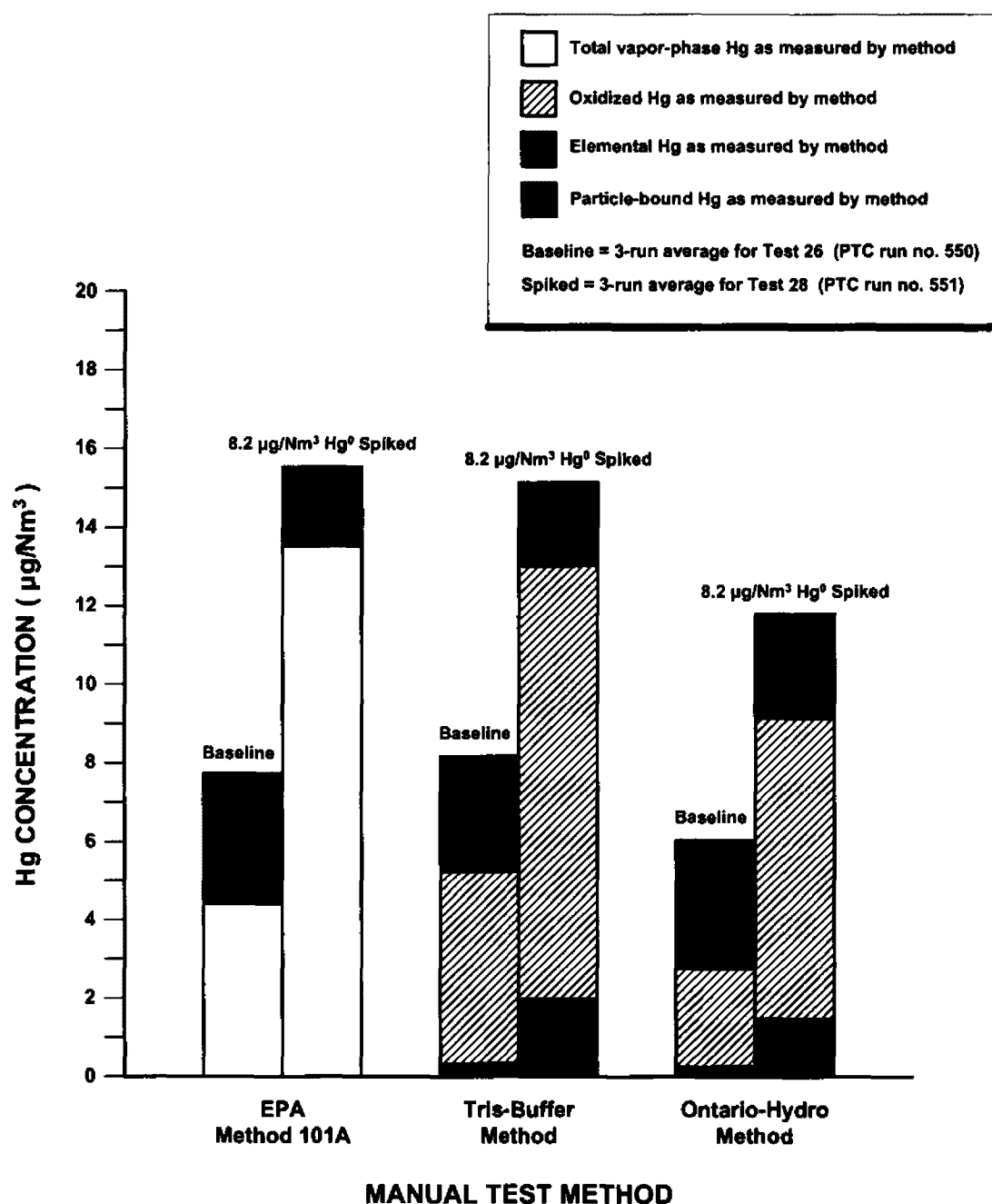
Figure 4-2. Comparison of Hg speciation measured by manual test methods from UND/EERC pilot-scale evaluation tests firing Blacksville bituminous coal and sampling and spiking Hg⁰ at FF inlet (source: graph prepared using test data presented in Appendix B to Reference 1).
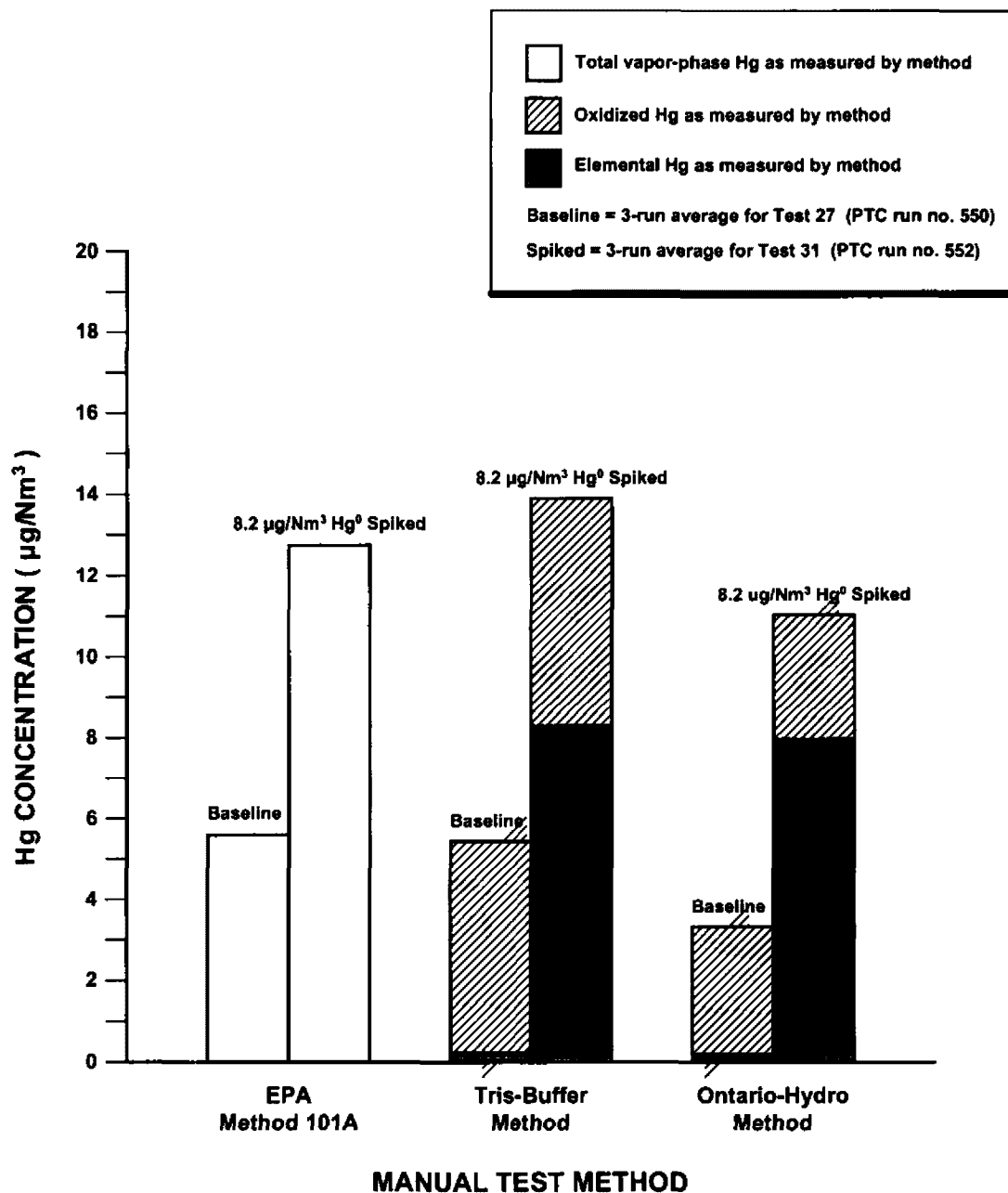
Figure 4-3. Comparison of gaseous Hg speciation measured by manual test methods from UND/EERC pilot-scale evaluation tests firing Blacksville bituminous coal and sampling and spiking Hg⁰ at FF outlet (source: graph prepared using test data presented in Appendix B to Reference 1).

discussed above.[1] Both Draft EPA Method 101B and the OH Method were selected for formal EPA Method 301 validation testing. Method 301 is EPA's accepted guidance for validation of source testing methodologies.[6] For these validation tests, all sampling and dynamic spiking of Hg^0 and $HgCl_2$ into a flue gas stream were performed at the outlet of the high efficiency fabric filter (FF), while burning a blend of Ohio No. 5 and Ohio No. 6 coals.[1] Validation testing was not performed at the PM control device inlet location.

A summary of the Method 301 validation results is shown in Table 4-2. The tests verified that both the OH Method and the draft EPA Method 101B achieved acceptable performance as defined by Method 301.[1] The precision of the OH Method for total gaseous Hg was determined to be less than 11 percent relative standard deviation (RSD) for Hg concentrations greater than 3 $\mu g/Nm^3$ and less than 34 percent RSD for Hg concentrations less than 3 $\mu g/Nm^3$. These values were within the acceptable range, based on the criteria established in EPA Method 301 (less than 50 percent RSD). In all cases, the laboratory bias for these tests based on a calculated correction factor was not statistically significant, though some oxidation (less than 15 percent) of the Hg^0 spike was observed even when spiking and sampling was done at the outlet of the fabric filter. The draft EPA Method 101B also met Method 301 validation requirements, though it did not perform as well as the OH Method.[1] As a result, the OH Method was selected as the most appropriate method for Hg speciation measurements in coal combustion gases.[1]

Final approval by the ASTM of the OH Method as an international test procedure is still pending as of the date of this report. The OH Method, in its current draft form, is available from the EPA Office of Air Quality Planning and Standards (OAQPS) Emission Measurement Center (EMC).[4] The draft version of the OH Method submitted to ASTM states that the method is applicable for sampling elemental, oxidized, and particle-bound Hg at the inlet and outlet of emission control devices and is suitable for measuring Hg concentrations ranging from approximately 0.5 to 100 $\mu g/Nm^3$.[4] Measurement sensitivity/detection levels can be extremely important where control technology performance is being determined in relatively low Hg coal content applications.

In summary, while several manual methods for Hg speciating measurements exist, the OH Method is the most thoroughly examined and accepted of these methods, and has met EPA Method 301 validation requirements. Application to air pollution control device inlet locations should be considered with caution due to the known catalytic and sorptive effects of certain coal fly ash PM. These measurement artifacts do not affect the use of the OH Method for total Hg measurements.

4.3 Continuous Emission Monitors for Hg Measurements

Continuous emission monitors (CEMs) are preferable for multiple reasons to using manual methods for measuring Hg. A CEM is capable of providing a real-time or near-real-time response for Hg measurements. A CEM can be used to obtain continuous Hg measurements

Table 4-2. Results from EPA Method 301 evaluation tests for the Ontario-Hydro Method (sources: References 1 and 4).

Ontario-Hydro Method [a]	Total Vapor-Phase Hg			Oxidized Hg			Elemental Hg		
	Mean[b], $\mu g/Nm^3$	Standard Deviation	RSD[c], %	Mean[b], $\mu g/Nm^3$	Standard Deviation	RSD, %	Mean[b], $\mu g/Nm^3$	Standard Deviation	RSD, %
Baseline	23.35	2.05	8.79	21.24	2.13	10.02	2.11	0.65	30.69
Hg⁰ Spike (15.0 $\mu g/Nm^3$)	38.89	2.00	5.13	23.32	2.08	8.94	15.57	1.09	6.97
HgCl₂ Spike (19.9 $\mu g/Nm^3$)	42.88	2.67	6.23	40.22	2.87	7.14	2.66	0.89	33.31

a. The correction factor in all cases was not statistically significant and is not shown.
b. For each mean result, there were 12 replicate samples (four quad trains).
c. RSD = Relative standard deviation.

over long periods in time. Conversely, manual methods are capable of only infrequent "snapshot" Hg measurements over time. As a result, CEMs are able to distinguish the magnitude and duration of short-term emission characteristics as well as perform long-term emission measurements to truly characterize a process's temporal emissions. Again, manual methods are not capable of performing these functions. It is for these reasons that Hg CEMs are extremely valuable tools supporting the understanding and control of Hg emissions from coal-fired electric utility power plants. This section discusses the state-of-the-art of using CEMs for Hg measurements and the associated measurement issues.

In general, Hg CEMs are a relatively new and yet unproven technology. Although CEMs that measure total Hg only are used to support regulatory applications in several European countries, the use of these CEMs is limited. Several total Hg CEMs are available commercially and are primarily of European origin.[7,8] In the United States., Hg CEMs have been limited to research applications with respect to coal-fired combustion emissions monitoring. As with the manual methods, CEMs capable of Hg speciation measurement are of the most value to supporting research on the characterization and control of Hg emissions from coal-fired electric utility boilers. The speciating Hg CEMs currently available should be considered prototypes.

The CEMs being developed for measuring Hg are similar to most other types of CEMs used for combustion processes in that the combustion gas sample typically must be extracted from the stack and then transferred to the analyzer for detection. However, continuous Hg monitoring is complicated by the fact that Hg exists in different forms (i.e., Hg^0, Hg^{2+}, and Hg_p) and that quantitative transport of all these forms is difficult.

Typically, Hg CEMs measure (i.e., detect) only Hg^0. These CEMs measure total Hg through the use of a conversion system that converts (reduces) the gaseous non-elemental or Hg^{2+} forms to Hg^0 for detection. Mercuric chloride is considered to be the primary oxidized form of Hg, though recent research suggests that other oxidized forms of Hg do indeed exist.[9,10] Although particulate-bound Hg can also be reduced to the gaseous elemental form, particulate sample delivery issues make this impractical. As a result, for most commercially available CEMs, the total Hg measured is in fact total gaseous Hg (TGM).

The conversion of gaseous, non-Hg^0 is commonly accomplished using a liquid reducing agent (e.g., stannous chloride). This technique is least preferable, though more established. The use of wet chemical reagents is considered to be a limitation to Hg CEM use. The wet chemicals typically possess corrosive properties and require frequent replenishment. The spent reagents may possess hazardous properties that result in waste disposal concerns. In addition, the reducing ability of reagents such as stannous chloride can be affected by high levels of SO_2.[11]

In addition to the more established wet chemistry conversion methods, dry conversion methods are also available. These techniques use high temperature catalysts or thermal reduction units to not only convert non-Hg^0, but also condition the sample for analysis by removing selective interferants. This approach does much to minimize the size of the conversion system as well as maintenance requirements. However, these systems have not been well characterized for

coal combustion gas Hg measurement applications.

Because the particulate form is difficult to transfer and is also often a measurement interferant, the particulate is typically filtered out and Hg_p remains unmeasured. This could potentially impart a negative bias to the total Hg measurements. This bias could be further amplified as certain types of particulate may actually capture gas-phase Hg. This may not be a significant issue for sources where Hg_p is not present in appreciable quantities, but may be a significant issue for high particulate-emitting sources (e.g., sources with minimal PM control) or in cases where the Hg measurements are conducted upstream of PM control devices. Therefore, the capability of a CEM to measure Hg_p is important and should not be ignored.

Similarly, there are known complications with the quantitative transfer of mercuric chloride.[9] Mercuric chloride ($HgCl_2$) is water soluble and reactive with many surfaces. Losses due to adsorption are the major concern. As a result, recent emphasis has been placed on locating the non-Hg^0 conversion systems as close as possible to the source so that the elemental form is transferred from the source to the detection unit instead of transporting the oxidized forms long distances.

In general, Hg CEMs can be distinguished by their Hg measurement detection principle. Detection systems include: cold-vapor atomic absorption spectrometry (CVAAS); cold-vapor atomic fluorescence spectrometry (CVAFS); *in-situ* ultraviolet differential optical absorption spectroscopy (UVDOAS); and atomic emission spectrometry (AES).[1,7,8,9]

The majority of Hg CEM systems employ CVAAS or CVAFS as the detection technique. These detection techniques are susceptible to measurement interferences resulting from the presence of common combustion process emissions. Gases such as NO_X, SO_2, HCl, and Cl_2 can act as measurement interferants as well as degrade the performance of concentrating devices (e.g., gold amalgams). As such, conditioning systems and/or techniques that remove or negate the effects of these interfering gases prior to sample delivery to the detector are required. The SO_2 is a major spectral interferant with most CVAA detection systems. The effects of SO_2 are commonly negated through the use of a gold trap. The sample gas is directed through a gold trap, where the Hg amalgams with the gold surface. Once the trap is loaded, it is heated and flushed with a SO_2-free carrier gas to the detector. The trapping also serves to improve measurement sensitivity by concentrating the sample. A trapping device is required of CVAFS systems to achieve optimum sensitivity; not because of the concentrating aspect, but because the carrier gas will enable maximum sensitivity. Oxygen and nitrogen have spectral quenching effects that suppress measurement sensitivity. Conditioning of the sample gas prior to reaching the gold trap is often required. HCl and NO_X in combination can poison the gold surface, preventing amalgamation with the Hg. Removal of both or either of these constituents is required.

An alternative to the Hg^0 measurement approach is AES. With this technique, the Hg is ionized by a high-energy source (e.g., plasma) and the emission energy detected. The advantage to this technique is that all forms of Hg, including particulate-bound Hg, are capable of being

ionized and detected. Although this technology is not quite as developed, another major advantage of AES is that the ionization source and detector can be located directly at the source, avoiding sample delivery issues. In addition, AES is not as susceptible to spectral interferences from common flue gas constituents.

Speciated Hg measurements are important to characterize combustion process emissions and evaluate Hg control strategies. While there are no commercially available CEMs that directly measure the various speciated forms of Hg, several total gaseous Hg CEMs, both commercial and prototype, have been enhanced to indirectly measure speciated Hg (the elemental and oxidized forms) by determining the difference between Hg^0 and total gaseous Hg. This difference is recognized as the oxidized form. Separate Hg measurements are made before and after the conversion step in order to calculate the oxidized form. This indirect speciation method is referred to as "speciation by difference." Based on the current understanding that the oxidized species of primary interest is mercuric chloride and that mercuric chloride is the dominant form of oxidized Hg present, the "speciation by difference" technique is considered an acceptable approach to obtaining speciated Hg measurements.

A key to performing the speciated Hg measurement is being able to perform reliable Hg^0 measurements. The Hg^{2+} must be removed without adding to the true amount of Hg^0 in the sampled gas stream. This is often accomplished using a liquid reagent to remove the water-soluble Hg^{2+}. These reagents also may serve to neutralize the effects of measurement interferants. The greatest concern is the reliability of the speciated Hg measurement. Measurement artifacts exist that bias the speciation, primarily by over-reporting the level of the oxidized species. The largest cause of this bias comes from the reactivity of certain types of PM (as discussed in Section 4.2). The PM may possess catalytic properties whereby, at the conditions of Hg CEM PM filtering environments, Hg^0 can be oxidized across the PM surface. This is not an issue from a TGM measurement standpoint (unless transport of oxidized Hg is an issue). However, it may have major implications when measuring Hg in gas streams possessing high PM loadings. This bias is minimized in low PM loading gas streams, consistent with Hg measurements downstream of PM control devices. Another potentially significant source of speciated Hg measurement bias takes place in the liquid phase. In combustion gases where Cl_2 is present, under certain conditions the Cl_2 may react in the liquid phase to oxidize Hg^0.[12] There is evidence that this problem can be mitigated.

As stated previously, the current, primary application of Hg CEMs is as a research tool/process monitor. Speciating Hg CEMs are integral to the DOE/EPA/EPRI Hg control technology development and evaluation research program. These Hg CEMs are used to characterize existing Hg emissions and distributions, including control technology performance. More importantly, these speciating Hg CEMs are used to better understand and optimize potential Hg control technologies so that absolute emissions can be established through OH sampling. Ultimately, it is desired to accept the quality and performance of Hg CEMs and measurements data so as to replace the reliance on OH measurements. Several pilot-scale and field tests have been performed specifically to evaluate and determine the measurement performance of both total and speciating Hg CEMs.

Several tests have been conducted specifically to evaluate total Hg CEMs as a compliance assurance tool. The first such test, sponsored by the EPA Office of Solid Waste (OSW), evaluated the performance of three Hg CEMs to measure total Hg emissions from a cement kiln that burned hazardous waste as a fuel.[13] Measurement performance was evaluated following the proposed "*Performance Specification 12 -- Specifications and Test Procedures for Total Mercury Continuous Monitoring Systems in Stationary Sources*" (PS-12).[14] At the time, this was a relatively new test procedure and had yet to be implemented. In fact, the guidance called for Hg^0 and $HgCl_2$ gas standards that had yet to be developed and proven. The tests were only marginally successful. None of the Hg CEMs tested met the performance test requirements. Based on the test results, the EPA/OSW concluded that Hg CEMs should not be considered as a compliance tool for hazardous waste combustors.[13] In retrospect, the harshness of the cement kiln's exhaust gas stream was concluded as a major cause of the test program's lack of success.[8,13] The cement kiln chosen for the EPA/OSW Hg CEM testing was not equipped with acid gas controls and had relatively high PM loading, resulting in severe interferences and operational difficulties for the CEMs.

The DOE Mixed Waste Focus Area (MWFA) has sponsored several tests determining the measurement performance of a single total Hg CEM under hazardous waste incineration conditions.[15,16] Measurement performance was also evaluated following PS 12. These tests demonstrated not only Hg CEM performance, but also that additional elements of the PS 12 test procedures could be implemented. A prototype Hg^0 compressed gas standard was used for the first time. While these tests have been relatively successful, they are still limited in scope and application.

The EPA's Environmental Technology Verification (ETV) Program, in collaboration with the NRMRL, has completed testing of four commercially available Hg CEMs from three vendors using the unique capabilities of NRMRL's pilot-scale combustion test facility. These tests examined the measurement performance of both total and speciated Hg CEMs under two distinct and diverse combustion conditions. Coal and chlorinated waste combustion conditions were simulated. These verification tests used PS 12 as guidance, but also considered specific measurement issues of interest and innovative approaches that better examined these issues. The pilot-scale tests were unique in that specific measurement issues were investigated as variables. The pilot-scale combustion facility enabled independent control of Hg concentration and species. As a result, the total Hg measurement could be challenged by the distribution of oxidized and Hg^0. Interference flue gas constituents were also independently examined. The ETV testing made use of several new quality assurance and quality control (QA/QC) tools. Newly developed Hg^0 compressed gas standards were used to determine Hg CEM calibration drift and system bias. As a result, not only were Hg CEMs evaluated, but also improved techniques for evaluating Hg CEMs were demonstrated. Performance data for the participating Hg CEMs are not yet available.

The UND/EERC has evaluated the performance of Hg CEMs during field tests at eight different coal-fired electric utility power plants representing facilities that burn lignite, subbituminous coal, or bituminous coal.[11,17] A variety of air pollution control devices and

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configurations were encountered, including ESPs, FFs, wet FGD scrubbers, spray dryer absorbers, and venturi scrubbers. For these tests, the Hg CEMs evaluated demonstrated the ability to measure total gaseous Hg within ± 20 percent of the OH Method measurements. The field-testing also examined the measurement performance of several Hg CEMs at low stack Hg emissions levels. These tests demonstrated a distinct advantage of the AF-based systems over the AA-based system (see Figure 4-4). Below concentrations of 5 $\mu g/m^3$, the AA-based systems exhibited higher signal to noise ratios. At these concentrations, the AF-based systems are a better choice.

The EPA/OAQPS/EMC has recently initiated a study to determine the measurement performance of two commercially available total Hg CEMs at a coal-fired electric utility power plant. Measurements of performance will be recorded to determine potential monitoring applications based on measurement performance achieved. Data from this study, and future studies of Hg CEM measurement performance at additional source categories, should aid in the future crafting of a performance specification for application of total Hg CEMs to a variety of different Hg emission source categories.

Performance testing of Hg CEMs has focused primarily on total Hg CEMs; total Hg CEMs are the most widely available commercially. However, with respect to the development and evaluation of Hg control technologies for coal-fired electric utility power plants, the most urgent need is for a speciating Hg monitor. As stated previously, the primary use of speciating Hg CEMs is as a research tool though application as a process monitor is also appealing. Of those speciating Hg CEMs in use, most are commercially available total or Hg^0 CEMs modified for use as a speciating Hg CEM. Very few speciating Hg CEMs are available commercially. The major distinction among speciating Hg CEMs is not the analyzer or detection principle, but the approach for managing potential interferants and method for converting oxidized forms of Hg to the detectable, elemental form.

Performance testing of speciating Hg CEMs to support Hg control technology research has also been performed under pilot- and field-scale operations and research continues in this area. Work performed by the UND/EERC has also focused on the research and development of speciating Hg CEMs, particularly the development and evaluation of pretreatment/conversion systems that can be used with multiple, commercially available Hg CEMs. The EERC has used speciating Hg CEMs to support field measurement activities in conjunction with OH Method measurements. Figure 4-5 compares the measurement performance of several speciating Hg CEMs to OH Method measurements made during testing at a coal-fired electric utility power plant.

A key to assessing measurement performance and validating measurement data quality is the development Quality Assurance/Quality Control (QA/QC) tools such as elemental and oxidized Hg gas standards. The tools are needed for instrument calibration, continuing calibration or drift checks, and system bias checks. The EPA/ORD has been active in the development of both elemental and $HgCl_2$ gas standards. A commercial compressed gas standard for Hg^0 has been evaluated for stability and accuracy. While the stability of the Hg^0 compressed
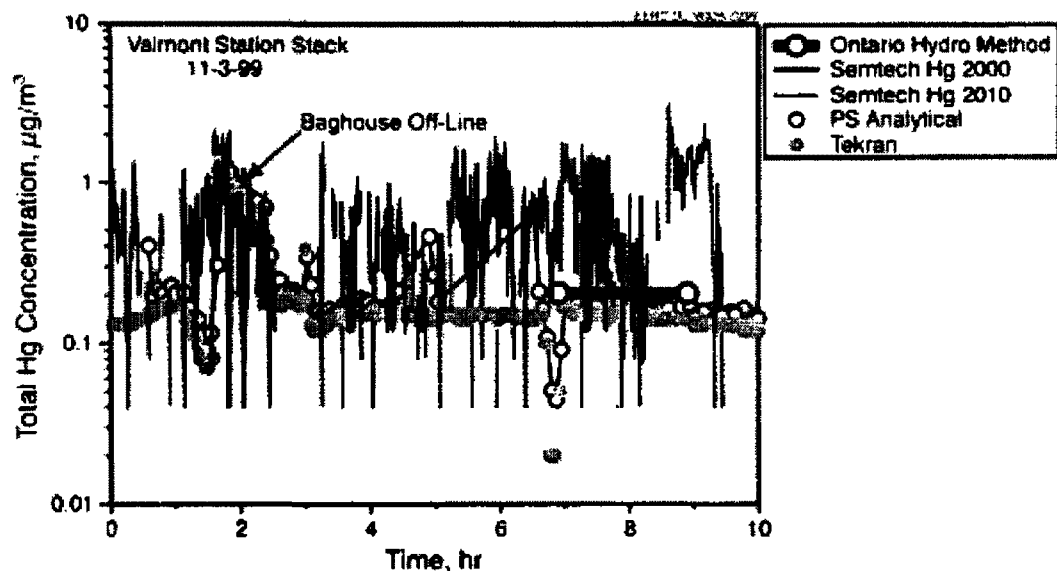
Figure 4-4. Comparison of total Hg results for CEMs at low Hg levels.

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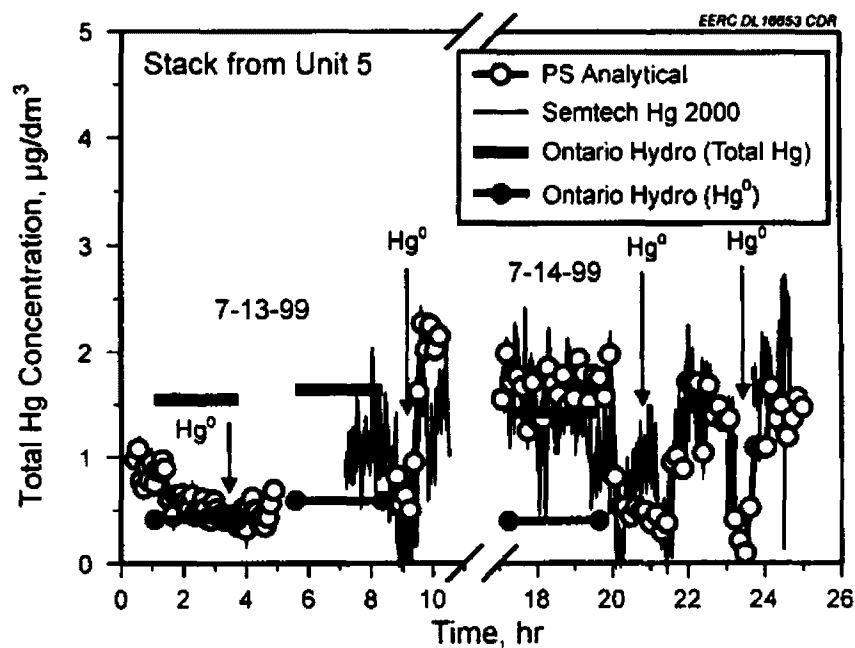
Figure 4-5. Comparison of Hg speciation results for CEMs at low Hg levels.

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gas standard has been confirmed, techniques for establishing the standard's true concentration have not. As a result, quantitative use of the standard is limited. Similarly, acceptance of a $HgCl_2$ standard is valuable: this standard is used to assess Hg conversion system effectiveness as well as overall sampling system delivery efficiency and reactivity, parameters not challenged by an Hg^0 gas standard. This is particularly relevant in measurement applications where oxidized Hg may be the predominant Hg form present. Moreover, several Hg CEMs vendors have developed QA/QC capabilities to perform their own instrument calibration drift and system bias checks from internal Hg^0 gas sources. These capabilities are needed for routine daily operational performance verification.

In summary, Hg CEMs are currently the tool of choice for evaluating the performance of candidate Hg control technologies. As different control technologies are evaluated, the associated measurement issues are encountered and addressed. Measurement issues are primarily associated with the oxidized Hg conversion systems as well as particulate bias effects, particularly at pollution control device inlet measurement locations. Both wet chemistry and dry conversion/conditioning systems are used to support these control technology research programs. It is the conversion/conditioning system that requires the most attention during operation of Hg CEM systems. It is also this frequent need for attention that limits their application to short measurement intervals. As a result, consideration as a compliance assurance tool is hindered. Clearly, in order to function as a dedicated process monitor and/or compliance tool, additional research is needed to develop and/or evaluate more reliable and less labor intensive Hg conversion/sample conditioning systems. These objectives are likely to be furthered as a result of control technology demonstration and evaluation activities.

4.4 Summary, Conclusions, and Recommendations

Valid and reliable Hg measurements, by either manual methods or using CEMs, are critical to the characterization and future reduction of Hg emissions from coal-fired electric utility power plants. Although these measurement techniques are tools that support a larger research objective, the quality, applicability, and specificity of these measurements directly impact the ability to conduct Hg emission control research. Measurement techniques that determine both the Hg^{2+} and Hg^0 gaseous forms of Hg are preferred over those techniques that can measure only total gaseous Hg. Conversely, speciated Hg measurement techniques are more complex and more susceptible to measurement biases. Although viable measurement techniques exist and measurement performance has been demonstrated for certain measurement situations, acceptable measurement techniques are not available to meet all measurement needs. Additional research and development is still needed to enable quality measurements from all necessary measurement environments.

The OH Method is the only manual method that is currently recognized in the United States for speciated Hg measurements in coal combustion gases. The OH Method appears to provide valid speciation results at sampling locations downstream of PM control devices in

which most of the fly ash has been removed from the gas stream. However, measurements made upstream of PM control devices are susceptible to measurement artifacts that bias the measurements of the different Hg species causing potential uncertainty in results. However, these artifacts do not affect the measurement of total Hg.

A limited number of both private prototype and commercial Hg CEMs are available for the measurement of total gas-phase Hg and to a lesser extent, speciated gas-phase Hg. Because of the diversity and severity of associated measurement environments, numerous measurement obstacles exist (e.g., PM artifacts, interferences, conversion systems, sample conditioning/delivery) that have not been adequately addressed, particularly with respect to speciated measurements. While Hg CEMs are used being used as a tool by researchers, these devices are not yet suitable for routine Hg monitoring applications at coal-fired electric utility power plants. As a research tool, Hg CEMs are suitable for short-term measurement needs. However, the technology has not advanced to the extent that acceptable, long-term measurement performance has been demonstrated. This must be accomplished for Hg CEMs to be considered suitable for any purpose beyond use as a research tool. The primary obstacle is the lack of sample conditioning/conversion systems suitable for long-term, minimal attention operation.

Improved methods for the sampling and analysis are critical to support the development of Hg emission control technologies, for use for Hg monitoring and control (process control), and for potential use as compliance tools. Specifically, research is needed to:

1. Develop improved sample conditioning/conversion systems (particularly dry, non-wet chemical) capable of long-term, minimal maintenance, operation,

2. Develop and demonstrate improved Hg CEM measurement techniques that address known and potential measurement obstacles (e.g., PM artifacts, interferences/biases, conversion systems, sample conditioning/delivery),

3. Develop accepted QA/QC tools (e.g., elemental and oxidized Hg gas standards) for validating instrument performance and data quality,

4. Develop and verify a manual test method suitable for measuring total and speciated Hg at sampling locations upstream of PM control devices,

5. Develop and verify a manual test method (e.g., modified OH Method) that can simultaneously measure speciated Hg and other trace metals,

6. Develop and demonstrate measurement techniques that are capable of directly identifying and quantifying trace levels of individual ionic species of Hg [e.g., $HgCl_2$, $HgCl$, HgS, $HgSO_4$, $Hg(NO_3)_2$],

7. Verify the ability of Hg CEMs to accurately measure total gas-phase Hg and speciated gas-phase Hg at diverse stack conditions representative of fuel type and pollution control device configurations (e.g., downstream of PM control devices and wet FGD scrubbers),

8. Verify the ability of Hg CEMs to accurately measure total gas-phase Hg and speciated gas-phase Hg at measurement locations upstream of PM control devices,

9. Demonstrate Hg CEM long-term monitoring performance, including operational requirements,

10. Identify and evaluate alternative, cost-effective semi-continuous methods for measuring the stack emission of total Hg, and

11. Demonstrate the use of Hg CEMs and semi-continuous monitoring methods as potential Hg emission compliance tools.

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Chapter 5
Mercury Speciation and Capture

5.1 Introduction

The source of Hg emissions from coal-fired electric utility boilers is the Hg that naturally exists in coal and is released during the combustion process. As discussed in Chapter 2, the Hg content of a coal varies by coal type and where it is mined. When the coal is burned in an electric utility boiler, most of the Hg bound in the coal is released into the combustion product gases. This chapter provides an introduction to Hg chemistry and behavior of Hg as it leaves the combustion zone of the furnace and passes in the flue gas through the downstream boiler sections, air heater, and air pollution control devices. Recent research on Hg chemistry in coal-fired electric utility boiler flue gas is summarized.

5.2 General Behavior of Mercury in Coal-fired Electric Utility Boilers

The majority of Hg in coal exists as sulfur-bound compounds and compounds associated with the organic fraction in coal. Small amounts of elemental Hg may also be present in the coal. Figure 5-1 presents a simplified schematic of the coal combustion process. The primary products of coal combustion are carbon dioxide (CO_2) and water (H_2O). In addition, as discussed in Chapter 3, significant quantities of the pollutants sulfur dioxide (SO_2) and nitrogen oxides (NO_x) are also formed. When the coal is burned in an electric utility boiler, the resulting high combustion temperatures in the vicinity of 1,500 °C (2,700 °F) vaporize the Hg in the coal to form gaseous elemental Hg. Subsequent cooling of the combustion gases and interaction of the gaseous elemental Hg with other combustion products result in a portion of the Hg being converted to other forms.

There are three basic forms of Hg in the flue gas from a coal-fired electric utility boiler: (1) elemental Hg (represented by the symbol Hg^0 in this report); (2) compounds of oxidized Hg (collectively represented by the symbol Hg^{2+} in this report); and (3) particle-bound mercury (represented by the symbol Hg_p in this report). Oxidized mercury compounds in the flue gas from a coal-fired electric utility boiler may include mercury chloride ($HgCl_2$), mercury oxide (HgO), and mercury sulfate ($HgSO_4$). Some researchers refer to oxidized mercury compounds collectively as *ionic mercury*. This is because, while oxidized mercury compounds may not exist as mercuric ions in the boiler flue gas, these compounds are measured as ionic mercury by the
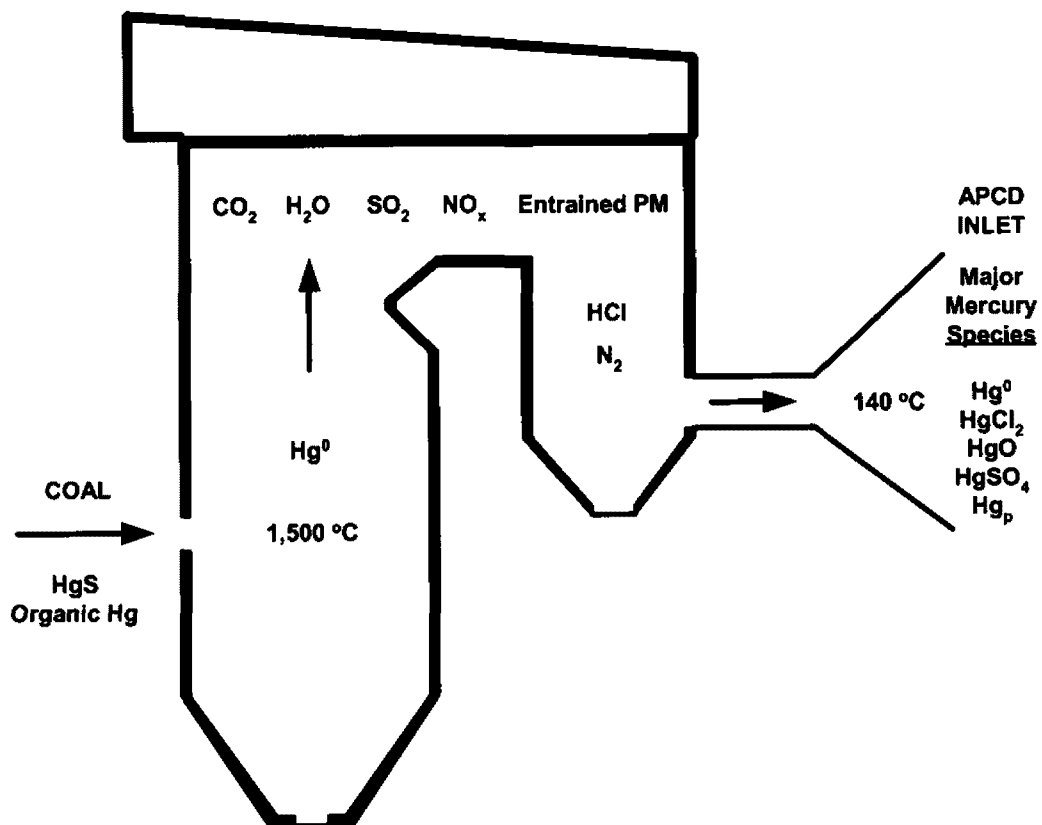
Figure 5-1. Mercury species distribution in coal-fired electric utility boiler flue gas.

speciation test method used to measure oxidized Hg (discussed in Chapter 4). Similarly, particle-bound Hg is referred to as *particulate mercury* by some researchers. The term *particle-bound mercury* is the preferred and is used in this report to emphasize that the mercury is bound to a solid particle.

The term *speciation* is used to denote the relative amounts of these three forms of Hg in the flue gas of the boiler. At present, speciation of Hg in the flue gas from a coal-fired electric utility is not well understood. A number of laboratory and field studies have been conducted, or are ongoing, to improve the understanding of the transformation of Hg^0 to the other Hg forms in the flue gas downstream of the boiler furnace. Data obtained to date indicate that combinations of site-specific factors affect the speciation of Hg in the flue gas. These factors include:

- Type and properties of the coal burned.
- Combustion conditions in the boiler furnace.
- Boiler flue gas temperature profile.
- Boiler flue gas composition.
- Boiler fly ash properties.
- Post-combustion flue gas cleaning technologies used.

The current understanding of the mechanisms by which Hg^0 transforms to Hg^{2+} and Hg_p in the flue gas from coal-fired electric utility boilers is discussed in subsequent sections of this chapter. It is important to understand how Hg speciates in the boiler flue gas because the overall effectiveness of different control strategies for capturing Hg often depends on the concentrations of the different forms of Hg present in the boiler flue gas. This topic will be discussed in detail in Chapters 6 and 7.

5.3 Speciation of Mercury

As mentioned above, high temperatures generated by combustion in the boiler furnace vaporize Hg in the coal. The resulting gaseous Hg^0 exiting the furnace combustion zone can undergo subsequent oxidation in the flue gas by several mechanisms. The predominant oxidized Hg species in boiler flue gases is believed to be $HgCl_2$. Other possible oxidized species may include HgO, $HgSO_4$, and mercuric nitrate monohydrate $Hg(NO_3)_2 \cdot H_2O$. The potential mechanisms for oxidation of Hg^0 in the boiler flue gas include:

- Gas-phase oxidation.
- Fly ash mediated oxidation.
- Oxidation by post-combustion NO_x controls.

Each of these oxidation mechanisms is discussed in the following sections.

5.3.1 Gas-phase Oxidation

As mentioned above, Hg in coal is believed to completely vaporize and convert into gaseous Hg^0 in the combustion zone of a boiler system. As gaseous Hg^0 travels with the flue gas in the boiler, it can undergo gas-phase oxidation to form gaseous Hg^{2+}, most of which is believed to be $HgCl_2$. Recent research [1] has speculated that the major gas-phase reaction pathway to form gaseous $HgCl_2$ is the reaction of gaseous Hg^0 with gaseous atomic chlorine (Cl). The latter is formed when chlorine in coal vaporizes during combustion.

At the furnace exit, the temperature of the flue gas is typically in the vicinity of 1400 °C (2552 °F). The flue gas cools as it passes through the heat exchanging equipment in the post-combustion region. At the outlet of the air heater (the last section of heat exchanging equipment), the temperature of the flue gas ranges from 127 to 327 °C (261 to 621°F). Chemical equilibrium calculations predict that gas-phase oxidation of Hg^0 to Hg^{2+} starts at about 677 °C (1251 °F) and is essentially complete by 427 °C (801 °F). Based on these results, Hg should exist entirely as Hg^{2+} downstream of the air heater. However, flue-gas measurements of Hg at air heater outlets indicate that gaseous Hg^0 is still present at this location, and that Hg^{2+} ranges from 5 to 95 percent of the gas-phase Hg. These data suggest that, due to kinetic limitations, the oxidation of Hg^0 does not reach completion.

As mentioned previously, gas-phase oxidation of Hg^0 is believed to take place via reaction with gaseous Cl. At furnace flame temperatures, a major portion of the chlorine in the coal exists as gaseous chlorine atoms, but as gas cools in post-combustion, the chlorine atoms combine to form primarily hydrogen chloride (HCl) and minor amounts of molecular chlorine (Cl_2). The rapid decrease in Cl concentration results in "quenched" Hg^{2+} concentrations corresponding to equilibrium values around 527 °C (981 °F).

Figures 5-2 and 5-3 show predicted distributions of Hg species in coal-fired electric utility flue gas as a function of flue gas temperature. The predicted distributions are based on equilibrium calculations of gas-phase oxidation of Hg^0 in flue gas from the combustion of a bituminous coal [1] and a subbituminous coal [2], respectively. Figure 5-2 shows that 80 percent of gaseous Hg^0 is oxidized to $HgCl_2$ by 527 °C (981°F). Figure 5-3 indicates no oxidation of Hg^0 at or above 527 °C (981°F). As mentioned above, the gas-phase oxidation of Hg^0 is believed to be kinetically limited, proceeding only to equilibrium levels around 527 °C (981 °F).

The difference in the equilibrium oxidation levels at 527 °C (800 K) in Figures 5-2 and 5-3 is attributed to the different chlorine levels in the model coals used in the calculations. The calculated data in Figure 5-2 are based on a bituminous coal with a relatively high chlorine concentration of several hundred parts per million by weight (ppmw). In contrast, the calculated data in Figure 5-3 are based on a typical western subbituminous coal with a relatively low chlorine content of 26 ppmw. Research indicates that coals with relatively high chlorine contents tend to produce more Hg^{2+} than coals with relatively low chlorine contents.[3]
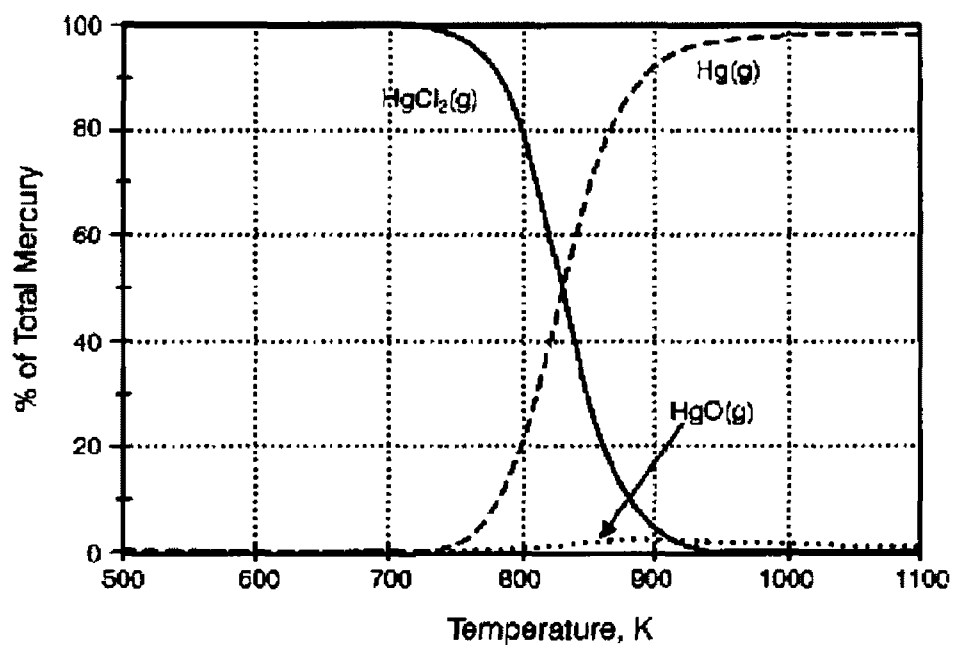
Figure 5-2. Predicted distribution of Hg species at equilibrium, as a function of temperature for a starting composition corresponding to combustion of a bituminous coal (Pittsburgh) in air at a stoichiometric ratio of 1.2 (source: Reference 2).
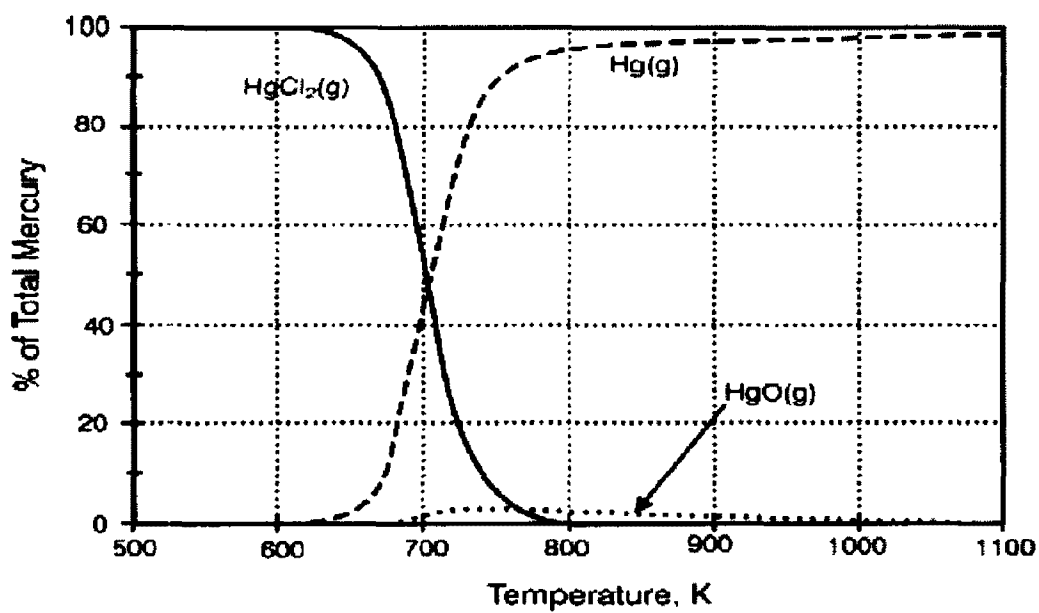
Figure 5-3. Predicted distribution of Hg species at equilibrium, as a function of temperature for a starting composition corresponding to combustion of a subbituminous coal (Powder River Basin) in air at a stoichiometric ratio of 1.2 (source: Reference 2).

In addition to being kinetically limited by Cl concentration, recent research conducted at EPA has found that gas-phase oxidation of Hg^0 is also inhibited by the presence of SO_2 and water vapor. [4] As shown in Figure 5-1, SO_2 and water vapor are constituents in the flue gas from coal-fired electric utility boilers. Figure 5-4 shows results from bench-scale experiments examining the effects of SO_2 and water vapor on the oxidation of gaseous Hg^0. These experiments were carried out using a simulated flue gas containing a base composition of 40 parts per million by volume (ppmv) Hg^0, 5 mole % carbon dioxide (CO_2), 2 mole % oxygen (O_2), and a balance of nitrogen (N_2); the temperature of the flue gas was 754 °C (1,389 °F). The effects of SO_2, water vapor, and HCl were studied by adding these constituents to the base flue gas. HCl was added to the simulated flue gas at three concentrations typical of coal combustion flue gas (50, 100, and 200 ppmv); SO_2 and water vapor were added with the HCl at 500 ppmv and 1.7 mole %, respectively.

As shown in Figure 5-4, the oxidation of Hg^0 was inhibited by the presence of SO_2 and water vapor. HCl is not believed to react directly with Hg^0 to cause its oxidation (a chlorinating agent such as atomic chlorine or Cl_2 is needed). HCl may produce trace quantities of the chlorinating agent in the flue gas. It is speculated that SO_2 and water vapor may inhibit gas-phase oxidation of Hg^0 by scavenging the chlorinating agent.

In addition to experimental studies, research has also been reported on the development of a kinetic model that is used to better understand the reaction mechanism involved in gas-phase Hg oxidation. A detailed chemical kinetics model using a chemical mechanism consisting of 60 reactions and 21 chemical species was developed recently to predict Hg speciation in combustion flue gas. [5] The speciation model accounts for the chlorination and oxidation of key flue gas components, including Hg^0. The performance of the model is very sensitive to temperature. For low reaction temperatures (< 630 °C), the model produced only trace amounts of Cl and Cl_2 from HCl, leading to a drastic under-prediction of Hg chlorination compared with experimental data. For higher reaction temperatures, model predictions were in good accord with experimental data. For conditions that produce an excess of Cl and Cl_2 relative to Hg, chlorination of Hg is determined by the competing influences of the initiation step, $Hg + Cl \rightarrow HgCl$, and the recombination reaction, $2Cl \rightarrow Cl_2$. If the Cl recombination is faster, Hg chlorination will eventually be determined by the slower pathway $Hg + Cl_2 \rightarrow HgCl_2$.

Another attempt has been made to formulate an elementary reaction mechanism for gas-phase Hg oxidation. [6] The proposed eight-step Hg oxidation mechanism quantitatively describes the reported extents of Hg oxidation for broad ranges of HCl and temperature. In the proposed mechanism, Hg is oxidized by a Cl atom recycle process, and, therefore, the concentrations of both Cl and Cl_2 are important. Once a pool of Cl atoms is established, Hg^0 is first oxidized by Cl into HgCl, which, in turn, is oxidized by Cl_2 into $HgCl_2$. The second step regenerates Cl atoms. Since the concentrations of Hg species are small in coal combustion flue gases, independent reactions establish and sustain the pool of Cl atoms. The pool is governed by the chemistries of moist CO oxidation, Cl species transformations, and nitrogen oxide (NO) production. The model predictions show that O_2 weakly promotes homogeneous Hg oxidation, whereas moisture is a strong inhibitor as it inhibits the decomposition of HCl to Cl_2. NO was identified as an effective inhibitor for Hg^0 oxidation through its effect on reducing the concentration of hydroxyl (OH)
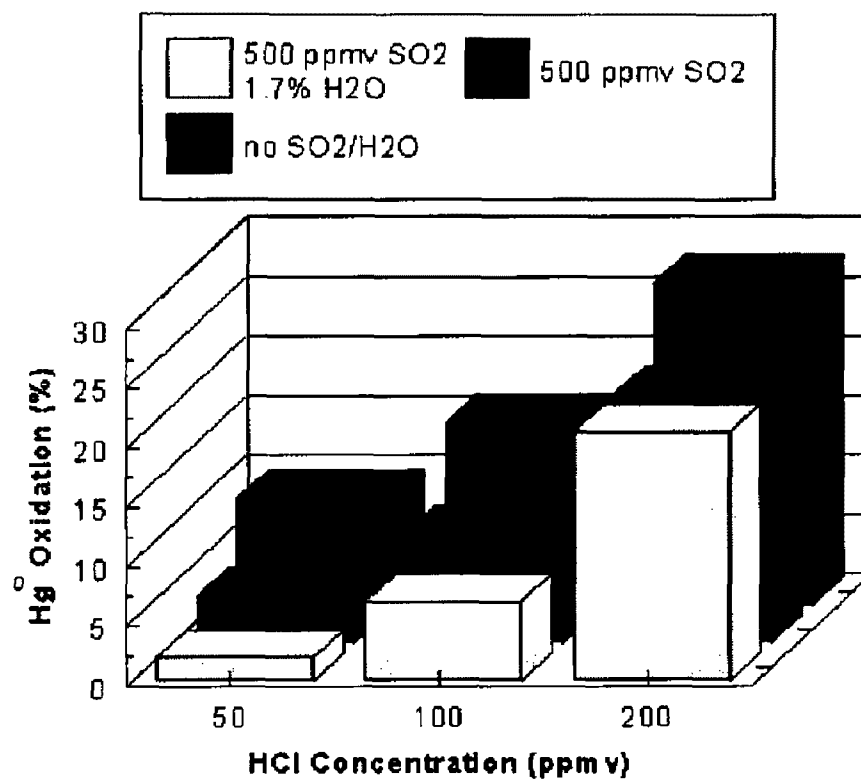
Figure 5-4. Effects of SO$_2$ and water vapor on the gas-phase oxidation of Hg^0 at 754 °C and at three different HCl concentrations.

in the flue gas. The formation of HOCl from OH and Cl is essential for the oxidation of Hg, which oxidizes HgCl into $HgCl_2$ and OH. The elimination of OH via $OH+NO+M = HONO+M$ is believed to inhibit Hg^0 oxidation.

5.3.2 Fly Ash Mediated Oxidation

In fabric filtration, flue gas penetrates a layer of fly ash as it passes through the filtering unit. The intimate contact between the flue gas and the fly ash on the filter provides an opportunity for the latter to oxidize some of the incoming gaseous Hg^0. However, this phenomenon does not occur across ESPs because the flue gas does not pass through a collected layer of fly ash (see Chapter 3 for a description of the operation of FFs and ESPs).

Certain fly ashes have been shown to promote oxidation of Hg^0 across a FF more actively than others. For example, fly ashes from bituminous coals tend to oxidize Hg^0 at higher rates than fly ashes from subbituminous coals and lignite. Differences in oxidation appear to be attributable to the composition of the fly ash, the presence of certain flue gas constituents, and the operating conditions of FFs.

Bench-scale tests were conducted at EPA to investigate the effects of fly ash composition and flue gas parameters on the oxidation of gaseous Hg^0.[4,7] In these experiments, a simulated flue gas containing Hg^0 (and other species) was passed through a fixed bed of simulated or actual coal fly ash, and oxidation of Hg^0 was measured across the reactor. Experimental results indicated two possible reaction pathways for fly-ash-mediated oxidation of Hg^0. One possible pathway is the oxidation of gaseous Hg^0 by fly ash in the presence of HCl, and the other is the oxidation of gaseous Hg^0 by fly ash in the presence of NO_X. The research also reflected that the iron content of the ash appeared to play a key role in oxidation of Hg^0. This EPA research is described in the ensuing paragraphs.

Coal fly ash is a mixture of metal oxides found in both crystalline and amorphous forms. Glasses are common ash constituents, composed primarily of the oxides of silicon and aluminum (known as aluminosilicate glasses) that can contain a significant amount of cations such as iron, sodium, potassium, calcium, and magnesium. Iron oxide (in the form of magnetite or hematite) is also as commonly found in ash as calcium oxide and calcium sulfate. In the presence of sufficiently high flue-gas concentrations of HCl or Cl_2, metallic oxides in fly ash may be converted to metal chlorides such as cuprous chloride (CuCl). Three-component model fly ashes were prepared by adding Fe_2O_3 or CuO at various weights to a base mixture of Al_2O_3 and SiO_2. An additional three-component fly ash was prepared by adding CuCl to a base mixture of Al_2O_3 and SiO_2. Municipal waste combustion fly ashes contain significant amounts of copper compared to coal combustion fly ashes that contain only trace levels of copper. Model fly ashes were prepared and tested in order to understand the effect of differences in copper content on the oxidation of Hg^0. Four-component fly ashes were prepared by adding various weights of CaO, and Fe_2O_3 or CuO to a base mixture of Al_2O_3 and SiO_2. Actual coal fly ashes were obtained from the combustion of three different coals (two subbituminous and one bituminous) from a pilot-size, pulverized-coal-fired furnace.

Model flue gas compositions were simulated to represent the temperature and composition of coal-fired electric utility flue gas as it enters a FF. The temperature of coal combustion flue gas as it enters a FF typically ranges from 150 °C (302 °F) to 250 °C (482 °F). Potentially important flue gas species (in terms of Hg^0 oxidation) include chlorine (primarily in the form of HCl at FF temperatures), NO_x (primarily in the form of NO at FF temperatures), SO_2, and water vapor. The base flue gas consisted of 40 ppbv Hg^0, 2 mole % O_2, 5 mole % CO_2, and the balance N_2 at a temperature of 250 °C (482 °F). HCl (50 ppmv), NO (200 ppmv), SO_2 (500 ppmv), and/or water vapor (1.7 mole %) were added to the base gas to determine their effect on oxidation. About 10 percent of NO_2 (10 ppmv) was measured when 200 ppmv of NO was added to the base flue gas which contains 2 mole % of O_2. The mixture of NO and NO_2 in flue gas is referred to collectively as NO_x. Table 5-1 shows the simulated and actual fly ashes and simulated flue gas tested.

Oxidation Behavior of Model Fly Ashes. HCl and NO_X were identified as the active components in flue gases for the oxidation of Hg^0. NO_x were more active than HCl. Cupric oxide (CuO) and ferric oxide (Fe_2O_3) were identified as the active components in model fly ashes for Hg^0 oxidation. In the presence of NO_x, inert components of model fly ashes such as alumina (Al_2O_3) and silica (SiO_2) appeared to become active in oxidation of Hg^0. Steady-state oxidation of Hg^0 promoted by the four-component model fly ashes (containing calcium oxide, CaO) was reached at much slower rates compared to those obtained using the three-component model fly ashes that contained no CaO (Figures 5-5 and 5-6). The partial removal of gas-phase HCl by CaO in the CaO-containing model fly ashes may have reduced the available chlorinating agent and resulted in slower oxidation of Hg^0.

Oxidation Behavior of Actual Coal Fly Ashes. As shown in Table 5-1, the Blacksville fly ash (derived from a bituminous coal) completely oxidized Hg^0 in the presence of NO (base + NO), but showed little oxidation in the presence of HCl (base + HCl).[7] The Comanche fly ash (derived from a subbituminous coal) did not oxidize Hg^0 in the presence of NO or HCl. The Absaloka coal (derived from a subbituminous coal) showed 30 to 35 percent oxidation of Hg^0 in the presence of NO, but no oxidation in the presence of HCl. It is believed that the high reactivity of the Blacksville coal in NO is related to its relatively high Fe_2O_3 concentration (22 percent); this observation is in agreement to that seen for the high iron (approximately 14 percent) three- and four-component model fly ashes.

More tests were conducted recently at EPA on actual fly ash samples with different coal ranks and iron contents in order to get a better understanding of the effects of iron in coal fly ashes on speciation of Hg.[8] It was observed that one subbituminous (3.7 percent iron) and three lignite coal fly ash (1.5 to 5.0 percent iron) samples tested with low iron content did not oxidize Hg^0 in the presence of NO and HCl. However, a bituminous coal fly ash sample (Valmont Station) with a low iron content (2.3 percent iron) completely oxidized Hg^0 in the presence of NO and HCl. It was also found that, upon adding Fe_2O_3 to the low iron content subbituminous and lignite fly ash samples to reach an iron content similar to that of the Blacksville sample, significant Hg^0 oxidation reactivity was measured (33 to 40 percent oxidation of Hg^0) for these iron-doped samples.
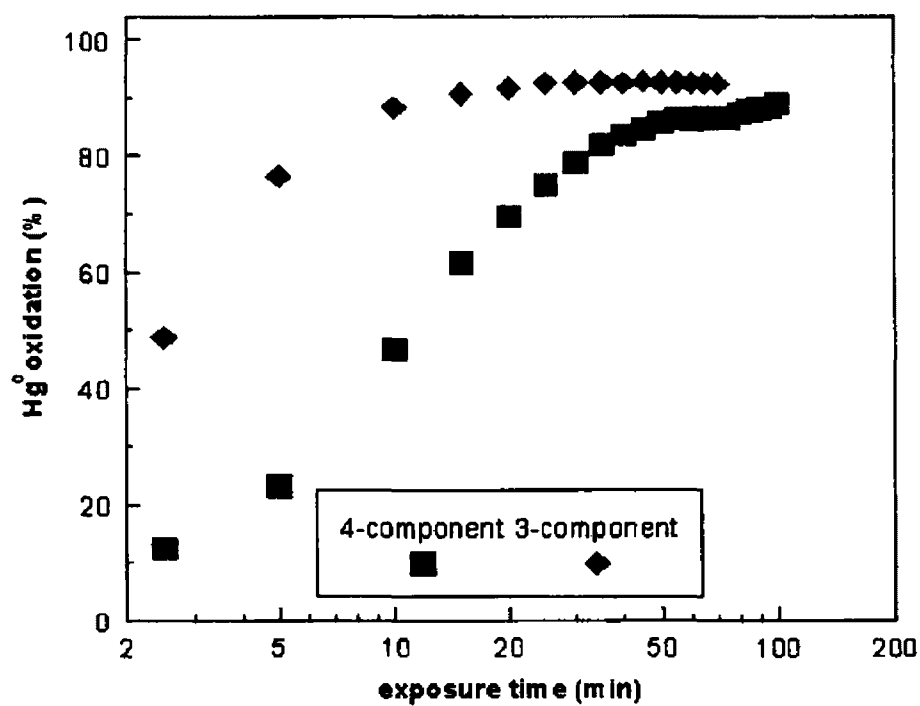
3-Component: silica/alumina (3.5/1) and 14 wt% Fe2O3
4-Component: silica/alumina (3.5/1), 13 wt% Fe2O3, and 6 wt% CaO

Figure 5-5. Hg^0 oxidation in the presence of the three- and four-component model fly ashes containing <u>iron</u> at a bed temperature of 250 °C (source: Reference 4).
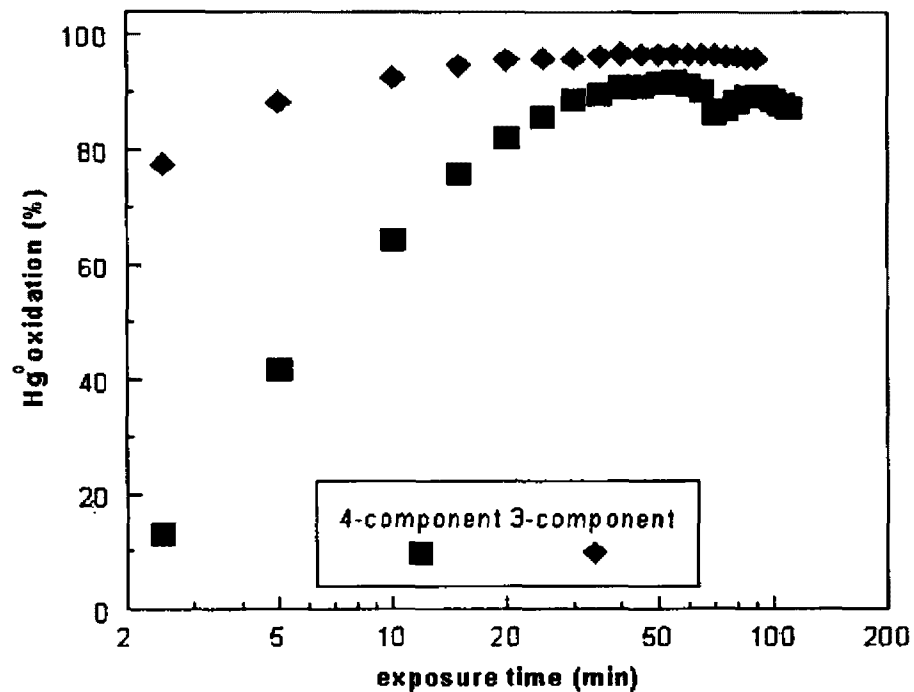
3-Component: silica/alumina (3.5/1) and 1 wt% CuO
4-Component: silica/alumina (3.5/1), 1 wt% CuO, and 6 wt% CaO

Figure 5-6. Hg⁰ oxidation in the presence of the three- and four-component model fly ashes containing <u>copper</u> at a bed temperature of 250 °C (source: Reference 4).

Table 5-1. Percent oxidation of Hg^0 by simulated and actual coal-fired electric utility boiler fly ash (source: Reference 4).

Fly Ash Composition (by weight percentages)	% Oxidation of Hg^0 by fly ash					
	Base[a]	Base + HCl	Base + HCl, SO_2	Base + HCl, SO_2, H_2O	Base + NO	Base + NO, SO_2
2-Component Model Fly Ash						
22% Al_2O_3 + 78% SiO_2	[b]	0			39	4
5-Component Model Fly Ashes						
19% Al_2O_3 + 67% SiO_2 + 14% Fe_2O_3	0	92	88	54	93	80
22% Al_2O_3 + 77% SiO_2 + 1% Fe_2O_3		67	43	37	48	26
22% Al_2O_3 + 78% SiO_2 + 0.1% Fe_2O_3		15			11	3
22% Al_2O_3 + 77% SiO_2 + 1% CuO		93	89	84	70	16
22% Al_2O_3 + 78% SiO_2 + 0.1% CuO		92	86	63	35	3
22% Al_2O_3 + 72% SiO_2 + 7% CaO	0	0	13	14	0.86	13
22% Al_2O_3 + 78% SiO_2 + 0.1% CuCl	87	77		23		
4-Component Model Fly Ashes						
21% Al_2O_3 + 71% SiO_2 + 1% CuO + 7% CaO		91	82	43		
18% Al_2O_3 + 63% SiO_2 + 13% Fe_2O_3 + 6% CaO		87	93	49		
Actual Fly Ash Samples						
Blacksville coal fly ash (bituminous) 22% Fe_2O_3, 6% CaO		6			100	
Comanche coal fly ash (subbituminous) 5% Fe_2O_3, 32% CaO		0			0	
Absaloka coal fly ash (subbituminous) 4% Fe_2O_3, 24% CaO					30-35	

(a) Base gas consisted of 40 ppbv Hg^0, 2 mole% O_2, 5 mole% CO_2, and balance N_2 at a temperature of 523 K. HCl, NO, SO_2, and water vapor were added to the base gas in the following concentrations 50 ppmv, 200 ppmv, 200 ppmv, and 1.7 mole%, respectively.
(b) Blank cells mean test not conducted.

The physical, chemical, and carbon properties of the Blacksville and Valmont samples were also characterized. It was found that the two fly ash samples have different unburned carbon contents (3.4 percent for Valmont and 16.8 percent for Blacksville). Based on this finding, it appears that iron content may not be the only ash-related factor that affects the Hg^0 oxidation reactivity of bituminous coal fly ashes. The effect of physical properties, such as surface area, and the effects of chemical properties, such as sodium content and alkalinity, in the fly ash may also determine the propensity of different fly ashes to oxidize Hg in flue gas.

Research for obtaining a better understanding of the roles of NO_X and Fe_2O_3 in the heterogeneous oxidation of Hg^0 was reported recently by UND/EERC.[9] In UND/EERC's reported research, the effects of NO_X and hematite (α-Fe_2O_3) on Hg transformations were studied by injecting them into actual coal combustion flue gases produced from burning bituminous (Blacksville), subbituminous (Absaloka), and lignite (Falkirk) coals in a 7-kW combustion system. It was found that the Blacksville fly ash has high Fe_2O_3 content (12.1 percent), and the Absaloka and Falkirk fly ashes have significantly lower Fe_2O_3 contents (4.5 and 7.9 percent, respectively). Portions of the Fe_2O_3 in Blacksville and Falkirk fly ashes are present as maghemite (γ-Fe_2O_3), and a portion of the Fe_2O_3 in Absaloka fly ash is present as hematite (α-Fe_2O_3). The flue gas generated from the combustion of Blacksville coal contained Hg^{2+} as the predominant Hg species (77 percent), whereas Absoloka and Falkirk flue gases contained predominantly Hg^0 (84 and 78 percent, respectively). Injections of NO_2 (80 to 190 ppm) at 440 to 880 °C and α-Fe_2O_3 (6 and 15 percent) at 450 °C into Absoloka and Falkirk coal combustion flue gases did not change Hg speciation. The UND/EERC researchers suggested that the lack of transformation from Hg^0 to Hg^{2+} in the 7-kW combustion system was possibly due to components of either Absoloka and Falkirk coal combustion flue gases, or their fly ashes, inhibiting the α-Fe_2O_3 catalyzed heterogeneous oxidation of Hg^0 by NO_X. The researchers also believed that an abundance of Hg^{2+} in Blacksville coal combustion flue gas and γ-Fe_2O_3 in the corresponding fly ash, and the inertness of injected α-Fe_2O_3 with respect to heterogeneous Hg^0 oxidation in Absoloka and Falkirk flue gases, are indications that γ-Fe_2O_3 rather than α-Fe_2O_3 catalyzes Hg^{2+} formation.

A study of the role of fly ash in the speciation of Hg in coal combustion flue gases was reported by Iowa State University.[10] In this study, bench-scale laboratory tests were performed in a simulated flue gas stream using two fly ash samples obtained from the ESPs of two full-scale coal-fired electric utility boilers. One fly ash was derived from burning a western subbituminous coal (Powder River Basin) while the other was derived from an eastern bituminous coal (Blacksville). Each of the two samples was separated into three subsamples with particle sizes greater than 10, 3, and 1 μm using three cyclones. The amount of sample collected in these three size ranges was 85 to 90 percent, 10 to15 percent, and 1 percent of the total ash, respectively. Only the two largest sized subsamples were tested for Hg^0 oxidation reactivity. The Blacksville sample was also separated into strongly magnetic (20 percent), weakly magnetic (34 percent), and nonmagnetic (46 percent) fractions using a hand magnet for testing Hg^0 oxidation reactivity of the individual fractions. Since magnetism of the fly ash samples is contributed mainly by iron oxides in the samples, the iron oxide content of the magnetically separated samples is in the following order: strongly magnetic > weakly magnetic > nonmagnetic. The low iron content PRB fly ash is nonmagnetic and was not magnetically

separated for testing. Scanning electron microscopy with energy-dispersive x-ray analysis (SEM-EDX) was used to examine the surface morphology and chemical composition of the fly ash samples. X-ray diffraction (XRD) was also used to examine the mineralogical composition of the whole and fractionated fly ash samples. XRD identifies only crystalline components of the samples. This is important since coal combustion fly ashes typically contain a considerably amount of glassy, amorphous material.

It was observed that, although the fly ashes tested were chemically and mineralogically different, there were no large differences in the catalytic potential for oxidizing Hg^0.[10] The Blacksville fly ash tended to show somewhat more catalytic reactivity (16 to 19 percent Hg^0 oxidation) than the PRB fly ash (4 to 10 percent Hg^0 oxidation). The researchers of this project suggested that the difference in reactivity could be due largely to the larger surface area (3.4 m^2/g) of the Blacksville fly ash compared to that (1.5 m^2/g) of the PRB fly ash. It was found from the SEM-EDX analyses that the iron-rich (highly magnetic) phases in the greater than 10 μm size fraction of the Blacksville sample contained about 25 percent (atomic) Fe, 10 percent each of Al and Si, 2 percent Ca, and lesser amounts of Na, S, K, and Ti. The nonmagnetic Blacksville fly ash fraction in the greater than 10 μm size range contained only 4 percent Fe, 10 percent Al, 20 percent Si, and lesser amounts of Na, S, K, and Ti. For the PRB fly ash (all nonmagnetic), both the greater than 10 μm and greater than 3 μm fractions contained about 3 percent Fe, 10- 20 percent Al and Si, about 10 percent Ca, and 2 percent or less of Mg, S, K, and Ti. The XRD results showed that the whole Blacksville ash contained primarily quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$), magnetite (Fe_3O_4), hematite (Fe_2O_3), and a trace of lime (CaO). The PRB fly ash contained mostly quartz and lesser amounts of lime, periclase (MgO), and calcium aluminum oxide ($Ca_3Al_2O_6$). No magnetite or hematite was found in this ash. It is interesting to note that the nonmagnetic fractions actually showed substantially higher amounts of oxidized Hg than the magnetic fractions. The reported test results of this study indicated that the nonmagnetic fraction resulted in 24 percent of the Hg being oxidized, while 3 percent of the Hg oxidized when using the magnetic ash. It has been suspected that the magnetic (iron-rich) fraction in fly ash would be more catalytic than the nonmagnetic (aluminosilicate-rich) fraction because of its mineralogy (predominantly iron oxides), and possibly because the magnetic phase tends to be enriched in transition metals that could also serve as Hg^0 oxidation catalysts. However, under the experimental conditions employed in this study, the test results do not support this. It was found that the surface area of the nonmagnetic fraction is about four times that of the magnetic fraction. From this study it appears that surface area is a dominant factor in determining the ash's Hg^0 oxidation reactivity.

Because major differences were not observed with the two fly ashes, a set of tests involving a full factorial design was conducted using only the Blacksville fly ash in order to apply statistical techniques for identifying the important factors in determining Hg^0 oxidation.[10] The statistical analysis results indicated that the composition of the simulated flue gas used in the tests and whether or not ash was present in the gas stream were the two most important factors. The presence of HCl, NO, NO_2, and SO_2 and all two-way gas interactions of the four gases listed above were found statistically significant for Hg^0 oxidation. The HCl, NO_2, and SO_2 appeared to contribute to Hg^0 oxidation, while the presence of NO appeared to suppress Hg^0 oxidation. NO_2 was found to be the most important of the four reactive gases tested; next were HCl and NO.

However, the effect of NO depended on whether NO_2 was present. Although the presence of NO_2 was statistically significant as a main factor, it was found more important in its interactions with other gas components. Based on the statistical analysis results, the researchers of this project concluded that the interactions of flue gases with fly ash to cause Hg^0 oxidation are extremely complex, and the difficulty in understanding the Hg chemistry in coal combustion flue gases is not surprising. It is noted that the EPA study showed significant Hg oxidation reactivity of the Blacksville ash, while studies at UND/EERC and Iowa State University show little Hg oxidation reactivity of Blacksville ash. Since the ash samples used in the above studies were generated at three different plant operating conditions, these conditions may play an important role in contributing to the reactivity of the ashes.

5.3.3 Oxidation by Post-combustion NO_X Controls

There are indications that post-combustion NO_X controls SCR and SNCR may oxidize some of the Hg^0 in the flue gas of a coal-fired electric utility boiler. The research on this issue is ongoing. For current understanding of this subject, the reader is referred to Chapter 6.

5.3.4 Potential Role of Deposits, Fly Ash, and Sorbents on Mercury Speciation

Gaseous Hg (both Hg^0 and Hg^{2+}) can be adsorbed by the solid particles in the coal-fired electric utility boiler flue gas. Adsorption is the phenomenon where a vapor molecule in a gas stream contacts the surface of a solid particle and is held there by attractive forces between the vapor molecule and the solid. Solid particles are present in all coal-fired electric utility boiler flue gas as a result of the ash that is generated during combustion of the coal. Ash that exits the furnace with the flue gas is called fly ash. Other types of solid particles may be introduced into the flue gas stream (e.g., lime, powdered activated carbon) for pollutant emission control. Both types of particles may adsorb gaseous Hg in the boiler flue gas. This section addresses the adsorption of gaseous Hg by fly ash. Adsorption of Hg by sorbent particles introduced into the flue gas stream and subsequently captured in a downstream PM control device is discussed in Chapter 6 as related to specific control technologies that may be implemented to increase overall Hg removal from the boiler flue gas.

Gaseous Hg can be adsorbed by fly ash in the flue gas (sometimes called "in-flight" adsorption). In-flight adsorption of gaseous Hg by fly ash occurs in the post-combustion region where the flue gas contains its highest concentration of fly ash (i.e., prior to the first PM control device). The type of coal from which a fly ash originates appears to strongly influence its ability to adsorb Hg. Pilot-scale[11] and field data[12] have indicated that fly ashes from subbituminous coals (specifically, those from the Powder River Basin in Wyoming) adsorb more gaseous Hg than fly ash from lignite and bituminous coals. Test data show 30 percent in-flight adsorption of gaseous Hg by fly ashes from boilers burning these subbituminous coals compared to 10 to 20 percent adsorption by the fly ashes from boilers burning lignite or bituminous coals. It has been suggested that the measured removals of Hg by fly ash can be inflated based on the sampling method, but in most cases are below 15 percent. General trends indicate that in-flight field capture of Hg from combustion of subbituminous coals is higher than from combustion of bituminous coals.[13]

The carbon content of fly ash is another parameter that may influence adsorption of gaseous Hg (the carbon in fly ash is unburned coal). Conditions that result in increased amounts of carbon in fly ash tend to increase the amount and subsequent capture of particle-bound Hg. Hg has been found to concentrate in the carbon-rich fraction of fly ash.[14,15] For similar coals, both laboratory[16] and pilot- and large-scale data[11] have shown a positive correlation between adsorption of gas-phase Hg and carbon content in fly ash. A research project conducted at full-scale coal-fired electric utility boilers in Colorado indicates that certain fly ashes adsorb significant levels of Hg from flue gas. Chapter 7 describes the methodology and results of this study in detail. Many of these fly ashes have carbon content greater than 7 percent, but one low-carbon content fly ash has also been identified. This research project and the possibility of using fly ash re-injection for Hg control is discussed in Chapter 6.

Gaseous Hg also can be adsorbed by fly ash collected on the surface of a FF. In a FF, there is contact of gaseous Hg in the flue gas with the collected layer of fly ash on the FF bags as the gases flow through the FF. Pilot-scale tests of a low-carbon fly ash (less than 0.5 percent carbon) showed that the fly ash adsorbed 65 percent of the gaseous Hg^0 entering a FF; the data indicate that fly ash properties other than just carbon content may affect adsorption. The tested fly ash was produced from the combustion of a subbituminous coal from the Powder River Basin in Wyoming. Western subbituminous coals generally contain high concentrations of CaO and tend to adsorb high levels of Hg^0. At this time, the mechanisms by which these Western coals adsorb Hg^0 are not known; however, the CaO content may be a factor. It has been shown in a pilot-scale study that combustion of western coals tends to produce relatively high particle-bound Hg emissions.[17]

5.4 Capture of Mercury by Sorbent Injection

Mercury can be captured and removed from a flue gas stream by injection of a sorbent into the exhaust stream with subsequent collection in a PM control device such as an electrostatic precipitator or a fabric filter. The implementation of this type of Hg control strategy requires the development, characterization, and evaluation of low-cost and efficient Hg sorbents. Experimental methods for characterization and evaluation are presented below. Further, efforts to develop better sorbents, with greater capacity and lower cost, are also discussed.

5.4.1 Sorbent Characterization

Sorbents are characterized by their physical and chemical properties. The most common physical characterization is surface area. The interior of a sorbent particle is highly porous. The surface area of sorbents is determined using the Brunauer, Emmett, and Teller (BET) method of N_2 adsorption.[18] Nitrogen is adsorbed at the normal boiling point of -195.8 °C and the surface area is determined based on mono-molecular coverage. Surface areas of sorbents range from 5 m^2/g for Ca-based sorbents to over 2000 m^2/g for highly porous activated carbons. Mercury capture often increases with increasing surface area of the sorbent. However, recent research[19] has suggested that pore surface area in the micropores is more important than the total surface area for the removal of part per billion concentrations of Hg from coal combustion flue gases.

Particle size distribution is another physical characteristic that is used to describe sorbents. Activated carbons that are used for Hg control are powdered with a size on the order of 44 μm or less. Particle size is measured using sieves or a scanning electron microscope (SEM). Generally, the smaller the particle size of an activated carbon, the better the access to the surface area and the faster the rate of adsorption kinetics. Careful consideration of particle size distribution can provide significant operating benefits, both in fabric filter applications, where pressure drop must be considered, and in ESP (or duct injection) applications, where mass transfer limitations in the short residence time mean that adsorption is a function of sorbent particle size.

Determination of the pore size distribution of an activated carbon is an extremely useful way of understanding the performance characteristics of the material. Pore sizes are based on the diameter of the pore and are categorized using the following IUPAC conventions: micropores <2 nm, mesopores 2-50 nm, and macropores >50 nm. Micropore volume can be estimated from CO_2 adsorption at 273 K using the Dubinin-Radushkevich (DR) equation. Total pore volume can be determined using N_2 adsorption.

Some of the chemical properties of activated carbons that influence Hg capture include sulfur content, iodine content, chlorine content, and water content. Functional groups of a sorbent have been shown to play an important role in adsorption behavior. Many carbon-oxygen functional groups have been identified in activated carbon including carbonyl, carboxyl, quinone, lactones, and phenol groups. Many methods have been used to study the functional groups present in carbonaceous materials including neutralization of bases, direct analysis of the oxide layer by chemical reaction, infrared spectroscopy, and x-ray photoelectron spectroscopy. For example, specific surface oxygen functional groups can be estimated by using the data measured from the base titration based on the following assumptions: $NaHCO_3$ titrates carboxyl groups; NaOH titrates carboxyl, lactone, and phenol groups; CO_2 is a decomposition product of carboxyl and lactone groups; and CO is a decomposition product of phenol and carbonyl groups.[20] The NaOH and HCl titration values can estimate the acidity and basicity of a carbon, respectively.

5.4.2 Experimental Methods Used in Sorbent Evaluation

In order to evaluate the performance of a specific Hg sorbent, several types of experimental reactors are used. The first step is testing in a bench-scale reactor system, which may be a fixed-bed, entrained-flow, or a fluidized-bed system. Sorbents that perform well in bench-scale tests are then tested in a pilot-scale system and may eventually be tested in a full-scale system. These systems are discussed below.

5.4.2.1 Bench-scale Reactors

Bench-scale reactors are the smallest category of reactors, hence the term "bench-scale." There are several types of bench-scale reactors that are used to evaluate Hg sorbents. The first type that will be discussed is a fixed-bed or packed-bed system. This type of reactor simulates Hg^0 capture that would occur in a FF. Another type of bench-scale reactor is an entrained-flow

reactor, which simulates in-flight capture of Hg^0 upstream of an ESP. It is important to highlight the major differences between these two reactors as shown in Table 5-2.

Fixed-bed Reactor. A schematic of the experimental apparatus used by EPA to study the capture of Hg^0 and $HgCl_2$ is shown in Figure 5-7. A detailed description of the apparatus can be found elsewhere.[21] In this system the Hg vapor generated is carried into a manifold by a nitrogen stream where it is mixed with SO_2, HCl, CO_2, O_2, and water vapor (as required by each particular experiment). The sorbent to be studied (approximately 0.02 g diluted with 2 g inert glass beads; bed length of approximately 2 cm) is placed in the reactor and maintained at the desired bed temperature by a temperature controller. A furnace kept at 850 °C is placed downstream of the reactor to convert any Hg^{2+} (as in $HgCl_2$) to Hg^0. According to thermodynamic predictions, the only Hg species that exists at this temperature is Hg^0.[22] Quality control experiments, in the absence of HCl in the simulated flue gas, also showed that all the $HgCl_2$ could be recovered as Hg^0 across this furnace. The presence of the furnace enables detection of non-adsorbed $HgCl_2$ as Hg^0 by the on-line ultraviolet (UV) Hg^0 analyzer, thus providing actual, continuous Hg^0 or $HgCl_2$ capture data by the fixed bed of sorbent. The UV Hg^0 analyzer used in this system responds to SO_2 as well as Hg^0. Signal effects due to SO_2 are corrected by placing an on-line SO_2 analyzer (UV) downstream of the Hg^0 analyzer and subtracting the measured SO_2 signal from the total response of the Hg analyzer; the SO_2 analyzer is incapable of responding to Hg in the concentration range generally used.

In each test, the fixed bed is exposed to the Hg-laden gas for 7 hours or until 100 percent breakthrough (saturation) is achieved (whichever comes first). During this period the exit concentration of Hg is continuously monitored. The instantaneous removal of Hg^0 or $HgCl_2$ at any time (t) is obtained as follows:

Instantaneous removal at time t (%) = $100*[(mercury)_{in} - (mercury)_{out}]/(mercury)_{in}$.

The specific amount of Hg uptake (q, cumulative removal up to time t; weight Hg species/weight sorbent) is determined by integrating and evaluating the area under the removal curves. Selected experiments conducted using this experimental setup have been run in duplicate and indicated a range of $\pm 10\%$ about the mean in the experimental results. It was found that differences in equilibrium $Hg^0/HgCl_2$ capacities, at 200-300 mg/Nm^3 inlet concentration, are statistically significant if the $Hg^0/HgCl_2$ capacities are at least $\pm$ 10 percent different from one another.

Entrained-flow Reactor. An example of a bench-scale entrained-flow reactor[23] is shown in Figure 5-8. This EPA reactor is constructed of quartz and is 310.5 cm long with an inside diameter of 4 cm. Three gas-sampling ports are located along the length of the reactor and are labeled SP1, SP2, and SP3. The reactor is heated with three Lindberg, 3-zone electric furnaces in series. The baseline Hg^0 concentration is measured in the absence of activated carbon using an ultraviolet (UV) analyzer (Buck Scientific, model 400A). Once the baseline is established, activated carbon is fed into the top of the reactor using a fluidized-bed feeder (0.2-0.5 std. L/min). The gas-phase Hg^0 concentration is then measured at one of the sample ports by pulling a gas sample (0.5 std. L/min) through a 1 μm filter to remove any particles, then through a

Table 5-2. Comparison of bench-scale fixed-bed with entrained-flow reactors.

Test Condition	Fixed-Bed Reactor	Entrained-Flow Reactor
Simulation of capture in	Fabric filter	Upstream of an ESP
Sorbent exposure	Minutes/Hours/Days	Less than 4 seconds
Sorbent evaluation based on	Breakthrough or uptake capacity	Reactivity
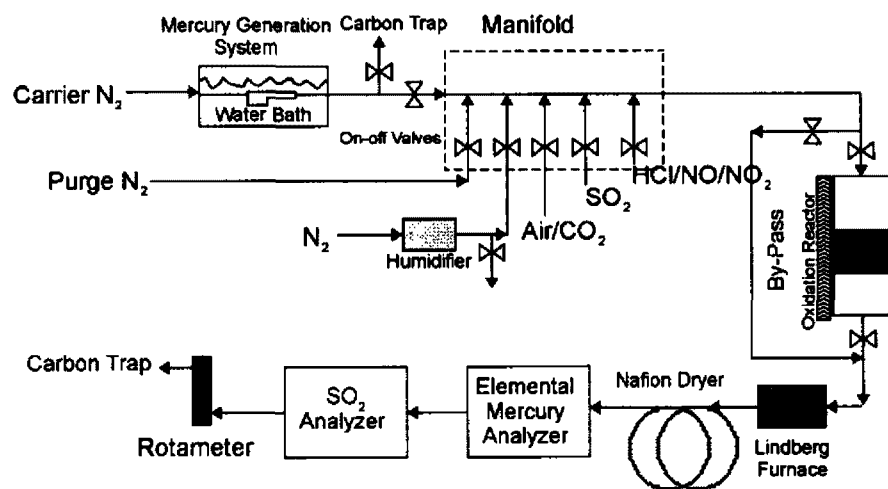
Figure 5-7. Schematic of bench-scale fixed-bed reactor (source: Reference 21).
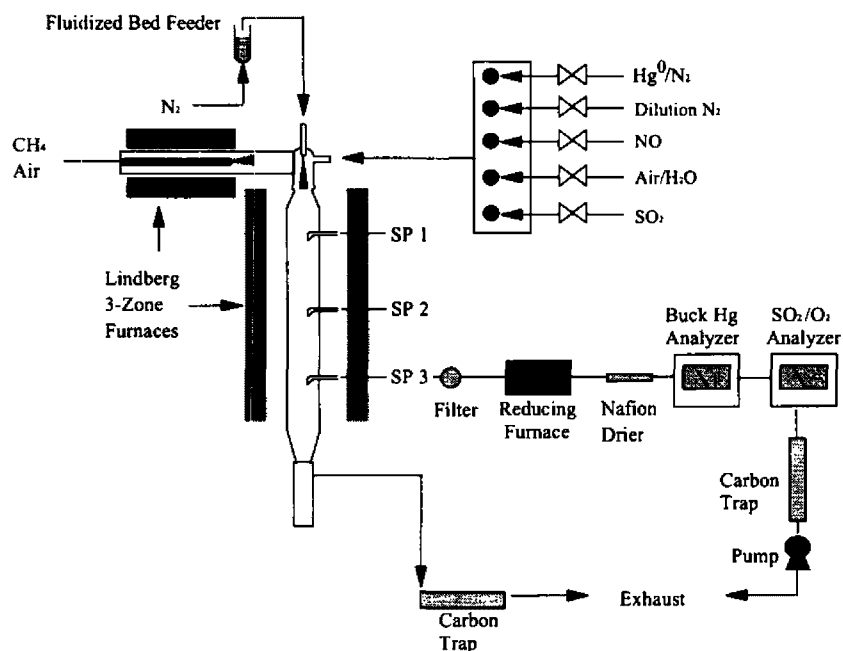
Figure 5-8. Schematic of bench-scale flow reactor with methane burner (source: Reference 23).

reducing furnace to convert any oxidized Hg to Hg^0. The reduction method is described elsewhere.[21] After the reducing furnace, the gas is dried using a Nafion® gas sample dryer (Perma Pure, Inc.) and is finally sent to a Buck analyzer.

Initial tests are conducted using nitrogen (N_2) as the carrier gas with later tests performed in a flue gas from a methane flame. In the N_2 carrier gas tests, industrial grade N_2 (1 std. L/min) flows over a Hg^0 permeation tube that is housed in a permeation oven (VICI Medtronic's, model 190) to generate a Hg^0-laden gas stream. The N_2/Hg^0 stream is diluted with a second N_2 stream (12 std. L/min) to the desired concentration before entering the top of the reactor. Other gases (SO_2, NO_X, O_2, water vapor) can be blended into the N_2 carrier gas in the mixing manifold.

A fluidized-bed feeder is used to inject sorbent into the reactor. An inlet line of N_2 is used to fluidize and carry the activated carbon to the reactor. The carbon feed rate is adjusted by varying the amount of N_2 (0.2 to 0.5 std. L/min) entering the feeder.

Because the UV analyzer used to detect Hg^0 is sensitive to particles, a filter is used to remove any carbon that may have been carried with the gas. Tests have been conducted to determine if carbon particles accumulate on the filter, as this would act like a packed bed and the reactor's removal of Hg^0 would be a combination of in-flight and filter (packed-bed) capture. In these tests, activated carbon was injected in the absence of Hg^0, and a gas sample was pulled through the filter. After 1 minute, Hg^0 was added to the gas stream to see if there was a lag in the time it takes for the baseline to return. The results were the same as for a blank filter, suggesting that the filter does not have an effect on the results.

The total flow through the reactor is typically 13 std. L/min, which gives residence times of 5.2, 11.5, and 17.7 s at ports SP1, SP2, and SP3, respectively. The velocity of the particles through the reactor is assumed to be the same as that of the gas flow since the terminal velocity of the particles is smaller than the velocity of the gas through the reactor by a factor of 3.

Fluidized-bed Reactor. Another type of bench-scale reactor that is used to evaluate sorbents is a fluidized-bed reactor,[24] shown in Figure 5-9. The advantage of this type of reactor is the extended contact time between the sorbent and the Hg-laden gas. Bench-scale Hg removal tests can be performed on a fluidized-bed reactor apparatus. In a typical experiment, an $Hg/NO/SO_2$ mixture, nitrogen, and dry air are metered through rotameters to produce 12 scfh of a dry simulated flue gas of 300 ppmv NO_X, 600 ppmv SO_2, 8 percent O_2, and varying Hg concentrations. This gas is preheated to reaction temperature (80 °C) and humidified with vaporized water to an average 10.5 mol % water. The resulting wet simulated flue gas is then passed through a vertical reactor loaded with fluidized sorbent and sand, and then passed through a filter to remove any entrained particulate to protect the downstream equipment. The reactor and filter assembly are housed in an oven maintained at 80 °C. The test stand is equipped with a bypass of the reactor and filter assembly to allow for bias checks. Sorbent is exposed to simulated flue gas for 30 minutes. Water is removed from the spent flue gas with a NAFION™ Dryer. Dry gas is then serially analyzed with Hg, SO_2, and NO_x continuous emission monitors (CEMs).
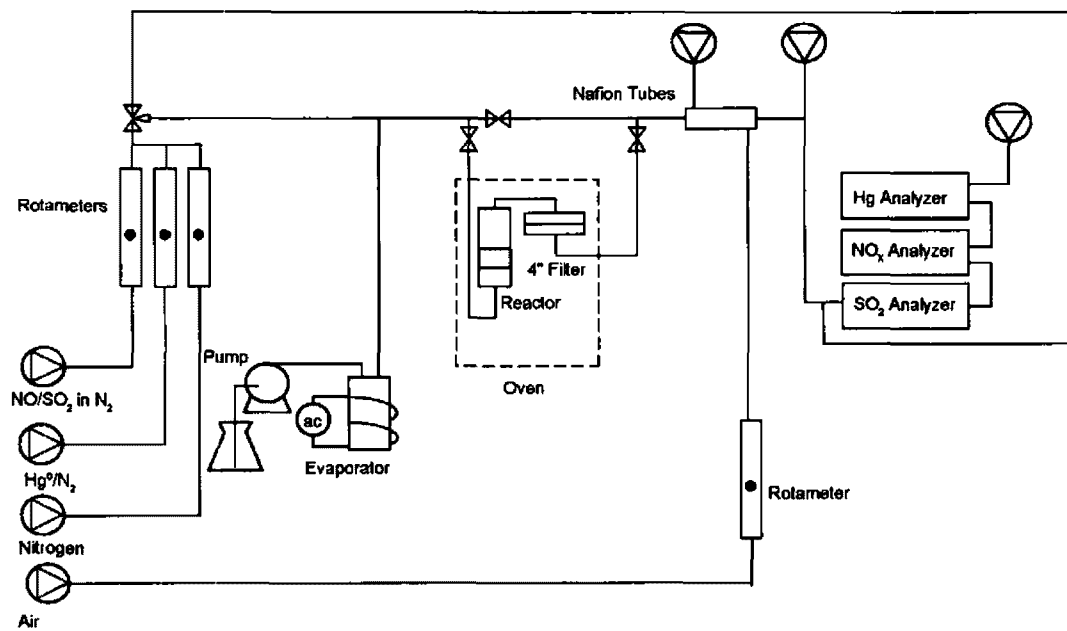
Figure 5-9. Schematic of bench-scale fluidized-bed reactor system (source: Reference 24).

5.4.2.2 Pilot-scale Systems

Initial design and testing is done in bench-scale reactors. Once the fundamentals of Hg capture have been tested in a bench-scale system, the next step is to move up to a larger or pilot-scale system. The main difference between bench- and pilot-scale systems involves testing sorbents in a more realistic situation involving coal combustion flue gas. This gas is generated in a pilot-scale combustor that contains a FF or ESP for particulate control. An example of this is the pilot-scale combustor operated by DOE (see Figure 7-3). This system burns coal at a rate of 500 lb/hr and is equipped with a FF. Sorbents, such as activated carbon, are injected upstream of the PM control device. Mercury removal is determined by gas-phase sampling upstream of the sorbent injection point and downstream of the PM control device.

Pilot-scale Hg removal can also be examined using a flue gas slipstream from a full-scale unit. An ESP or FF is attached to the slipstream and tested. A portable FF was developed by EPRI and called a COHPAC (COmpact Hybrid PArticulate Collector) unit. [26] This unit was tested for Hg removal using activated carbon. The URS Corporation (formerly Radian International) also developed a reactor system that uses a slipstream of actual flue gas withdrawn from a power plant to evaluate sorbents or catalysts in a fixed bed. [27] It should be noted that the slipstream reactor, which uses actual coal combustion flue gas, does not always produce the same Hg captive behavior of a sorbent that a similar laboratory system does using simulated flue gas. [28] It is important to perform pilot-scale tests prior to conducting full-scale tests to eliminate uncertainties and costly redesign of a process. With the data collected in the pilot-scale studies, full-scale tests can be initiated.

5.4.2.3 Full-scale Tests

Most of work to date in Hg control has been done in bench- or pilot-scale systems. These reduced-scale systems provide insight into many issues, but cannot fully account for the impacts that additional control technologies have on plant-wide equipment. Therefore, it is necessary to scale up and perform full-scale tests to document actual performance in a full-scale boiler. These tests are based on the results obtained in bench- and pilot-scale tests. Screening tests in bench- and pilot-scale systems identify sorbents that are effective in capturing Hg. These sorbents are then tested in a full-scale coal-fired electric utility power plant to determine full-scale performance.

Each full-scale unit is unique in terms of the pollution control equipment that is present as well as the operating conditions. Some of the factors that are evaluated include:

- Type of particulate control equipment that is used (ESP or FF),

- Impact of cake thickness and cleaning frequency in a FF, and

- Removal of Hg by the fly ash in the system. Subbituminous coal ashes have been shown to be effective in capturing Hg.

5.4.3 Research on Sorbent Evaluation

5.4.3.1 Sorbent Evaluation Using Enhanced-flow Reactors

A flow reactor was designed to simulate Hg^0 capture through a duct or ESP and to obtain kinetic rate constants for the adsorption of Hg^0 onto sorbents. Several researchers have predicted that, under certain conditions, dispersed-phase capture would be limited by mass transfer.[29,30] Calculations were performed to determine the required operating conditions to minimize external mass transfer effects in the flow reactor, and experimental tests were performed to verify these calculations.[23,31,32] The first test involved changing the diffusion coefficient by changing the gas in the system from N_2 to helium (He) and to argon (Ar) while holding all other parameters constant (particle size, residence time, temperature, and Hg^0 concentration). The diffusion coefficient increased by an order of magnitude by changing the gas from N_2 to He. Using a lignite-based commercially available carbon (Norit FGD) at 100 °C and a Hg^0 concentration of 86 ppb, Hg^0 removal was 6 percent at a carbon to Hg ratio (C:Hg) of 1,500:1 and increased to 30 percent at a C:Hg of 8,000:1. Experimental results were similar when He was used as compared to N_2. If external mass transfer were controlling, then a higher Hg^0 removal would have been obtained using He, since the mass transfer coefficient increased.

A second test involved using two commercially available activated carbons, Norit FGD and Calgon WPL at 100 °C and 124 ppb Hg^0 in dry N_2. Removal for the FGD carbon ranged from 9 percent (C:Hg=2200:1) to 23 percent (C:Hg=6400:1). Removal for the WPL carbon ranged from 11 percent (C:Hg=340) to 94 percent (C:Hg=5000:1). If dispersed-phase capture in the flow reactor were film-mass-transfer limited, the two activated carbons would have removed similar amounts of Hg^0 at a given C:Hg, assuming each carbon had sufficient Hg^0 capacity.

The flow reactor has been used to examine the effect of temperature, particle size, residence time, carbon type, and gas composition on Hg^0 removal.[31-33] The effect of particle size on Hg^0 removal for Darco FGD at 100 °C and a Hg^0 concentration of 86 ppb is shown in Figure 5-10. Several particle sizes (4-8, >8-16, >16-24, and >24-44 μm) were injected into the flow reactor at C:Hg ratios ranging from 2000 to 11,000:1. The gas was sampled at SP2, resulting in a gas contact time of 8.4 s. Figure 5-11 shows that greater Hg^0 removal is achieved by increasing the feed rate and by decreasing the particle size. At a C:Hg of 5000:1, a 5 percent reduction was obtained with the >24-44 μm size fraction as compared to a 20 percent reduction with the 4-8 μm fraction. Thus by using a smaller particle a higher removal can be obtained at a given C:Hg. Both external and internal mass transfers are dependent on particle size: the effect of mass transfer increases with an increase in particle size.

5.4.3.2 Sorbent Evaluation Using Packed-bed Reactors

Recent bench-scale studies at the University of North Dakota's Energy and Environmental Research Center (UND/EERC) have focused on the interactions of gaseous flue gas constituents on the adsorption capacity of activated carbon for Hg.[34] Bench-scale studies were performed using a fixed bed of carbon. The tested carbon was a commercially available lignite-based activated carbon (LAC) commercially known as Darco FGD™ from Norit
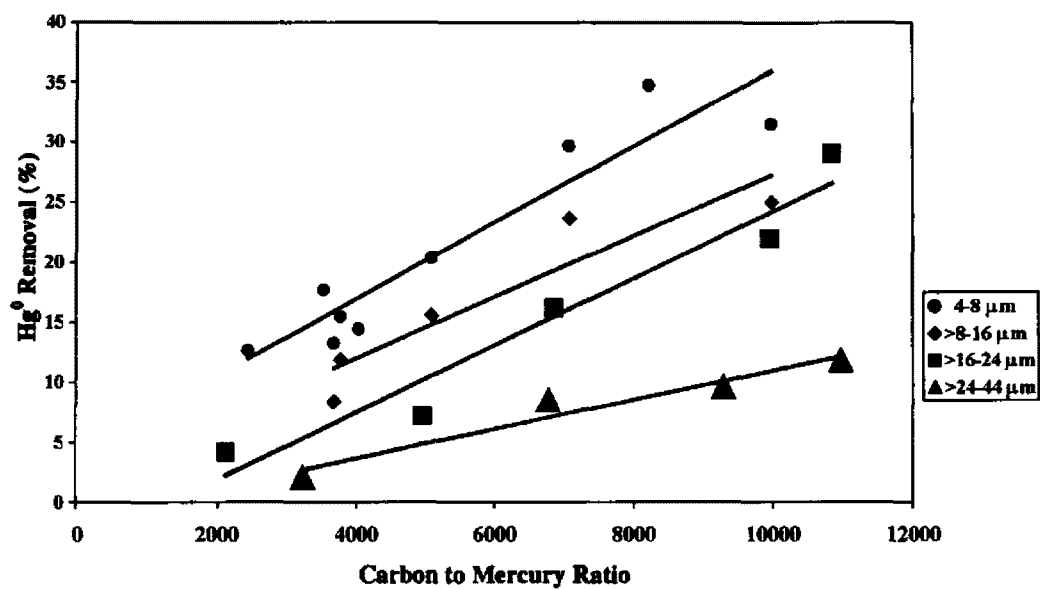
Figure 5-10. Effect of particle size on adsorption for Darco FGD at 100 °C, 86 ppb Hg⁰ concentration, and 8.4 s contact time (source: Reference 31).

Americas, Inc. A simulated flue gas containing a nominal concentration of 15 $\mu g/Nm^3$ of gaseous Hg^0 was passed through the fixed bed of carbon. In addition to Hg, the baseline test gas contained 6 percent O_2, 12 percent CO_2, 8 percent H_2O, and the balance N_2. Various flue gas constituents (SO_2, HCl, NO, and NO_2) were added individually and in combination to the baseline test gas to determine the effects of flue gas constituents on Hg adsorption. Temperature effects were also examined. Table 5-3 shows the various compositions of gas tested.

For each adsorption test, a Hg CEM was used to monitor total or elemental Hg. Measurements were alternated between the inlet and outlet locations of the test bed. For a given test, measurements took place primarily at the outlet location; however, occasionally the inlet location was tested to confirm that a constant concentration of gaseous Hg^0 was entering the test bed. For each test, the analyzer was set to measure total gaseous Hg at the outlet; however, occasionally the analyzer was set to measure only gaseous Hg^0 at the outlet. The purpose of measuring only gaseous Hg^0 at the outlet was to determine if any incoming gaseous Hg^0 was being oxidized by carbon in the bed (evident if the concentration of gaseous Hg^0 in the outlet gas was less than the concentration of total gaseous Hg in the outlet gas).

For adsorption to take place (assuming attractive forces exist between a particular gaseous specie and sorbent), the adsorbing specie must have sufficient time to reach the surface of a sorbent and diffuse into its pores (where most adsorption takes place). If any of the adsorbing specie in a gas stream passing through a fixed bed of sorbent cannot reach the surface of the sorbent (mainly its pore surfaces), the specie will pass through the bed unadsorbed. Researchers conducted preliminary tests to show that the gaseous Hg in the test gas had sufficient time (under the conditions tested) to contact the sorbent and to diffuse into its pores. Proving this point was important since some of the adsorption tests showed immediate breakthrough of Hg in the outlet gas. In these cases, immediate breakthrough was not due to insufficient contact time but rather the carbon's inability to adsorb all of the gaseous mercury.

Figure 5-11 shows an example of the sampling and measurements taken during testing of the baseline test gas with HCl, NO_2, and SO_2 (as noted in the graph, SO_2 was added to the baseline test gas 2.5 hours after the start of the test). Except where noted, the Hg concentrations in Figure 5-11 are those in the outlet test gas and represent concentrations of total gaseous Hg. Mercury concentrations in the graph are quantified as a percentage of the inlet concentration of gaseous Hg^0. The percentage of Hg in the outlet test gas is called percent breakthrough. Figure 5-11 indicates that the analyzer sampled and measured total gaseous Hg in the outlet gas at all times during testing except at approximately 5.2 hours, at which time the analyzer sampled and measured Hg in the inlet gas. At approximately 5.15 hours the analyzer measured gaseous Hg^0 instead of total gaseous Hg in the outlet test gas; the drop in the concentration curve at this time from approximately 150 percent to zero percent indicates that Hg in the outlet test gas consisted entirely of gaseous Hg^{2+}. Thus, while only gaseous Hg^0 was in the test gas entering the carbon bed, the Hg^0 was oxidized to Hg^{2+} as it passed through the bed. (Why some of the outlet concentrations of total gaseous Hg exceeded 100 percent of the inlet Hg concentration for this run is explained further on in this section.)

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Table 5-3. Composition of test gases to simulate coal combustion flue gas used for UND/EERC bench-scale study (source: Reference 34).

SO₂ ppmv	HCl ppmv	NO ppmv	NO₂ ppmv
Baseline test gas*			
0	0	0	0
Baseline test gas plus 1 additional gas			
1600	0	0	0
0	50	0	0
0	0	300	0
0	0	0	20
Baseline test gas plus 2 additional gases			
1,600	50	0	0
1,600	0	300	0
1,600	0	0	20
0	50	0	20
0	50	300	0
0	0	300	20
Baseline test gas plus 3 additional gases			
1,600	50	300	0
1,600	50	0	20
1,600	0	300	20
0	50	300	20
Baseline test gas plus 4 additional gases			
1600	50	300	20

(a) Prior to adding SO_2, HCl, NO, and/or NO_2, the baseline test gas contained 15 μg/nm³ of gaseous Hg°; 6 percent O_2; 12 percent CO_2; 8 percent H_2O; and the balance N_2.
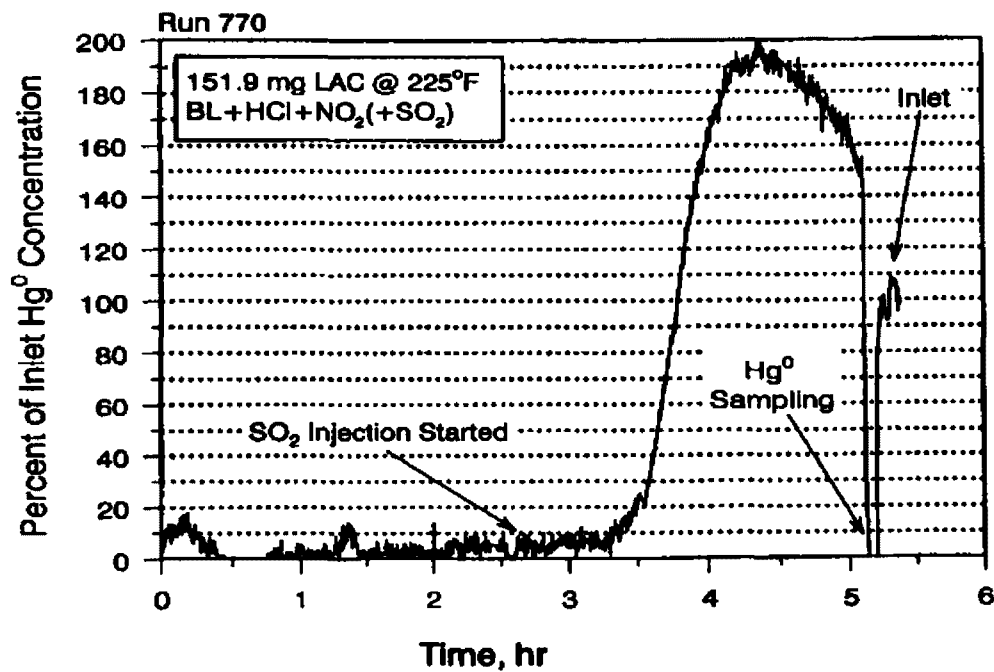
Figure 5-11. Example of the sampling and measurements taken during testing of the baseline test gas with HCl, NO_2, and SO_2. (source: Reference 34).

Graphs of the adsorption tests with the 15 remaining gases in Table 5-3 can be found elsewhere;[13] the cited graphs are similar to Figure 5-11 in that Hg concentrations (primarily outlet concentrations of total gaseous Hg) are plotted versus the time of the adsorption test.

The following summarizes the detailed test results:

- When the sorbent was exposed to the baseline gas only, the sorbent initially captured 10 to 20 percent of the incoming gaseous Hg^0; the rest of the Hg passed through the bed (i.e., was not adsorbed).

- When the sorbent was exposed to SO_2 in addition to the baseline gas, Hg capture improved slightly.

- Under exposure of the sorbent to HCl, NO, or NO_2 added one at a time to the baseline gas, the Hg capture of the sorbent improved to 90 to 100 percent.

- An apparently significant interaction between SO_2 and NO_2 gases and the sorbent caused a rapid breakthrough of Hg as well as conversion of the Hg to its volatile oxidized form. This effect occurred at both 107 and 163 °C (225 and 325 °F) and with or without the presence of HCl and NO.

- In the presence of all four acid gases (SO_2, HCl, NO, and NO_2), rapid breakthrough and oxidation of the Hg occurred at both 107 and 163 °C (225 and 325 °F). This suggests that the interactions between the sorbent and NO_2 and SO_2 gases produced poor sorbent performance, which may be a major effect. This may be likely to occur over a variety of conditions typical of coal-fired electric utility boilers, and represents a hurdle that must be overcome to achieve effective Hg control by carbon adsorption.

The UND/EERC is continuing to investigate the interactions of gaseous flue gas constituents on the adsorption capacity of activated carbon for Hg. In addition, other types of sorbents are being developed and investigated under similar simulated flue gas conditions. Other gaseous flue gas constituents are also being examined to assess their impact on the adsorption of Hg.

5.4.3.3 Sorbent Evaluation Using Fluidized-bed Reactors

Under DOE's Small Business Innovative Research (SBIR) Program, Environmental Elements Corporation (EEC) has been developing a circulating fluidized bed (CFB)[24] to promote agglomeration of fine PM, allowing for its capture in an ESP. In addition, a single injection of iodide-impregnated activated carbon was added to the fluidized bed to adsorb gaseous Hg. High residence time, as a result of particle recirculation, allows for effective utilization of the carbon and high collection of the fine particles. Laboratory tests with heated air indicate that, with a high density of fly ash at a 4-second residence time within the bed, fine particle emissions are reduced by an order of magnitude.

Results from the laboratory-scale testing indicate that spiked gaseous Hg^0 was significantly reduced when passed through the fluidized bed of fly ash (50 percent Hg removed) with a further reduction to essentially zero, when activated carbon was injected into the bed (25 $\mu g/m^3$ to zero) at 110 °C (230 °F). The iodide-impregnated activated carbon was fully utilized after greater than 2 hours within the bed. An adsorption capacity was calculated to be 770 $\mu g/g$ for the carbon and 480 $\mu g/g$ for the bed of ash. Other field tests were conducted at Public Service Electric and Gas' Mercer Station with similar results.[24]

5.5 Sorbent Development

The implementation of an effective and efficient Hg control strategy using sorbent injection requires the development of low-cost and efficient Hg sorbents. Of the known Hg sorbents, activated carbon and calcium-based sorbents have been the most actively studied. However, improved versions of these sorbents and new classes of Hg sorbents can be expected, as this is still a very active field.

5.5.1 Powdered Activated Carbons

Activated carbons have been extensively studied for their Hg capture capability. Activated carbon is the reference sorbent for Hg control in municipal waste combustors. Many factors may affect the adsorptive capability of the activated carbon sorbent. These include the temperature and composition of the flue gas, the concentration of Hg in the exhaust stream, and the physical and chemical characteristics of the activated carbon (or functionalized/impregnated carbon). Some specific efforts at understanding these effects are given below.

5.5.1.1 Effects of Temperature, Mercury Concentration, and Acid Gases

The effects of bed temperature, Hg concentration, presence of acid gases (HCl and SO_2), and presence of water vapor on the capture of Hg^0 and $HgCl_2$ by thermally activated carbons (FGD and PC-100) and Ca-based sorbents [Ca (OH)$_2$ and a mixture of Ca(OH)$_2$ and fly ash] were examined in a fixed-bed, bench-scale system.[21] Sorption studies indicated an abundance of $HgCl_2$ adsorption sites in calcium-based sorbents. Increasing the $HgCl_2$ concentration increased its uptake, and increasing the bed temperature decreased its uptake. Gas-phase $HgCl_2$ concentration had a very strong effect on its adsorption, while bed temperature had a small influence on adsorption. The observed temperature and concentration trends suggest that the process is adsorption-controlled and that the rate of $HgCl_2$ capture is determined by how fast molecules in the vicinity of the active sites are being adsorbed. Mixtures of Ca(OH)$_2$ and fly ash with 7 times higher surface area than Ca(OH)$_2$ and a totally different pore size distribution exhibited identical $HgCl_2$ capture to that of Ca(OH)$_2$. The presence of acid gases (1000 ppm SO_2 and 50 ppm HCl) drastically decreased the uptake of $HgCl_2$ by Ca(OH)$_2$. The inhibition effect of SO_2 was more drastic that HCl, and essentially controlled the $HgCl_2$ uptake. It was hypothesized that the inhibition effect is due to competition between these acid gases and $HgCl_2$ for the available alkaline sites.

Sorption studies further indicated that the available active sites for capturing Hg^0 in the activated carbons are limited, suggesting that it is more difficult to control Hg^0 emissions than $HgCl_2$ emissions. Increasing the Hg^0 inlet concentration and decreasing the bed temperature increased the saturation capacities of the activated carbons, the time needed to reach this capacity, and the initial rate of Hg^0 uptake. Unlike $HgCl_2$ capture by $Ca(OH)_2$, bed temperature had a very strong effect on the Hg^0 adsorption by the activated carbons, and gas-phase Hg^0 concentration had a small influence on such adsorption. PC-100, with twice the surface area of FGD, consistently exhibited higher saturation capacities (3-4 times higher) than FGD. The presence of acid gases had a positive effect on the capture of Hg^0 by a lignite-coal-based activated carbon (FGD) and had no influence on Hg^0 capture by a bituminous-coal-based activated carbon (PC-100). This difference was related to a higher concentration of Ca (acid gas sorbent) in FGD. It appears that adsorption of these acid gases by FGD creates active S and Cl sites, which are instrumental in capturing Hg^0, through formation of S-Hg and Cl-Hg bonds in the solid phase (chemisorption). These results indicate that the optimum region for the control of Hg^0 by injection of activated carbon is upstream of the acid gas removal system.

5.5.1.2 Role of Surface Functional Groups

The content of oxygenated acidic and alkaline surface functional groups (SFGs) on the surface of two activated carbons was manipulated to investigate their role in Hg^0 and $HgCl_2$ capture.[35] Acidic SFGs on the surface of activated carbons were neutralized by a variety of alkaline washes. The alkaline-treated activated carbon showed no enhancement in Hg^0 and $HgCl_2$ capture, thus indicating that acidic SFGs play no role in capturing Hg species. The alkaline SFGs content was increased by a thermal treatment process. The thermally treated activated carbons did not exhibit any improvement with regard to their Hg^0 and $HgCl_2$ capture capabilities as compared to the untreated ones. The activated carbons were then treated with a very dilute HCl solution to decrease their alkaline SFGs content. The HCl-treated activated carbon showed a very significant improvement in its Hg^0 and $HgCl_2$ capture capabilities. This observation was contrary to the initial hypothesis that alkaline sites are needed to capture acidic $HgCl_2$ from the flue gas. It was then hypothesized that HCl treatment increases the number of active surface chlorine sites, which subsequently enhance Hg^0 and $HgCl_2$ capture. An analytical technique, Energy-Dispersive X-ray Spectroscopy (EDXS), was used to quantify surface Cl sites. A strong correlation between the increased amount of surface Cl and $Hg^0/HgCl_2$ uptake enhancement was observed. The role of SFGs containing Cl atoms in providing $Hg^0/HgCl_2$ active sites was established. Future investigation using SEM/EDXS and Fourier Transform Infrared (FTIR) will focus on understanding the nature of Cl bonds on the surface of carbon, so that more effective Hg species sorbents can be manufactured.

5.5.1.3 In-flight Capture of Mercury by a Chlorine-impregnated Activated Carbon

Activated carbon duct injection seems to be the most promising Hg control technology for coal-fired electric utility boilers equipped with ESPs. In this technology, the injected activated carbon removes Hg only while contacting the flue gas during very limited sorbent/gas contact time (<3 seconds). Prior investigations have shown that very high, and rather costly, carbon-to-Hg weight ratios (>50,000) are needed to achieve adequate Hg removal. In order to

reduce the operating cost of the carbon injection process, either a more efficient sorbent that can operate at a lower carbon-to-Hg weight ratio or a lower-cost activated carbon (or possibly both) are required. In this study[33], a cost-effective Cl-impregnation process was successfully implemented on an inexpensive virgin activated carbon. The Cl-impregnated carbon was produced in a 5 pound large batch, and its in-flight Hg^0 removal efficiency was evaluated in a flow reactor (as previously discussed in Section 5.4.2.1) with gas/solid contact times of 3 to 4 seconds. The Hg^0 removal efficiency of more than 80 percent was obtained in a flue gas containing the effluent of natural gas combustion doped with coal combustion levels of NO_X and SO_2 at carbon-to-Hg weight ratios of about 3000. Hg^0 removal was rather insensitive to the adsorption temperature in the range of 100-200 °C. Cost analysis showed that this Cl-impregnation process can produce a very active and cost-effective activated carbon that can be used as a practical sorbent in a duct injection control technology in ESP-equipped coal-fired electric utility boilers. Preliminary cost estimates indicated that approximately 53 percent reduction of the total annual cost of Hg control could be possible when using Cl-impregnated FGD in lieu of virgin activated carbon. Future investigations would be focused on evaluating the Cl-impregnated activated carbon in a pilot-scale, 21-kW (90,000-Btu/hr) refractory-lined, furnace fired with pulverized coal.[33]

5.5.2 Calcium-based Sorbents

Work conducted by EPA and ARCADIS Geraghty & Miller, Inc. [funded by the Illinois Clean Coal Institute (ICCI)] indicates that the injection of calcium-based sorbents into flue gas can result in significant removal of Hg.[36,37] Researchers examined the high-temperature/short-gas-phase residence time removal of Hg using injection of lime while burning an Illinois #6 coal in a pilot-scale combustor. The lime was injected as a slurry at a calcium-to-sulfur (Ca:S) ratio of 2.0 mol/mol at 968 °C (1775 °F). Under these conditions, 77 percent of the total Hg was removed from the flue gas (Table 5-4). Based on these results, they concluded, "injection of lime in the high temperature regions of coal-fired processes upstream of air pollution control systems can efficiently transfer Hg from the gas to the solid phase." Summaries of work follow.

5.5.2.1 Capture of Low Concentrations of Mercury Using Calcium-based Sorbents

The capture of Hg^0 and mercuric chloride ($HgCl_2$), the Hg species identified in coal flue gas, by three types of calcium-based sorbents differing in their internal structure, was examined in a packed-bed, bench-scale study under simulated flue gas conditions for coal-fired electric utility boilers.[38] The results obtained were compared with Hg^0 and $HgCl_2$ capture by an activated carbon (FGD) under identical conditions. Tests were conducted with and without SO_2 to evaluate the effect of SO_2 on Hg^0 and $HgCl_2$ control by each of the sorbents.

The Ca-based sorbents showed insignificant removal of Hg^0 in the absence of SO_2. However, in the presence of SO_2, Hg^0 capture was enhanced for the three Ca-based sorbents. It was postulated that the reaction of hydrated lime with SO_2 would result in pore mouth closure as evidenced by the sharp drop in the SO_2 removal rate after the initial 10 minutes of exposure. Despite the loss of internal surface area, the relatively high uptake of Hg^0, observed for these sorbents in the presence of SO_2, suggests that Hg^0 and SO_2 do not compete for the same active

Table 5-4. Mercury removal by lime sorbent injection as measured by EPA bench-scale tests (source: Reference 36).

Test	Total Hg Concentration, µg/dscm	Total Gaseous Hg, percent	Total Particle-bound Hg, percent
Baseline	5.7	100	0
Lime sorbent injection	8.0	23	77

sites, and that the sites for Hg^0 capture are influenced positively by the presence of SO_2. Moreover, the capture of Hg^0 in the presence of SO_2 increased with sorbent surface area and internal pore structure.

Conversely, the three Ca-based sorbents showed decreased removal of $HgCl_2$ in the presence of SO_2. In the absence of SO_2, roughly 25 percent of the incoming $HgCl_2$ was captured. The alkaline sites in the Ca-based sorbents were postulated to be instrumental in the capture of acidic $HgCl_2$. SO_2 not only competed for these alkaline sites but also, as mentioned, likely closed pores with subsequent reduction in accessibility of the interior of the Ca-based sorbent particles to the $HgCl_2$ molecules.

It was hypothesized that the capture of Hg^0 in the presence of SO_2 may occur through a chemisorption mechanism, while the nature of the adsorption of $HgCl_2$ molecules may be explained through a physisorption mechanism. The effect of temperature studies further supported this hypothesis. Increasing the system temperature caused an increase in Hg^0 uptake by the sorbents in the presence of SO_2. However, the increase in temperature resulted in a significant decrease in the $HgCl_2$ uptake in the absence or presence of SO_2. Increased sorbent surface area and internal pore structure had no observable effect on $HgCl_2$ capture in the presence of SO_2.

With the relatively large quantities of Ca needed for SO_2 control at coal-fired electric utility boilers, the above results suggest that Ca-based sorbents, modified by reaction with fly ash, can be used to control total Hg emissions and SO_2 cost effectively. The most effective calcium-based sorbents are those with significant surface area (for SO_2 and $HgCl_2$ capture) and pore volume (for Hg^0 capture).

5.5.2.2 Simultaneous Control of Hg^0, SO_2, and NO_X by Oxidized-calcium-based Sorbents

Multipollutant sorbents have been developed that can remove both Hg^0 and Hg^{+2} as effectively as FGD activated carbon in fixed-bed simulations of coal-fired electric utility boiler flue gas at 80 °C.[39] Oxidant-enriched, calcium-based sorbents proved far superior to activated carbon with respect to SO_2 uptake on the same fixed-bed simulations. These oxidant-enriched, calcium-based sorbents also performed better with respect to NO_X and SO_2 uptake than baseline lime hydrates for fixed- and fluid-bed simulations at 80 °C.

Preliminary economic analyses suggest that silicate sorbents with oxidants are 20 percent of the cost of activated carbon for Hg removal, while oxidant-enriched lime hydrates offer reduced, but significant savings. Credits for SO_2 and NO_X increase the savings for multipollutant sorbents over activated carbon.

The apparent superiority of multipollutant lime and silicate hydrates enhanced with oxidants has been confirmed at conditions typical of gas-cooled, semi-dry adsorption processes on boilers; performance of sorbents at higher-temperature conditions of duct sorbent injection technologies remains to be evaluated. Planned field evaluations of both semi-dry adsorption and

duct sorbent injection will allow better economic and performance comparisons of activated carbon sorbents to that of oxidant-enriched lime and silicate hydrates.

A technology for the efficient capture of Hg through in furnace injection of a calcium-based sorbent has been developed by McDermott Technologies recently. A discussion of the full-scale tests of the technology is presented in Chapter 7.

5.5.3 Development of Low-cost Sorbents

Since 1995, EPRI has supported a sorbent development program for removal of Hg emissions from coal-fired electric utility power plants at several research organizations including Illinois State Geological Survey (ISGS), University of Illinois (UI), and URS Corporation. The development of effective Hg sorbents that can be produced at lower costs than existing commercial activated carbons is the main objective of the program. The development efforts were documented in three EPRI Reports.[40-42] A significant number of sorbents were derived from a variety of precursor materials, including coal, biomass, waste tire, activated carbon fibers, fly ash, and zeolite, through this work. Different preparation methods were used to determine the effects of sorbent properties, such as pore size distribution, pore volume, surface area, particle size, and sulfur content, on the ability to remove Hg. The effects of different processing methods, including steam activation, grinding, size-fractionation, and sulfur-impregnation, on sorbent performance were also investigated in laboratory tests. Promising low-cost sorbents were further evaluated in actual flue gas at several full-scale coal-fired electric utility power plants.

Results of the EPRI sorbent development work showed that effective sorbents can be prepared from inexpensive precursor materials using simple activation steps. One notable example is that a char produced from corn fiber, a by-product from a corn-to-ethanol production process, showed a Hg^0 adsorption capacity over twice that of the commercial FGD carbon sorbent, after the char was activated in CO_2 at 865 °C for 3.5 hours.[40] Inactivated corn char had no capacity for $HgCl_2$, and only a low capacity for Hg^0. It appears that the composition of the flue gas has a significant effect on the Hg adsorption capacities of the coal-derived activated carbons.[41] The EPRI-funded study found that the presence of acid gases (SO_2 and HCl) inhibits Hg^0 and $HgCl_2$ adsorption for both lignite- and bituminous-coal-derived activated carbons. However, research conducted by EPA showed that the presence of acid gases enhanced the capture of Hg^0 by a lignite activated carbon and had no influence on the adsorption by a bituminous-coal-derived activated carbon.[21] In a later more extensive follow-up study funded by EPRI and ICCI, the effects of acid gases on the $HgCl_2$ and Hg^0 adsorption capacities of activated carbons were found to vary, depending on the precursor materials and characteristics of the carbons.[43] For example, carbons derived from tire and corn fiber had much higher $HgCl_2$ and Hg^0 adsorption capacities when they were tested in a high-SO_2 concentration flue gas simulating the combustion of Eastern bituminous coals compared to those when they were tested in the low-SO_2 concentration flue gas simulating Western subbituminous coal combustion. Complex interactions occurring between the characteristics of the carbons and the acid gases may lead to the observed varying effects of the acid gases on Hg adsorption behaviors of the carbon sorbents.

More fundamental research is needed to understand and predict the effects of acid gases on the performance of sorbents derived from different precursor materials.

The most effective sorbents were obtained by the sulfur-impregnation of activated carbons derived from waste material and carbon fibers.[40] Researchers at the University of Pittsburgh demonstrated that impregnation of heteroatoms such as sulfur[44] and chloride[45] is an effective method to improve the vapor-phase Hg adsorption capacities of activated carbons. It has been suggested that sorbent-impregnation studies should focus on highly microporous sorbents since the presence of active surface functional groups, sulfur as an example, in the micropores through impregnation is likely to provide the most reactive sites for Hg adsorption from coal combustion flue gas.[19] They stressed that the micropore surface area of sorbent is an important physical property for vapor-phase Hg adsorption. Most of the commercial activated carbons are used for liquid-phase applications and contain a large mesopore surface area, in addition to micropores, that are less effective for adsorption of ppb levels of Hg from coal combustion flue gases. EPA researchers[46] have observed the importance of active functional groups in the micropores for vapor-phase Hg adsorption. After treating an activated carbon with an aqueous sulfuric solution, they found that most of the mesopores of the carbon are filled with water due to the presence of the hydroscopic sulfuric acid, and the carbon becomes a highly microporous sorbent. The Hg^0 adsorption capacity of the sulfuric-acid-treated carbon is much higher than that of the as-received carbon due to the presence of the active sulfuric acid functional groups in the micropores of the treated carbon.

The most recent research conducted by ISGS, UI, and URS Corporation showed that relatively low surface area microporous biomass-based carbon sorbents, such as those derived from pistachio nut shells and from corn fiber, are as effective as the commercial FGD carbon sorbent for Hg adsorption.[43] They found that the Hg adsorption capacities of the biomass-based carbon sorbents, which contained negligible (0.09 percent) sulfur, are comparable to those of the coal- and tire-derived carbons that have substantial sulfur contents (0.98 to 2.1 percent). The biomass-based carbon sorbents also have very little chlorine functional groups. It appears that more oxygen, another heteroatom, remained in the biomass-based carbon sorbents after the pyrolysis of the oxygen-rich biomass from the carbon-making process contributing to the significant Hg adsorption capacities of such sorbents. It has been suggested recently by EPA researchers[47] that the Hg^0 adsorption capacity of an activated carbon is correlated to the concentrations of the oxygen functional groups of the carbon. They changed the oxygen functional group concentrations of a carbon by heating the carbon sample to 900 °C in an inert atmosphere to remove the functional groups. Also, more oxygen functional groups were introduced to the carbon sample by oxidizing the carbon sample in an aqueous nitric acid solution. They suggested that lactone and carbonyl groups introduced during the oxidization of the carbon by nitric acid treatment might be the active sites for Hg^0 adsorption.

5.5.4 Modeling of Sorbent Performance

The Hg adsorption data produced from bench-scale tests provide a relative indication of performance for different sorbents; however, the actual Hg removal performance of the sorbents in full-scale systems cannot be predicted based on bench-scale results alone. To predict Hg

removal in full-scale systems, mass transfer considerations have to be combined with laboratory data. Such an approach was applied by by EPRI recently to develop a model for predicting sorbent performance in full-scale systems.[48] The model is also capable of determining when mass transfer limits Hg removal and when it is limited by sorbent capacity. By incorporating the appropriate mass transfer expressions, the model relates the adsorption characteristic data for a given sorbent tested under a given set of flue gas conditions in the laboratory to the expected Hg removal performance across a FF or an ESP.

Results of the sorbent performance predicted by the model agree reasonably well with data of the same sorbent measured by pilot-scale tests for both ESP and FF applications. The pilot-scale facilities used for the tests consisted of an ESP with a 160-acfm wire-tube ESP, and a FF with a 4000-acfm transportable pulse-jet FF operating in the COHPAC configuration. Results of the pilot-scale tests and modeling both showed that a carbon sorbent with 15 μm diameter and 1000 μg/g Hg adsorption capacity achieved about 80 percent Hg removal in a FF operated at about 140 °C (280 °F) with 3 lb/Macf sorbent injection rate and cleaning cycle of 45 min. However, test and modeling results both showed that Hg removal decreases to less than 20 percent when the same sorbent was injected upstream of an ESP under conditions similar to the above.

Laboratory tests which have been conducted to evaluate the adsorption characteristics of potential sorbents for Hg removal seem to suggest that reactivity of the sorbent might be more important than its equilibrium adsorption capacity for sorbent injection. Currently, an ESP is more widely used than a FF as a PM control device for coal-fired electric utility boilers in the United States. Sorbent reactivity is the important parameter determining Hg removal when injecting a powdered sorbent upstream of an ESP, where adsorption of Hg occurs mainly in-flight with short residence times (about 2 seconds). When injecting sorbent upstream of a FF, additional Hg removal can occur due to the presence of accumulated sorbent in the filter cake, resulting in improved mass transfer and sorbent utilization. Sorbent capacity becomes a more important parameter than reactivity in such cases.

5.6 Capture of Mercury in Wet FGD Scrubbers

5.6.1 Wet Scrubbing

Mercuric chloride is readily soluble in water. Thus, the oxidized fraction of Hg vapors in flue gas is efficiently removed when a power plant is operated with a wet scrubber for removing SO_2. The elemental fraction, on the other hand, is insoluble and is not removed to any significant degree. A DOE-funded study[49] conducted by CONSOL, Inc. showed that the nominal Hg removal for wet FGD systems on units firing bituminous coals is approximately 55 percent, with the removal of Hg^{2+} between 80 and 95 percent. Studies conducted by McDermott Technologies, Inc. at its 10-MWe research facility suggested a possible conversion of the Hg^{2+} captured in the scrubbing media and reemissions as Hg^0.[50] McDermott Technologies performed follow up tests to investigate the use of additives to prevent the conversion of adsorbed Hg^{2+} to gaseous Hg^0.[51] These tests are described in more detail in Chapter 7.

5.6.2 Oxidation

The challenge to Hg removal in wet scrubbers for SO_2 is to find some way to oxidize the elemental Hg vapor before it reaches the scrubber or to modify the liquid-phase of the scrubber to cause oxidation to occur there.

URS Radian International has conducted various laboratory and field-test studies to investigate adsorption and catalytic oxidation of gaseous Hg^0 in coal-fired electric utility flue gas. The results of the bench-scale testing are discussed below. The additional pilot- and full-scale testing conducted by URS Radian International are discussed in Chapter 7.

Different compositions of catalysts and fly ashes were tested in a bench-scale, fixed-bed configuration to identify materials that adsorb and/or oxidize gaseous Hg^0.[52] Mixing sand with a particular catalyst or fly ash created fixed beds of sorbents. A simulated coal-fired electric utility boiler flue gas containing gaseous Hg^0 was then passed through the bed. The flue gas was tested at the inlet and outlet of each sorbent bed to determine Hg adsorption and/or oxidation across the bed. Table 5-5 lists the simulated flue gas conditions and the most active catalysts and fly ashes identified during testing for oxidation of gaseous Hg^0.

Figure 5-12 is an example of the adsorption/oxidation of gaseous Hg^0 with time by one of the iron catalysts in Table 5-5. In this figure, the oxidation of gaseous Hg^0 increases as the breakthrough of Hg from the catalyst bed increases (breakthrough is quantified as a percentage of the incoming Hg). At 100 percent breakthrough when the catalyst is no longer adsorbing any of the incoming Hg (i.e., the catalyst has reached its equilibrium adsorption capacity for the incoming Hg^0), all of the Hg^0 passing through the bed is being oxidized to Hg^{2+}.

Figure 5-13 shows adsorption/oxidation results for all of the catalysts in Table 5-5. Adsorption and oxidation of gaseous Hg^0 was greater at 149 °C (300 °F) than at the higher temperature of 371 °C (700 °F). The adsorption and oxidation activity of the activated carbon was considered the highest among the materials tested because a lower mass was utilized during the tests compared to the other materials.

Figure 5-14 shows the adsorption/oxidation results for the fly ashes from Table 5-5. Like the catalysts, the fly ashes showed higher adsorption and oxidation of gaseous Hg^0 at 149 °C (300 °F) than at 371 °C (700 °F); for this reason, only the lower temperature results are shown in Figure 5-14. The subbituminous and bituminous coal fly ashes generally showed higher oxidation rates than the lignite coal fly ashes. As seen, the #2 bituminous coal fly ash had varying adsorption and oxidation rates depending upon where the fly ash samples were collected. Samples collected from the hoppers of the first field of the ESP indicated lower oxidation of gaseous Hg^0 but a higher adsorption of Hg compared to the finer fly ash collected in the fifth and final field of the ESP. Although not shown, fly ash captured by a cyclone in the Hg speciation sampling train indicated a higher adsorption but no oxidation of the gaseous Hg^0. Fly ash from the fifth field of the ESP indicated the highest rate of oxidation and the lowest size-fractionated particles. This may be associated with the size differences of the fly ash and/or the surface

Table 5-5. Simulated flue gas conditions with the most active catalysts and fly ashes indicated for oxidation of gaseous Hg^0 to gaseous Hg^{2+}(source: Reference 52)

Parameter	Baseline Conditions	Most Active Catalysts	Most Active Fly Ashes
Fixed-bed Temperature	300 and 700 °F	Fe #1 (1000 mg)	Subbituminous #1
Hg^0 Injection	45 to 60 µg/Nm³	Pd #1 (1000 mg)	Subbituminous #2
Oxygen	7 percent	Fe #2 (200 mg)	Bituminous #1
Carbon Dioxide	12 percent	Fe #3 (200 mg)	Bituminous #2-Field 1*
Moisture	7 percent	NO_x Catalysts (1000 mg)	Bituminous #2-Field 5*
Sulfur Dioxide	1600 ppmv	Fe #4 (1000 mg)	Bituminous #3
HCl	50 ppmv	Pd #2 (1000 mg)	Lignite #1
Gas Flow Rate	1 L/min	Carbon (20 mg)	Oil-Fired #1

(a) Fly ash collected at the first and fifth field of the ESP at the EPRI ECTC.
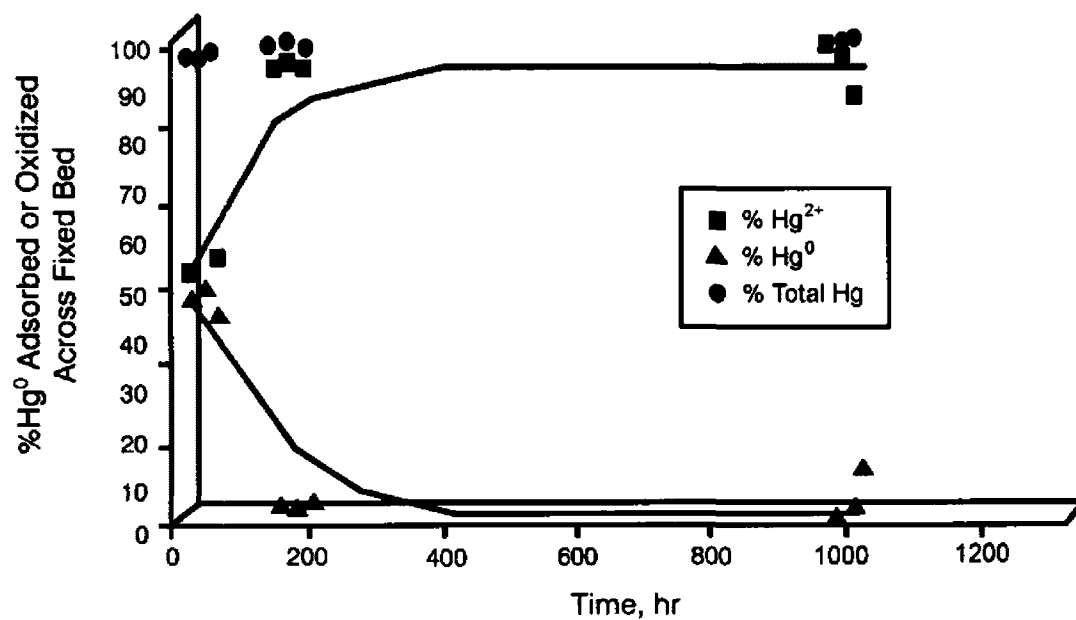
Figure 5-12. Adsorption and subsequent oxidation of gaseous Hg^0 in a simulated flue gas at 149°C (300 °F) (source: Reference 52).
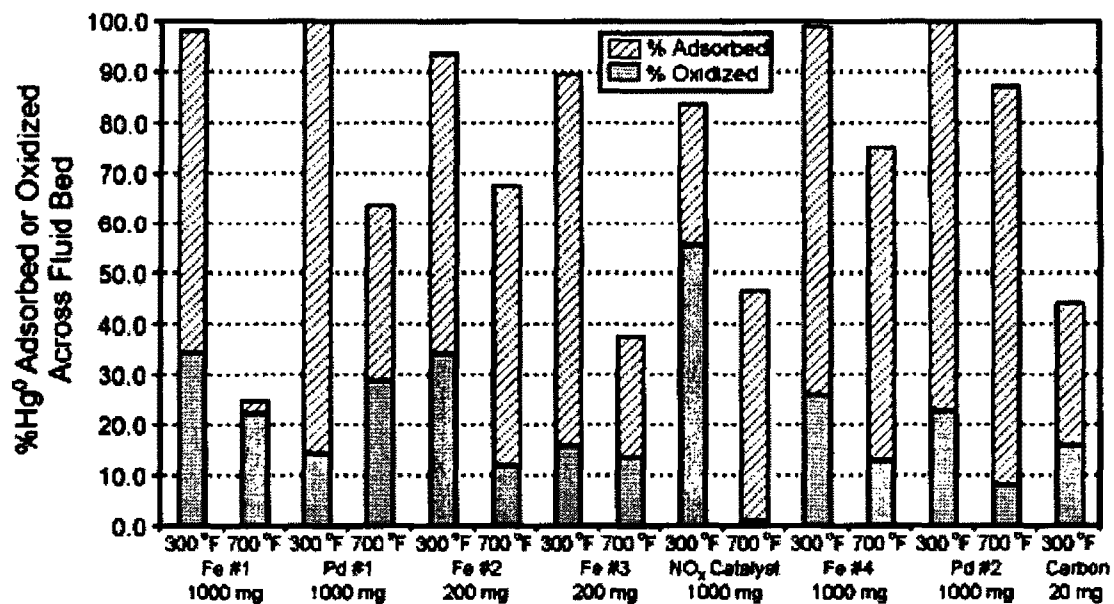
Figure 5-13. Adsorption and oxidation of gaseous Hg⁰ by various catalysts at 149 °C (300 °F) and 371 °C (700 °F) (source: Reference 52).
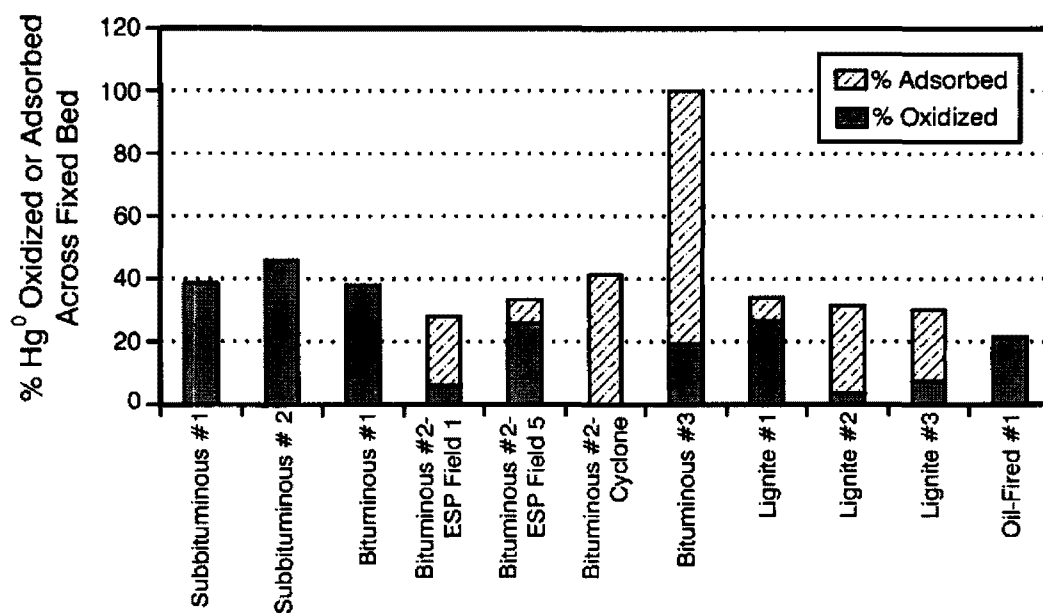
Figure 5-14. Adsorption and oxidation of gaseous Hg⁰ by various coal fly ashes at 149 °C (300 °F) and 371 °C (700 °F) (source: Reference 52).

chemistry of the finer fly ash being enriched in trace metals or other condensed or adsorbed compounds from the flue gas during the combustion of the bituminous coal.

5.6.3 Gas and Liquid Oxidation Reagents

Argonne National Laboratory has been investigating the use of oxidizing agents that could potentially convert gaseous Hg^0 into more soluble species that would be absorbed in wet FGD systems.[53] Current research is focused on a process concept that involves introduction of an oxidizing agent into the flue gas upstream of the scrubber. The oxidizing agent employed is NOXSORB™, which is a commercial product containing chloric acid and sodium chlorate. When a dilute solution of this agent was introduced into a gas stream containing gaseous Hg^0 and other typical flue-gas species at 300 °F (149 °C), it was found that nearly 100 percent of the gaseous Hg^0 was removed from the gaseous phase and recovered in process liquids. A significant added benefit was that approximately 80 percent of the NO was removed at the same time. Thus, the potential exists for a process that combines removal of SO_2, NO, Hg^0, and, perhaps, PM.

Continuing laboratory research efforts are acquiring the data needed to establish a mass balance for the process. In addition, the effects of such process parameters as reagent concentration, SO_2 concentration, NO concentration, and reaction time (residence time) are being studied. For example, SO_2 has been found to decrease slightly the amount of gaseous Hg^0 oxidized while appearing to increase the removal of NO from the gaseous phase. Preliminary economic projections, based on the results to date, indicate that the chemical cost for NO oxidation could be less than $5,000/ton NO removed; while for gaseous Hg^0 oxidation, it would be about $20,000/lb Hg^0 removed. These results will be refined as additional experimental results are obtained.

5.7 Observations and Conclusions

When coal is burned in an electric utility boiler, the resulting high combustion temperatures in the vicinity of 1500 °C (2700 °F) vaporize the Hg in the coal to form gaseous Hg^0. Subsequent cooling of the combustion gases and interaction of the gaseous Hg^0 with other combustion products result in a portion of the Hg being converted to other forms, viz., Hg^{2+} and Hg_p. The term *speciation* is used to denote the relative amounts of these three forms of Hg in the flue gas of the boiler. It is important to understand how Hg speciates in the boiler flue gas because, as discussed in Chapters 6 and 7, the overall effectiveness of different control strategies for capturing Hg often depends on the concentrations of the different forms of Hg species present in the boiler flue gas.

The speciation of Hg results from oxidation of Hg^0 in the boiler flue gas, with the predominant oxidized Hg species believed to be $HgCl_2$. The mechanisms for this oxidation include gas-phase oxidation, fly-ash-mediated oxidation, and oxidation by post-combustion NO_X controls. Data reveal that gas-phase oxidation is kinetically limited and occurs due to reactions

of Hg with oxidizers such as Cl and Cl_2. Research also suggests that gas-phase oxidation may be inhibited by the presence of NO, SO_2, and water vapor.

Certain fly ashes have been shown to promote oxidation of Hg^0 more than others. The differences in oxidation appear to be attributable to the composition of the fly ash and the presence of certain flue gas constituents. The results of bench-scale research conducted at EPA reflect that the presence of HCl and NO_X in flue gas and iron in fly ash assists in oxidation. Other research indicates that γ-Fe_2O_3 may be causing Hg^{2+} formation, and that surface area may be a dominant factor in this regard. Also, there are indications that HCl, NO_2, and SO_2 in the flue gas may contribute to Hg^0 oxidation, while the presence of NO may suppress Hg^0 oxidation.

The understanding of Hg speciation in the flue gas of coal-fired electric utility boilers is far from being mature, and research and development efforts are currently underway to develop more information.

Mercury can be captured and removed from a flue gas stream by injection of a sorbent into the exhaust stream with subsequent collection in a PM control device such as an electrostatic precipitator or a fabric filter. However, adsorptive capture of Hg from flue gas is a complex process that involves many variables. These include the temperature and composition of the flue gas, the concentration of Hg in the exhaust stream, and the physical and chemical characteristics of the sorbent (and associated functional group). The implementation of an effective and efficient Hg control strategy using sorbent injection requires the development of low-cost and efficient Hg sorbents. Of the known Hg sorbents, activated carbon and calcium-based sorbents have been the most actively studied. However, improved versions of these sorbents and new classes of Hg sorbents can be expected, as this is still a very active field of study.

Adsorption of elemental Hg is enhanced by the presence of functional groups and/or catalytically active sites (that oxidize the Hg to Hg^{2+}). Oxidation of elemental Hg to ionic species by the catalytic components that may be present in fly ash (especially iron compounds) is a critical step before adsorption of the species by the fly ash or some injected sorbents. Both the oxidant and binding sites for the adsorption of elemental Hg may also be provided by the injected sorbents. Also, alkaline components of the fly ash exhibit sorptive properties for oxidized Hg. Fly ashes, which contain higher unburned carbon contents, such as those produced from low-NO_X burner systems, may have significant catalytic and sorptive properties. The unburned carbon appears to have some oxidant/adsorption sites similar to those that existed in the activated carbon sorbents.

Activated carbon binding sites may be enhanced by impregnation with an active additive (e.g., S, Cl, I) or pretreatment (e.g., with H_2SO_4 or HCl). It appears that the presence of hetroatoms, such as sulfur and chlorine, on the activated carbon surfaces greatly enhance the adsorption of Hg. Other non-carbon-based sorbents may be enhanced by oxidant/catalyst additions. The enhancement is caused by the oxidation of the elemental Hg either by the added oxidant or by the added catalyst to the sorbents. A promising alternative appears to be the replacement of the coal-based activated carbons with a low cost, high-capacity, reactive sorbent. Such sorbents are currently under development.

Oxidized Hg is readily absorbed by alkaline solutes/slurries or adsorbed by alkaline PM (or by sorbents). Flue gas desulfurization systems, which use alkaline materials to neutralize the acidic SO_2 gas, remove oxidized Hg effectively in the flue gas. Current research is focusing on optimization of the existing desulfurization systems as a retrofit technology for controlling oxidized Hg emissions and on development of new multipollutant control technologies for simultaneously controlling both SO_2 and oxidized Hg emissions.

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Chapter 6

MERCURY CAPTURE BY EXISTING CONTROL SYSTEMS USED BY COAL-FIRED ELECTRIC UTILITY BOILERS

6.1 INTRODUCTION

Existing coal-fired electric utility boilers in the United States use a variety of emission control technologies to meet air standards for sulfur dioxide (SO_2), nitrogen oxides (NO_X), and particulate matter (PM). The EPA's ICR data presented in Chapter 3 of this report indicate that most electric utilities are controlling NO_X emissions from their coal-fired boilers by combustion modification techniques and controlling SO_2 emissions by burning low-sulfur coal. All of the coal-fired electric utility boilers use some type of post-combustion control device to meet PM emission standards. Of these PM controls, electrostatic precipitators (ESPs) are the predominant control type used on coal-fired boiler units (83 percent) with the second most common control device being a fabric filter (14 percent). Use of post-combustion SO_2 controls is less common: approximately 20 percent of the boiler units use either wet flue gas desulfurization (FGD) systems (15 percent) or spray dryer absorber (SDA) systems (5 percent). While the use of either selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) on coal-fired electric utility boilers for NO_X emission control presently is very limited (less than 4 percent), the application of these post-combustion NO_X controls is becoming more prevalent.

The implementation of post-combustion controls is not specifically intended to control mercury emissions from coal-fired utility boilers. However, these controls capture mercury in varying degrees depending on the control technologies used and the mercury speciation at the inlet to the control device(s). This chapter discusses mercury capture by existing post-combustion control systems used by coal-fired utility boilers. An estimate of nationwide mercury emissions from existing coal-fired utility boilers is presented. The mechanisms by which existing post-combustion control systems capture mercury are reviewed. The ICR mercury emission test data for mercury capture by the existing post-combustion control systems used for coal-fired utility boilers are presented and discussed.

6.2 EPA ICR PART III DATA

As introduced in Chapter 1 of this report, the EPA conducted a three-part data collection effort to gather information about the coal-fired utility boilers operating in the United States in 1999[1]. The Part I ICR data consist of information on the coal types burned, the boiler furnace types, and the air pollutant control devices used for the 1,143 coal-fired utility boilers in the United States having a capacity equal to or greater than 25 MWe. These data are summarized and discussed in Chapters 2 and 3 of this report. The Part II ICR data

consist of information on the quantity, mercury content, and other selected properties of coal burned by each of the identified 1,143 boiler units during calendar year 1999. A summary and evaluation of these data are presented in Section 2.7 and Appendix A of this report. For Part III of the information collection effort, the EPA selected a subset of the coal-fired electric utility boilers for which field source testing was performed to obtain mercury emission data for the air pollutant control devices now being used for these units. This chapter presents a summary and analysis of the emissions data collected by Part III of EPA's information collection effort.

The EPA ICR Part III data are composed of mercury emission source test results for 80 coal-fired electric utility boilers. These boiler units were selected by the EPA to be generally representative of the nationwide population of coal-fired utility boilers according to the type of boiler used, the type of coal burned, and the air emission controls used. For each of the tested boiler units, the flue gas mercury measurements were generally made at the inlet and outlet of control device(s). The mercury measurements were made using the OH Method for speciated mercury (this test method is discussed in Section 4.1 of this report). Also, samples of the coal being burned in the boiler unit during the source test were collected and analyzed for mercury content.

For boiler units that use a control configuration consisting of a single PM control device, the flue gas samples were collected at the inlet to the PM control device and in the stack. For units using SDA systems, the flue gas measurements were made at the inlet to the SDA and in the stack. For units using an ESP or FF followed by a wet FGD scrubber, the flue gas measurements were taken at the inlet to the wet scrubber inlet (i.e., downstream of the PM control device) and in the stack. For units equipped with a PS and a wet FGD scrubber, measurements were made at the inlet to the PS device and in the stack.

Of the three IGCC plants located in the United States, two of the plants (Polk Power Station and Wabash River Repowering Project) were included as part of the Part III ICR test program. At both facilities, combustion gas measurements using the OH Method were made at the exhaust stack of the gas turbines. During testing, coal feed rates to the coal-gasification units were recorded. Coal samples were collected during testing and analyzed for total mercury.

A summary of 81 boiler and coal type configurations for which mercury emission data were collected is given in Table 6-1. Of these boiler units, 65 were pulverized-coal-fired (PC-fired) boilers. Such boilers account for the vast majority of the 1,143 coal-fired electric utility boilers operating in the United States in terms of both total units and nationwide generating capacity as shown Table 2-4.

Table 6-1
Distribution of ICR Mercury Emission Test Data
By Boiler-coal Type Configurations

Boiler Unit Type	Number of Boiler Units Tested				Total Number of Units Tested
	Fuel Burned In Boiler Unit				
	Bituminous Coal	Subbituminous Coal	Lignite	Other(a)	
Pulverized-coal-fired	26	29	9	1	65
Cyclone-fired	3	2	2	0	7
Fluidized-bed Combustor	1	0	2	2	5
Stoker-fired	2	0	0	0	2
IGCC (b)	2	0	0	0	2
Total Number of Units Tested	34	31	13	3	81

(a) Some units used coal wastes or a blend of fuels.
(b) Integrated coal gasification combined cycle unit.

A summary of the flue gas cleaning devices installed on the PC-fired test units is given in Table 6-2 as a function of type of fuel burned in each unit in 1999. These data show that:

- A total of 28 test units were equipped with a CS-ESP (14), HS-ESP (8), or FF (6).
- The 11 dry FGD units were equipped with either a SDA/ESP (3) or SDA/FF (8).
- The 20 wet FGD units were equipped with a PS + Wet FGD (6), CS-ESP + Wet FGD (6), HS-ESP + Wet FGD (6), or FF + Wet FGD (2).
- Two units were equipped with a CS-ESP + FF.
- One was equipped with a PS.

Table 6-2
Distribution of ICR Mercury Emission Test Data for Pulverized-coal-fired Boilers By Post-combustion Emission Control Device Configuration

Post-combustion Control Strategy	Post-combustion Emission Control Device Configuration	Number of Boiler Units Tested				
		Fuel Burned In Boiler Unit				Total
		Bituminous Coal	Subbituminous Coal	Lignite	Other	
PM Control Only	CS-ESP	7	5	1	1	14
	HS-ESP	4	4	0	0	8
	FF	4	2	0	0	6
	CS-ESP + FF	0	0	2	0	2
	PS	0	1	0	0	1
PM Control and Dry SO$_2$ Scrubber System	SDA + CS-EP	0	3	0	0	3
	SDA + FF	3	3	2	0	8
	DI + CS-ESP	1	0	0	0	1
PM Control and Wet SO$_2$ Scrubber System	PS + wet FGD	1	4	1	0	6
	CS-ESP + wet FGD	1	3	2	0	6
	HS-ESP + wet FGD	1	5	0	0	6
	FF + wet FGD	2	0	0	0	2
Other Control Device Configuration		2	0	0	0	2
Number of Units Tested		27	29	8	1	65

PM Controls
CS-ESP = cold-side electrostatic precipitator
HS-ESP = hot-side electrostatic precipitator
FF = fabric filter
PS = particle scrubber

SO$_2$ Controls
DI = dry injection
FGD = flue gas desulfurization system
SDA = spray dryer adsorber system

6.3 MERCURY CONTENT OF UTILITY COALS BURNED IN 1999

The analysis results of more than 39,000 coal samples were reported in the Part II ICR data. These results include the mercury content of as-fired coals and supplemental fuels burned in electric utility boilers in 1999. A comparison of the mercury contents of the different major coal types and supplemental fuels burned by electric utilities in 1999 and normalized by fuel heating value is shown Figure 6-1. Waste bituminous coal and waste anthracite had the highest mercury contents expressed in lb Hg/10^{12} Btu. The mercury content of the bituminous coal, subbituminous coal, and lignite (the three most commonly used fuels) was generally less than 15 lb/10^{12} Btu. Statistical information on each type of fuel burned in coal-fired utility boilers is presented in Table 6-3.
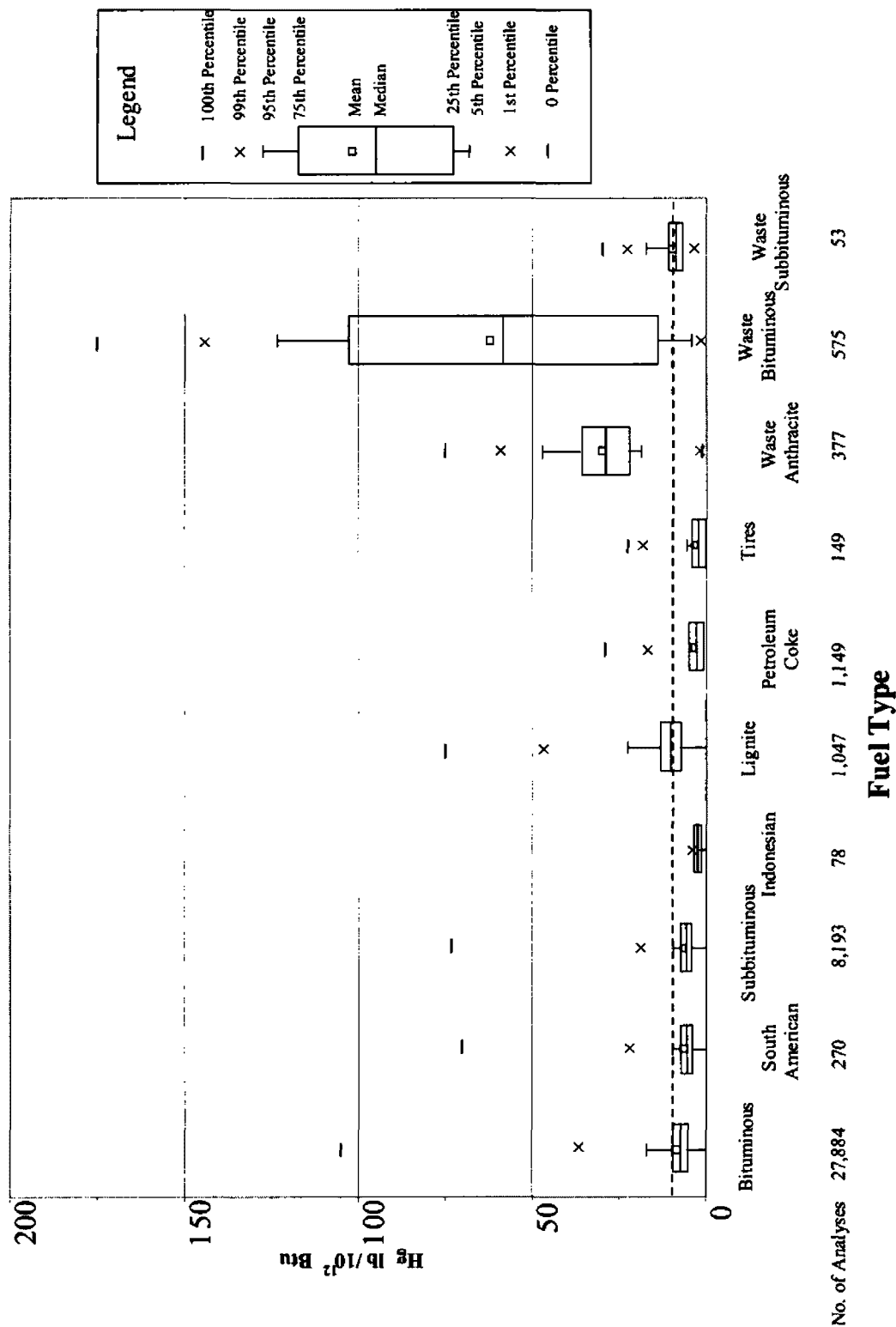
Figure 6-1. 1999 ICR data analyses – mercury in fuels.

Table 6-3
Comparison of Mercury Content Normalized By Heating Value
In As-fired Coals and Supplemental Fuels for Electric Utility Boilers in 1999

Fuel Type	Number of Analyses	Ratio of Mercury to Fuel Heat Content (lb Hg per 10^{12} Btu)			
		Range	Mean	Median	Standard Deviation
Anthracite coal	114	5.02 – 35.19	15.28	13.37	6.23
Bituminous coal	27,884	0.04 – 103.81	8.59	7.05	6.69
South American bituminous coal (a)	270	0.70 – 66.81	5.94	4.91	5.28
Subbituminous coal	8,193	0.39 – 71.08	5.74	5.00	3.59
Indonesian subbituminous coal (b)	78	0.79 – 4.61	2.51	2.39	0.86
Lignite	1,047	0.93 – 75.06	10.54	7.94	9.05
Waste anthracite coal	377	2.49 – 73.02	29.31	27.77	11.94
Waste bituminous coal	575	2.47 –172.92	60.50	53.32	44.35
Waste subbituminous coal	53	5.81 – 30.35	11.42	10.79	4.66
Petroleum coke	1,149	0.06 – 32.16	23.18	2.16	3.18
Tire-derived fuel	149	0.38 – 19.89	3.58	2.79	2.78

(a) Bituminous coal imported from South America and burned at one power plant in Florida and one power plant in Texas.
(b) Subbituminous coal imported from Indonesia and burned at a coal-fired power plant in Hawaii.

6.4 POTENTIAL MERCURY CAPTURE IN EXISTING UNITS

Mercury capture in existing units depends on Hg speciation at the inlet to the control device(s) and the type(s) of control technologies used. Units that burn bituminous coals have relatively high concentrations of Hg^{2+} at the inlet to the control device(s). Units that burn subbituminous coal or lignite typically have relatively low concentrations of Hg^{2+} and high concentrations of Hg^0 at the inlet to the control device(s).

The effects of coal and combustion conditions are attributed primarily to the flue gas composition and properties of fly ash that affect the speciation and capture of Hg. While OH measurements made upstream of PM control devices do not always provide quantitatively accurate information on Hg speciation, they do provide semi-quantitative information relative to the amounts of Hg_p, Hg^{2+}, and Hg^0 in flue gas from the combustion of different types of

coals. They also provide useful information on the potential for the oxidization of the Hg^0 and the capture of the resulting reaction products in downstream control devices.

The relatively high concentrations of chlorine in bituminous coals are believed to result in the oxidization of Hg^0 to form Hg^{2+}, primarily $HgCl_2$. By contrast, both subbituminous coal and lignite have lower amounts of chlorine and higher amounts of alkaline material (calcium and sodium) than bituminous coals. Chlorine from the combustion of subbituminous coal and lignite tends to react with the alkaline materials in flue gas, and little if any chlorine is available for the oxidization of Hg. Therefore, flue gas from combustion of subbituminous coal and lignite tends to have relatively low concentrations of Hg^{2+}.

6.4.1 Units with an ESP or FF

Approximately 77 percent of the coal-fired utility boilers currently operating in the United States are equipped with only an ESP or an FF. Gaseous mercury (both Hg^0 and Hg^{2+}) can potentially be adsorbed on fly ash and be collected in a downstream ESP or FF. The modern ESPs or FFs that are now used on most coal-fired units achieve very high capture efficiencies for total particulate matter (see Table 3-3). As a consequence, these PM control devices are also effective in capturing Hg_p in the boiler flue gases.

The degree to which mercury can be adsorbed onto fly ash for subsequent capture in PM control is dependent on the speciation of mercury, the flue gas concentration of fly ash, and the properties of fly ash. It is currently believed that mercury is primarily adsorbed onto the unburned carbon in fly ash (see Section 5.3). Approximately 80 percent of the coal ash in PC-fired boilers is entrained with the flue gas as fly ash. PC-fired boilers with low-NO_X burners have higher levels of carbon in the fly ash with a correspondingly higher potential for mercury adsorption. Cyclone and stoker boilers tend to have high levels of carbon in the fly ash, but have lower flue gas concentrations of fly ash than PC-fired boilers. Fly ash concentrations in fluidized-bed combustors tend to be higher than those in PC-fired boilers. Also, the carbon content of fluidized-bed combustor fly ash is generally higher than that of PC-boiler fly ash.

The syngas from a coal gasifier is composed mainly of hydrogen, carbon monoxide, carbon dioxide, and nitrogen. This gas also contains vaporous trace elements, such as mercury, as well as dust and aerosols containing trace elements. The source of mercury in syngas is the mercury that is naturally present in coal and is released during the gasification processes, which typically takes place at 950 °C (1750 °F). Mercury that is not retained in the solid residue from the gasification process is released almost exclusively as Hg^0.

Gas-phase mercury in units equipped with an ESP can be adsorbed on the entrained fly ash upstream of the ESP. The gas-phase mercury in units equipped with a FF can be adsorbed by entrained fly ash or it can be adsorbed as the flue gas passes through the filter cake on the surface of the FF. The degree to which gaseous mercury adsorbs on the filter cake typically depends on the speciation of gaseous mercury in the flue gas; in general, gaseous Hg^{2+} is easier to adsorb than gaseous Hg^0 (see discussion in Section 5.3.1).

6.4.2 Units with SDA Systems

An SDA system operates by the same principle as a wet FGD system using a lime scrubbing agent, except that the flue gas is mixed with a fine mist of lime slurry instead of a bulk liquid (as in wet scrubbing). The SO_2 is absorbed in the slurry and reacts with the hydrated lime reagent to form solid calcium sulfite and calcium sulfate. The heat of the flue gas, leaving dry solid particles of calcium sulfite and calcium sulfate, evaporates the water in the mist. Entrained particles (unreacted sorbent particles, reaction products, and fly ash) are captured in the downstream PM control device (either an ESP or FF).

The performance of SDA systems in controlling SO_2 emissions is dependent on the difference between the SDA outlet temperature and the corresponding flue gas water vapor saturation temperature. SDA systems on coal-fired boilers typically operate about 20 °F (11 °C) above the saturation temperature (i.e., a 20 °F [11 °C] approach to saturation temperature). The relatively low flue gas temperatures afforded by SDA systems increase the potential for mercury capture. The caking or buildup of moist fly ash deposits, which can plug the SDA reactor and coat downstream surfaces, dictates the minimum flue gas temperatures, which can be employed at the outlet of SDAs.

Hg_p is readily captured in SDA systems. Both Hg^0 and Hg^{2+} can potentially be adsorbed on fly ash, calcium sulfite, or calcium sulfate particles in the SDA. They can also be adsorbed and captured as the flue gas passes through the ESP or FF, whichever is used for PM control. In addition, gaseous Hg^{2+} may be absorbed in the slurry droplets and react with the calcium-based sorbents within the droplets. Nearly all of the Hg_p can be captured in the downstream PM control device. If the PM control device is a FF, there is the potential for additional capture of gaseous mercury as the flue gas passes through the bag filter cake composed of fly ash and dried slurry particles.

6.4.3 Units with Wet FGD Systems

Approximately 15 percent of coal-fired utility boilers in the United States use wet FGD systems to control SO_2 emissions. In each of these systems, a PM control device is installed upstream of the wet FGD scrubber. PM control devices used with wet FGD scrubbers include particulate scrubbers (PS), CS-ESPs, HS-ESPs, and FF baghouses. As described in Chapter 3, wet FGD systems remove gaseous SO_2 from flue gas by absorption. In wet scrubbers, gaseous species are mixed with a liquid in which they are soluble. For SO_2 absorption, gaseous SO_2 is mixed with a caustic slurry, typically water and limestone or water and lime.

Gaseous compounds of Hg^{2+} are generally water-soluble and can absorb in the aqueous slurry of a wet FGD system. However, gaseous Hg^0 is insoluble in water and therefore does not absorb in such slurries. When gaseous compounds of Hg^{2+} are absorbed in the liquid slurry of a wet FGD system, the dissolved species are believed to react with

dissolved sulfides from the flue gas, such as H_2S, to form mercuric sulfide (HgS); the HgS precipitates from the liquid solution as sludge. In the absence of sufficient sulfides in the liquid solution, a competing reaction that reduces/converts dissolved Hg^{2+} to Hg^0 is believed to take place. When this conversion takes place, the newly formed (insoluble) Hg^0 is transferred to the flue gas passing through the wet FGD system. The transferred Hg^0 increases the concentration of Hg^0 in the flue gas passing through the wet FGD (since the incoming Hg^0 is not absorbed), thereby resulting in a higher concentration of gaseous Hg^0 in the flue gas exiting the wet FGD compared to that entering. Transition metals in the slurry (originating from the flue gas) are believed to play an active role in the conversion reaction since they can act as catalysts and/or reactants for reducing oxidized species.

Recent research on the capture of mercury in wet scrubber systems is discussed in Section 5.6.

6.4.4 Units with Other Control Devices

Some units use PS systems, primarily venturi scrubbers, to control PM emissions. Capture of Hg in these systems is limited to soluble Hg compounds such as $HgCl_2$. PS systems are typically poor fine PM collectors and, if Hg_p in the flue gas is associated with fine PM, capture of Hg_p by such scrubbers may be poor. Hg^0 is insoluble and will not typically be captured by the scrubber. It is possible to capture Hg^{2+} in the wet scrubbers, but the scrubber chemistry, and the manner in which the scrubber is operated, will determine whether it is effectively removed, or whether it is stripped, from the scrubbing liquor. Stripping can occur if the Hg^{2+} is not adsorbed on the particles, or reacted chemically with liquid-phase reactants within the scrubber.

Mechanical collectors such as cyclones do a poor job of capturing fine PM, and mercury capture in these control devices should be limited to the capture of Hg_p associated with particles larger than 10 μm.

6.5 EPA'S PART III ICR DATA EVALUATION APPROACH

The methods used to evaluate the Part III ICR data were based on two interrelated objectives. The first objective was to estimate the amount, speciation, and geographical distribution of national mercury emissions from coal-fired power plants in 1999. The second was to characterize the effects of coal properties, combustion conditions, and flue gas cleaning methods on the speciation and capture of mercury. The satisfaction of the first objective involved the development of mercury emission factors as a function of the type of coal burned, the type of boiler, and the air pollution control device(s) used.

6.5.1 Evaluation Method

The development of emission factors for different classes of coal-fired units was based on hypotheses derived from current understanding of mercury speciation and capture, as discussed in Chapter 5. The hypotheses are:

- Mercury speciation and capture are dependent on the coal properties, combustion conditions, and flue gas cleaning methods that are used for any specific test unit,

- Hg^{2+} is more readily absorbed in aqueous media than Hg^0, and therefore can be captured in wet scrubbers, while Hg^0 cannot,

- Gas-phase mercury can be adsorbed onto the unburned carbon in fly ash, which can catalyze oxidation of Hg^0,

- Hg_p can be readily captured in an ESP or an FF,

- The potential for mercury capture increases with decreasing flue gas temperatures, and

- Flue gas from combustion of bituminous coals typically has a higher fraction of Hg^{2+} than the gas from subbituminous and lignite coals.

Combinations of coal, boiler, and control technologies that are expected to behave in a similar manner with respect to speciation and capture of mercury can be grouped into data sets called coal-boiler-control technology classes or bins. Many of these data sets in the ICR database consist of tests at one or two units, and this small number of samples results in relatively large uncertainties concerning the central values and variability of the underlying populations. However, the mean values and statistical behavior of the classes with a large number of test units can be investigated, and the results can be compared with the results of classes with a small number of test sites. If the relative behavior of the large and small data sets is consistent with our theoretical expectations, then we can have some confidence that the speciation and capture estimates for the smaller sets are reasonable.

The ICR Part III emission data were sorted into coal-boiler-control classes. Next, the data in each class were evaluated for consistency, and the data between classes were evaluated according to the postulated behavior criteria given above. With few exceptions, the differences in speciation and capture of mercury between the different classes were consistent with the above-hypothesized behavior. Based on this observation, emission factors were developed for use in estimating the amount and speciation of mercury emissions from coal-fired electric utility boilers in 1999. The data in the coal-boiler-control classes were also used to conduct further evaluations of the effects of coal properties, combustion conditions, and flue gas cleaning conditions on the control of mercury emissions at existing coal-fired power plants.

6.5.2 Measures of Performance

Measures used to evaluate the effect of the coal, boiler, and control device variables on the capture of mercury included the inlet and outlet concentrations of Hg_p, Hg^{2+}, Hg^0, and Hg_T, and the reduction of Hg_T. Emission factors, defined in this report to be the fraction of mercury emitted to the atmosphere relative to the amount that enters the first air pollution control device, were also calculated and used to evaluate the emission of speciated Hg and

Hg_T.

The fraction of Hg_T captured in air pollution control device(s) can be used interchangeably with the emission factor for Hg_T [EMF_T]:

EMF_T = 1 - Capture Hg_T

Where the fractional capture is:

Capture Hg_T = [Hg_T (inlet) - Hg_T(outlet)]/Hg_T(inlet) = 1 - Hg_T(outlet)/Hg_T(inlet)

And the percentage reduction (%Red) across the control device(s) is:

%Red = 100 x [1 - Hg_T(outlet)/Hg_T(inlet)]

The %Red can be determined from either (1) the inlet and outlet concentrations of Hg_T as measured by the OH Method, or (2) inlet concentration estimates made from Part III coal samples and outlet concentrations obtained with the OH Method. When the OH measurements are used to evaluate the reduction in emissions or emission factors, the inlet and outlet concentrations must be expressed on a common basis µm/dscm at 3% O_2) or lb of $Hg/10^{12}$ Btu of coal burned to account for air in-leakage through fans or across the air pollution control device(s).

The results of the OH Method emission tests for Hg_T are shown in Figures 6-2 and 6-3. Figure 6-2 is a scatter plot of the inlet versus the outlet concentrations of Hg_T. In general, the outlet Hg_T concentration increases with increasing inlet Hg_T concentrations. The increasing outlet Hg_T concentrations that appear linear with respect to Hg_T inlet concentrations are indicative of a constant percentage reduction across the control device(s). ESPs exhibit this type of performance for the control of PM. These types of devices are called constant reduction devices. Note that there are also a number of data points distributed just above the x-axis; i.e., zero outlet concentration. These data points are indicative of constant outlet devices with low emission concentrations. FF baghouses tend to operate like constant outlet devices.

Figure 6-3 is a scatter plot showing inlet Hg_T concentration versus percent reduction in Hg_T across the control device(s). There are no discernable trends in the capture of Hg_T as a function of inlet concentration. The negative emission reductions represent cases for which the outlet Hg_T concentration is higher than the inlet concentration. This can result from one or a combination of factors. For example, negative emission reductions can occur when (1) temperature changes within the test unit increase the desorption of Hg, (2) ESP rapping cycles result in the reentrainment of Hg_p, and (3) small differences between Hg inlet and outlet concentrations cannot be accurately quantified because of imprecision in the OH Method.
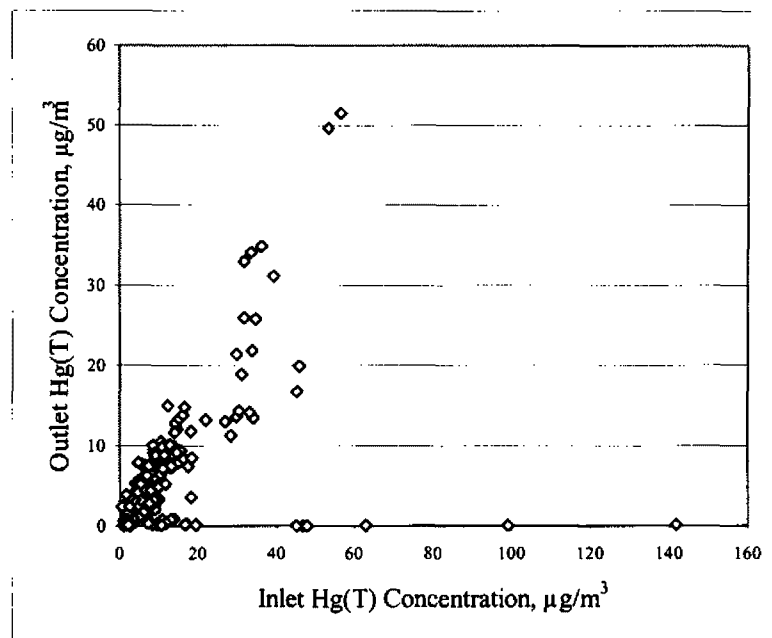
Fig. 6-2. Inlet versus outlet mercury concentration for all tests.
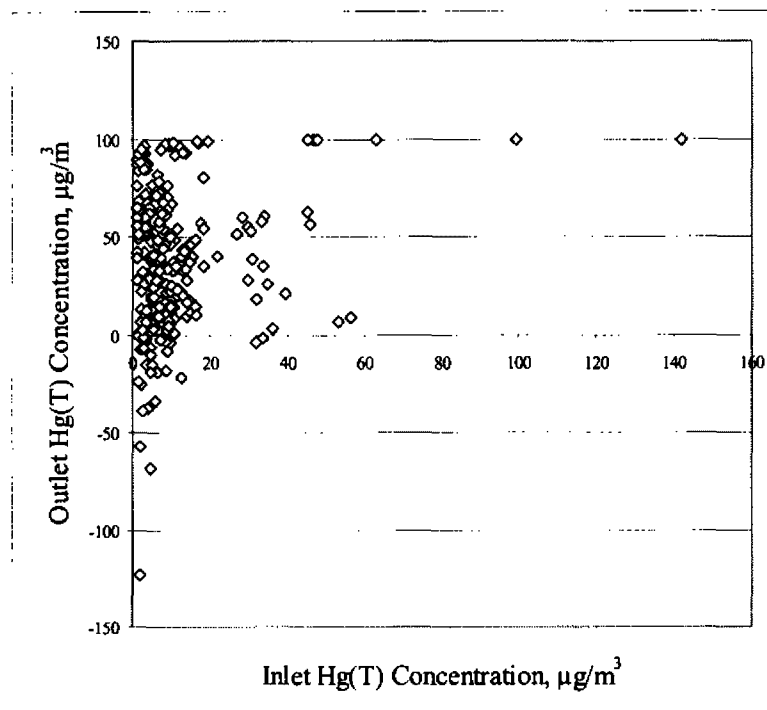
Fig. 6-3. Inlet mercury concentration versus percent reduction for all tests.

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Emission factors for speciated Hg can be developed by dividing or normalizing the stack Hg species by the concentration of Hg_T at the inlet to the first control device. In the development of these emission factors, it is assumed that all of the Hg in the as-burned coal is equal to the value of Hg_T measured at the inlet sampling location by the OH method. The emission factors for Hg_p (EMF_p), Hg^{2+} (EMF^{2+}), and Hg^0 (EMF^0) are calculated by:

$$EMF_p = Hg_p \text{ (outlet) } / Hg_T \text{ (inlet)},$$

$$EMF^{2+} = Hg^{2+} \text{(outlet) } / Hg_T \text{ (inlet), and}$$

$$EMF^0 = Hg^0 \text{ (outlet) } / Hg_T \text{ (inlet)}.$$

For situations where Hg_T (outlet) is higher than Hg_T (inlet), the stack emission factors are calculated by replacing the Hg_T (inlet) value with the corresponding Hg_T (outlet) value:

$$EMF_p = Hg_p \text{ (outlet)}/Hg_T \text{ (outlet)}, \quad [\text{for } Hg_T \text{ (outlet) } > Hg_T \text{ (inlet)}],$$

$$EMF^{2+} = Hg^{2+} \text{ (outlet)}/Hg_T \text{ (outlet)}, \quad [\text{for } Hg_T \text{ (outlet) } > Hg_T \text{ (inlet)}], \text{ and}$$

$$EMF^0 = Hg^0 \text{ (outlet)}/Hg_T \text{ (outlet)}, \quad [\text{for } Hg_T \text{ (outlet) } > Hg_T \text{ (inlet)}].$$

In the latter case, it should be noted that $EMF_p + EMF^{2+} + EMF^0 = 1$.

In addition to the above emission factors, speciation factors (SPFs) are calculated and used to characterize Hg speciation at both the inlet and outlet sampling locations. The SPFs represent the fractions of Hg_T in the inlet or outlet samples that are present as Hg_p, Hg^{2+}, or Hg^0. For the inlet sampling train:

$$SPF_p = Hg_p \text{ (inlet) } / Hg_T \text{ (inlet)},$$

$$SPF^{2+} = Hg^{2+} \text{ (inlet) } / Hg_T \text{ (inlet), and}$$

$$SPF^0 = Hg^0 \text{ (inlet) } / Hg_T \text{ (inlet)}.$$

For the outlet sampling train:

$$SPF_p = Hg_p \text{ (outlet) } / Hg_T \text{ (outlet)},$$

$$SPF^{2+} = Hg^{2+} \text{ (outlet) } / Hg_T \text{ (outlet), and}$$

$$SPF^0 = Hg^0 \text{ (outlet) } / Hg_T \text{ (outlet)}.$$

In all cases:

$$SPFp + SPF^{2+} + SPF^0 = 1.$$

Emission factors and speciation factors for units equipped with an ESP, FF, PM scrubber, mechanical collector, SDA/ESP, or SDA/FF were calculated using inlet OH measurements for Hg_T and outlet OH measurements for speciated and Hg_T. For units with wet FGD scrubbing systems, emission factors were determined by multiplying the average emission factor for the PM control device that precedes the scrubber by the emission factors for the scrubber as determined by OH measurements. For example, the estimated EMFs for a PC-fired boiler burning subbituminous coal and equipped with cold-side ESP and wet FGD system are calculated as follows:

The class average CS-ESP EMF_T for a PC-boiler firing subbituminous coal is 0.91, and the class average wet FGD EMF_T for a PC-boiler firing subbituminous coal is 0.71. The EMFT across both control devices is therefore:

$$EMF_T \text{ (CS-ESP + FGD)} = EMF_T \text{ (CS-ESP)} \times EMF_T \text{ (FGD)}$$

$$= 0.91 \times 0.71 = 0.65.$$

The corresponding level of control across both devices is:

$$\%Reduction \text{ (CS-ESP + FGD)} = 100 * [1 - EMF_T \text{ (CS-ESP + FGD)}]$$

$$= 100 (1 - 0.65) = 35 \%.$$

Emission factors for coal gasification units were calculated using the Hg content of the feed coal and the OH measurements made in the stack.

6.5.3 Comparisons of Hg_T (Inlet) Using OH Measurement and Coal Hg Data

Emission factors for speciated and total Hg relative to inlet Hg concentrations can be determined using two methods. The first method uses the Hg_T inlet concentrations from OH sampling train measurements. The second method involves the calculation of total Hg inlet values using coal Hg data and sampling train data (flue gas flow rate, moisture concentration, O_2 concentration, and temperature).

Emission factor estimates determined using the OH Method train data and the ICR Part II coal data often give significantly different results. The best estimate can sometimes be obtained by discarding outliers, by reviewing the test reports for tests conditions that can lead to questionable results, and by comparison of the results relative to tests at other test sites. In some cases, it is not possible to arrive at a best estimate, and there is a significant amount of uncertainty leading to a range of estimates.

Mercury capture (percent reduction in emissions) and emission factors for Hg_p, Hg^{2+}, Hg^0, and Hg_T were then calculated using the average stack values for each data set as determined by both coal and OH Method sample train data. Emission factors based on the OH Method sampling train data provided the most consistent results. The inlet

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concentrations and percentage reduction reflected in the body of this report correspond primarily to test results obtained using the OH Method.

6.5.4 Development of Data Sets for Coal-boiler-control Classes

As described earlier, unit classes are defined as those combinations of coal, boiler, and control technologies that are expected to provide similar results in the speciation and capture of Hg. Data sets for different classes of units were developed by sorting the unit tests by coal type, boiler type, NO_x control method, PM control method, and SO_2 control method. Data sets were consolidated whenever the joint sets appeared to provide the same results as the initial groupings. Thus, wall- and tangentially fired PC boilers were consolidated into a single conventional PC boiler set. Units that reported no NO_x controls were consolidated with low-NO_x burners, overfire-air staging, and concentric firing systems.

6.5.5 Questionable Nature of OH Speciation Measurements Upstream of PM Controls

Initial evaluations of the Part III ICR data dealt with comparisons of the coal-boiler-control classes using the results of OH speciation measurements at both the inlet and outlet sampling locations. Comparisons were also made of the results obtained using either the Part III ICR coal data or the inlet OH data to evaluate emission reduction trends. The comparison of speciation at the inlet and outlet locations produced, in some cases, results contrary to the expected behavior of Hg between the inlet and outlet of the control devices.

Previous research has shown that the OH sampling method provides valid measurements for Hg_T at both the inlet to flue gas cleaning devices and in the stack. Also, the OH Method has been shown to provide valid Hg speciation measurements when samples are taken downstream of an efficient PM control device. However, the OH Method can give erroneous speciation measurements for locations upstream of PM control devices.

The OH sampling train consists of a probe, a particulate filter, a series of impingers, a gas flow meter, and a sample pump. The filter captures particulate matter and Hg_p, while the downstream impingers separate Hg^{2+} from Hg^0. Fly ash captured by the sampling train filter can absorb gas-phase Hg (Hg^{2+} and Hg^0) and oxidize Hg^0 resulting in physical and chemical transformations within the sampling train. The rates of these transformations are dependent on the properties of fly ash, the amount of fly ash, the temperature, the flue gas composition, and the sampling duration. Samples collected downstream of efficient PM control devices do not contain enough fly ash to significantly alter Hg speciation within the sampling train, but samples collected upstream of PM control devices can give erroneous results because of fly-ash-induced transformations.

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Table 6-4
ICR Mercury Emission Test Allocations by Coal-boiler-control Class

No. Ea Group	Coal-boiler Control Class	No. of Test Runs	Test Unit Name (Bold numbers in parentheses indicate no. of test runs)
	POST-COMBUSTION CONTROLS: COLD-SIDE ESPS		
1	Bituminous Coal, PC Boiler with CS-ESP	21	Brayton Point 1 (3), Brayton Point 3 (3), Gibson 0300 (3), Gibson 1099 (3), Meramec (3), Jack Watson (3), Widow Creek (3)
2	Bituminous Coal and Pet Coke, PC Boiler with CS-ESP	6	Presque Isle 5 (3), Presque Isle 6 (3)
3	Bituminous Coal, PC Boiler with SNCR and CS-ESP	3	Salem Harber (3)
4	Subbituminous Coal, PC Boiler with CS-ESP	9	Montrose (3), George Neal South (3), Newton (3)
5	Subbituminous/ Bituminous Coal, PC Boiler with CS-ESP	3	St. Clair (3)
6	Lignite, PC Boiler with CS-ESP	3	Stanton 1 (3)
	POST-COMBUSTION CONTROLS: HOT-SIDE ESPS		
1	Bituminous Coal, PC Boiler with HS-ESP	9	Cliffside (3), Gaston (3), Dunkirk (3)
2	Subbituminous Coal, PC Boiler (Dry Bottom) with HS-ESP	6	Cholla 3 (3), Columbia (3)
3	Subbituminous Coal, PC Boiler (Wet Bottom) with HS-ESP	6	Platte (3), Presque Isle 9 (3)
4	Subbituminous/ Bituminous Coal, PC Boiler with HS-ESP	3	Clifty (3)
	POST-COMBUSTION CONTROLS: FF BAGHOUSES		
1	Bituminous Coal, PC Boiler with FF Baghouse	6	Sammis (3), Valmont (3)
2	Bituminous Coal/Pet. Coke, PC Boiler with FF Baghouse (Measurements not valid, disregard)	3	Valley (3)
3	Bituminous/Subbituminous Coal, PC Boiler with FF Baghouse	3	Shawnee (3)
4	Subbituminous Coal, PC Boiler with FF Baghouse	6	Boswell 2 (3), Comanche (3)
	POST-COMBUSTION CONTROLS: MISCELLANEOUS PM CONTROLS		
1	TX Lignite, PC Boiler with CS-ESP and FF (COHPAC)	6	Bigbrown (3), Monticello 1-2 (3)
2	Subbituminous Coal, PC Boiler with PM Scrubbers	3	Boswell 3 (3)
	POST-COMBUSTION CONTROLS: DRY FGD SCRUBBERS		
1	Bituminous Coal, PC Boiler with DSI and CS-ESP	3	Washington (3)
2	Subbituminous Coal, PC Boiler with CS-ESP/SDA	9	GRDA (3), Laramie 3 (3), Wyodak (3)
3	Bituminous Coal, PC Boiler with SDA/FF	3	Mecklenburg (3)
4	Bituminous Coal, PC Boiler with SCR and SDA/FF	6	Logan (3), SEI (3)
5	Subbituminous Coal, PC Boiler with SDA/FF	9	Craig 3 (3), Rawhide (3), NSP Sherburne (3)
6	ND Lignite, PC Boiler with SDA/FF	6	Antelope Valley (3), Stanton 10 (3)
7	Bituminous Coal, Stoker with SDA/FF	3	Dwayne Collier (3)
	POST-COMBUSTION CONTROLS: WET FGD SCRUBBERS		
1	Bituminous Coal, PC Boiler with PS and Wet FGD Scrubbers	3	Bruce Mansfield (3)
2	Subbituminous Coal, PC Boiler with PS and Wet FGD Scrubbers	12	Boswell 4 (3), Cholla 2 (3), Colstrip (3), Lawrence (3)
3	ND Lignite, PC Boiler with PS and Wet FGD Scrubbers	3	Lewis and Clark (3)
4	Bituminous Coal, PC Boiler with CS-ESP and Wet FGD Scrubbers	6	AES Cayuga (3), Big Bend (3)
5	Subbituminous Coal, PC Boiler with CS-ESP and Wet FGD Scrubbers	9	Jim Bridger (3), Laramie River 1 (3), Sam Seymore (3)
6	TX Lignite, PC Boiler with CS-ESP and Wet FGD Scrubbers	6	Monticello 3 (3), Limestone (3)
7	Bituminous Coal, PC Boiler with HS-ESP and Wet FGD Scrubbers	6	Charles Lowman (3), Morrow (3)
8	Subbituminous Coal, PC Boiler with HS-ESP and Wet FGD Scrubbers	12	Coronado (3), Craig 1 (3), Navajo (3), San Juan (3)
9	Bituminous Coal, PC Boiler with FF and Wet FGD Scrubber	6	Clover (3), Intermountain (3)
	CYCLONE-FIRED BOILERS		
1	Lignite, Cyclone Boiler with CS-ESP	2	Leland Olds (2)
2	Subbituminous Coal/Pet. Coke, Cyclone Boiler with HS-ESP	3	Nelson Dewey (3)
3	Lignite, Cyclone Boiler with Mechanical Collector	3	Bay Front (3)
4	Lignite, Cyclone Boiler with SDA/FF	2	Coyote (2)
5	Bituminous Coal, Cyclone Boiler with PS and Wet FGD Scrubbers	3	Lacygne (3)
6	Bituminous Coal, Cyclone Boiler with CS-ESP and Wet FGD Scrubbers	3	Bailly (3)
	FLUIDIZED-BED COMBUSTORS		
1	Lignite, FBC with CS-ESP	3	R.M. Heskett (3)
2	Anthracite Coal Waste, FBC with FF	3	Kline Township (3)
3	Bituminous Coal Waste, FBC with FF	3	Scrubgrass (3)
4	Bituminous Coal/Pet. Coke, FBC with SNCR and FF	3	Stockton Cogen (3)
5	Subbituminous Coal, FBC with SCR and FF	3	AES Hawaii (3)
6	Lignite, FBC with CS-FF	3	TNP (3)

The effects of filtered solids on a filter in the OH sampling train are shown in Figure 6-4. These test results were obtained from pilot-scale coal combustion experiments conducted by the DOE Federal Energy Technology Center (FETC) [now the National Energy Technology Laboratory (NETL)]. The OH sampling train speciation data shown in Figure 6-4 were collected simultaneously in two different manners. In the first, tests designated by the symbols OH-n (n=1, 2, 3...), samples were collected by running the sampling train in the prescribed method by collecting an isokinetic sample with the probe nozzle facing upstream. In the second manner, tests designated by MOH-n (n=1, 2, 3, ...) were run with the probe nozzle facing downstream so that the PM entering the train would be minimal[2].
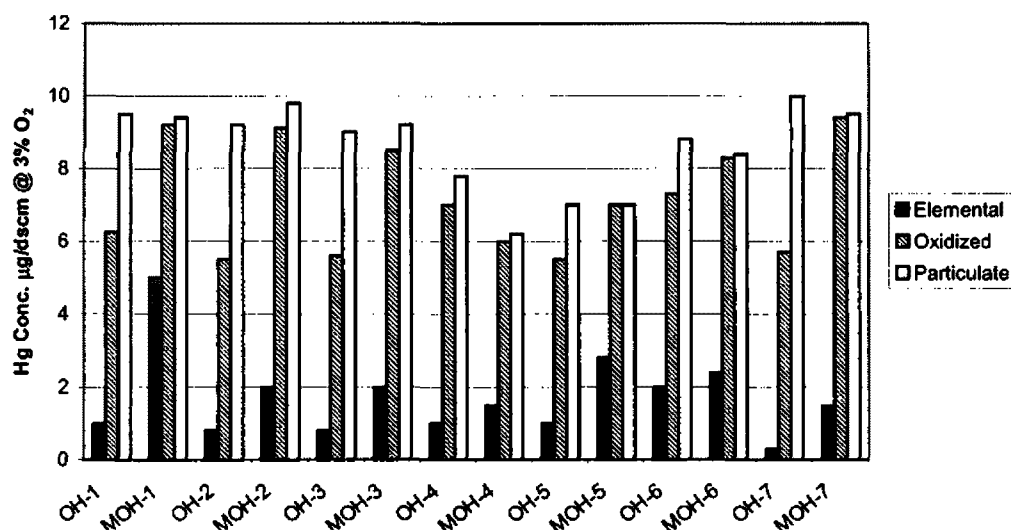
Figure 6-4. Effect of OH sample filter solids on Hg speciation.

The results of these experiments show that, for each of the simultaneous runs, the values of Hg_T can be considered to be equal when taking into account sample variations resulting from the imprecision of the OH Method. However, the samples taken with the probe facing upstream indicated higher concentrations of Hg_p and Hg^{2+} than the samples with the nozzles facing downstream. This provides evidence that PM collected on the filter of the train facing upstream resulted in the oxidization and adsorption of Hg as flue gas passed through the sampling train. This and other evidence indicate that in some cases the use of the OH Method to collect speciation samples upstream of PM control devices provides questionable results[3].

6.6 FUEL, BOILER, AND CONTROL TECHNOLOGY EFFECTS

Based on current understanding of speciation and capture of mercury, it is believed that the ICR data represent a number of subpopulations corresponding to fuel-boiler-control combinations. Sections 6.6 and 6.7 provide an interpretation of physical and chemical phenomena that can be used to characterize the roles that coal, combustion, and flue gas cleaning variables play in the speciation and capture of Hg. Section 6.8 provides a summary of national emission estimates that were based on data described in Sections 6.6 and 6.7. Conclusions are provided in Section 6.9.

The interpretations in Sections 6.6 and 6.7 are based on previous bench-, pilot-, and full-scale tests, plus a number of different modeling efforts related to speciation and capture of Hg in coal-fired boilers. While we have attempted to provide an internally consistent interpretation of the data, some of the observed results are inconsistent with the current theories on the behavior of Hg. In these instances, either our interpretations may be incorrect and other factors may account for the apparent discrepancies in results, or the data may be incorrect. It is believed that some discrepancies result from questionable OH Method or from

errors in reporting test results.

The evaluation of ICR Phase III data indicates that air pollution control technologies now used on coal-fired utility boilers exhibit levels of control that range from 0 to 99 percent reduction of Hg_T. The level of control varies with the coal, combustion conditions, and flue gas cleaning methods used at individual sites. In some instances, there is substantial variation in the three tests conducted at individual sites. The run-to-run variations at any given site can result from actual variations in emissions or with problems associated with the measurement method.

The OH Method is relatively complex, and measurement method problems can result from errors that occur:
- during the collection of samples,
- in extracting samples from the sampling train,
- from the chemical extraction of Hg from the nozzle and probe wash, from the sample train filter, and from the different impingers,
- from Hg analysis, and
- from data reduction and transcription.

Some errors are inevitable in spite of the best efforts of everyone involved in the measurement process.

In statistical terms, the OH data represent a very small number of samples of the underlying population. Each individual test represents the average of flue gas concentration of speciated Hg during a short "snapshot" in time. Run-to-run variations at any given site result from temporal variations in coal properties, combustion conditions, and emission control technology process conditions. There are also site-to-site variations within a given coal-boiler-control class and variations between classes. Even considering these sample population variations, the ICR data provide a great deal of information, when evaluated in the context of current knowledge on the behavior of Hg in coal-fired electrical generating units.

Table 6-5 shows differences in the average reduction in Hg_T emissions for coal-boiler-control classes that burn pulverized coal. Plants that employ only post-combustion PM controls display class average Hg_T emission reductions ranging from 1 to 90 percent. Units with FFs obtained the highest average levels of control. Decreasing average levels of control were generally observed for units equipped with a CS-ESP, HS-ESP, and PS. For units equipped with dry scrubbers, the class average Hg_T emission reductions ranged from 2 to 98 percent. The estimated class average reductions for wet FGD scrubbers were similar and ranged from 10 to 98 percent.

For PC-fired boilers, the amount of Hg captured by a given control technology is greater for bituminous coal than for either subbituminous coal or lignite. For example, the average capture of Hg based on OH inlet measurements in PC-fired plants equipped with a CS-ESP is 36 percent for bituminous coal, 9 percent for subbituminous coal, and 1 percent for lignite.

Table 6-5
Average Mercury Capture by Existing Post-combustion Control
Configurations Used for PC-fired Boilers

Post-combustion Control Strategy	Post-combustion Emission Control Device Configuration	Average Mercury Capture by Control Configuration		
		Coal Burned in Pulverized-coal-fired Boiler Unit		
		Bituminous Coal	Subbituminous Coal	Lignite
PM Control Only	CS-ESP	36 %	3 %	-4 %
	HS-ESP	9 %	6 %	not tested
	FF	90 %	72 %	not tested
	PS	not tested	9 %	not tested
PM Control and Spray Dryer Adsorber	SDA+ESP	not tested	35 %	not tested
	SDA+FF	98 %	24 %	0 %
	SDA+FF+SCR	98 %	not tested	not tested
PM Control and Wet FGD System(a)	PS+FGD	12 %	-8 %	33 %
	CS-ESP+FGD	74 %	29 %	44 %
	HS-ESP+FGD	50 %	29 %	not tested
	FF+FGD	98 %	not tested	not tested

(a) Estimated capture across both control devices

CS-ESP = cold-side electrostatic precipitator   HS-ESP = hot-side electrostatic precipitator
FF = fabric filter   PS = particle scrubber
SDA = spray dryer adsorber system

6.6.1 Coal Effects

While OH speciation measurements may not provide an accurate characterization of the speciation at the inlet sampling location, transformations within the sampling train provide an indication of the fly ash reactivity, and potential for Hg adsorption. SPFs for selected coal-boiler-control classes are summarized in Table 6-6. The data in Table 6-6 are class average SPFs for PC-fired boilers at the inlet and outlet sampling locations. Data are shown for bituminous, subbituminous, ND lignite, and TX lignite. Relatively high levels of SPF_p at the inlet indicate that the Hg was either present as Hg_p in the flue gas, or it was readily absorbed by fly ash on the sampling train filter. Relatively high levels of Hg^{2+} at the inlet indicate that Hg at the inlet sampling location was either already oxidized or oxidized as the flue gas passed through the sampling train. Relatively high levels of measured Hg^0 indicate that there were relatively high levels of Hg^0 in the inlet flue gas.

The units burning bituminous coal exhibited relatively high levels of SPF_p and SPF^{2+} in the inlet samples. It is hypothesized that high levels of $SPF_p + SPF^{2+}$, or alternatively low SPF^0, in the inlet sampling train indicates a high probability that Hg can be readily captured in downstream APCD(s). For the bituminous-coal-fired units, values of SPF_p and SPF^{2+} ranged from 0.03 to 0.92, while values of SPF^0 ranged from 0.01 to 0.37. The HS-ESP unit exhibited the highest level of Hg^0 followed by units equipped with SDA/FF systems. HS-ESP units

operate at temperatures where Hg^0 is not easily oxidized or captured. The SDA/FF units exhibited a 98 percent capture of Hg_T, and the relative concentrations of the SPF^{2+} and SPF^0 measurements at the stack sampling location were 0.22 and 0.77, respectively. This could result from the efficient capture of Hg^{2+} in these units.

The PC-fired units burning subbituminous coal exhibit inlet SPF^0 values ranging from 0.44 to 0.84. The summed $SPF_p + SPF^{2+}$ values for the CS-ESP and HS-ESP units were similar. Both of these classes of units exhibited Hg_T captures of 9 percent. The moderately low Hg_T captures for the SDA/ESP (38 percent) and SDA/FF (25 percent) are reflected by the summed inlet $SPF_p + SPF^{2+}$ values for these units. The units with FF systems (72 percent average capture) had measured average inlet SPF^0 values of 44 percent.

There were a limited number of tests for units firing lignite. The units burning ND lignites tend to have a higher SPF^0 values than units burning TX lignites. The CS-ESP units burning ND lignite exhibited an average inlet SPF^0 value of 0.98. While there was no comparable test unit that fired TX lignite, a unit equipped with a CS-ESP + FF exhibited an average inlet SPF^0 of 0.60. While the inlet measurements for the CS-ESP + FF unit were taken downstream of the CS-ESP, a higher SPF^0 would have been expected if the TX lignite were to provide similar speciation results as the ND lignite. Moderate to average SPF^0 values (0.47) were also noted for the CS-ESP + wet FGD units using TX lignite. Inlet measurements for these units were also made downstream of a CS-ESP.

The similarities between inlet and outlet SPF values can also be used to identify instances where the measured inlet speciation values provide a good estimate of the true Hg speciation in the flue gas at the inlet sampling location. Units with similar inlet and outlet SPFs are identified by an (a) in Table 6-6. These cases correspond to tests in which the capture of Hg_T is ≤ 25 percent for many of the units firing subbituminous coals and ND lignite (e.g., comparison of the respective inlet and outlet values for SPF_p).

Table 6-6
Effects of Coal and Control Technology Inlet and Outlet SPF
and Capture for PC-fired Boilers

Coal-Control Class	Inlet			Outlet			% Red
	SPF_p	SPF^{2+}	SPF^0	SPF_p	SPF^{2+}	SPF^0	Hg_T
Bituminous							
CS-ESP	0.35	0.58	0.07	0.02	0.78	0.20	36
SNCR and CS-ESP	0.92	0.03	0.05	0.20	0.35	0.45	91
HS-ESP (a)	0.09	0.53	0.37	0.04	0.59	0.37	9
FF	0.92	0.04	0.04	0.01	0.52	0.47	90
SDA/FF	0.59	0.28	0.15	0.01	0.22	0.77	98
SCR and SDA/FF	0.82	0.17	0.01	0.05	0.46	0.48	98
Subbituminous							
CS-ESP (a)	0.05	0.25	0.70	0.00	0.31	0.69	3
HS-ESP (a)	0.02	0.15	0.83	0.00	0.17	0.83	6
FF	0.33	0.23	0.44	0.01	0.87	0.12	72
SDA/ESP	0.13	0.26	0.61	0.00	0.05	0.94	35
SDA/FF (a)	0.01	0.06	0.84	0.01	0.05	0.94	24
ND Lignite							
CS-ESP (a)	0.01	0.01	0.98	0.00	0.04	0.96	-4
SDA/FF (a)	0.03	0.04	0.93	0.00	0.03	0.97	0
TX Lignite							
CS-ESP + FF	0.09	0.31	0.60	0.00	0.70	0.30	NA
CS-ESP + Wet FGD	0.00	0.52	0.47	0.01	0.14	0.85	44

(a) Units with similar inlet and outlet SPF values.

6.6.2 <u>Control Technology Effects</u>

Control technology effects are inseparable from coal and boiler effects. In the following sections, post-combustion control technology effects will be evaluated in terms of the three major types of controls currently used for coal-fired utility boilers: PM controls, dry FGD scrubbing controls, and wet FGD controls. These evaluations will be discussed initially in terms of control technology and coal effects on PC-fired boilers. The speciation and capture of Hg from cyclone-fired combustors, FBCs, and IGCC units will then be discussed.

A summary of test results for each of the coal-boiler-control classes for which ICR Hg emission data were collected is given in Table 6-7. The data include information on the number of tests for each class, the average emission factors for Hg_p, Hg^{2+}, Hg^0, and Hg_T, and the average and range of Hg_T emission reductions.

Table 6-7
Average Mercury Emission Factors and Percent Reduction for Coal-boiler-control Classes

No. Ea Group	COAL-BOILER-CONTROL CLASS	No. of Tests	Hg_T, µg/dscm Inlet	Hg_T, µg/dscm Outlet	Average Bin EMF (a) Hg_g	Hg^{2+}	Hg^0	Hg_T	Red in Hg_T, % Range	Ave.
	POST-COMBUSTION CONTROLS: COLD-SIDE ESPs									
1	Bituminous Coal, PC Boiler with CS-ESP	21	13.82	10.31	0.04	0.48	0.15	0.64	81.01 - 0.00	36.03
2	Bituminous Coal and Pet Coke, PC Boiler and CS-ESP	6	4.47	1.73	0.01	0.19	0.20	0.40	70.84 - 50.29	60.14
3	Bituminous Coal, PC Boiler with SNCR and CS-ESP	3	4.41	0.41	0.02	0.03	0.04	0.09	93.06 - 87.07	90.90
4	Subbituminous Coal, PC Boiler with CS-ESP	9	10.05	9.57	0.00	0.31	0.66	0.97	17.46 - (-)0.10	8.75
5	Subbituminous/ Bituminous Coal, PC Boiler with CS-ESP	3	6.79	5.36	0.00	0.20	0.59	0.79	35.63 - 8.71	21.33
6	Lignite, PC Boiler with CS-ESP	3	11.67	12.06	0.00	0.04	1.00	1.04	4.42 - 0.00	1.47
	POST-COMBUSTION CONTROLS: HOT-SIDE ESPs									
1	Bituminous Coal, PC Boiler with HS-ESP	9	9.07	7.95	0.05	0.53	0.33	0.91	42.51 - 0.00	15.09
2	Subbituminous Coal, PC Boiler (Dry Bottom) with HS-ESP	6	9.12	8.41	0.00	0.16	0.77	0.94	27.34 - 0.00	8.80
3	Subbituminous Coal, PC Boiler (Wet Bottom) with HS-ESP	6	10.63	10.92	0.00	0.09	0.95	1.03	26.93 - 0.00	4.50
4	Subbituminous/ Bituminous Coal, PC Boiler with HS-ESP	3	14.51	9.57	0.02	0.32	0.32	0.66	36.99 - 29.51	34.03
	POST-COMBUSTION CONTROLS: FF BAGHOUSES									
1	Bituminous Coal, PC Boiler with FF Baghouse	6	8.13	0.64	0.00	0.07	0.03	0.10	93.04 - 84.15	89.67
2	Bituminous Coal/Pet. Coke, PC Boiler with FF Baghouse (Measurements not valid, disregard)	3	2.20	2.31	0.02	0.77	0.19	0.98	5.67 - (-)25.15	-6.73
3	Bituminous/Subbituminous Coal, PC Boiler with FF Baghouse	3	4.61	1.38	0.00	0.13	0.16	0.30	72.62 - 66.73	69.95
4	Subbituminous Coal, PC Boiler with FF Baghouse	6	7.80	2.42	0.00	0.24	0.04	0.28	87.45 - 52.67	72.43
	POST-COMBUSTION CONTROLS: MISCELLANEOUS CONTROLS									
1	TX Lignite, PC Boiler with CS-ESP and FF (COHPAC)	6	50.05	59.65	0.00	0.75	0.40	1.15	28.69 - 0.00	4.93
2	Subbituminous Coal, PC Boiler with PM Scrubbers	3	6.18	5.63	0.00	0.01	0.90	0.91	13.81 - 5.25	8.74
	POST-COMBUSTION CONTROLS: DRY FGD SCRUBBERS									
1	Bituminous Coal, PC Boiler with DSI and CS-ESP	3	17.03	9.32	0.00	0.37	0.18	0.55	52.61 - 40.68	44.89
2	Subbituminous Coal, PC Boiler with CS-ESP/SDA	9	12.64	7.78	0.01	0.05	0.99	1.04	62.53 - 0.00	37.94
3	Bituminous Coal, PC Boiler with SDA/FF	3	13.59	0.24	0.00	0.00	0.02	0.02	99.23 - 96.91	97.91
4	Bituminous Coal, PC Boiler with SCR and SDA/FF	6	15.22	0.28	0.00	0.01	0.01	0.02	98.72 - 96.56	98.05
5	Subbituminous Coal, PC Boiler with SDA/FF	9	9.56	7.39	0.01	0.03	0.72	0.76	47.31 - 0.00	25.40
6	ND Lignite, PC Boiler with SDA/FF	6	9.65	9.69	0.00	0.04	0.96	1.00	8.49 - 0.00	1.95
7	Bituminous Coal, Stoker with SDA/FF	3	2.39	0.14	0.01	0.01	0.03	0.06	95.43 - 92.84	94.25

(continued)

Table 6-7 (cont'd)

Average Mercury Emission Factors and Percent Reduction for Coal-boiler-control Classes

No. Ea Group	COAL-BOILER-CONTROL CLASS	No. of Tests	Hg_T, μg/dscm		Average Bin EMF (a)				Red in Hg_T, %	
			Inlet	Outlet	Hg_0	Hg^{2+}	Hg^p	Hg_T	Range	Ave.
	POST-COMBUSTION CONTROLS: WET FGD SCRUBBERS									
1	Bituminous Coal PC Boiler with PS and Wet FGD Scrubbers	3	11.15	9.75	0.00	0.17	0.70	0.88	14.94-7.42	12.39
2	Subbituminous Coal PC Boiler with PS and Wet FGD Scrubbers	12	6.30	6.42	0.02	0.06	1.00	1.08	74.27-0.00	10.15
3	ND Lignite PC Boiler with PS and Wet FGD Scrubbers	3	23.64	15.09	0.00	0.02	0.65	0.67	50.75-8.81	12.77
4	Bituminous Coal PC Boiler with CS-ESP and Wet FGD Scrubbers	6	7.77	2.64	0.00	0.03	0.31	0.34	76.06-64.01	70.68
5	Subbituminous Coal PC Boiler with CS-ESP and Wet FGD Scrubbers	9	11.22	8.24	0.00	0.02	0.72	0.75	57.53-1.51	26.78
6	TX Lignite PC Boiler with CS-ESP and Wet FGD Scrubbers	6	44.03	25.00	0.00	0.08	0.48	0.56	56.07-21.31	43.71
7	Bituminous Coal PC Boiler with HS-ESP and Wet FGD Scrubbers	6	10.46	5.83	0.01	0.18	0.39	0.58	59.20-27.96	44.61
8	Subbituminous Coal PC Boiler with HS-ESP and Wet FGD Scrubbers	12	5.12	3.74	0.01	0.03	0.74	0.78	41.48-(-)16.05	18.17
9	Bituminous Coal PC Boiler with FF and Wet FGD Scrubbers	6	1.88	0.50	0.01	0.08	0.19	0.28	98.95-96.78	97.80
	CYCLONE-FIRED BOILERS									
1	Lignite Cyclone Boiler with CS-ESP	2	6.80	5.60	0.00	0.16	0.77	0.93	33.26-0.00	16.63
2	Subbituminous Coal/Pet Coke Cyclone Boiler with HS-ESP	3	2.77	3.00	0.02	0.08	1.00	1.11	0.13-0.00	0.04
3	Lignite Cyclone Boiler with Mechanical Collector	3	3.13	4.98	0.25	0.76	0.56	1.57	0.34-0.00	0.11
4	Lignite Cyclone Boiler with SDA/FF	2	17.82	16.34	0.00	0.01	0.90	0.91	11.81-5.48	8.64
5	Bituminous Coal Cyclone Boiler with PS and Wet FGD Scrubbers	3	9.88	7.57	0.01	0.04	0.72	0.77	24.53-22.17	23.29
6	Bituminous Coal Cyclone Boiler with CS-ESP and Wet FGD Scrubbers	3	5.61	3.11	0.00	0.06	0.49	0.55	54.95-54.11	54.43
	FLUIDIZED-BED COMBUSTORS (FBCs)									
1	Lignite FBC with CS-ESP	3	10.46	5.95	0.03	0.06	0.53	0.62	54.49 - 11.09	38.29
2	Anthracite Coal Waste FBC with FF	3	44.69	0.12	0.00	0.00	0.00	0.00	99.74 - 99.73	99.74
3	Bituminous Coal Waste FBC with FF	3	128.83	0.13	0.00	0.00	0.00	0.00	99.92 - 99.85	99.89
4	Bituminous Coal/Pet Coke FBC with SNCR and FF	3	2.24	0.12	0.01	0.02	0.02	0.06	96.09 - 92.16	94.25
5	Subbituminous Coal FBC with SCR and FF	3	1.71	0.73	0.00	0.01	0.41	0.43	64.91 - 51.35	57.37
6	Lignite FBC with CS-FF	3	35.98	15.11	0.00	0.31	0.12	0.43	61.88 - 54.07	57.05

(a) See Section 6.5.2 for discussion of emission factors.

6-23

6.6.3 Post-combustion PM Controls

In 1999, 72 percent of the coal-fired electric utility boilers in the U.S. used post-combustion controls that consisted only of PM controls. The Phase I ICR revealed that there were 890 units that used only post-combustion PM controls. This included 791 units using either CS- or HS-ESPs and 80 units that used FF baghouses. The number of boiler units in the U.S. equipped only with PM controls is shown in Table 6-8 along with the number of test units in each PM control category.

Table 6-8
Number of Coal-fired Utility Boilers Equipped with Particulate Matter Controls Only

Particulate Matter Control	Number of Units	
	Utility Industry	Test Units
CS- or HS-ESP (a)	791	25
Two ESPs in series	2	2
Fabric Filter	80	12
ESP w/ Fabric Filter	6	2
Particulate Scrubber	5	1
ESP w/ Particulate Scrubber	4	0
Mechanical Collector	2	1

(a) 14 CS-ESPs and 9 HS-ESPs were tested

6.6.3.1 Cold-side ESPs

A total of 14 PC-fired units equipped with CS-ESPs were tested. The types of fuels that were used in these tests are given in Table 6-9.

Table 6-9
Type of Fuel Used in PC-fired Units Equipped with CS-ESP

Type of Fuel	No. of Test Units
Bituminous	8
Bituminous & Pet. Coke	2
Subbituminous	3
Subbituminous/Bituminous	1
Total	14

One of the units burning bituminous coal was also equipped with an SNCR system for NO_x control. One cyclone-fired unit that burned lignite was also tested. The results of Hg emission tests on PC-fired units equipped with a CS-ESP are given in Table 6-10.

Table 6-10
Post-combustion Controls: Cold-side ESPs

Plant ID	Run											
Bituminous Coal, PC Boiler with CS-ESP												
Brayton Point 1	1	2.01	3.34	0.32	5.68	6.80	0.77	3.83	0.23	4.84	14.73	28.86
Brayton Point 1	2	2.61	3.69	0.25	6.55	4.21	0.75	3.19	0.25	4.18	36.11	0.68
Brayton Point 1	3	2.17	3.50	0.26	5.93	5.01	0.77	3.02	0.24	4.02	32.19	19.64
Average												
Brayton Point 3	1	3.14	3.67	0.36	7.17	8.55	0.78	3.18	0.46	4.43	38.21	48.20
Brayton Point 3	2	1.83	3.14	0.34	5.31	5.30	0.96	2.47	0.37	3.80	28.47	28.27
Brayton Point 3	3	1.40	3.26	1.60	6.26	5.58	0.01	3.43	1.70	5.15	17.70	7.71
Average												
Gibson 0300	1	1.94	31.74	4.39	38.08	13.69	0.00	32.03	7.51	39.54	-3.85	-188.83
Gibson 0300	2	1.25	38.06	2.92	42.23	13.33	0.01	32.21	5.80	38.01	9.98	-185.13
Gibson 0300	3	1.75	44.44	1.65	47.85	13.53	0.01	42.87	4.17	47.05	1.66	-247.76
Average												
Gibson 1099	1	5.53	10.33	2.34	18.20	14.00	0.03	6.06	5.03	11.12	38.92	20.62
Gibson 1099	2	27.57	3.78	1.25	32.60	15.09	0.05	8.41	5.00	13.46	58.69	10.76
Gibson 1099	3	4.60	11.02	1.58	17.20	14.69	0.03	11.03	4.65	15.71	8.68	-6.93
Average												
Meramec	1	7.61	0.49	0.14	8.23	8.46	0.00	0.76	0.80	1.56	81.01	81.54
Meramec	2	9.34	1.36	0.44	11.15	10.72	0.01	2.20	1.13	3.35	69.97	68.77
Meramec	3	5.65	1.93	0.62	8.19	5.89	0.00	1.51	0.79	2.30	71.96	60.99
Average												
Jack Watson	1	3.60	1.22	0.92	5.74	4.70	0.05	2.57	1.87	4.49	21.71	4.39
Jack Watson	2	4.91	1.16	0.25	6.32	5.67	0.05	2.99	0.89	3.94	37.70	30.53
Jack Watson	3	4.64	0.60	0.23	5.46	6.20	0.06	2.92	0.89	3.88	29.04	37.45
Average												
Widows Creek	1	3.36	0.44	0.54	4.34	3.11	0.14	1.48	0.78	2.40	44.75	22.95
Widows Creek	2	2.98	0.45	0.51	3.94	2.67	0.01	1.28	0.68	1.97	50.00	26.25
Widows Creek	3	2.87	0.47	0.50	3.83	2.15	0.01	0.65	0.67	1.34	65.11	37.81
Average												
Minimum		1.25	0.44	0.14	3.83	2.15	0.00	0.65	0.23	1.34	-3.85	-247.76
Maximum		27.57	44.44	4.39	47.85	15.09	0.96	42.87	7.51	47.05	81.01	81.54
STDEV		5.62	13.05	1.09	13.86	4.35	0.34	12.01	2.24	13.67	23.90	88.31
Bituminous Coal and Pet Coke, PC Boiler with CS-ESP												
Presque Isle 5	1	4.56	0.48	0.14	5.17	4.27	0.01	0.72	1.06	1.80	65.29	57.92
Presque Isle 5	2	3.60	0.66	0.57	4.82	3.48	0.00	0.82	1.02	1.84	61.87	47.14
Presque Isle 5	3	5.06	0.45	0.12	5.63	3.93	0.02	0.71	0.91	1.64	70.84	58.19
Average												
Presque Isle 6	1	2.73	0.63	0.17	3.52	2.29	0.06	0.84	0.70	1.60	54.54	30.10
Presque Isle 6	2	2.97	0.72	0.25	3.94	4.34	0.03	1.00	0.93	1.96	50.29	54.87
Presque Isle 6	3	2.96	0.62	0.17	3.75	3.85	0.03	0.73	0.81	1.57	58.00	59.17
Average												
Minimum		2.73	0.45	0.12	3.52	2.29	0.00	0.71	0.70	1.57	50.29	30.10
Maximum		5.06	0.72	0.57	5.63	4.34	0.06	1.00	1.06	1.96	70.84	59.17
STDEV		0.96	0.11	0.17	0.86	0.75	0.02	0.11	0.13	0.15	7.44	11.25

(continued)

Table 6-10 (cont'd)
Post-combustion Controls: Cold-side ESPs

Unit ID	Run											
Bituminous Coal, PC Boiler with SNCR and CS-ESP												
Salem Harbor	1	4.12	0.32	0.32	4.76	3.44	0.07	0.28	0.27	0.62	87.07	82.11
Salem Harbor	2	4.09	0.04	0.16	4.29	2.35	0.10	0.07	0.15	0.32	92.57	86.40
Salem Harbor	3	3.96	0.06	0.15	4.17	3.27	0.08	0.08	0.14	0.29	93.06	91.16
Average		*(illegible)*			4.41	3.02		0.14	0.19	0.42	90.90	86.55
Subbituminous Coal, PC Boiler with CS-ESP												
Montrose	1	1.94	1.85	6.00	9.79	44.90	0.03	2.57	5.48	8.08	17.46	82.01
Montrose	2	0.91	2.52	4.93	8.36	51.99	0.02	2.60	5.94	8.56	-2.31	83.54
Montrose	3	1.63	2.85	4.68	9.16	47.76	0.02	2.30	5.69	8.01	12.54	83.22
Average		*(illegible)*			9.10	48.21	0.02	2.49	5.70	8.22	9.23	82.92
George Neal So.	1	0.17	4.78	6.34	11.29	3.96	0.03	4.07	5.47	9.58	15.18	-6.90
George Neal So.	2	0.07	4.35	8.24	12.66	7.82	0.06	4.60	6.87	11.53	8.89	-47.37
George Neal So.	3	0.02	3.53	3.77	7.32	10.19	0.02	4.74	6.39	11.15	-52.29	-9.36
Average		*(illegible)*			10.42	7.99	0.04	4.47	6.24	10.75	-12.04	-21.21
Newton	1	0.04	0.58	9.70	10.32	9.07	0.00	2.26	8.07	10.33	-0.10	-14.00
Newton	2	0.04	0.63	9.85	10.52	8.05	0.00	1.66	7.13	8.80	16.33	-9.28
Newton	3	0.08	1.65	9.26	11.00	9.34	0.00	2.04	8.03	10.07	8.46	-7.82
Average		*(illegible)*			10.61	8.82	0.00	1.99	7.74	9.73	8.23	-10.36
Average		0.54	2.53	6.91	10.05	21.01	0.02	2.98	6.56	9.57	2.09	17.12
Minimum		0.02	0.58	3.77	7.32	7.82	0.00	1.66	5.47	8.01	-52.29	-47.37
Maximum		1.94	4.78	9.85	12.66	51.99	0.06	4.74	8.07	11.53	17.46	83.54
STDEV		0.76	1.50	2.34	1.61	19.75	0.02	1.16	1.02	1.30	21.75	50.89
SPF		0.05	0.25	0.69	1.00	1.00	0.00	0.31	0.69	1.00		
Subbituminous/ Bituminous Coal, PC Boiler with CS-ESP												
St Clair	1	2.53	2.29	1.97	6.79	16.26	0.01	1.35	3.01	4.37	35.63	73.13
St Clair	2	2.87	2.13	1.40	6.39	14.36	0.01	1.39	3.74	5.14	19.65	64.24
St Clair	3	0.98	1.94	4.28	7.20	17.71	0.01	1.33	5.24	6.57	8.71	62.89
Average		2.13	2.12	2.55	6.79	16.11	0.01	1.35	4.00	5.36	21.33	66.75
Lignite, PC Boiler with CS-ESP												
Stanton 1	1	0.04	0.15	11.96	12.15	31.51	0.04	0.42	11.16	11.62	4.42	63.13
Stanton 1	2	0.13	0.13	10.81	11.06	41.24	0.02	0.43	11.68	12.14	-9.70	70.56
Stanton 1	3	0.08	0.05	11.66	11.79	19.94	0.01	0.45	11.97	12.43	-5.41	37.67
Average		0.08	0.11	11.48	11.67	30.90	0.02	0.44	11.60	12.06	-3.57	57.12

The test units with a CS-ESP display significant run-to-run differences (variations) in the Hg_T (inlet), Hg_T (outlet), and % Hg_T reduction. These differences may result from the changing Hg_T inlet concentrations, changing boiler and control device operating conditions, or sampling and analysis problems. Two important variables that affect Hg capture are changes in Hg inlet concentration and unit operating temperatures.

Run-to-run variations for test units burning bituminous coal in PC-fired boilers equipped with CS-ESPs are shown in Figure 6-5. While the class average Hg_T reduction for these units was 36 percent, the run-to-run emission reductions in Hg_T range from 0 to 81 percent. All inlet and outlet Hg_T concentrations for the Widow Creek, Jack Watson, Brayton 3, and Brayton 1 were similar. The Meramec plant exhibited relatively high Hg_T reductions as did run 2 on Gibson 1099. Gibson 0300 exhibited high stack gas concentrations of Hg_T, and run 1 on Gibson 0300 had a higher outlet Hg_T concentration than at the inlet. The unit-to-unit variations in Hg_T emission reductions for these same units are shown in Figure 6-6. The average emission reduction for the seven 3-run tests shown in Figure 6-6 is still 37 percent, but unit-to-unit emission reductions range from 3 percent for Gibson 0300 to 74 percent for Meramec. The speciation of Hg for the bituminous coals is predominantly Hg^{2+}.

In Figure 6-6, there are two unit test averages given for Gibson. Both averages are for the same unit, Gibson 0300. The unit average for Gibson 1099 is for tests conducted in October 1999, while the average for Gibson 0300 is for tests conducted in March 2000. The tests in October and March used coal from the same source. Average unit reductions in Hg_T for the October and March tests were 35 and 3 percent, respectively. The apparent discrepancy in the test results led plant engineers to investigate. The investigation indicated that steam-cleaning of the air preheater during the collection of OH samples was the probable cause of these inconsistencies.

The Hg speciation and Hg_T reductions for PC-fired units equipped with CS-ESPs and burning subbituminous coal and lignite are shown in Figure 6-7. Hg emission reductions for the units range from -4 to 12 percent, exhibiting little if any Hg capture. The relative concentrations of Hg^0 in the stack gas are higher than those observed for units firing bituminous coal.
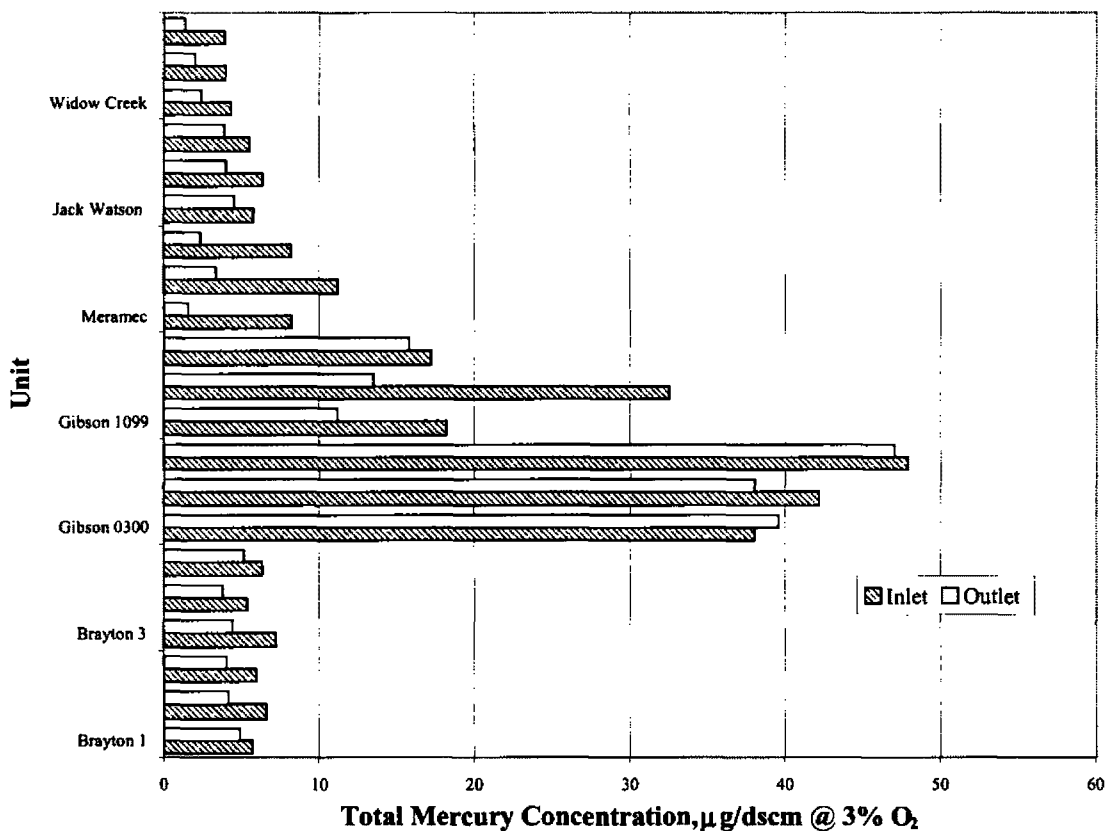
Figure 6-5. Inlet and outlet mercury concentrations for bituminous PC-fired boilers with CS-ESP.

Figure 6-6. Mercury emissions from bituminous-coal-fired PC boilers with CS-ESP.
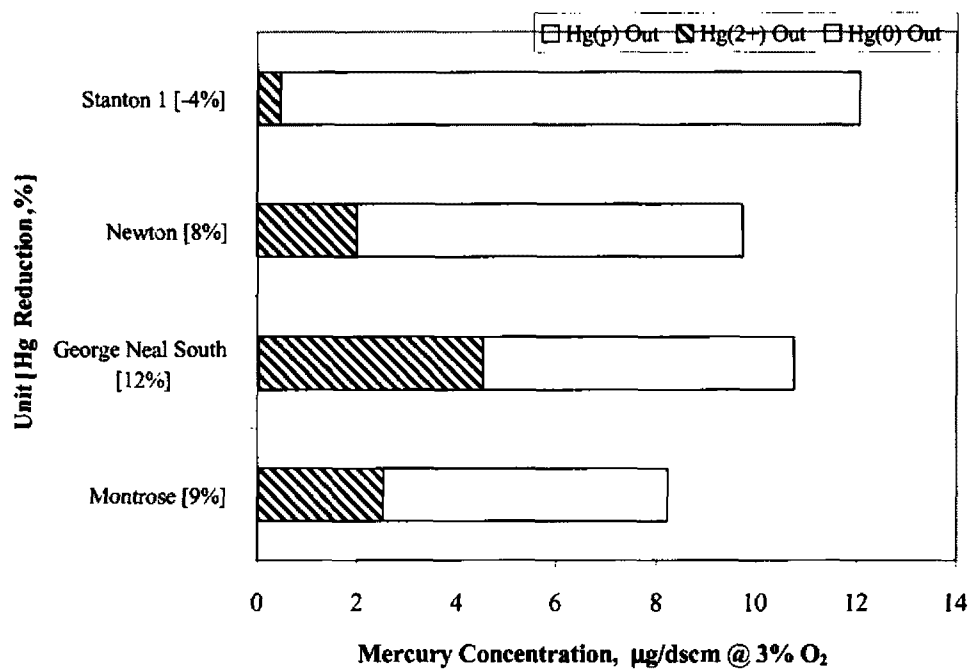
Figure 6-7. Mercury emissions for subbituminous- and lignite-fired PC boilers with CS-ESP.

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Run-to-run variations on a given unit can be attributed to operating variables such as inlet Hg concentrations, operating temperature, soot blowing, reentrainment losses within an ESP, or the imprecision of the OH Method.

Mercury outlet concentrations can be expressed by:

Hg_T (outlet) = Hg_T (inlet) − Hg_p (captured in the control device)

+ Hg_p (reentrained and escapes the control device)

- Hg^0 or Hg^{2+} (adsorbed and captured within the control device)

+ Hg_p, Hg^{2+}, or Hg^0 (desorbed or is reentrained and escapes capture)

Deposits or captured fly ash between the inlet and outlet sampling location (the stack) can adsorb or desorb gas-phase Hg, depending on time-dependent changes in the inlet Hg concentration and operating temperatures downstream of the inlet sampling location. Temperature effects can be understood by considering the deposits and collected fly ash between the inlet and stack locations to be a complex system that adsorbs and desorbs Hg. If the system has reached equilibrium in terms of operating conditions, there will be a constant relationship between the inlet and outlet concentrations of Hg. Increases in operating temperatures within the system can increase the rate at which Hg is desorbed, resulting in increased outlet concentrations relative to the inlet concentrations. Temperature decreases can increase Hg adsorption within the system. This can cause a decrease in the Hg outlet concentrations relative to the inlet concentrations.

Temporal changes in inlet and outlet Hg concentrations are the result of hysteresis or history effects. Hypothetical changes in Hg reduction for three tests on a single unit that could occur because of the time lag between changing inlet and outlet Hg concentrations are illustrated in Figure 6-8. In this illustration, Hg emission reductions during runs 1, 2, and 3 averaged 30, -15, and 40 percent, respectively. The -15 percent indicates that the measured outlet Hg concentrations were higher than the inlet concentrations.
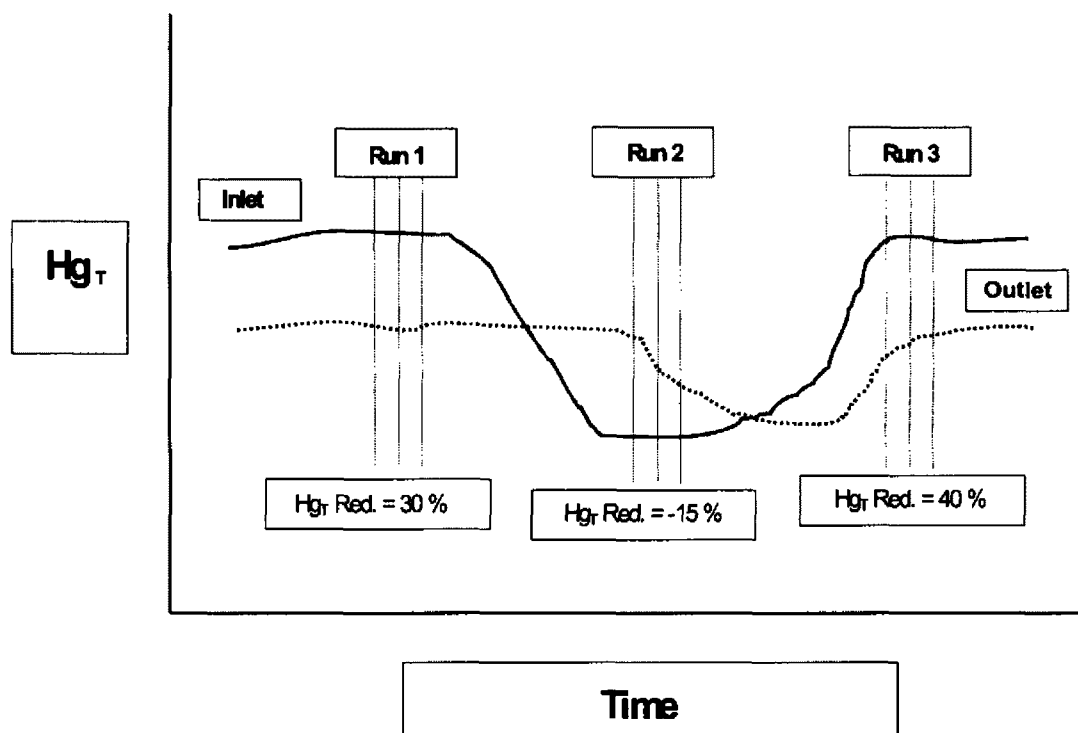
Figure 6-8. Hypothetical effect of inlet and outlet Hg_T concentration changes on run-to-run Hg_T capture.

Changes in the fly ash carbon content, changes in unit operating conditions such as load, and diurnal changes in temperature may also result in hysteresis effects. The ICR tests for each unit represent a snapshot in time. Additional OH Method tests or tests with Hg CEMs are needed over an extended period of time to more fully characterize the effects of coal, combustion, and control technology variables on stack emissions of Hg.

6.6.3.2 Hot-side ESPs

Eight ICR units that burn pulverized coal and that were equipped with an HS-ESP were tested. Three of these units burned bituminous coal; four burned subbituminous coal; and one burned subbituminous and bituminous coal. A ninth, a cyclone-fired unit equipped with an HS-ESP, burned subbituminous coal and petroleum coke. Hg test data for the eight PC-fired units are given in Table 6-11.

Table 6-11
Post-combustion Controls: Hot-side ESPs

Bituminous Coal, PC Boiler with HS-ESP												
Cliffside	1	0.17	3.72	3.31	7.20	5.43	0.41	2.79	3.95	7.14	0.86	-31.58
Cliffside	2	0.09	3.54	3.33	6.95	3.84	0.10	2.27	1.95	4.31	38.00	-12.17
Cliffside	3	0.08	4.15	7.27	11.49	8.80	0.10	3.97	2.54	6.61	42.51	24.94
Average												
Gaston	1	4.28	0.86	2.64	7.77	5.20	0.74	4.70	2.34	7.78	-0.19	-49.56
Gaston	2	2.57	0.71	3.56	6.84	6.27	0.40	5.80	3.47	9.66	-41.37	-54.19
Gaston	3	0.43	3.94	2.83	7.20	4.70	1.15	4.73	2.04	7.92	-10.00	-68.41
Average												
Dunkirk	1	0.09	8.56	2.82	11.47	10.06	0.21	6.89	3.67	10.77	6.08	-7.09
Dunkirk	2	0.01	8.91	1.43	10.36	10.30	0.08	4.57	2.46	7.12	31.27	30.90
Dunkirk	3	0.01	9.15	3.20	12.36	9.65	0.03	6.40	3.82	10.25	17.08	-6.26
Average												
Minimum		0.01	0.71	1.43	6.84	3.84	0.03	2.27	1.95	4.31	-41.37	-68.41
Maximum		4.28	9.15	7.27	12.36	10.30	1.15	6.89	3.95	10.77	42.51	30.90
STDEV		1.52	3.28	1.59	2.30	2.55	0.37	1.54	0.80	2.02	26.41	34.54
Subbituminous Coal, PC Boiler (Dry Bottom) with HS-ESP												
Cholla 3	1	0.07	0.37	1.93	2.37	51.98	0.01	0.51	1.87	2.40	-1.30	95.39
Cholla 3	2	0.51	0.32	0.46	1.28	54.43	0.01	0.01	1.00	1.02	20.42	98.12
Cholla 3	3	0.45	0.43	0.61	1.49	40.48	0.01	0.39	1.27	1.67	-12.28	95.87
Average												
Columbia	1	0.01	0.93	14.27	15.22	9.85	0.00	2.74	11.71	14.45	5.02	-46.78
Columbia	2	0.01	5.82	13.40	19.24	10.30	0.00	2.16	11.82	13.98	27.34	-35.71
Columbia	3	0.01	0.46	14.65	15.12	10.35	0.00	2.65	12.68	15.34	-1.47	-48.18
Average												
Minimum		0.01	0.32	0.46	1.28	9.85	0.00	0.01	1.00	1.02	-12.28	-48.18
Maximum		0.51	5.82	14.65	19.24	54.43	0.01	2.74	12.68	15.34	27.34	98.12
STDEV		0.23	2.18	7.21	8.26	21.77	0.00	1.24	5.87	7.09	14.88	76.82
Subbituminous Coal, PC Boiler (Wet Bottom) with HS-ESP												
Platte	1	0.03	4.15	9.82	14.00	11.10	0.01	1.45	8.76	10.23	26.93	7.88
Platte	2	0.02	1.92	11.31	13.25	9.65	0.01	0.78	16.86	17.65	-33.20	-82.85
Platte	3	0.03	4.39	11.63	16.04	6.05	0.01	1.51	14.90	16.43	-2.40	-171.57
Average												
Presque Isle 9	1	0.04	0.14	6.70	6.89	9.86	0.00	0.57	6.30	6.88	0.10	30.22
Presque Isle 9	2	0.01	0.14	6.89	7.05	8.92	0.00	0.67	6.74	7.41	-5.23	16.87
Presque Isle 9	3	0.01	0.10	6.43	6.55	9.91	0.00	0.54	6.38	6.92	-5.76	30.11
Average												
Minimum		0.01	0.10	6.43	6.55	6.05	0.00	0.54	6.30	6.88	-33.20	-171.57
Maximum		0.04	4.39	11.63	16.04	11.10	0.01	1.51	16.86	17.65	26.93	30.22
STDEV		0.01	2.03	2.41	4.27	1.72	0.01	0.44	4.69	4.91	19.13	82.08
Subbituminous/Bituminous Coal, PC Boiler with HS-ESP												
Clifty	3	0.01	3.41	11.46	14.87	7.84	0.07	5.50	3.80	9.37	36.99	-19.53
Clifty	1	0.40	2.35	11.17	13.92	8.02	0.70	3.60	4.67	8.96	35.58	-11.78
Clifty	2	0.02	3.58	11.13	14.73	7.66	0.01	5.04	5.34	10.39	29.51	-35.57
Average												

As shown in Figure 6-9, the units that fired bituminous coal exhibited average emission reductions of 18 percent (Dunkirk), -17 percent (Gaston), and 27 percent (Cliffside). In Figure 6-10, the HS-ESP units that burned subbituminous coal and lignite exhibit Hg emission reductions of 2 percent (Cholla), -1 percent (Columbia), -3 percent (Platte), and -6 percent (Presque Isle). Stack concentrations of Hg^0 were substantially higher for the units burning subbituminous coal than for those burning bituminous coal.

Hot-side ESPs tend to exhibit poor capture because they operate over a temperature range where the oxidization and adsorption of Hg^0 is limited.

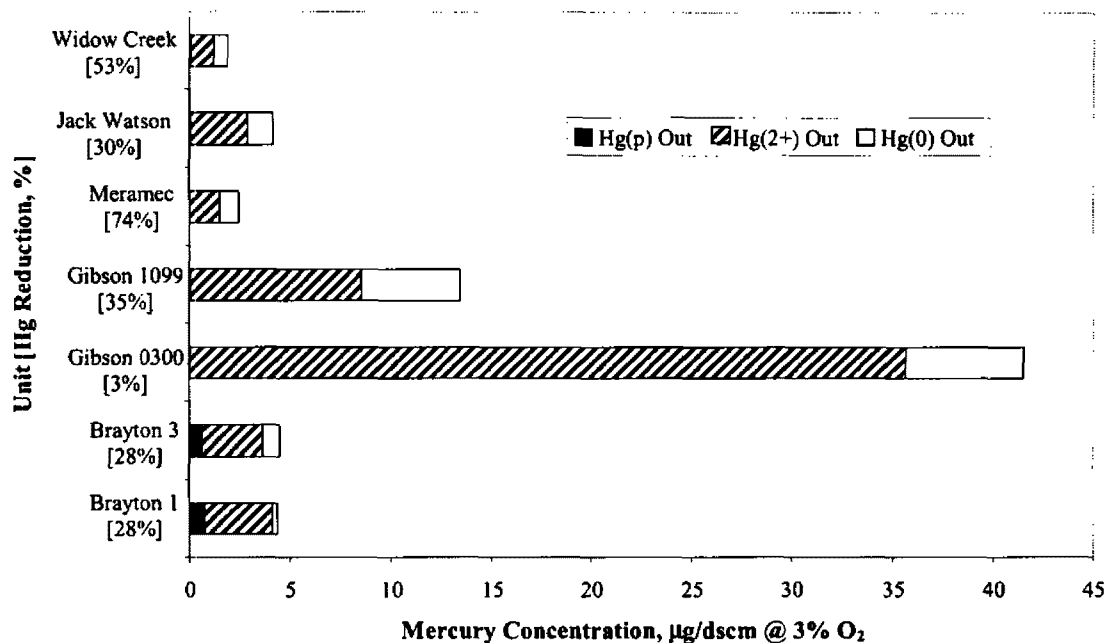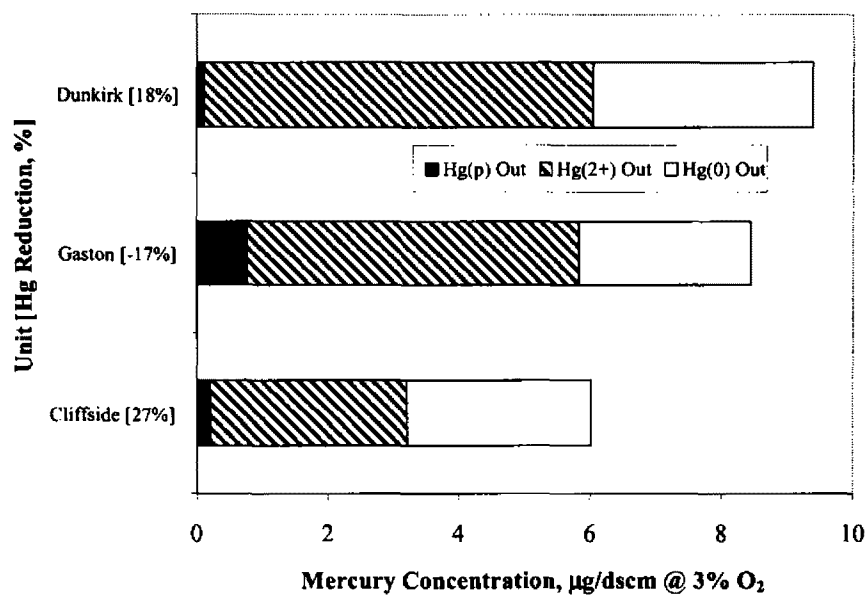Figure 6-9. Mercury emissions from bituminous-fired PC boilers with HS-ESP.
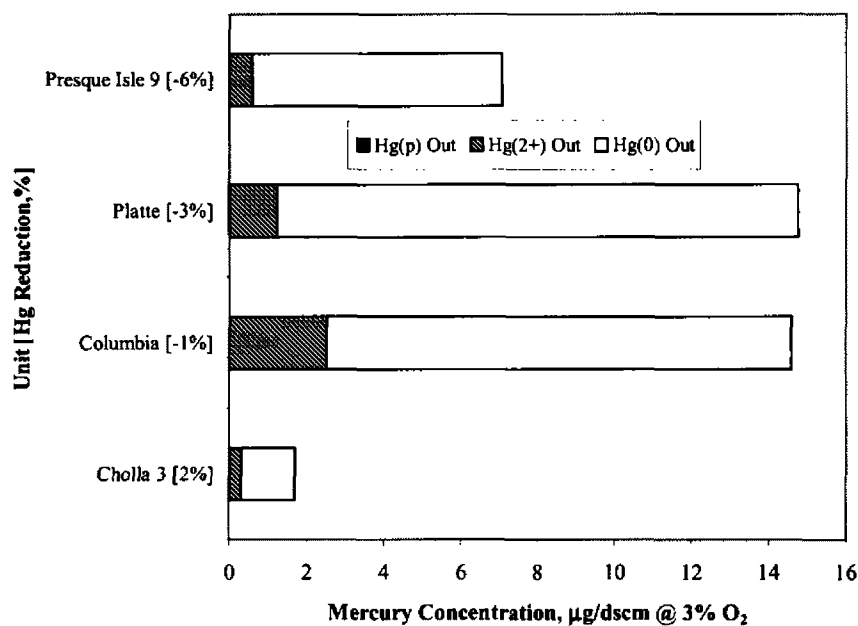
Figure 6-10. Mercury emissions for subbituminous- and lignite-fired PC boilers with HS-ESP.

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6.6.3.3 FF Baghouses

Six PC-fired units with FF baghouses were tested. The results of one test unit (Valley) were omitted from the results because of data quality problems. The unit name, type of coal burned, and reduction in Hg_T are given in Table 6-12 for the five units with valid test data.

Table 6-12
Mercury (Hg_T) Reduction at PC-fired Units with FF Baghouses

Unit	Coal	Reduction in Hg_T, %
Sammis	Bituminous	92
Valmont	Bituminous	87
Shawnee	Bituminous/subbituminous	70
Boswell 2	Subbituminous	83
Comanche	Subbituminous	62

Detailed test results for the five units listed in Table 6-12 are given in Table 6-13. The average run-to-run Hg_T reductions for the FF units ranged from 53 to 92 percent. The class average emission reductions for the two bituminous-coal-fired units was 90 percent, the average for the single unit that fired bituminous and subbituminous coals was 70 percent, and the class average for the two units that fired subbituminous coal was 72 percent. There were generally high stack concentrations of Hg^{2+} for all FF units. Hg^0 can be oxidized as it passes through the FF, either from reactions with fly ash on the filter cake or from reactions with bag filter material. This can lead to relatively low concentrations of Hg^0 in the stack gas. These observations may not apply to all bag filter materials, or units that burn either lignite or subbituminous coal.

6.6.3.4 Comparison of ESPs and FFs

The average unit-to-unit reductions in Hg_T in the inlet and outlet of PC-fired units equipped with a CS-ESP, HS-ESP, or FF baghouse are shown in Figure 6-11. Stack concentrations and speciation results are shown in Figure 6-12. SPF results are shown in Figure 6-13.

The best Hg capture is exhibited for units equipped with a FF (72 to 90 percent average reductions). This is followed by units that are equipped with a CS-ESP and that burn bituminous coal or bituminous coal and petroleum coke (35 to 54 percent average reductions). Poor capture (-4 to 9 percent average reductions) is shown for all units that are equipped with a HS-ESP and for units that are equipped with a CS-ESP and burn either subbituminous coal or lignite. Units, which exhibit poor Hg_T capture, display higher SPF^0 values than units that have good Hg_T capture. In units that burn bituminous coal or bituminous coal and petroleum

coke, Hg^{2+} constitutes more than half of the total Hg in the stack gas. This is also true for the unit that is equipped with a FF and burns subbituminous coal.

Table 6-13
Post-combustion Controls: FF Baghouses

Unit	Test No.										
Bituminous Coal, PC Boiler with FF Baghouse											
Sammis	1	11.78	0.48	0.61	12.86	6.64	0.01	0.49	0.61	1.11	91.37	83.28
Sammis	2	15.35	0.50	0.54	16.38	9.54	0.01	0.58	0.55	1.14	93.04	88.05
Sammis	3	14.62	0.51	0.52	15.65	9.55	0.02	0.51	0.57	1.10	92.97	88.48
Average												
Valmont	1	0.92	0.12	0.18	1.22	0.80	0.00	0.12	0.04	0.16	86.98	80.04
Valmont	2	0.92	0.07	0.14	1.12	0.44	0.00	0.10	0.02	0.12	89.53	73.26
Valmont	3	1.23	0.10	0.17	1.51	0.60	0.00	0.21	0.03	0.24	84.15	60.16
Average												
Average												
Minimum		0.92	0.07	0.14	1.12	0.44	0.00	0.10	0.02	0.12	84.15	60.16
Maximum		15.35	0.51	0.61	16.38	9.55	0.02	0.58	0.61	1.14	93.04	88.48
STDEV		7.16	0.22	0.22	7.59	4.49	0.01	0.22	0.30	0.52	3.54	10.76
Bituminous Coal/Pet. Coke, PC Boiler with FF Baghouse (Measurements not valid, disregard)											
Valley	1	0.04	1.44	1.21	2.69	0.95	0.11	2.02	0.41	2.54	5.67	-165.84
Valley	2	0.05	1.49	0.45	1.99	1.33	0.04	1.55	0.42	2.00	-0.70	-50.84
Valley	3	0.04	1.22	0.67	1.92	1.52	0.00	1.89	0.52	2.41	-25.15	-58.75
Average												
Bituminous/Subbituminous Coal, PC Boiler with FF Baghouse											
Shawnee	1	3.18	0.58	0.72	4.48	2.39	0.01	0.63	0.84	1.49	66.73	37.66
Shawnee	2	3.01	0.98	0.66	4.65	4.29	0.02	0.61	0.75	1.37	70.51	68.03
Shawnee	3	3.44	0.57	0.67	4.68	2.66	0.01	0.60	0.68	1.28	72.62	51.82
Average												
Subbituminous Coal, PC Boiler with FF Baghouse											
Boswell 2	2	1.99	1.26	1.46	4.71	4.35	0.00	0.35	0.23	0.59	87.45	86.43
Boswell 2	3	0.83	1.15	2.49	4.46	5.20	0.00	0.58	0.12	0.70	84.32	86.54
Boswell 2	1	2.75	1.81	1.60	6.16	8.35	0.07	1.26	0.14	1.47	76.06	82.34
Average												
Comanche	1	1.81	3.93	5.71	11.46	15.91	0.00	3.33	0.27	3.60	68.58	77.37
Comanche	3	5.27	1.28	3.67	10.22	14.24	0.00	3.20	0.33	3.52	65.52	75.26
Comanche	2	2.59	1.45	5.77	9.82	17.08	0.00	3.99	0.65	4.65	52.67	72.80
Average												
Average												
Minimum		0.83	1.15	1.46	4.46	4.35	0.00	0.35	0.12	0.59	52.67	72.80
Maximum		5.27	3.93	5.77	11.46	17.08	0.07	3.99	0.65	4.65	87.45	86.54
STDEV		1.50	1.06	1.94	3.06	5.59	0.03	1.57	0.20	1.72	12.91	5.85
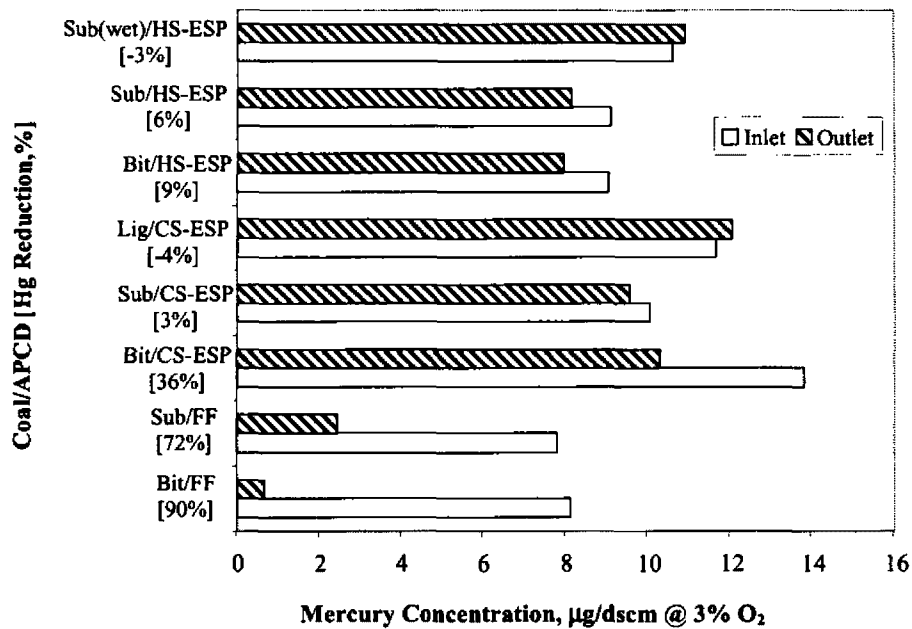
Figure 6-11. Mercury emission reductions for PC-fired boilers with ESPs and FFs.
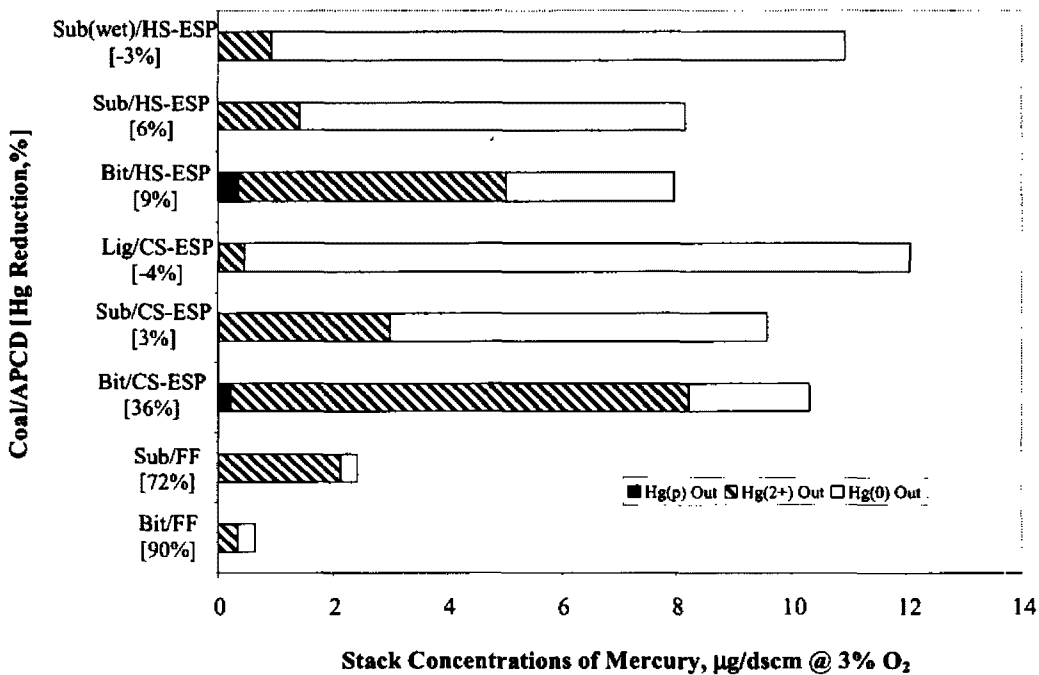
Figure 6-12. Mercury speciation for PC-fired boilers with ESPs and FFs.

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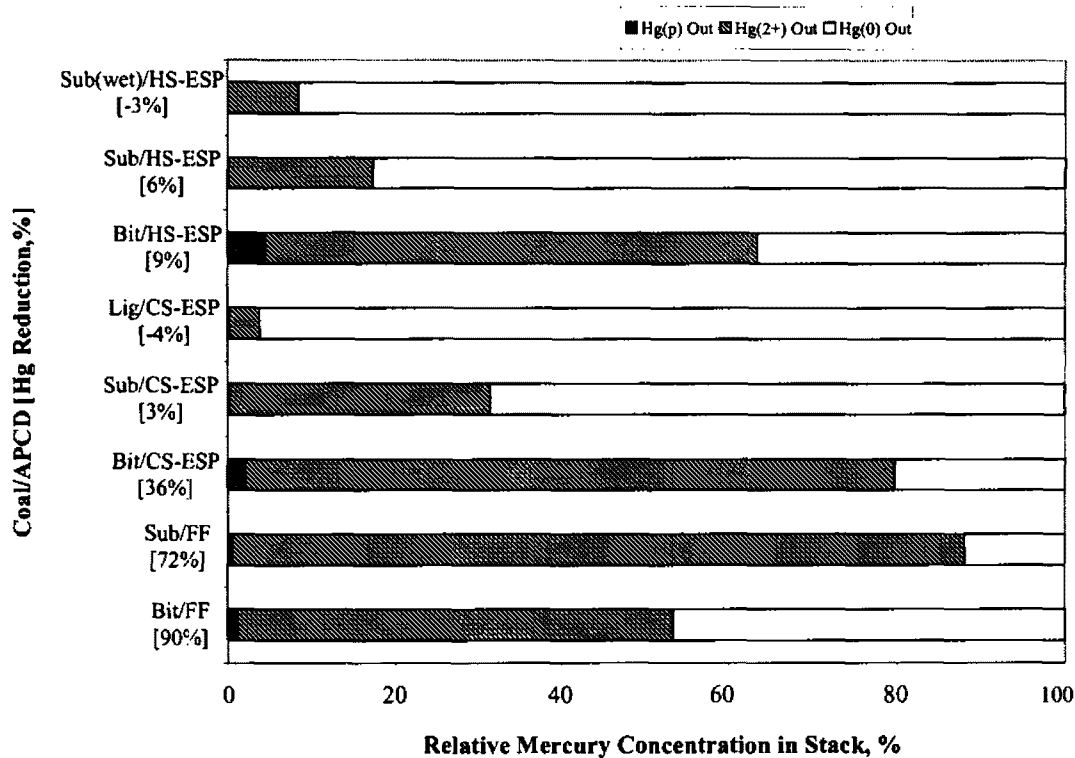
Figure 6-13. Relative mercury speciation for PC-fired boilers with ESPs and FFs.

6.6.3.5 Other PM Controls

Other PM control methods that were tested included two units firing TX lignite and equipped with a CS-ESP followed by a pulse-jet FF baghouse, and one PC-fired unit burning subbituminous coal and equipped with a PM scrubber (see Table 6-14). The three-run average Hg_T reduction across the PM scrubber on this latter unit was 9 percent.

At the Bigbrown and Monticello units, the inlet and outlet Hg measurements were made across the baghouse. There is little consistency between three runs for the Monticello unit, and the data may not be valid. Bigbrown exhibited negligible Hg_T capture across the FF. While some Hg_p and Hg^{2+} may have been captured in the upstream ESP, the low amounts of fly ash captured in the downstream FF probably account for the lack of Hg_T capture in the baghouse.

Table 6-14
Post-combustion Controls: Miscellaneous PM Controls

TX Lignite, PC Boiler with CS-ESP and FF (COHPAC)												
Bigbrown	1	2.59	8.35	31.24	42.18	50.86	0.01	16.58	25.20	41.80	0.92	17.82
Bigbrown	2	0.54	10.37	27.31	38.21	49.95	0.01	17.66	25.47	43.13	-12.88	13.65
Bigbrown	3	0.14	14.14	21.93	36.21	46.92	0.01	18.49	22.12	40.62	-12.20	13.42
Average												
Monticello 1-2	1	15.97	22.54	8.82	47.34	53.79	0.17	32.01	1.58	33.76	28.69	37.23
Monticello 1-2	2	0.37	14.82	46.29	61.48	54.09	0.11	78.08	14.93	93.11	-51.46	-72.13
Monticello 1-2	3	7.97	22.74	44.19	74.90	84.65	0.08	86.89	18.51	105.48	-40.84	-24.61
Average												
Minimum		0.14	8.35	8.82	36.21	46.92	0.01	16.58	1.58	33.76	-51.46	-72.13
Maximum		15.97	22.74	46.29	74.90	84.65	0.17	86.89	25.47	105.48	28.69	37.23
STDEV		6.31	6.03	14.07	15.16	13.94	0.07	32.27	8.99	31.13	26.49	39.61
Subbituminous Coal, PC Boiler with PM Scrubber												
Boswell 3	1	0.01	0.25	6.06	6.32	5.00	0.00	0.05	5.82	5.87	7.16	-17.51
Boswell 3	2	0.01	0.31	6.00	6.32	6.38	0.00	0.06	5.39	5.45	13.81	14.54
Boswell 3	3	0.06	0.62	5.21	5.89	5.79	0.00	0.06	5.51	5.58	5.25	3.60
Average												

6.6.4 Hg Capture in Units with Dry FGD Scrubbers

Thirteen units with dry scrubbing systems were tested. One unit uses dry sorbent injection in combination with a CS-ESP, three units use SDA/ESP systems, and the remaining nine units are equipped with SDA/FF systems. Two of the units equipped with SDA/FFs were also equipped with a SCR system. Hg emission test results for the dry scrubber units are summarized in Table 6-15.

At the Port Washington unit, sorbent is injected downstream of the air preheater. OH inlet measurements were made upstream of the preheater, and outlet measurements were made in the duct downstream of the CS-ESP. The average capture of Hg_T for the Port Washington dry sorbent injection unit was 45 percent. The SPF^{2+} and SPF^0 values for this unit fell within the range of values exhibited by PC-fired boilers that are equipped with a CS-ESP and burn bituminous coal. The three pulverized subbituminous-coal-fired units equipped with a SDA/ESP system exhibited average Hg_T captures of 25 percent (GRDA), 40 percent (Laramie 3), and 41 percent (Wyodak).

As mentioned above, nine units equipped with a SD/FF system were tested. One unit firing bituminous coal had a Hg_T capture of 98 percent. The two units firing bituminous coal and also equipped with an SCR system had a class average Hg_T capture of 99 percent. Three SDA/FF units fired with subbituminous coal had Hg_T captures of 36, 32, and 5 percent.

Table 6-15
Post-combustion Controls: Dry FGD Scrubbers

Plant ID	Run No.										
Bituminous Coal, PC Boiler with DSI and CS-ESP											
Washington	1	0.00	4.33	11.63	15.97	13.01	0.00	6.41	3.06	9.47	40.68	27.22
Washington	2	0.00	7.75	11.02	18.77	13.36	0.00	5.84	3.05	8.90	52.61	33.42
Washington	3	0.00	6.40	9.95	16.36	13.33	0.04	6.52	3.04	9.59	41.37	28.06
Average												
Subbituminous Coal, PC Boiler with CS-ESP/SDA												
GRDA	1	0.13	4.42	7.77	12.31	11.22	0.01	1.55	5.58	7.13	42.06	36.42
GRDA	2	0.53	2.97	6.50	9.99	10.73	0.01	1.28	11.12	12.42	-24.23	-15.70
GRDA	3	0.51	8.78	3.71	13.01	12.24	0.01	0.34	5.41	5.76	55.72	52.94
Average												
Laramie 3	1	0.03	0.22	0.63	0.88	15.03	0.03	0.10	3.87	4.00	0.00	73.40
Laramie 3	2	1.69	0.52	8.53	10.75	17.67	0.03	0.04	4.52	4.58	57.35	74.05
Laramie 3	3	4.55	0.44	9.28	14.27	14.94	0.03	0.04	5.27	5.35	62.53	64.22
Average												
Wyodak	1	2.49	3.88	11.63	18.00	4.46	0.05	0.07	9.97	10.09	43.95	-126.38
Wyodak	2	3.05	4.71	9.42	17.17	6.41	0.05	0.17	10.11	10.32	39.87	-61.16
Wyodak	3	2.25	3.57	11.51	17.34	8.17	0.05	0.25	10.11	10.41	39.99	-27.41
Average												
Average												
Minimum		0.03	0.22	0.63	0.88	4.46	0.01	0.04	3.87	4.00	-24.23	-126.38
Maximum		4.55	8.78	11.63	18.00	17.67	0.05	1.55	11.12	12.42	62.53	74.05
STDEV		1.54	2.72	3.60	5.28	4.32	0.02	0.57	2.91	3.06	28.72	70.07
Bituminous Coal, PC Boiler with SDA/FF												
Mecklenburg	1	11.34	3.40	6.16	20.91	11.52	0.00	0.07	0.09	0.16	99.23	98.60
Mecklenburg	2	5.66	4.21	0.02	9.89	13.28	0.00	0.07	0.23	0.31	96.91	97.70
Mecklenburg	3	6.90	3.04	0.02	9.96	11.50	0.00	0.01	0.23	0.24	97.60	97.92
Average												
Bituminous Coal, PC Boiler with SCR and SDA/FF												
Logan	1	12.87	7.22	0.21	20.31	18.28	0.02	0.08	0.16	0.26	98.71	98.57
Logan	2	12.74	4.36	0.35	17.46	18.14	0.02	0.13	0.17	0.32	98.16	98.23
Logan	3	12.45	4.59	0.25	17.29	17.51	0.01	0.04	0.17	0.22	98.72	98.74
Average												
SEI	1	13.48	0.30	0.14	13.92	11.79	0.01	0.34	0.13	0.48	96.56	95.94
SEI	2	9.47	0.25	0.18	9.90	11.74	0.01	0.09	0.12	0.22	97.79	98.13
SEI	3	12.01	0.25	0.16	12.42	11.97	0.02	0.08	0.11	0.21	98.34	98.28
Average												
Average												
Minimum		9.47	0.25	0.14	9.90	11.74	0.01	0.04	0.11	0.21	96.56	95.94
Maximum		13.48	7.22	0.35	20.31	18.28	0.02	0.34	0.17	0.48	98.72	98.74
STDEV		.41	2.98	0.08	3.82	3.38	0.00	0.11	0.03	0.10	0.81	1.03

(continued)

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Table 6-15 (cont'd)
Post-combustion Controls: Dry FGD Scrubbers

Subbituminous Coal, PC Boiler with SDA/FF												
Craig 3	1	0.57	0.65	0.20	1.42	1.20	0.00	0.04	0.90	0.94	33.79	21.49
Craig 3	2	0.92	0.50	0.17	1.60	1.06	0.00	0.04	0.89	0.93	41.83	11.88
Craig 3	3	0.90	0.23	0.12	1.25	0.93	0.00	0.03	0.82	0.86	31.67	7.38
Average												
Rawhide	1	0.25	1.38	12.46	14.09	8.09	0.12	0.76	10.80	11.68	17.16	-44.36
Rawhide	2	1.92	0.83	12.85	15.59	7.33	0.01	0.69	9.91	10.60	32.03	-44.61
Rawhide	3	3.76	0.46	14.79	19.01	9.24	0.03	0.98	9.00	10.01	47.31	-8.41
Average												
NSP Sherburne	1	0.03	0.53	10.92	11.48	8.29	0.12	0.20	8.42	8.74	23.81	-5.43
NSP Sherburne	2	0.03	0.23	10.92	11.18	8.27	0.14	0.18	12.09	12.40	-10.94	-49.92
NSP Sherburne	3	0.03	0.19	10.24	10.46	7.73	0.27	0.24	9.84	10.35	1.05	-34.01
Average												
Minimum		0.03	0.19	0.12	1.25	0.93	0.00	0.03	0.82	0.86	-10.94	-49.92
Maximum		3.76	1.38	14.79	19.01	9.24	0.27	0.98	12.09	12.40	47.31	21.49
STDEV		1.23	0.37	6.08	6.63	3.59	0.09	0.36	4.68	4.97	18.96	27.38
ND Lignite, PC Boiler with SDA/FF												
Antelope Valley	1	0.16	0.38	7.80	8.34	13.85	0.01	0.25	omit	NA	NA	NA
Antelope Valley	2	0.21	0.42	7.82	8.45	16.03	0.02	0.79	8.16	8.98	-6.27	44.01
Antelope Valley	3	0.16	0.16	7.67	8.00	12.50	0.02	0.33	6.97	7.32	8.49	41.45
Average												
Stanton 10	1	0.22	0.24	10.23	10.70	12.82	0.02	0.40	10.14	10.56	1.24	17.63
Stanton 10	2	0.27	0.36	9.86	10.49	15.63	0.01	0.17	10.58	10.76	-2.54	31.15
Stanton 10	3	0.50	0.69	9.45	10.64	9.45	0.01	0.01	10.81	10.83	-1.77	-14.61
Average												
Minimum		0.16	0.16	7.67	8.00	9.45	0.01	0.01	6.97	7.32	-6.27	-14.61
Maximum		0.50	0.69	10.23	10.70	16.03	0.02	0.79	10.81	10.83	8.49	44.01
STDEV		0.13	0.20	1.18	1.32	2.67	0.01	0.29	1.69	1.53	5.53	23.91
Bituminous, Stoker with SDA/FF												
Dwayne Collier	1	2.19	0.03	0.06	2.28	3.37	0.06	0.02	0.08	0.16	92.84	95.16
Dwayne Collier	2	2.14	0.18	0.42	2.75	3.48	0.03	0.03	0.09	0.15	94.48	95.64
Dwayne Collier	3	1.99	0.03	0.11	2.13	3.29	0.01	0.03	0.06	0.10	95.43	97.04
Average												

The average Hg_T captures in two units firing lignite were 1 and -1 percent. A single stoker-fired boiler burning bituminous coal had a total average Hg capture of 94 percent.

The reduction in emissions for each SDA test class is shown in Figure 6-14. The stack concentrations of Hg_p, Hg^{2+}, Hg^0, and Hg_T are shown in Figure 6-15 along with the average total Hg_T capture for each SDA class. The relative Hg speciation for the same coal-fired boiler classes is shown in Figure 6-16. The predominance of Hg^0 in the stack emissions from units fired with subbituminous coal and lignite is attributed to low levels of Hg^0 oxidization and the relative ease of Hg^{2+} capture.
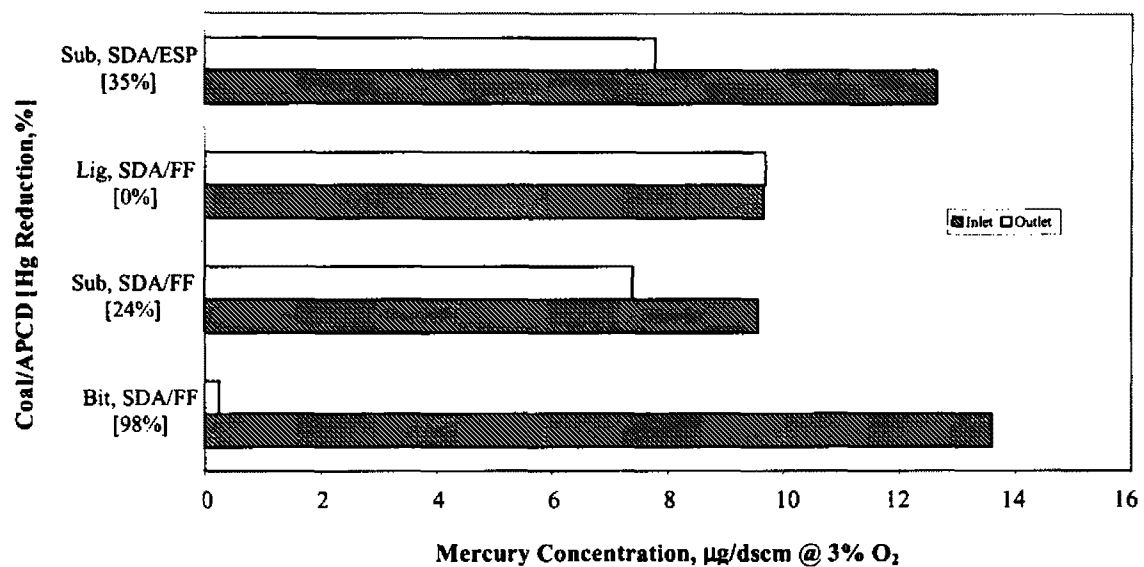
Figure 6-14. Mercury control for dry FGD scrubbers.
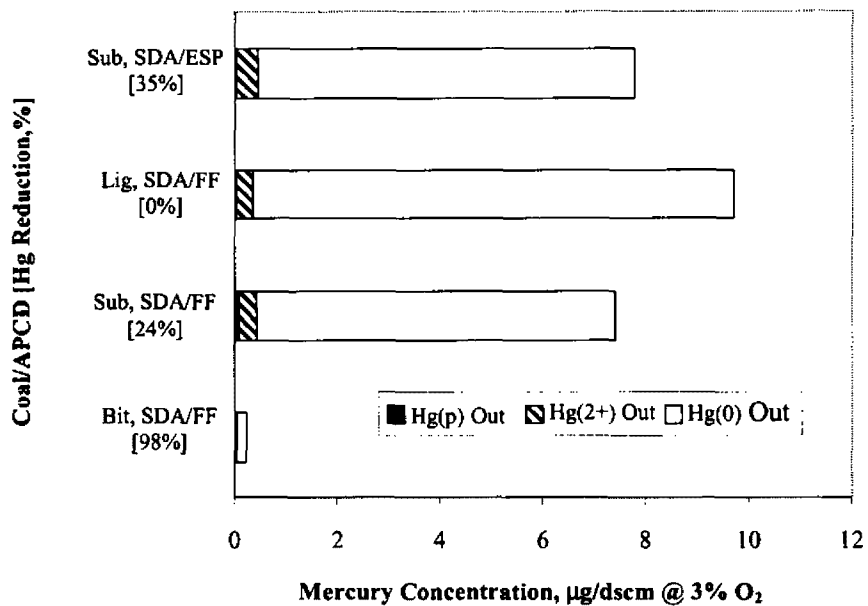
Figure 6-15. Mercury speciation for PC boilers with SDA.
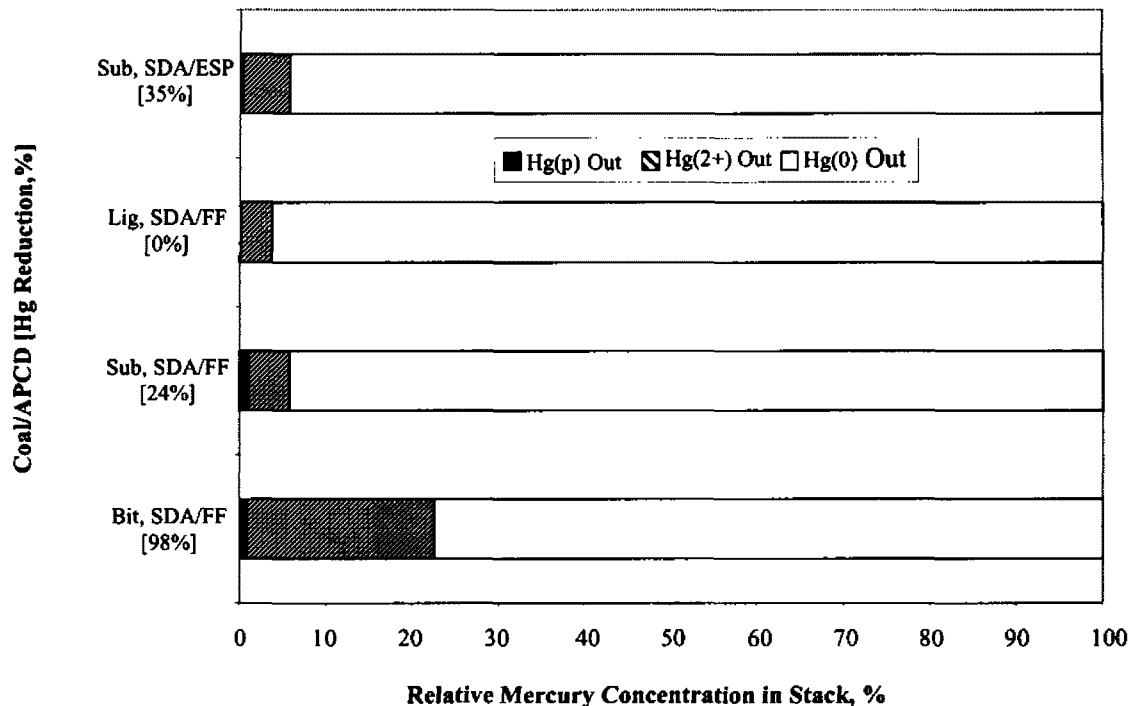
Figure 6-16. Relative mercury speciation for PC boilers with SDA.

6.6.5 Hg Capture in Units with Wet FGD Scrubbers

The wet FGD scrubber systems that were tested consisted of units equipped with four PM control device configurations. These different configurations are expected to have different effects on the speciation and capture of Hg. These different configurations included units equipped with a PS, a CS-ESP, an HS-ESP, or a FF baghouse. Inlet and outlet measurements on the PS + wet FGD units were made across both control devices. Inlet measurements on the systems with an ESP or FF were made between the PM control device and the FGD scrubber. Outlet measurements were made in the stack.

A total of 23 units with wet FGD systems were tested. Seven units used PM scrubber systems to control particulate emissions, eight used CS-ESPs, six used HS-ESPs, and two used FF baghouses. Twenty-one of the test units burned pulverized coal. The other two test units burned bituminous coal in cyclone-fired boilers. One unit was equipped with a PM scrubber, and the other had a CS-ESP. The number of PC-fired test units in each coal-control class is shown in Table 6-16. (Also see Tables 6-4 and 6-6.)

Table 6-16
PC-fired Boiler PM Controls for Wet FGD Systems

PM Control	Number of Test Units			Totals
	Bit.	Subbit.	Lignite	
PS	1	4	1	6
CS-ESP	2	3	2	7
HS-ESP	2	4	0	6
FF	2	0	0	2
				21

The results of emission tests on wet FGD systems are summarized in Table 6-17. The next to last column in Table 6-17 shows the percent reduction in Hg_T across the wet FGD scrubber as determined by the OH sampling train measurements. The last column is an estimate of the reduction in Hg_T across the PM control device and wet FGD scrubber. These estimates were made using the class PM average coal-boiler-control EMF that is applicable to each test unit (see Section 6.5.2).

Class average emission test results for the PC-fired boilers with wet FGD units are shown in Figures 6-17, 6-18, and 6-19. Each of these figures is based on capture estimates across the PM control device and wet FGD scrubber combinations. Figure 6-17 shows the class average stack concentrations of Hg_p, Hg^{2+}, and Hg^0. Figure 6-18 shows the average inlet and outlet concentrations of Hg_T and percent reduction for each class. Figure 6-19 shows the relative mercury speciation for PC-boilers with wet FGD scrubbers.

Table 6-17
Post-combustion Controls: Wet FGD Scrubbers

Plant ID	Run No.										
Bituminous Coal, PC Boiler with PS and Wet FGD Scrubber											
Bruce Mansfield	1	0.27	8.65	1.58	10.50	10.93	0.04	1.89	7.01	8.95	14.81	18.11
Bruce Mansfield	2	0.73	9.84	2.08	12.65	8.93	0.06	2.73	7.96	10.76	14.94	-20.57
Bruce Mansfield	3	0.27	8.34	1.70	10.31	11.82	0.04	1.22	8.29	9.55	7.42	19.25
Average		0.42	8.95	1.79	11.15	10.56	0.05	1.95	7.75	9.75	12.39	5.60
Subbituminous Coal, PC Boiler with PS and Wet FGD Scrubber											
Boswell 4	1	0.11	0.33	5.05	5.48	6.98	0.02	0.10	5.53	5.65	-3.08	19.00
Boswell 4	2	2.98	1.07	1.47	5.53	6.63	0.20	0.44	5.89	6.53	-18.25	1.41
Boswell 4	3	2.75	0.55	1.16	4.45	7.93	0.28	0.59	5.57	6.43	-44.40	18.91
Average		1.96	0.65	2.56	5.15	7.18	0.17	0.38	5.66	6.21	-21.91	13.11
Cholla 2	1	0.42	0.97	4.68	6.07	6.99	0.15	0.21	3.93	4.29	29.30	38.59
Cholla 2	2	1.11	0.93	2.62	4.66	6.37	0.19	0.14	4.67	5.01	-7.51	21.38
Cholla 2	3	0.41	2.06	2.99	5.46	5.09	0.11	0.14	4.22	4.46	18.29	12.27
Average		0.65	1.32	3.43	5.40	6.15	0.15	0.16	4.27	4.59	13.36	24.08
Colstrip	1	1.78	2.29	1.08	5.15	7.63	0.05	0.42	9.13	9.60	-86.54	-25.89
Colstrip	2	1.94	2.37	6.37	10.68	7.98	0.02	0.45	11.03	11.51	-7.74	-44.19
Colstrip	3	1.63	2.86	5.39	9.88	7.93	0.02	0.39	2.13	2.54	74.27	67.94
Average		1.78	2.51	4.28	8.57	7.85	0.03	0.42	7.43	7.88	-6.67	-0.71
Lawrence	1	0.23	1.65	4.99	6.86	6.24	0.01	0.49	6.37	6.87	-0.07	-10.01
Lawrence	2	0.53	0.63	4.41	5.58	5.47	0.08	0.53	6.71	7.32	-31.14	-33.75
Lawrence	3	0.24	0.65	4.96	5.86	6.03	0.09	0.51	6.20	6.81	-16.21	-12.96
Average		0.33	0.98	4.79	6.10	5.91	0.06	0.51	6.43	7.00	-15.81	-18.91
Average		1.18	1.36	3.76	6.30	6.77	0.10	0.37	5.95	6.41	-7.76	4.50
Minimum		0.11	0.33	1.08	4.45	5.09	0.01	0.10	2.13	2.54	-86.54	-44.19
Maximum		2.98	2.86	6.37	10.68	7.98	0.28	0.59	11.03	11.51	74.27	67.94
STDEV		1.02	0.85	1.82	1.96	0.98	0.09	0.17	2.34	2.40	39.47	31.96
ND Lignite, PC Boiler with PS and Wet FGD Scrubber											
Lewis and Clark	1	1.15	16.47	11.65	29.27	15.33	0.06	0.50	13.86	14.42	50.75	5.98
Lewis and Clark	2	1.68	13.64	8.43	23.75	15.54	0.00	0.35	14.19	14.55	38.74	6.41
Lewis and Clark	3	1.41	6.28	10.20	17.89	18.96	0.00	0.50	15.81	16.31	8.81	13.94
Average		1.41	12.13	10.09	23.64	16.61	0.02	0.45	14.62	15.09	32.77	8.78

CONTINUED

Table 6-17 (cont'd)
Post-combustion Controls: Wet FGD Scrubbers

Plant ID	Run No.	Hg-p in, lb/10^12	Hg-2 in, lb/10^12	Hg-0 in, lb/10^12	Hg-t in, lb/10^12	Hg in coal	Hg-p out, lb/10^12	Hg-2 out, lb/10^12	Hg-0 out, lb/10^12	Hg-t out, lb/10^12	Wet FGD %	PM+FGD %

Bituminous Coal, PC Boiler with CS-ESP and Wet FGD Scrubber

Plant ID	No.											
AES Cayuga	2	0.00	6.40	2.58	8.98	11.87	0.00	0.18	2.70	2.88	67.91	76.06
AES Cayuga	1	0.00	5.87	2.24	8.11	10.70	0.00	0.36	2.73	3.09	61.88	71.56
AES Cayuga	3	0.00	5.55	2.95	8.50	10.80	0.00	0.18	3.08	3.26	61.63	71.38
Average		**0.00**	**5.94**	**2.59**	**8.53**	**11.12**	**0.00**	**0.24**	**2.83**	**3.08**	**63.81**	**73.00**
Big Bend	1	0.09	4.86	2.40	7.34	17.52	0.05	0.21	2.18	2.44	66.70	75.16
Big Bend	2	0.05	4.92	2.31	7.29	11.25	0.00	0.12	1.75	1.87	74.37	80.88
Big Bend	3	0.02	4.26	2.13	6.41	12.01	0.03	0.23	2.05	2.31	64.01	73.15
Average		**0.05**	**4.68**	**2.28**	**7.01**	**13.59**	**0.03**	**0.19**	**1.99**	**2.21**	**68.36**	**76.39**
Average		**0.03**	**5.31**	**2.43**	**7.77**	**12.36**	**0.01**	**0.22**	**2.41**	**2.64**	**66.08**	**74.70**
Minimum		0.00	4.26	2.13	6.41	10.70	0.00	0.12	1.75	1.87	61.63	71.38
Maximum		0.09	6.40	2.95	8.98	17.52	0.05	0.36	3.08	3.26	74.37	80.88
STDEV		0.03	0.78	0.30	0.94	2.59	0.02	0.08	0.50	0.53	4.78	3.56

Subbituminous Coal, PC Boiler with CS-ESP and Wet FGD Scrubber

Plant ID	No.											
Jim Bridger	1	0.05	2.49	5.21	7.74	no coal flow	0.06	0.25	6.63	6.95	10.32	14.60
Jim Bridger	2	0.44	2.04	5.64	8.12	no coal flow	0.05	0.29	6.51	6.85	15.64	19.67
Jim Bridger	3	0.07	1.78	4.50	6.35	no coal flow	0.03	0.20	5.92	6.15	3.06	7.69
Average		**0.19**	**2.10**	**5.12**	**7.41**	**not include**	**0.05**	**0.25**	**6.34**	**6.65**	**9.68**	**13.99**
Laramie River 1	1	0.25	3.14	7.52	10.91	13.52	0.02	0.29	4.86	5.18	52.57	54.83
Laramie River 1	2	0.04	2.16	8.35	10.55	15.45	0.00	0.12	5.73	5.85	44.54	47.18
Laramie River 1	3	0.02	3.08	7.53	10.63	15.71	0.01	0.03	4.48	4.52	57.53	59.56
Average		**0.10**	**2.79**	**7.80**	**10.70**	**14.90**	**0.01**	**0.15**	**5.02**	**5.18**	**51.55**	**53.86**
Sam Seymour	1	0.03	3.00	9.10	12.13	60.48	0.06	0.24	12.25	12.54	1.51	1.51
Sam Seymour	2	0.01	4.08	13.10	17.19	43.20	0.11	0.29	13.33	13.74	23.90	23.90
Sam Seymour	3	0.01	5.39	11.96	17.35	51.04	0.06	0.35	11.99	12.39	31.99	31.99
Average		**0.01**	**4.16**	**11.39**	**15.56**	**51.58**	**0.07**	**0.29**	**12.53**	**12.89**	**19.13**	**19.13**
Average		**0.10**	**3.02**	**8.10**	**11.22**	**33.24**	**0.04**	**0.23**	**7.97**	**8.24**	**26.78**	**28.99**
Minimum		0.01	1.78	4.50	6.35	13.52	0.00	0.03	4.48	4.52	1.51	1.51
Maximum		0.44	5.39	13.10	17.35	60.48	0.11	0.35	13.33	13.74	57.53	59.56
STDEV		0.15	1.13	2.94	3.88	20.84	0.03	0.10	3.50	3.59	21.09	20.83

*Note the column title changes from coal to Wet FGD and PM+FGD   CONTINUED

(Intentionally Blank)

Table 6-17 (cont'd)
Post-combustion Controls: Wet FGD Scrubbers

| Plant ID	Run No.											
TX Lignite, PC Boiler with CS-ESP and wet FGD Scrubber												
Monticello 3	1	0.19	16.49	29.39	46.07	61.96	0.31	6.50	29.45	36.25	21.31	21.31
Monticello 3	2	0.11	19.77	28.15	48.03	63.13	0.18	0.44	25.52	26.14	45.57	45.57
Monticello 3	3	0.13	25.83	27.21	53.16	76.52	0.24	7.26	23.10	30.60	42.44	42.44
Average												
Limestone	1	0.01	23.55	13.38	36.94	14.49	0.04	2.69	15.96	18.69	49.40	49.40
Limestone	2	0.01	24.55	13.11	37.68	20.84	0.33	3.18	16.23	19.74	47.59	47.59
Limestone	3	0.02	28.15	14.11	42.29	15.29	0.12	1.27	17.18	18.58	56.07	56.07
Average												
Average												
Minimum		0.01	16.49	13.11	36.94	14.49	0.04	0.44	15.96	18.58	21.31	21.31
Maximum		0.19	28.15	29.39	53.16	76.52	0.33	7.26	29.45	36.25	56.07	56.07
STDEV		0.07	4.24	8.09	6.28	28.12	0.11	2.76	5.63	7.32	11.89	11.89
Bituminous Coal, PC Boiler with HS-ESP and wet FGD Scrubber												
Charles Lowman	1	2.64	3.33	2.09	8.06	23.49	0.06	1.68	3.39	5.13	36.44	44.29
Charles Lowman	2	1.55	3.98	2.17	7.69	21.50	0.07	1.86	3.50	5.44	29.31	38.03
Charles Lowman	3	3.45	3.55	2.02	9.01	23.94	0.05	2.06	3.19	5.30	41.18	48.44
Average												
Morrow	1	0.05	10.80	4.41	15.27	5.48	0.05	2.06	5.00	7.11	53.46	59.20
Morrow	2	0.01	8.31	4.10	12.42	5.42	0.03	1.79	4.50	6.31	49.18	55.45
Morrow	3	0.03	6.98	3.32	10.33	5.38	0.04	1.12	4.55	5.71	44.70	51.52
Average												
Average												
Minimum		0.01	3.33	2.02	7.69	5.38	0.03	1.12	3.19	5.13	29.31	38.03
Maximum		3.45	10.80	4.41	15.27	23.94	0.07	2.06	5.00	7.11	53.46	59.20
STDEV		1.50	3.05	1.08	2.91	9.65	0.02	0.35	0.75	0.75	8.74	7.66
Subbituminous Coal, PC Boiler with HS-ESP and wet FGD Scrubber												
Coronado	1	0.03	0.99	2.19	3.20	4.45	0.02	0.04	3.56	3.61	-12.95	-0.87
Coronado	2	0.03	0.82	1.86	2.71	4.76	0.08	0.07	1.83	1.98	26.82	34.64
Coronado	3	0.03	1.09	1.87	2.99	3.86	0.11	0.13	3.08	3.32	-11.30	0.60
Average												
Craig 1	1	0.04	0.33	3.61	3.97	2.45	0.00	0.13	2.13	2.26	43.05	49.14
Craig 1	2	0.04	0.29	2.52	2.85	2.79	0.00	0.11	2.09	2.20	22.93	31.17
Craig 1	3	0.04	0.16	1.99	2.19	2.30	0.01	0.09	2.03	2.14	2.44	12.87
Average												
Navajo	1	0.03	2.91	3.55	6.49	4.37	0.05	0.04	3.67	3.76	42.00	48.20
Navajo	2	0.03	0.45	3.93	4.41	2.63	0.02	0.04	3.79	3.85	12.65	21.99
Navajo	3	0.03	0.62	3.50	4.16	2.63	0.01	0.04	3.77	3.82	8.25	18.06
Average												
San Juan	1	0.02	6.25	5.81	12.08	7.94	0.05	0.45	7.14	7.64	36.74	43.50
San Juan	2	0.08	3.31	4.26	7.65	8.69	0.08	0.38	4.79	5.25	31.35	38.69
San Juan	3	0.02	5.07	3.62	8.70	11.00	0.05	0.31	4.66	5.02	42.31	48.48
Average												
Average												
Minimum		0.02	0.16	1.86	2.19	2.30	0.00	0.04	1.83	1.98	-12.95	-0.87
Maximum		0.08	6.25	5.81	12.08	11.00	0.11	0.45	7.14	7.64	43.05	49.14
STDEV		0.02	2.05	1.19	3.02	2.86	0.04	0.14	1.52	1.64	20.32	18.15
Bituminous Coal, PC Boiler with FF and wet FGD scrubber												
Clover	1	0.06	1.00	1.11	2.17	29.21	0.05	0.42	0.42	0.88	59.42	96.78
Clover	2	0.03	1.11	1.99	3.13	41.19	0.02	0.34	0.17	0.53	83.13	98.66
Clover	3	0.08	1.16	0.62	1.86	49.02	0.06	0.05	0.14	0.25	86.76	98.95
Average												
Intermountain	1	0.01	1.01	0.20	1.22	2.00	0.01	0.03	0.25	0.29	76.15	98.11
Intermountain	2	0.01	1.08	0.24	1.33	1.97	0.01	0.07	0.46	0.54	59.67	96.80
Intermountain	3	0.01	1.36	0.22	1.58	3.09	0.01	0.08	0.41	0.50	68.68	97.52
Average												
Average												
Minimum		0.01	1.00	0.20	1.22	1.97	0.01	0.03	0.14	0.25	59.42	96.78
Maximum		0.08	1.36	1.99	3.13	49.02	0.06	0.42	0.46	0.88	86.76	98.95
STDEV		0.03	0.13	0.71	0.70	21.47	0.02	0.17	0.14	0.23	11.66	0.92
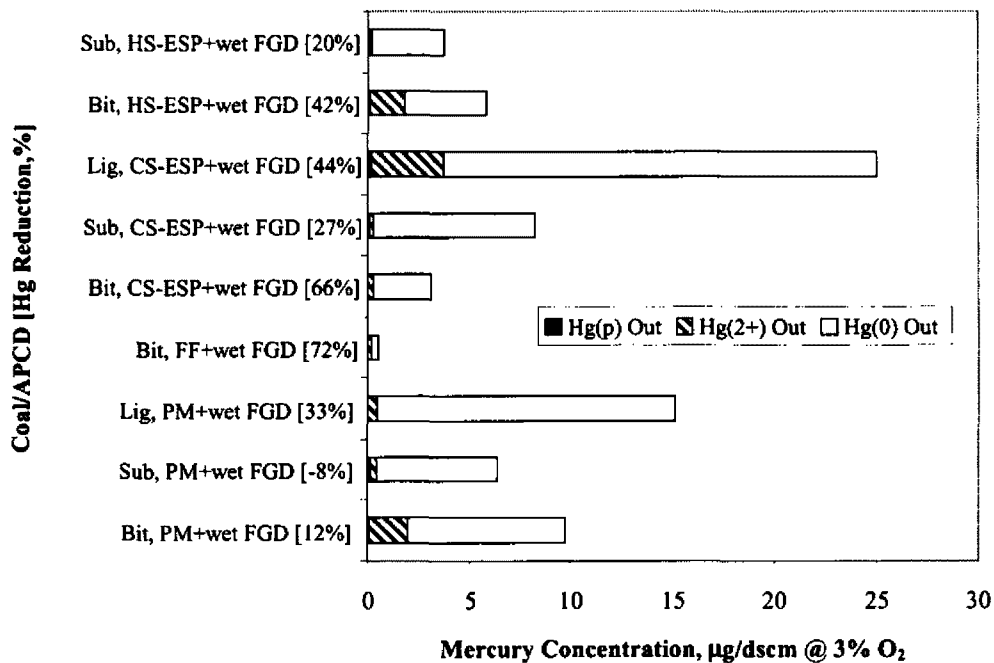
Figure 6-17. Mercury speciation for PC boilers with wet FGD.
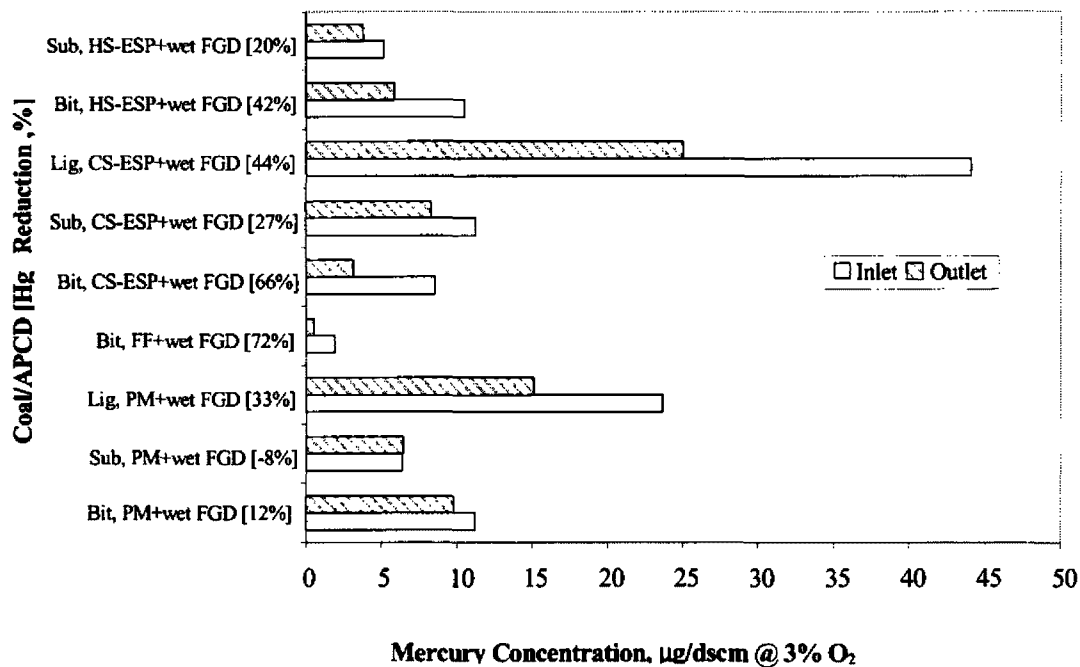
Figure 6-18. Mercury emissions for PC boilers with wet FGD.

6-45
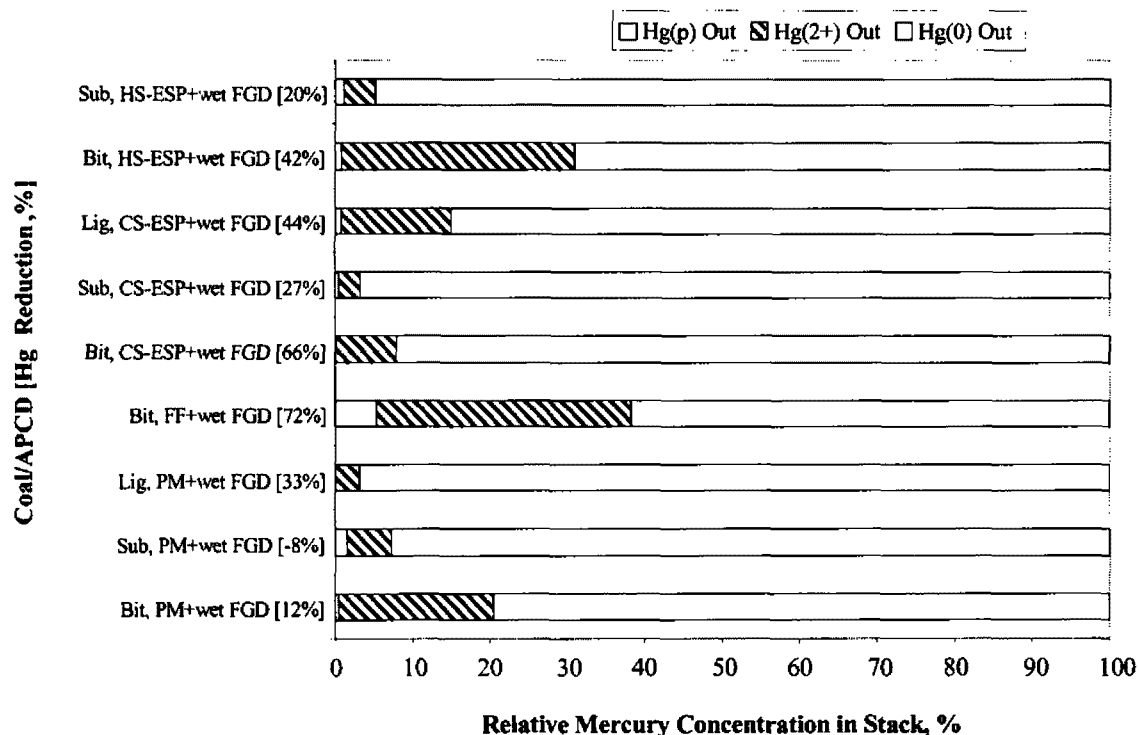
Figure 6-19. Relative mercury speciation for PC boilers with wet FGD.

The best levels of Hg_T capture are exhibited by units burning bituminous coal and equipped with a FF (98 percent), CS-ESP (75 percent), or HS-ESP (50 percent). The higher capture levels for bituminous-fired boilers equipped with the CS-ESP, HS-ESP, or FF control devices are consistent with the high levels of Hg^0 oxidization associated with these coal-boiler control classes (see Figures 6-12 and 6-13). The very high levels of Hg capture exhibited by the bituminous-coal-fired boiler units with a FF and wet FGD system can be attributed to high levels of Hg^0 oxidization and to the capture or conversion of Hg_p and Hg^{2+} as flue gas passes through the FF cake. Estimates of Hg_T capture across the wet FGD and PM + wet FGD combinations are shown in Table 6-18 for units burning bituminous coal. Detailed data for these units are given in Table 6-17. The best control is exhibited by wet FGD systems equipped with a FF followed by units equipped with a CS-ESP and a HS-ESP.

The Hg_T capture in one test unit burning bituminous coal and equipped with a PM scrubber + wet FGD system averaged 12 percent. Hg at the outlet of the scrubber was predominantly Hg^0.

Table 6-18
Wet FGD Scrubbers Burning Bituminous Coal

Controls and Test Unit	Reduction in Hg_T, %	
FF + Wet FGD	FGD	PM + FGD
Clover	76	98
Intermountain	68	97
Average	72	98
CS-ESP + Wet FGD		
Big Bend	68	76
AES Cayuga	64	73
Average	66	75
HS-ESP + Wet FGD		
Charles R. Lowman	36	44
Morrow	49	55
Average	43	50

The estimated capture of Hg_T in wet FGD units burning subbituminous coals is given in Table 6-19. The four PS units were Boswell 4, Cholla 2, Colstrip, and Lawrence. The inlet and outlet Hg_T data appeared reasonable except for runs 1 and 2 on Colstrip. All tests on Lawrence and Boswell 4 had Hg_T outlet concentrations higher than the corresponding Hg_T inlet concentrations. Cholla 2, which had Hg_T emission reductions ranging from -8 to 29 percent, appeared to exhibit hysterisis effects. One unit, Lewis and Clark, burned a ND lignite. This unit also appeared to exhibit hysterisis effects, with successive Hg_T reductions for the three tests of 51, 39, and 9 percent. The declining reductions in Hg_T capture were mirrored by inlet reductions of Hg_T and Hg^{2+}.

The erratic nature and differences in capture for the CS-ESP units are probably due to differences in the subbituminous coals being burned and the differences in the scrubber operating conditions. Except for the Coronado tests, the test results on HS units were fairly consistent. It is not known whether the sampling and analysis results from the Coronado unit are incorrect or whether differences in the coal and operating conditions caused the lower Hg_T capture results.

Table 6-19
Wet FGD Scrubbers Burning Subbituminous Coal

Controls and Test Unit	Reduction in Hg_T, %	
PS + Wet FGD	FGD	PM + FGD
Boswell 4	NA	-22
Cholla 2	NA	13
Colstrip	NA	-7
Lawrence	NA	-16
Average		-8
HS-ESP + Wet FGD		
Coronado	1	11
Craig 1	23	31
Navajo	21	29
San Juan	37	44
Average	20	29
CS-ESP + Wet FGD		
Jim Bridger	10	14
Laramie 1	52	54
Sam Seymour	19	19
Average	27	29

Two units, burning TX lignite and equipped with a CS-ESP, exhibited average Hg_T captures of 46 percent (see Table 6-20). The SPF^{2+} for limestone was 0.65 and the SPF^{2+} for Monticello 3 was 0.42, indicating moderately high relative concentrations of Hg^{2+} at the scrubber inlets of these two units. TX lignites appear to have a higher oxidization and capture potential than ND lignites.

Table 6-20
Wet FGD Scrubbers Burning TX Lignite

Controls and Test Unit	Reduction in Hg_T, %	
CS-ESP + Wet FGD	FGD	PM + FGD*
Limestone	51	51
Monticello 3	36	36
Average	44	44
*Estimated		

6.6.6 Potential Effects of Post-combustion NO_X Controls

Post-combustion NO_X controls convert NO_X in the boiler flue gases to molecular nitrogen and water using a catalytic process (selective catalytic reduction) or a noncatalytic process (selective noncatalytic reduction). For both processes, a reducing agent (usually ammonia) is injected into the boiler flue gas at a point upstream of any post-combustion PM or SO_2 control device. A limited amount of data is available in the ICR Hg emission database regarding the potential effects of these post-combustion NO_X controls on Hg capture. These data are presented in Table 6-21. Test results for pulverized-coal boilers burning bituminous coal with either SNCR or SCR systems are compared to the results of tests on similarly controlled units that do not use post-combustion NO_X controls.

Table 6-21
Potential Effects of Post-combustion NO_X Control Technologies on Mercury Capture in PC-fired Boilers Burning Bituminous Coal

Post-combustion Controls	Post-combustion NO_X Control	Number of Pulverized-coal-fired Boiler Units Tested	Average Mercury Capture by Control Configuration
CS-ESP	none	6	36%
	SNCR	1	91%
SDA + FF	none	2	98%
	SCR	1	98%

Tests on the single pulverized-coal boiler unit using a CS-ESP with SNCR shows an average Hg capture that is significantly higher than the six units tested with a CS-ESP using no post-combustion NO_X controls (91 percent with SNCR versus 36 percent without SNCR). It was reported that the fly ash from the boiler unit using SNCR contained unusually high levels of carbon. Because data are available only for this one test, it is not known whether

the high levels of Hg capture indicated by the test results are attributable to the high fly ash carbon content, the use of an SNCR system, a combination of both, or some other site-specific factor.

A comparison of tests for pulverized-coal boiler units using an SDA with an FF shows no discernable difference in Hg capture with or without the use of an SCR for post-combustion NO_X control. An average Hg capture of 98 percent was measured by the tests on the one unit equipped with an SCR compared to 98 percent Hg capture for the two similar units without SCR systems. Because of the very high levels of Hg capture by all of the tested control configurations, it is not possible to determine the effect of SCR on Hg capture.

Recent tests on a pilot-scale, pulverized-coal combustor, which was equipped with an SCR and a CS-ESP, showed increased Hg capture when bituminous coals were burned but not when a subbituminous coal was burned. Mercury emission reductions were observed when the SCR system was operated normally with the injection of ammonia upstream of the SCR catalyst. Improvement of Hg capture was also noted when ammonia was injected, but the SCR catalyst was bypassed. These tests provide evidence that SNCR and SCR systems may enhance Hg capture under some conditions.

6.7   COMBUSTION SYSTEM EFFECTS

LNBs and combustion modification techniques are believed to increase the unburned carbon in fly ash and increase the adsorption of Hg onto collectable fly ash. Since neither the fly ash carbon content nor the LOI was measured during the ICR field test, it is not possible to evaluate Hg capture performance benefits that accrue from the use of NO_X control combustion modification techniques. The ICR field test program included tests on six different unit classes using cyclone-fired boilers and six unit classes with FBCs. The results of ICR tests on units with cyclone-fired boilers and FBCs are shown in Tables 6-22 and 6-23, respectively.

Table 6-22
Cyclone-fired Boilers

ND Lignite, Cyclone Boiler with CS-ESP												
Leland Olds	1	0.56	0.23	3.30	4.09	5.63	0.00	0.82	4.04	4.86	-18.68	13.66
Leland Olds	2	0.26	0.46	8.80	9.51	10.18	0.00	1.09	5.26	6.35	33.26	37.64
Leland Olds	3	2.85	0.81	4.77	8.43	7.94	0.00	1.60	LS	NA	NA	NA
Average												
Subbituminous/Pet. Coke, Cyclone Boiler with HS-ESP												
Nelson Dewey	1	0.01	0.49	3.20	3.69	6.62	0.10	0.26	3.33	3.69	0.13	44.27
Nelson Dewey	2	0.01	0.24	2.19	2.43	6.47	0.04	0.16	2.40	2.60	-6.90	59.83
Nelson Dewey	3	0.01	0.12	2.06	2.18	6.09	0.04	0.25	2.44	2.73	-24.95	55.22
Average												
Lignite, Cyclone Boiler with Mechanical Collector												
Bay Front	1	0.76	0.78	2.17	3.70	3.58	1.19	0.60	1.91	3.69	0.34	-2.95
Bay Front	2	1.08	0.67	1.94	3.69	3.01	0.86	2.75	1.80	5.40	-46.54	-79.21
Bay Front	3	0.09	0.77	1.74	2.60	3.36	0.48	3.57	1.78	5.84	-125.00	-73.79
Average												
Lignite, Cyclone Boiler with SDA/FF												
Coyote	1	0.69	1.62	13.68	15.99	10.51	0.08	0.04	13.97	14.10	11.81	-34.23
Coyote	2	1.18	2.98	13.90	18.06	18.55	0.14	0.24	LS	NA	NA	NA
Coyote	3	1.69	3.07	14.91	19.66	11.39	0.08	0.44	18.06	18.58	5.48	-63.12
Average												
Bituminous, Cyclone Boiler with PS and Wet FGD Scrubbers												
Lacygne	1	6.70	3.99	1.30	12.00	no inlet flow	0.04	0.44	8.74	9.22	23.18	no inlet flow
Lacygne	2	6.52	3.34	0.60	10.46	no inlet flow	0.05	0.43	7.41	7.89	24.53	no inlet flow
Lacygne	3	5.98	0.59	0.61	7.18	no inlet flow	0.09	0.41	5.10	5.59	22.17	no inlet flow
Average												
Bituminous, Cyclone Boiler with CS-ESP and wet FGD Scrubber												
Bailly	1	0.04	3.18	2.57	5.79	4.41	0.00	0.36	2.85	3.22	54.24	27.09
Bailly	2	0.04	2.37	2.95	5.36	5.20	0.00	0.31	2.62	2.93	54.95	43.53
Bailly	3	0.09	3.01	2.58	5.68	4.08	0.00	0.39	2.78	3.17	54.11	22.31
Average												

Table 6-23
Fluidized Bed Combustors

Plant ID	Run No.	Hg-in O-H	Hg-in O-H	Hg-in O-H	Hg-in O-H	Hg-in Coal	Hg-out O-H	Hg-out O-H	Hg-out O-H	Hg-out O-H	%R O-H	%R Coal
Lignite, FBC with CS-ESP												
R.M. Heskett	1	4.73	5.39	3.83	13.95	13.54	1.06	1.44	4.57	7.07	49.29	47.76
R.M. Heskett	2	2.93	0.96	2.61	6.50	12.68	0.07	0.41	5.31	5.78	11.09	54.40
R.M. Heskett	3	7.43	0.44	3.08	10.94	11.11	0.05	0.18	4.74	4.98	54.49	55.19
Average		5.03	2.26	3.17	10.46	12.44	0.39	0.69	4.87	5.95	38.29	52.45
Anthracite Waste, FBC with FF												
Kline Township	1	44.54	0.12	0.45	45.11	148.68	0.00	0.06	0.06	0.12	99.74	99.92
Kline Township	2	43.12	0.06	0.40	43.58	212.95	0.00	0.06	0.06	0.12	99.73	99.95
Kline Township	3	44.97	0.06	0.34	45.37	153.77	0.00	0.06	0.06	0.12	99.74	99.92
Average		44.21	0.08	0.40	44.69	171.80	0.00	0.06	0.06	0.12	99.74	99.93
Bituminous Waste, FBC with FF												
Scrubgrass	1	184.04	0.68	0.19	184.91	100.09	0.00	0.07	0.08	0.15	99.92	99.85
Scrubgrass	2	124.11	0.42	0.09	124.62	101.35	0.00	0.05	0.07	0.12	99.91	99.89
Scrubgrass	3	76.68	0.22	0.07	76.97	100.25	0.00	0.04	0.07	0.11	99.85	99.89
Average		128.28	0.44	0.12	128.83	100.56	0.00	0.05	0.07	0.13	99.89	99.88
Bituminous/Pet. Coke, FBC with SNCR and FF												
Stockton Cogen	1	2.71	0.06	0.06	2.83	1.68	0.02	0.04	0.05	0.11	96.09	93.39
Stockton Cogen	2	1.56	0.07	0.06	1.69	1.44	0.03	0.05	0.05	0.13	92.16	90.80
Stockton Cogen	3	2.08	0.06	0.06	2.20	1.66	0.03	0.05	0.05	0.12	94.48	92.67
Average		2.12	0.07	0.06	2.24	1.59	0.03	0.05	0.05	0.12	94.25	92.29
Subbituminous, FBC with SCR and FF												
AES Hawaii	1	0.26	0.04	1.29	1.59	3.77	0.00	0.02	0.68	0.70	55.84	81.39
AES Hawaii	2	0.35	0.17	1.38	1.90	3.72	0.00	0.02	0.90	0.92	51.35	75.16
AES Hawaii	3	0.36	0.11	1.18	1.64	2.51	0.00	0.02	0.55	0.58	64.91	77.06
Average		0.32	0.10	1.28	1.71	3.33	0.00	0.02	0.71	0.73	57.37	77.87
Lignite, FBC with CS-FF												
TNP	1	21.65	8.68	7.42	37.74	63.81	0.04	12.13	4.74	16.91	55.20	73.50
TNP	2	10.65	4.51	6.09	21.25	44.22	0.03	6.78	2.94	9.76	54.07	77.93
TNP	3	28.12	13.78	7.04	48.94	95.04	0.04	13.54	5.07	18.66	61.88	80.37
Average		20.14	8.99	6.85	35.98	67.69	0.04	10.82	4.25	15.11	57.05	77.27

6.7.1 Cyclone-fired Boilers

Mercury capture and stack gas speciation for cyclone-fired boilers are shown in Figures 6-20 and 6-21. The percentage of total Hg capture in these units appears to be similar to the Hg captured in pulverized-coal-fired units burning similar fuels and equipped with comparable air pollution control devices (see Table 6-24). Except for the unit equipped with a mechanized collector, the Hg in flue gas consisted primarily of Hg^0.
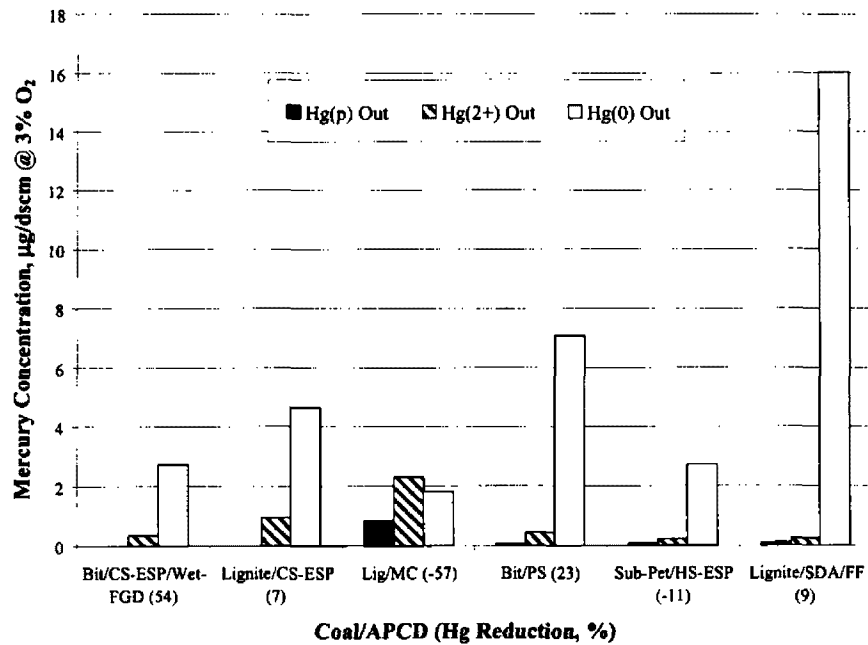
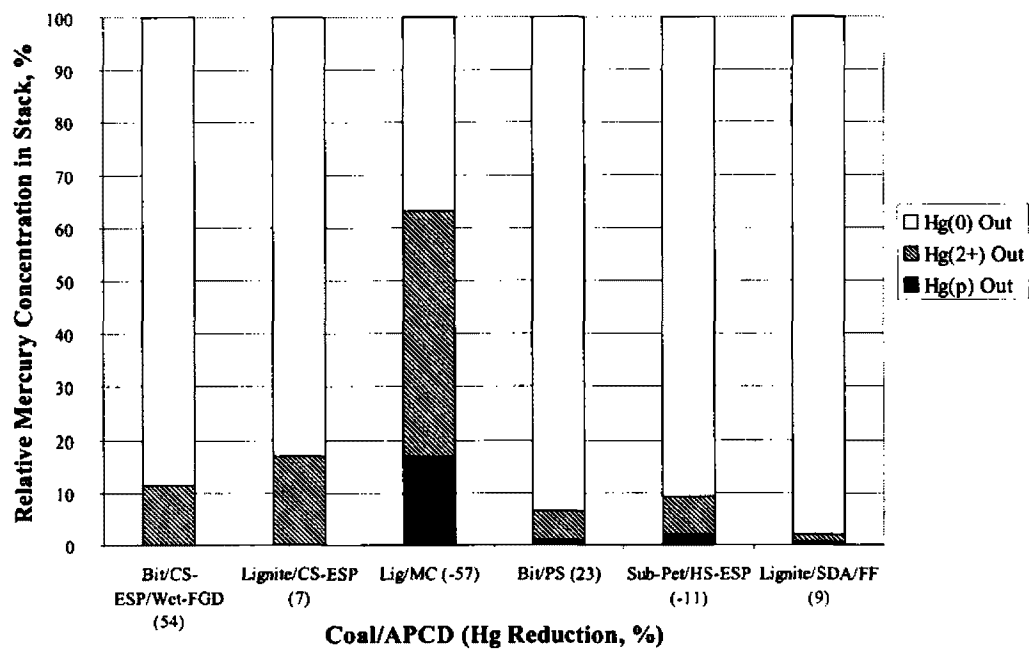**Figure 6-20. Mercury speciation for cyclone-fired boilers.**

Figure 6-21. Relative mercury speciation for cyclone-fired boilers.

Table 6-24
Comparison of Class Average
Hg_T Reductions for PC- and Cyclone-fired Boilers

Unit Class	Reduction in Hg_T, %	
	Cyclone	PC-Fired
Lignite, CS-ESP	9	36
Subbituminous/Pet Coke, HS-ESP	0	7
Lignite, Multicyclone	0	NA
ND Lignite, SDA/FF	7	2
Bituminous, PM scrubber + wet FGD	23	12
Bituminous, CS-ESP + wet FGD	54	81

6.7.2 Fluidized-bed Combustors

Six fluidized-bed combustors were tested on the ICR program. Test results for the fluidized-bed units are shown in Figures 6-22 and 6-23. All of the units injected limestone into the FBC to control SO_2 emissions. One unit was equipped with a CS-ESP while the remaining five units were equipped with a FF. One of the FF units was also equipped with an SNCR system. The unit equipped with the CS-ESP burned lignite. The capture of Hg_T for this unit averaged 38 percent. The reduction in Hg_T for units equipped with FF systems depended primarily on the type of fuel that was burned. The one unit that burned subbituminous coal was equipped with an SCR system and a FF. Inlet and outlet Hg_T concentrations for the two valid runs on this unit were 1.7 and 0.7 µg/dscm, respectively, resulting in a 57 percent capture efficiency. One unit that burned waste anthracite had an average Hg_T reduction efficiency of 99.7 percent, while another unit burning bituminous coal and petroleum coke had an average reduction of 94 percent.

The best performance for any unit tested during the Part III ICR program exhibited average Hg_T inlet concentrations of 185 µg/dscm, outlet concentrations of 0.15 µg/dscm, and an average Hg_T reduction of 99.9 percent.
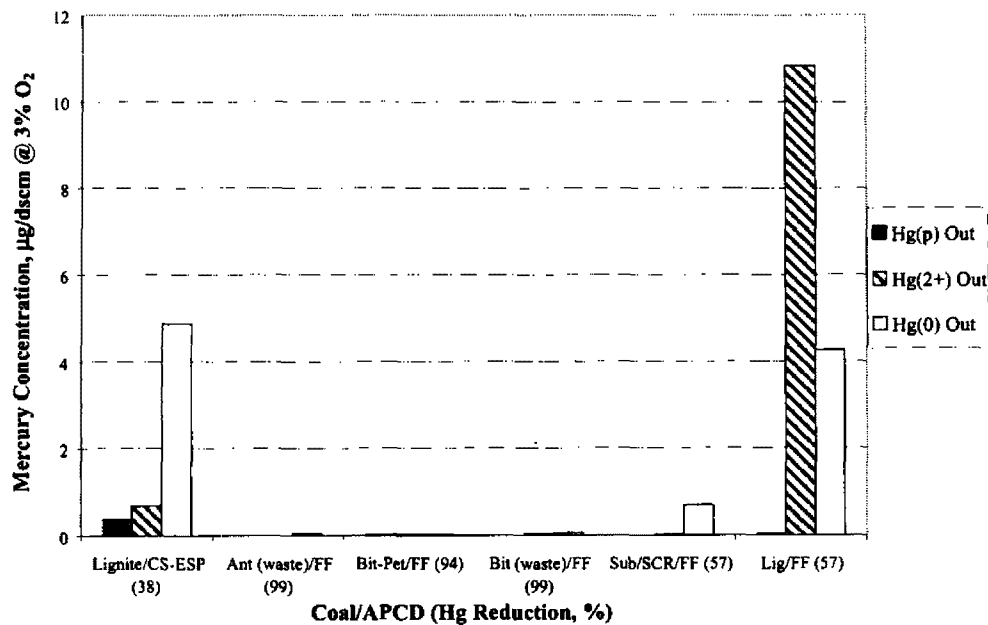
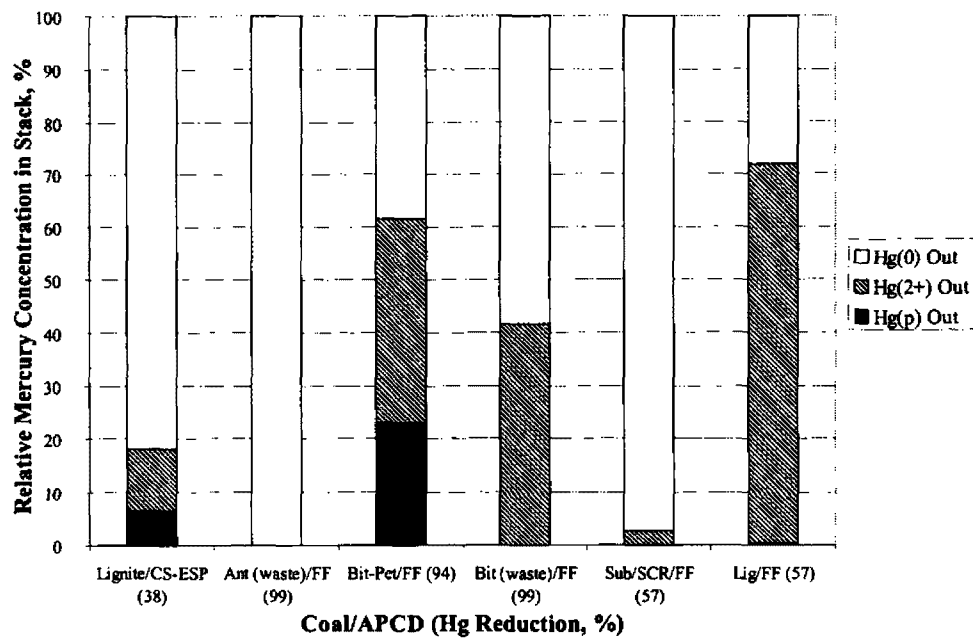**Figure 6-22. Mercury speciation for FBCs.**

Figure 6-23. Relative mercury speciation for FBCs.

6.7.3 IGCC Facilities

Table 6-25 summarizes the emission source test data and coal analysis data for the Tampa Electric Company Polk Power Project and Wabash River Coal Gasification Repowering Project. A more detailed presentation of the test data is included in Appendix C of this report. Coal data were used to calculate inlet feed rates of total Hg to the coal-gasification units. The total Hg in the exhaust gas from the gas turbine was determined by summing the three Hg species obtained using the OH Method during each test run (i.e., Hg_p, Hg^{2+}, and Hg^0).

Table 6-25
Calculated Mercury Removal in IGCC Power Plants Using Bituminous Coal

IGCC Facility	Test Run	Coal Fed to Gasifer			Gas Turbine Exhaust Gas Stream			Overall Mercury Removal (%)
		Coal Flow Rate (kg/hr, dry)	Total Hg Content (ppm, dry)	Total Hg Feed Rate (kg/hr)	Gas Stream Flow Rate (dscm/hr)	Total Hg Content [c] (µg/dscm)	Total Hg Emission Rate (kg/hr)	
Tampa Electric Company Polk Power Project	Run 1	91,454	ND [a]	0.0091 [b]	1,430,191	3.94 [d]	0.0056	38
	Run 2	88,707	ND [a]	0.0089 [b]	1,453,617	3.86 [d]	0.0056	37
	Run 3	71,373	ND [a]	0.0071 [b]	1,414,052	3.68 [d]	0.0052	27
	3-Run Average	83,845	- - - - -	0.0084	1,432,620	3.83 [d]	0.0055	34
Wabash River Coal Gasification Repowering Project	Run 1	90,663	0.064	0.0058	1,372,064	2.57 [e]	0.0035	40
	Run 2	89,629	0.068	0.0061	1,385,884	2.60 [e]	0.0036	41
	Run 3	89,493	0.070	0.0063	1,352,458	2.76 [e]	0.0037	41
	3-Run Average	89,928	0.067	0.0061	1,370,135	2.64 [e]	0.0036	41

(a) No mercury was detected by the test method used to analyze the coal.

(b) Feed rate calculated assuming total mercury content of the coal is at the detection limit for the analytical method (0.1 ppm).

(c) Total mercury content of the gas turbine exhaust stream determined using Ontario-Hydro Method results.

(d) No particle-bound mercury was detected by the Ontario-Hydro Method. To calculate total Hg content, it is assumed that particle-bound mercury concentration in gas stream is negligible. It is reasonable to assume that, consistent with good IGCC operating practices, the total particle concentration of the syngas burned in the gas turbine needs to be very low in order to prevent premature wear of the gas turbine blades.

(e) No particle-bound mercury or oxidized mercury was detected by the Ontario-Hydro Method. To calculate total Hg content it is assumed that particle-bound mercury and oxidized mercury concentrations in the gas stream are negligible. At the Wabash River facility the syngas is cleaned and conditioned before burning in the gas turbine by a barrier filter for particulate removal, a water scrubber for gas cooling, and an amine scrubber for removal of reduced-sulfur species. It is reasonable to assume that these filtration and scrubbing processes remove the particle-bound and oxidized mercury from the gas stream.

The operating difficulties experienced at the Pinon Pine IGCC facility demonstrate that good operating practices dictate the need for the concentration of particulate matter in the syngas to be continuously maintained at very low levels to prevent premature gas turbine blade erosion. The OH Method measurements obtained at both of the tested IGCC facilities are consistent with this operating practice. In both cases, the OH Method detected no particle-bound Hg in the gas turbine exhaust gas. With very low numbers of particles in the syngas

stream to begin with, the elemental Hg released during the coal gasification process has very few opportunities to be adsorbed on solid particles to form particle-bound Hg.

The OH Method test results show that elemental Hg is the predominant species in the gas turbine exhaust gas. For the Polk IGCC facility, the measured distribution of gaseous Hg species was approximately 90 percent elemental Hg and 10 percent Hg^{2+}. For the Wabash River IGCC facility, no Hg^{2+} was detected by the OH Method (i.e., 100 percent of the Hg_T in the exhaust gas stream was in the form of Hg^0). One possible explanation for these results is the different gas cleaning processes used at the two IGCC facilities. The syngas from the coal gasifier at the Wabash River IGCC facility is cleaned and conditioned using a system that includes a water scrubber for gas cooling and an amine scrubber for removal of reduced-sulfur species. Oxidized Hg is water-soluble and is readily absorbed by a wet scrubbing system. However, Hg^0 is insoluble and passes through a wet scrubbing system. Thus, it is reasonable to expect that the water and amine scrubbers used at the Wabash River IGCC facility effectively remove the oxidized Hg in the syngas before it is burned in the gas turbine.

The Polk IGCC facility uses a hot gas-cleaning system. There is no wet scrubbing process to remove any Hg^{2+} from the syngas before it is burned. The syngas is not cooled and remains at elevated temperatures until it is fed to the gas turbine. It cannot be determined from the test data how the elevated syngas temperatures and combustion process in the gas turbine combustors affect Hg speciation. However, it is believed that any Hg^{2+} in the syngas will be converted back to Hg^0 when the syngas is burned. The degree of oxidization will probably be limited by the combustion gas composition and the rate at which it is cooled before it is emitted to the atmosphere.

The last column in Table 6-25 provides an estimate of the overall amount of Hg in the coal removed by the IGCC process. Based on these two tests, approximately one-third of the Hg in the coal is removed. The Hg that remains in the combustion gas is primarily Hg^0.

6.8 NATIONAL AND REGIONAL EMISSION ESTIMATES

Estimates of the nationwide Hg emissions provide an indication of the overall level of Hg capture being achieved by existing control systems used by coal-fired utility boilers in the United States. A number of different approaches can be used for these estimates. The EPA evaluated four different methods for estimating nationwide Hg emissions using information from the ICR database. The method selected as being the best is outlined below:

- ICR Part II coal data were used to determine the average Hg content and the amount of coal burned in each of 1143 units supplying data for 1999.

- Mercury in the flue gas from coal burned in each boiler unit in 1999 was calculated assuming that all of the Hg in the coal was in the flue gas leaving the furnace.

- Each unit was assigned a coal-boiler-control class that best met the characteristics of the unit.

- Total Hg in the boiler flue gas for each unit was multiplied by the class emission factors for speciated and total Hg that had been assigned to the unit.

- Total and speciated Hg emissions for each unit were added to provide estimates of national Hg emissions from coal-fired utility boilers in 1999.

Computer runs using this procedure resulted in estimated national Hg emissions in 1999 of 43.5 tons.

Using the EPA's ICR database, EPRI independently estimated the nationwide Hg emissions from existing coal-fired utility boilers in the United States to be in the range of 45 to 48 tons in 1999. EPRI selected a different estimation methodology than the one used by EPA. EPRI's method is based on a model that correlates the level of Hg emissions with the amount of chlorine in coal and the ratio of chlorine to sulfur in the coal for the case of units with cold-side ESPs. Both the EPA and EPRI estimate that approximately 75 tons of Hg was in coals burned in 1999.

After EPA announced its decision to develop the NESHAP, the transfer of data from the field test reports to the emission databases was rechecked for errors. It was found that several test units had been assigned to the wrong coal-boiler-control classes. Also, the results of a number of tests failed data quality requirements and were removed from the analysis set. Subsequent computer evaluations resulted in the following estimates:

- 48 tons of Hg was emitted to the atmosphere from coal-fired utility boilers in 1999, and

- 27 tons of Hg was captured by existing flue gas cleaning devices.

Nationwide, approximately 25 tons (52 percent) of Hg was emitted from the combustion of bituminous coal, followed by 17 tons (36 percent) from the combustion of subbituminous coals, and 4 tons (8 percent) from the combustion of lignite. The total amounts of Hg emitted compared to the tonnage and types of coal burned in 1999 are presented in Table 6-26.

Table 6-26
Nationwide Coal Burned and Mercury Emitted
From Electric Utility Coal-fired Power Plants in 1999

Coal Type	Nationwide Total Coal Tonnage Burned In 1999 (dry tons) [a]	Percent of Total Coal Burned	Nationwide Total Mercury Emitted in 1999 (tons)	Percent of Total Mercury Emitted
Bituminous	427,572,000	56	25	52
Subbituminous	279,227,000	36	17	36
Lignite	50,932,000	7	4	8
Other	10,756,000	1	2	4
Total	768,487,000	100	48	100

(a) For wet tons (as received), nationwide total is 928,398,000 tons in 1999.
   Percentages for wet tons are 50% bituminous, 41% subbituminous, and 8% lignite.

6.9 SUMMARY AND CONCLUSIONS

Previous research has shown that the capture of Hg by flue gas cleaning devices is dependent on Hg speciation. Both Hg^0 and Hg^{2+} are in a vapor phase at flue gas cleaning temperatures. Hg^0 is insoluble in water and cannot be captured in wet scrubbers. The predominant Hg^{2+} compounds in coal flue gas are weakly-to-strongly soluble and can be generally captured in wet FGD scrubbers. Both Hg^0 and Hg^{2+} can be adsorbed onto porous solids such as fly ash, PAC, or calcium-based acid gas sorbents for subsequent collection in a PM control device. Hg^{2+} is generally easier to capture by adsorption than Hg^0. Hg_p is attached to solids that can be readily captured in ESPs and FFs.

The evaluation of ICR data provides valuable insights into relationships between the speciation and capture of Hg, the type of coal burned, the types of boilers used, and the types of post-combustion technologies used for flue gas cleaning. The evaluation of ICR data indicates that the behavior of Hg in conventional PC-fired utility boilers is primarily dependent on the type of coal burned and the control technologies used at each site. This behavior is consistent with the ensuing interpretations.

Bituminous Coals

The Hg^0 in flue gas from the combustion of bituminous coal is readily oxidized and converted to Hg_p or Hg^{2+}. The best technologies for controlling corresponding Hg emissions are dry or wet FGD scrubbers along with post-combustion PM controls. Dry scrubbing systems that use a SDA/FF are superior in performance to those that use a SDA/ESP. In SDA/FF systems, Hg can be absorbed on PM in the SDA, and particulate- and gas-phase Hg can be captured as it passes through the FF and its associated filter cake. SDA/ESP systems depend on the in-fight capture of Hg.

A PM control device always precedes wet FGD scrubbers. Four types of PM control devices are commonly used: FFs, CS-ESPs, HS-ESPs, and PM scrubbers. Units equipped with a FF exhibit the best capture followed by units equipped with a CS-ESP, HS-ESP, and PM scrubbers. Units that are equipped with FF + wet FGDs can capture Hg in FF and can convert Hg^0 to Hg^{2+} for subsequent capture in the scrubber. Hg capture in CS-ESP + wet FGD systems depends on the degree of Hg capture and oxidization as the flue gas passes through the CS-ESP. Hg capture in units equipped with HS-ESPs is generally lower than the capture in CS-ESPs because HS-ESPs operate at temperatures where the oxidization and capture of Hg is limited. The single test unit equipped with a PS + wet FGD system exhibited an average Hg_T capture of 12 percent.

Subbituminous Coals

Some subbituminous coals exhibit little, if any, Hg^0 oxidization in PC-fired boilers. Others display moderate amounts of Hg^0 oxidization. The use of low NO_X burners tends to increase the amount of unburned carbon and the potential for capturing gas-phase Hg. The ICR data show that the oxidization of Hg^0 can occur from gas-phase reactions or gas/solid reactions with fly ash or surface deposits in power plants. The unburned carbon in fly ash can oxidize Hg^0 or adsorb gas-phase Hg. Hg^{2+} is believed to be more readily captured by adsorption than Hg^0. Because of temperature considerations, the adsorption of Hg onto fly ash in units equipped with CS-ESPs is believed to occur as the flue gas flows through the air preheater and the ducting that leads to the ESP. Additional adsorption can also occur within the ESP.

Flue gas from the combustion of bituminous coal contains moderate to high levels of Hg^{2+}, primarily in the form of $HgCl_2$.

The EPA ICR database provides a massive amount of information that can be mined for additional information. However, its usefulness is limited by the uncertainty of some of the measurements and by information that the data set does not contain. Some of the uses and limitations of the ICR data are summarized below. The data provide:

- Reasonable estimates of National and Regional emissions for Hg_p, Hg^{2+}, Hg^0, and Hg_T. They cannot be used to predict the total and speciated Hg emissions of individual plants.

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- Information against which hypotheses and models of the speciation and capture of Hg in coal-fired boilers can be tested. It cannot be used to identify or confirm specific mechanisms that control the speciation and capture of Hg.

- Information needed to guide the development of control technologies and identify effective strategies for the control of Hg emissions.

Cautions:

- Mercury speciation measurements made with the OH Method upstream of the PM control devices should be used with caution. PM collected on the sampling train filter can result in physical and chemical transformations with the sampling train – with the result that OH Method speciation results do not accurately characterize the different forms of Hg in the flue gas where the samples were collected. The OH Method samples for Hg_T accurately reflect the concentration of Hg_T in the flue gas where the sample was collected. Also the samples collected at the inlet to air pollution control devices may not accurately represent the average Hg concentration because of flow stratifications near the sampling location.

- At low inlet and outlet concentrations, the precision of the OH Method can obscure real differences between these concentrations. When the capture across the control devices is being evaluated, the underlying imprecision of the measurements can show dramatic positive or negative reductions in emissions.

- It is believed that the positive variations in flue gas temperature can result in de-sorption of Hg_p collected within PM control devices, resulting in flue gas concentrations of Hg that are higher at the outlet than at the inlet. Reentrainment of Hg_p during rapping cycles of an ESP can also result in outlet concentrations that are higher than the inlet.

- There is uncertainty in the central values and statistical characteristics of the OH measurements. The samples represent a short snapshot in time, and the effects of long-term variations in coal properties and plant operating conditions are unknown.

- The adsorption of Hg onto fly ash is highly dependent on fly ash properties and particularly on the fly ash carbon content. The lack of information on coal and fly ash properties limits the ability to evaluate the effects of LNBs on the capture of Hg.

6.10 REFERENCES

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Chapter 7
Research and Development Status of
Potential Retrofit Mercury Control Technologies

7.1 Introduction

The Part III EPA ICR data show that ESP and FF control devices currently used to meet PM emission standards do capture particle-bound mercury (Hg_p) from coal-fired electric utility boilers (see Chapter 6). The data also suggest that SDA and wet FGD scrubbers in place to meet SO_2 emission standards do capture oxidized mercury (Hg^{2+}). However, these data also show that the air pollution control devices presently used at most electric utility power plants are not very effective in capturing elemental mercury (Hg^0). Consequently, to achieve further reductions in Hg emissions from existing coal-fired electric utility power plants, additional Hg reduction strategies must be implemented.

Potential Hg control strategies may be technology based (e.g., adding Hg emissions control devices), economics based (e.g., Hg emissions trading programs), or national energy policy based (e.g., switching from coal to alternative energy sources for electrical power production). This chapter discusses technology-based control strategies available for reducing Hg emissions from existing coal-fired electric utility power plants (Section 7.2). Current research and development is focused on retrofitting Hg control technologies to the coal-fired electric utility power plant's existing air pollution control systems (Section 7.3). This retrofit approach offers the potential for reduced costs of implementing Hg controls by enhancing the capability of the air pollution control equipment already in place to capture more Hg.

Building on the results of laboratory- and bench-scale research studies (discussed in Chapter 5), additional studies have been, and currently are being, conducted using pilot-scale test facilities to further investigate the more promising retrofit Hg control technologies (Section 7.4). For the many existing coal-fired electric utility boilers that are equipped with only ESPs or FFs, retrofit technologies under development are based on injecting sorbents into the flue gas upstream of the control device (Section 7.5). Retrofit technologies to improve wet FGD scrubber performance in capturing Hg are based on promoting oxidization of Hg^0 to soluble species by the addition of oxidizing agents or the installation of fixed oxidizing catalysts upstream of the scrubber (Section 7.6). The high levels of Hg control already achieved by the few existing boilers using SDA for control of PM and SO_2 may be further enhanced by coinjection of a second sorbent (Section 7.7). From a long-term perspective, the most cost-effective Hg controls may be those implemented under a multipollutant emission control strategy. New

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multipollutant control technologies, which potentially are effective in controlling Hg emissions, are under development (Section 7.8).

7.2 Technology-based Mercury Control Strategies for Existing Coal-fired Electric Utility Boilers

7.2.1 Remove Mercury Prior to Burning by Coal Cleaning

Reducing the amount of Hg in the coal burned in electric utility boilers would reduce the level of Hg emissions from these boilers without the need for additional post-combustion Hg controls. Switching coal suppliers to obtain coals with lower Hg contents raises complex economic and national energy policy issues that are beyond the scope of this report.

Physical cleaning of coal (discussed in Chapter 2) has traditionally been used at coal preparation plants to remove mineral matter (i.e., a source of coal combustion ash) and mineral-bound sulfur (pyrite) from the mined coal. Mercury and other trace metals are also removed by this cleaning depending on whether these metals are associated with the organic carbon structure of coal or coal mineral inclusions. However, the existing commercially available coal-cleaning methods remove only a portion of the Hg associated with the non-combustible mineral matter in the coal and none of the Hg associated with the organic carbon structure of the coal. Consequently, conventional physical coal cleaning can remove only a limited portion of the Hg content of specific coals and may not be applicable to all coals.

There is the potential for additional Hg reductions in the coal from several advanced physical coal-cleaning processes using selective agglomeration or column froth flotation now being developed. For example, Microcel™ is a type of column froth flotation available through ICF Kaiser and Control International. The company is the exclusive licensee for use of the technology for coal deposits east of the Mississippi River and has sold units for commercial operation in Virginia, West Virginia, and Kentucky. Ken-Flote™ is another type of column froth flotation cell coal-cleaning technology that is commercially available. Results of bench-scale studies indicate that the combination of conventional with advanced coal-cleaning techniques removes from 40 to 82 percent of the Hg contained in samples of raw coal.[1,2]

Advanced coal-cleaning processes using naturally occurring microbes and mild chemical treatments to reduce the Hg content in coal have been investigated under DOE-funded bench-scale studies. The results of these tests indicate that these chemical and biological coal-cleaning processes have the potential for further reduction in the Hg content of coals. However, DOE viewed the processes as potentially high-cost control technologies, and DOE currently is not funding development of these types of coal-cleaning technologies.[3]

From a near-term perspective, some reduction of the Hg content in certain coals burning at existing coal-fired electric utility power plants can be achieved by physical coal-cleaning processes. However, there are no easily identifiable coal deposits or coal types that will reliably benefit from cleaning, with respect to reducing Hg content. In addition, even with

implementation of widespread coal cleaning for Hg emissions control, significant quantities of Hg will remain in the coal after cleaning; this will require that other control techniques be used to achieve additional reductions in Hg emissions.

7.2.2 Retrofit Mercury Controls to Existing Air Pollution Control Systems

In addition to reducing the amount of Hg in the coal before it is burned in a coal-fired electric utility boiler, a second technology-based alternative is to remove more of the Hg in the boiler flue gas before it is vented out the stack. One strategy is to retrofit or adapt control technologies to the facility's existing air pollution control systems to increase the amount of Hg captured by these systems rather than install new, separate Hg control devices. The strategy offers the potential advantage of reducing the costs of implementing the Hg controls by enhancing the capability of the air pollution control equipment already in place to capture more Hg.

The existing air pollution controls used for a given coal-fired electric utility boiler depends on site-specific factors including the properties of the coal burned, age and size of the boilers, the geographic location of the facility, individual state regulatory requirements, and preferences of the facility owner or operator. For approximately 70 percent of the existing coal-fired electric utility boilers in the United States, the control device used is an ESP (see Table 3-6 in Chapter 3). These power plants typically burn low-sulfur coals to control SO_2 emissions and use combustion modifications for NO_X emissions control. Most boilers use a "cold-side" ESP where the control device is installed downstream of the boiler air heater (discussed in Section 3.4.1). Some of the boilers use a "hot-side" ESP where the control device is installed upstream of the boiler air heater. A small number of existing boilers (7 percent) that fire low-sulfur coal use FFs instead of ESPs. In general, FFs are being used at these coal-fired electric utility power plants to obtain better PM control or to solve ESP performance problems associated with high-resistivity fly ash. A FF can be used only downstream of the boiler air heater because of temperature limitations of the fabric filter bags.

Post-combustion SO_2 emissions controls are used at approximately 27 percent of existing coal-fired electric utility boilers. The SO_2 control technology most commonly used for these boilers is a wet FGD scrubber. In all cases, a PM control device, usually an ESP, precedes a scrubber. Wet FGD scrubbers remove gaseous SO_2 from flue gas by absorption. In absorption, gaseous species are contacted with a liquid in which they are soluble. For SO_2 absorption, gaseous SO_2 is contacted with a caustic slurry, typically water and limestone or water and lime. The newer semi-dry SO_2 scrubber technologies currently are used at small number of the existing coal-fired utility boilers (about 5 percent). However, for retrofit Hg control, these semi-dry scrubbers have the advantage of an existing sorbent delivery system coupled with, in most cases, a downstream FF to collect the reacted sorbent already in place. A detailed discussion of potential retrofit options and current research and development status is presented in following sections.

7.2.3 Integrate Mercury Control Under a Multipollutant Control Strategy

The most cost-effective, long-term Hg controls may be those implemented as part of a multipollutant control strategy. Selection and deployment of new SO_2, NO_X, and fine PM controls, which also control or contribute to the control of gaseous Hg in coal combustion flue gas, may reduce or eliminate the need for Hg-specific controls. For example, installation of a wet or semi-dry FGD unit should reduce oxidized Hg emissions by 90 to 95 percent over previous levels; adding upstream NO_X controls, which assist in oxidation of Hg^0, would further reduce total Hg emissions. Replacing or supplementing existing ESPs with FFs will likely remove additional Hg, especially for bituminous coal applications.

The remaining majority, Sections 7.3 through 7.7, discusses control technologies that reduce Hg emissions by improving the performance of existing air pollution control devices to capture the Hg in coal combustion flue gas. Section 7.8 discusses new multipollutant control technologies (other than serial SO_X-NO_X-PM control devices), which are under development and are potentially applicable to electric utility coal-fired electric utility power plants.

7.3 Post-combustion Mercury Control Retrofit

Retrofits that reduce Hg emissions from existing electric utility coal-fired electric utility power plants are implemented by modifying existing post-combustion emission control techniques already in place. Potential retrofit options are identified and discussed below. Options that are discussed may not be technically feasible or economically practical to install and operate at all facilities.

7.3.1 Cold-side ESP Retrofit Options

Add Flue Gas Cooling. Lowering the flue gas temperature entering the ESP assists natural fly ash sorption of Hg as well as improves the performance of any sorbents injected upstream for Hg control. However, the acid dew point temperature limits gas cooling when the flue gas has significant HCl or H_2SO_4 formation potential.

Add Sorbent Injection. Gaseous Hg can be converted to Hg_p by adsorption onto solid particles in flue gas. Injecting sorbents into the flue gas upstream of the ESP increases the amount of Hg captured in the form of Hg_p. This modification may require adding ducting between the sorbent injection point and the ESP, and adding a gas absorber/humidifier upstream of the ESP. This approach also may be limited by the ability of the ESP to collect high-resistivity sorbents. For coal-fired electric utility boilers with marginally performing ESPs that have difficulty meeting opacity requirements and may not be candidates for a sorbent injection retrofit, the following option may be preferred.

Add Downstream FF with Sorbent Injection. Adding a FF downstream of the existing ESP, while a more expensive retrofit option, allows a significant portion of the fly ash to be collected without reacted sorbent and enhances overall PM control efficiency where ESP performance is marginal. Further, because the FF would have a much lower particulate loading,

the collecting surface can be smaller (higher air-to-cloth ratio) or have longer cleaning cycles (good for sorbent performance and bag life).

ESP Modifications. Potential ESP modifications include converting the last field of the ESP to a wet ESP or a very compact pulsejet FF. These conversions would likely be made because of PM collection improvements needed, rather than Hg control considerations; nonetheless, associated Hg control benefits would also be likely.

7.3.2 Hot-side ESP Retrofit Options

Convert to Cold-side ESP with Sorbent Injection. Adding flue gas cooling is not an option for a hot-side ESP because of its location upstream of the air preheater. The only potential retrofit option for Hg capture without adding a new downstream PM control device is to convert the existing ESP from a hot-side configuration to a cold-side configuration. Depending on the plant layout and ESP design, this may be possible by reconfiguring the ducting and retuning the ESP to operate at the lower temperature. Adding sorbent injection with the modification would further improve Hg capture. The lower flue gas temperature entering the ESP enhances the adsorption of gaseous Hg onto fly ash or sorbent (if injected upstream) and subsequent collection of the particulate Hg in the ESP.

Add Downstream FF with Sorbent Injection. The same as for a cold-side ESP, adding a FF downstream of the existing ESP, while a more expensive retrofit option, allows a significant portion of the fly ash to be collected without reacted sorbent.

7.3.3 Fabric Filter Retrofit Options

Add Flue Gas Cooling. As is the case for ESPs, lowering the flue gas temperatures entering the FF enhances the adsorption of gaseous Hg onto fly ash or sorbent (if injected upstream). Again, the acid dew point temperature limits gas cooling when the flue gas has significant HCl or H_2SO_4 formation potential.

Add Sorbent Injection. Use of sorbent injection may require some internal FF modifications to ensure good sorbent performance. In general, existing FFs were not designed as adsorbers, so some modifications may be in order to ensure that sorbent particles stay entrained and become part of the filter cake. This may be accomplished by removing baffles, changing the point of gas entry, increasing gas velocity, or using smaller sorbent particles. Operating requirements of the FF may require more frequent cleaning with the additional sorbent loading.

FF Modifications. Potential FF retrofit options include replacing fabric bags with catalytic bags that oxidize Hg^0 to Hg^{++} and Hg_p or adding electrostatic augmentation to increase the bag cleaning cycle interval time and hence increase sorbent/gas contact time. This last improvement would be especially beneficial with higher-cost, high-capacity sorbents.

7.3.4 Spray Dryer Absorber Retrofit Options

Use Oxidation Additives. Existing SDA systems already achieve very high Hg removal on certain coals but show poor performance on other coals. Possible causes are low oxidation potential resulting from high alkaline fly ash content as well as low effective carbon content in fly ash. Therefore possible performance improvements include producing a higher carbon content fly ash by NO_x combustion control modifications, direct addition of activated carbon to the absorber with lime, and addition of oxidants to the absorber.

Replace Existing ESP with FF Control Device. Where the PM control device used for the absorber is an ESP, replacement of the unit with a FF would likely improve Hg removal as a result of enhanced PM control as well as greater conversion of Hg^{2+} to Hg_p.

7.3.5 Wet FGD Scrubber Retrofit Options

Use Oxidation Additives. Oxidation of the gaseous Hg^0 to gaseous Hg^{2+} can potentially increase the total Hg removed by wet scrubbing since gaseous Hg^{2+} is more readily captured by these systems than gaseous Hg^0. Several flue gas additives and scrubbing additives are being developed to increase the conversion of Hg^0 to Hg^+ prior to the scrubber inlet. Flue gas and scrubber additives are also being developed for use in preventing the conversion of absorbed Hg^{2+} to gaseous Hg^0 in wet FGD systems. The one caution is that increasing oxidants upstream or within the scrubber may also oxidize other species such as SO_2 and NO/NO_2 to sulfuric and nitric acid aerosols.

Add Fixed Oxidizing Catalysts Upstream of Scrubber. Improvements in wet scrubber performance in capturing Hg may be accomplished by installation of fixed oxidizing catalysts upstream of the scrubber to promote oxidization of Hg^0 to soluble species. Potential catalysts currently are being tested.

Wet FGD Scrubber Modifications. Several studies of pilot-scale wet FGD systems suggest that modifying the scrubber operation and design (as well as the control and design of upstream ESPs) may improve the capture of gaseous Hg^{2+} and reduce the conversion of absorbed Hg^{2+} to Hg^0. Specifically, these studies have found that the liquid-to-gas ratio and tower design of a wet FGD unit affect the absorption of gaseous Hg^{2+}, while the oxidation air influences the conversion of absorbed Hg^{2+} back to Hg^0 which is then emitted to the atmosphere in the scrubber exhaust gas.

7.3.6 Particle Scrubber Retrofit Options

A few existing power plants use wet scrubbers exclusively for control of PM emissions. Knowledge gained in the enhancing control of Hg emissions from wet FGD scrubbers by operating modifications also may be useful in improving the Hg removal performance of these particle scrubbers.

7.4 Retrofit Control Technology Research and Development Programs

None of the retrofit options discussed in Section 7.3 are routinely being used by the electric utility industry at this time. In addition, the Hg emissions control technologies that are successfully used for municipal waste combustors (MWCs) in the United States and Europe cannot be directly retrofitted to existing coal-fired electric utility boilers. Differences in flue gas properties, combustion unit design, and other factors (discussed in Section 7.4.1) prevent the Hg control devices now used for MWCs to be directly installed at coal-fired electric utility power plants. Consequently, development of effective retrofit control technologies for coal-fired electric utility boilers is the subject of bench-scale, pilot-scale, and full-scale test programs. Chapter 5 discusses laboratory studies investigating potential Hg control techniques for coal-fired electric utility boilers. To further develop the most promising of these control techniques for full-scale application to coal-fired electric utility boilers, pilot-scale and full-scale research studies are being funded by the EPA, DOE, EPRI, state agencies, and private companies. Section 7.4.2 describes several pilot-scale test units that are being used for research and development programs. Building upon the results obtain using these test facilities, a number of full-scale test programs currently are being conducted to provide a more thorough characterization of the performance and potential for widespread commercial application of specific retrofit Hg control technologies.

7.4.1 MWC Mercury Control Technology

Injection of activated carbon into the flue gas from a MWC and collecting the reacted sorbent in a downstream FF is one Hg control method widely used for MWCs.[4,5] Mercury removal levels in excess of 90 percent are achieved. However, the level of Hg control achieved by adding sorbents into the flue gas from a particular combustion unit is influenced by the particular characteristics of the flue gas from that unit including flue gas temperature, flow rate, Hg content, and chloride Hg content. Table 7-1 compares selected properties of the flue gas from a coal-fired utility boiler with those for a MWC flue gas. As shown in this table, Hg concentrations in MWC flue gas streams may be up to several orders of magnitude greater than those seen in utility flue gas streams. In addition, MWC flue gas contains mostly Hg^{2+}, while flue gas from coal-fired electric utility boilers can have substantial amounts of Hg^0, which generally is less likely to be adsorbed. Additionally the flue gas ductwork for a coal-fired utility boiler is substantially larger and more complex (multiple passes) than for a MWC, therefore duct injection of a sorbent is more complicated and its performance more difficult to predict for a coal-fired utility boiler due to variations in temperatures, residence time, and other factors.

Similarly, the wet scrubber technology used by European MWCs is not directly applicable to controlling emissions from coal combustion. European MWCs typically have two-stage scrubbers consisting of a low-pH water scrubber to control hydrochloric acid (HCl) emissions, produced as a result of the large quantities of plastics in the garbage burned, followed by an alkaline scrubber to control SO_2 emissions. In contrast, wet scrubbing systems typically used by the electric utility industry in the United States to control SO_2 emissions resulting from burning high sulfur coal consist of a single-stage wet scrubber using a limestone or lime scrubbing agent. As a consequence, there are significant differences in the underlying chemistry

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Table 7-1. Comparisons of typical uncontrolled flue gas parameters for coal-fired utility boiler versus municipal waste combustor (MWC).

Flue Gas Parameter	Coal-fired Electric Utility Boiler	Municipal Waste Combustor
Temperature (°C)	121 to 177	177 to 299 [a]
Hg Content (μg/dscm)	1 to 25	400 to 1,400 [b]
Chloride Content (μg/dscm)	1,000 to 140,000	200,000 to 400,00 [a]
Flow Rate (dscm/min)	11,000 to 4,000,000	80,000 to 200,000 [a]

(a) Temperature, chloride content, and flow rate data taken or determined from Reference 6
(b) Mercury content data taken from Reference 4.

of the scrubbing systems used for MWCs compared to those currently in use at coal-fired electric utility power plants.

7.4.2 Pilot-scale Coal-fired Test Facilities

To date, most of the retrofit control technology development has been conducted using pilot-scale test units that simulate full-scale coal-fired electric utility boiler combustion conditions. The DOE Federal Energy Technology Center, the Ohio Coal Development Office (OCDO), and McDermott Technology, Inc., jointly funded one program titled the Advanced Emissions Control Development Program (AECDP). This test program was conducted in three phases using a 10 MW coal-fired test faculty.[7,8,9] The test facility is capable of testing a full-flow ESP, a partial-flow pulsejet FF, and a wet FGD scrubber. All testing under the AECDP was performed firing Ohio bituminous coals. Figure 7-1 shows a schematic of the test facility. Specific AECDP test results related to specific retrofit options are discussed later in this chapter under the relevant topic headings.

For a DOE cooperative agreement test program, the project team of Public Service Company of Colorado (PSCO), ADA Technologies, and EPRI fabricated a pilot-scale particulate control module (PCM) to investigate Hg control in actual coal combustion flue gas by different dry sorbents.[10] Figure 7-2 shows a schematic of the PCM. The PCM draws a slipstream of flue gas (600 actual cubic feet per minute) from the 350-MWe coal-fired electric utility boiler (Unit 2) at PSCO's Comanche Station power plant. This boiler is an opposed-fired, pulverized-coal boiler firing Powder River Basin (PRB) subbituminous coal. Flue gas can be drawn either from the inlet (high particulate loading) or the outlet (essentially particle free) of the full-size Unit 2 reverse-gas FF. In addition, the PCM can be configured as an ESP, a reverse-gas or pulse-jet FF, and as EPRI's TOXICON pulse-jet FF. Gaseous Hg is injected into the flue gas to the PCM along with recycled fly ash and/or sorbent; the solids can be injected at various locations upstream of the PCM to investigate the effects of Hg adsorption at different in-flight residence times (0.5 to 3 seconds). The PCM is also equipped with in-duct heating and water spraying to investigate the effects of Hg adsorption at different temperatures. Specific results from testing using the PCM are discussed later in this chapter under the relevant topic headings.

The DOE National Energy Technology Laboratory (NETL) is conducting in-house research studies using a 500-lb/hr coal combustion unit to simulate a pulverized-coal-fired electric utility boiler.[11,12] Figure 7-3 shows a schematic of the DOE/NETL coal combustion test facility. The system consists of a wall-fired, pulverized-coal furnace equipped with a water-cooled convection system, a recuperative air heater, spray dryer, sorbent injection duct (SID) test section, and FF. Sorbent can be injected at numerous locations along the SID test section; this allows for a wide range of sorbent in-duct residence times relative to the FF and to the SID flue-gas sampling locations.
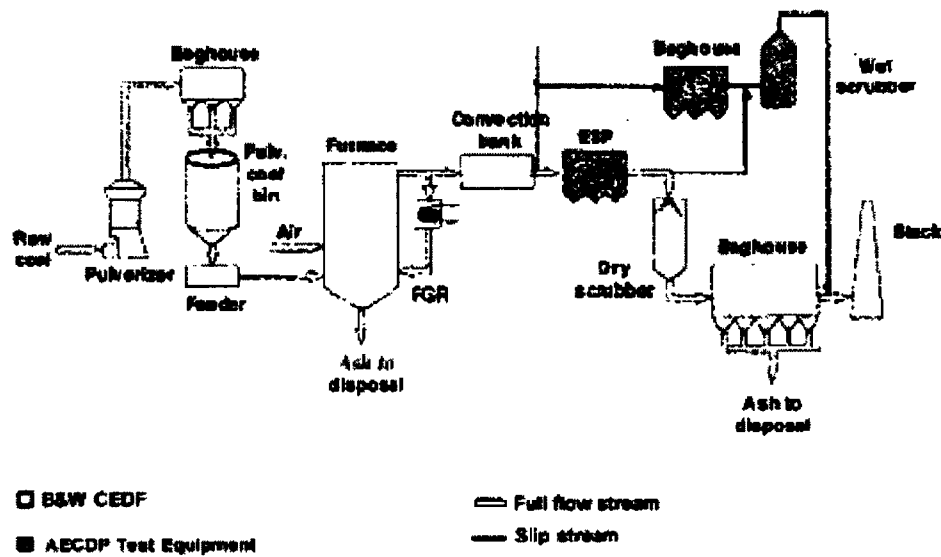
Figure 7-1. Schematic of 10-MWe coal-fired Babcock & Wilcox (B&W) Clean Environment Development Facility (CEDF) as used for Advanced Emissions Control Development Program (AECDP) (source: Reference 9).
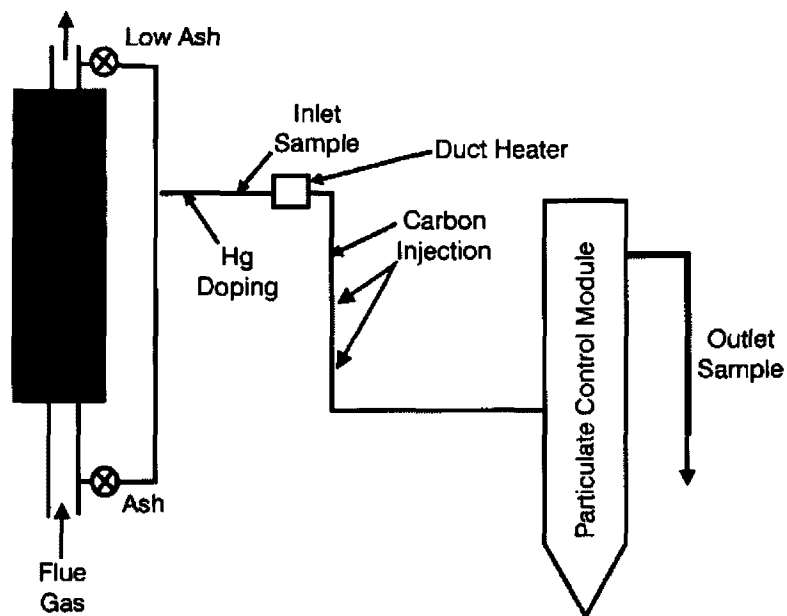
Figure 7-2. Schematic of Particulate Control Module (PCM) at Public Service Company of Colorado (PSCO) Comanche Station (source: Reference 10).
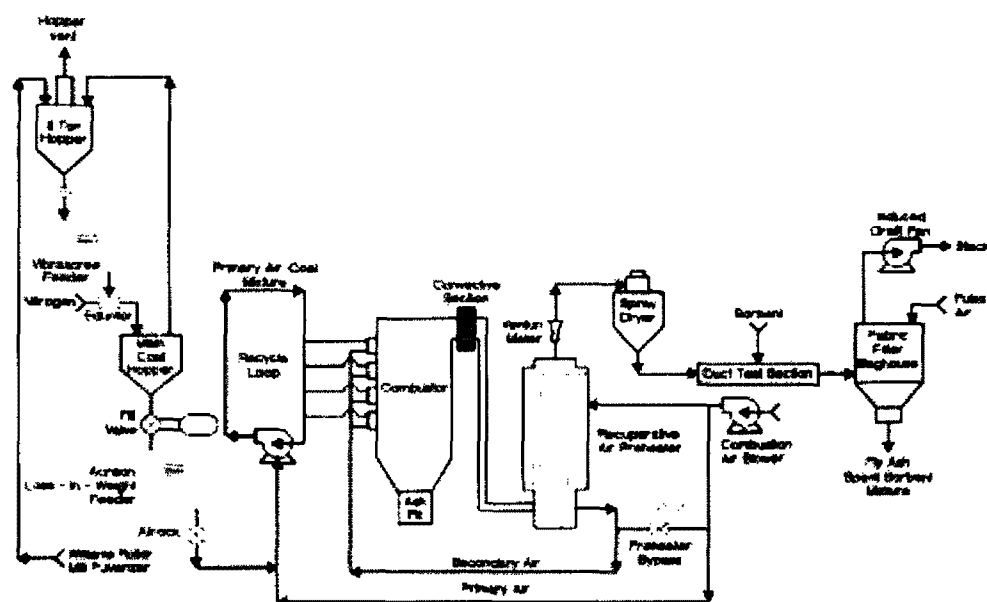
Figure 7-3. Schematic of DOE/NETL in-house 500-lb/hr coal combustion test facility (source: Reference 12).

7.5 Mercury Control Retrofits for Existing Coal-fired Electric Utility Boilers Using ESP or FF Only

The focus of research and development for existing coal-fired electric utility boilers equipped only with an ESP or FF has been the use of dry sorbent injection. As discussed in Chapter 5, gaseous Hg can be adsorbed onto solid particles in the flue gas. A solid particle that absorbs gaseous species is called a "sorbent." The flue gas from every electric utility boiler that directly burns coal (i.e., all boilers except for IGCC units) contains fly ash particles that adsorb gaseous Hg in the flue gas to various degrees. Other types of solid particles can be injected into the flue gas for the purpose of adsorbing gaseous Hg. Materials being investigated as possible sorbents for Hg control include activated carbon, calcium-based and sodium-based (trona) sorbents, various clays and zeolites, alkaline-earth sulfides, and lime and lime-silica multipollutant sorbents. An alternative sorbent-based Hg control approach that has been investigated is passing the flue gas through a fixed bed of a noble-metal-based sorbent.

7.5.1 Sorbent Injection Configurations

In general, four retrofit configurations are possible for injecting dry sorbent particles into the flue gas from a coal-fired utility boiler. It may not be technically feasible to implement one or more of these configurations at a given existing coal-fired power plant because of site-specific factors such as the existing flue gas duct configuration, availability of space to add additional ducting or new control device, use of a wet FGD scrubber, or other plant layout and operation considerations.

Configuration A - Sorbent injection into the flue gas duct upstream of existing ESP or FF. Cooling of the flue gas upstream of the sorbent injection point or modifications to the ducting may be needed.

Configuration B - Sorbent injection into the flue gas duct downstream of the existing PM control device followed by a new FF (to collect the reacted sorbent), with or without flue gas cooling upstream of the injection point. This configuration requires higher capital costs but reduces sorbent costs compared to Configuration A. The configuration also allows the fly ash collected by the upstream PM control device to be sold without being mixed with the injected sorbent.

Configuration C - Sorbent injection into a circulating fluidized-bed absorber (CFA) upstream of the existing ESP or FF, with or without flue gas cooling upstream of the CFA. The advantage to using a CFA is that it recirculates reacted materials with fresh sorbent to create an entrained bed with a high number of reaction sites resulting in higher sorbent utilization and enhanced capture of Hg and other pollutants.

Configuration D - Sorbent injection into a CFA downstream of the existing PM control device and followed by a new FF (to collect the reacted sorbent). Like Configuration B, this configuration allows the fly ash collected by the upstream PM control device to be sold without being mixed with the injected sorbent.

The level of Hg capture using sorbent injection with a downstream ESP depends on in-flight adsorption of Hg by entrained sorbent particles. Mercury capture in a downstream FF occurs by this same in-flight adsorption process as well as a second mechanism when flue gas must pass through the filter cake collected on the FF bags. This filter cake contains a mixture of previously captured fly ash and sorbent particles, and provides good contact between gaseous Hg and captured particles. Filter cake retention times between bag cleaning cycles may be as long as 60 minutes, greatly increasing the adsorption of Hg on the sorbent particles. This compares with the relatively short time that in-flight adsorption occurs upstream of the control device (nominal times for in-flight adsorption are 0.5 to 1.5 seconds). In addition, FFs generally are more efficient than ESPs in collecting fine particles and any associated Hg_p (see Table 3-3). The extra contact time and higher collection efficiency provided by a FF reduces the amount of sorbent needed for adsorption compared to what is needed for an ESP to achieve a given level of control.

Cooling the flue gas before the sorbent injection point can improve Hg adsorption by the sorbent, which in turn may reduce the amount of sorbent needed for a given level of control. However, the temperature to which the flue gas may be cooled is limited because sulfuric acid (and perhaps hydrochloric acid) mists may be formed if the flue gas temperature drops below the acid dew point(s) of the flue gas. For all four configurations, sorbent capacity may be maximized by recycling and reinjecting sorbent and fly ash collected in the PM control device(s) located downstream of the injection point.

7.5.2 Sorbent Adsorption Theory

Gas-phase adsorption occurs when a gaseous specie contacts the surface of a solid and is held there by attractive forces between the gaseous specie and the solid. In adsorption terminology, the gaseous specie being adsorbed is called the "adsorbate," and the solid is called the "adsorbent" or "sorbent." While all solids have the potential to adsorb gaseous species, adsorption is not very pronounced unless a solid has a large surface area. As a result, most solids for gas-phase adsorption are highly porous and in the form of particles or granules. The porosity of the solids provides large amounts of internal surface area where most adsorption takes place. When a gaseous specie is adsorbed onto the surface of a solid particle, the gaseous specie becomes a particle-bound specie.

Gas-phase adsorption may be classified as chemisorption or physical adsorption depending on the nature of the attractive force between the adsorbate and sorbent. In chemisorption, the adsorbate reacts with the surface of the sorbent, thus, the attractive force between the adsorbate and sorbent is similar to a chemical bond. Chemisorption often involves the use of sorbents impregnated with compounds that are reactive with the adsorbate. In physical adsorption, the attractive force between an adsorbate and sorbent is electrostatic in nature (similar to the attraction between metal filings and a magnet, where the metal filings are analogous to the adsorbate and the magnet is analogous to the sorbent). Different adsorbates have different attractive forces for a given sorbent due to differences in molecular weight, normal boiling point (or vapor pressure), degree of unsaturation, polarity, and structural configuration. When a sorbent is exposed to more than one adsorbate, preferential adsorption

tends to take place due to differences in the attractive forces between the different adsorbates and the sorbent particles.

Equilibrium adsorption capacity is the maximum amount of adsorbate a given mass of sorbent can hold at a given temperature and adsorbate gas concentration. Generally, the adsorption capacity of a sorbent for a given adsorbate increases with increased adsorbate concentration and decreases with increases adsorption temperature.

In a dynamic adsorption system (i.e., an adsorption system involving a moving gas stream), a gas stream containing one or more adsorbates is passed through a fixed or fluidized bed of sorbent particles or the sorbent particles are injected directly into the gas stream. In dynamic adsorption systems, the contact time between the sorbent particles and the adsorbate in the gas stream is critical. While contact time does not affect the equilibrium adsorption capacity of the sorbent, it directly affects the sorbent's ability to capture the adsorbate from the gas stream. Maximum capture of adsorbate from the gas stream will not take place unless the adsorbate has sufficient time to contact the sorbent and diffuse into its pores. Thus, increasing the contact time increases Hg capture by the sorbent.

7.5.3 Pilot-scale and Full-scale Research and Development Status

The laboratory studies of using dry sorbents for Hg control based on bench-scale reactor testing are discussed in Section 5.4. This section discusses the results from field studies testing different sorbents in pilot-scale or full-scale systems.

7.5.3.1 Coal Fly Ash Reinjection

As discussed in Chapter 5, fly ash generated naturally when burning certain coals in a utility boiler adsorbs some of the gaseous Hg in the flue gas. The adsorption of gaseous Hg by the fly ash vented in the flue gas from the boiler, referred to by some researchers as "native fly ash," is believed to occur at active sites on the ash surface similar to those on sorbent (e.g., fly ash carbon analogous to activated carbon or fly ash alkaline species akin to injected lime). As part of the DOE cooperative agreement test program to investigate dry sorbents, the project team of PSCO, ADA Technologies, and EPRI evaluated Hg removal rates by the fly ash in the flue gas from burning two types of Western coals and the potential for Hg removal by reinjection of low levels of collected fly ash back into the flue gas upstream of the particulate control device.[10] The use of reinjected fly ash for Hg control avoids the potentially adverse impact on the commercial viability of selling the fly ash collected in the downstream particulate control devices. The use of activated carbon as a Hg sorbent may increase the level of carbon in the collected fly ash/activated carbon mixture above allowable maximum levels for some commercial fly ash applications (e.g., sale of fly ash for use as a concrete additive).

Full-scale testing was conducted at three PSCO coal-fired electric utility power plants to characterize gaseous Hg removal by the native fly ash in flue gas at each facility; a boiler using a FF for PM control was tested. At one facility, a second boiler using an ESP was also tested. Two of the three power plants burned subbituminous coal from the Powder River Basin (PRB),

and the other burned a Colorado-mined bituminous coal. Flue gas measurements were taken concurrently at the inlet and outlet of each particulate control device. At two of the power plants, testing was conducted in both the summer and winter in order to investigate the effect of ambient temperature on the adsorption of Hg on the fly ash.

Results of the full-scale tests are summarized in Table 7-2. Mercury removal measured across the three FFs ranged from 61 to 99 percent. Mercury removal across the ESP was significantly lower at 28 percent. The two boilers units demonstrating Hg removals above 80 percent (Arapahoe 4 and Cherokee 3) were equipped with low-NO_x burner retrofits. The use of these burners often causes elevated levels of unburned carbon in the fly ash. Measuring unburned carbon by the "loss-on-ignition" (LOI) test, the fly ashes from Arapahoe 4 and Cherokee 3 had LOI contents approximately 7 to 14 times higher than the fly ashes from the other two boilers. The Hg levels measured for the Cherokee 3 unit was essentially the same in both summer and winter, indicating no adverse temperature effects on adsorption. In contrast, the Arapahoe 4 tests showed better adsorption at cooler test conditions (i.e., winter versus summer).

To examine the use of fly ash reinjection for Hg emissions controls, a series of pilot-scale tests were conducted by collecting the fly ash samples from the three power plants and injecting the collected fly ash into the PCM located at the Comanche Station (discussed in Section 7.4.2). For the recycled fly ash tests, the PCM was configured as a reverse-gas FF and drew fly-ash-free flue gas from the outlet side of the FF serving the coal-fired boiler. The flue gas was spiked with gaseous Hg to produce a Hg concentration of approximately 10 $\mu g/Nm^3$. The gaseous Hg concentration was sampled at the inlet and outlet of the PCM using a Hg continuous emissions monitor (Perkin Elmer MERCEM). Recycled fly ash was injected into the flue gas just downstream of the inlet sampling port. Except during one test, the injected fly ash samples were not treated in any way to enhance their Hg-adsorbing properties. For one test, a sample of fly ash from the Comanche 2 unit was treated with a hot nitrogen purge in an attempt to desorb any Hg on the ash particles.

Table 7-3 summarizes Hg removal data for the fly ashes tested. Reinjected subbituminous coal fly ash removed 84 to 86 percent of the gaseous Hg across the PCM. In contrast, reinjecting fly ash from the boiler burning bituminous coal showed only a 10 percent removal of gaseous Hg. The removal efficiency for bituminous coal fly ash was increased to 31 percent when this ash was thermally pretreated to desorb Hg before injection into the PCM. The results in Table 7-3 show that the recycled fly ashes from the Cherokee and Arapahoe boilers had additional capacity to adsorb gaseous Hg (beyond what they had adsorbed from their source flue gas), while the untreated recycled fly ash from the Comanche 2 boiler appeared to be saturated or no longer reactive. The LOI contents of the Cherokee 3 and Arapahoe 4 fly ash samples were 8 and 14 percent, respectively. The LOI contents of the Comanche 2 fly ash samples were 0.3 to 0.4 percent. As was observed during the full-scale testing, fly ashes with the highest LOI contents (those from the Arapahoe 4 and Cherokee 3 boilers) adsorbed more Hg than fly ashes with lower LOI contents (those from the Comanche 2 boiler).

Table 7-2. Hg removal by native fly ashes measured across PM control devices at PSCO power plants burning selected western coals (source: Reference 10).

Power Plant	Type of Coal Burned	PM Control Device	Ash Carbon Content (% LOI[b])	Gaseous Hg Removal (%)
PSCO[a] Cherokee	Bituminous (Colorado)	Reverse-gas FF (Boiler Unit #3)	7.6	98 (summer) 99 (winter)
PSCO Arapahoe	Subbituminous (Powder River Basin)	ESP (Boiler Unit #1)	< 1	28
		Reverse-gas FF (Boiler Unit #4)	14.4	62 (summer) 82 (winter)
PSCO Comanche	Subbituminous (Powder River Basin)	Reverse-gas FF (Boiler Unit #2)	0.4	61

(a) PSCO = Public Service Company of Colorado
(b) LOI = Loss on ignition

Table 7-3. Hg removals by fly ash reinjection measured across PCM at PSCO Comanche power plant for selected western coals (source: Reference 10).

Reinjected Fly Ash Coal Source (PSCO power plant)	Flue Gas Temperature (°F)	Ash Reinjection Rate (grains/acf)	Ash Carbon Content (% LOI[a])	Gaseous Hg Removal (%)
PRB Subbituminous coal (Arapahoe 4)	320	0.13	14.4	84
PRB Subbituminous coal (Cherokee 3)	320	0.33	7.6	86
Colorado Bituminous coal (Comanche 2)	280	1.13	0.42	10
	280	1.21	0.26	31 [b]

(a) LOI = Loss on ignition
(b) Deadsorbed ash.

In addition to evaluating the adsorption capacity of recycled fly ashes, several tests were made using the PCM to evaluate the effects of temperature on fly ash adsorption. For the temperature tests, fly-ash-laden flue gas was extracted from the inlet of the FF serving the Comanche 2 boiler and passed through the PCM; gaseous Hg was injected upstream of the PCM. Hg adsorption across the PCM was monitored as the temperature of the flue gas through the PCM was varied. Table 7-4 summarizes the results of the temperature tests. For the baseline tests (no heating or cooling), the temperature of the flue gas through the PCM was in the range of 135 °C (275 °F); at this temperature, the Comanche 2 fly ash removed 20 to 40 percent of the gaseous Hg present in the flue gas. When the flue gas was heated to around 152 °C (305 °F), the fly-ash Hg removal dropped to zero, while spray cooling to reduce the flue gas temperature to about 110 °C (230 °F) increased the Hg removal to around 60 percent. As expected, the data from these tests show that adsorption is greatly affected by temperature, with adsorption increasing with decreasing flue gas temperature.

7.5.3.2 Activated Carbon Sorbent Injection

The most frequently tested activated carbon for Hg removal from coal combustion gases has been a commercially available carbon manufactured by Norit Americas, Inc. (trade name Darco FGD™). The Darco FGD™ carbon is produced from lignite specifically for the removal of heavy metals and other contaminants from MWC flue gas streams. Other commercially available activated carbons and experimental carbons also have been tested.

A full-scale test program jointly funded by EPRI and Public Service Electric and Gas (PSE&G) evaluated the potential of activated carbon injection for Hg control.[13] The tests were performed at the PSE&G Hudson Generating Station, which fires low-sulfur bituminous coal and uses an ESP for PM control. Two types of activated carbon were tested, the Darco FGD™ carbon and an experimental carbon identified as AC-1. Results from these tests are shown in Table 7-5. The data indicate a distinct reduction in total Hg removal efficiency with increased temperature. The maximum Hg removal measured was 83 percent using the Darco FGD™ carbon at a C:Hg ratio of 45,000:1 and an ESP operating temperature of 221 °F. Full-scale ESP operation at this low temperature is not practical, however, due to potential problems with acid condensation.

Sorbent injection using Darco FGD™ carbon and an ESP was also tested as part of the AECDP Phase III studies.[9] For this test, the coal burned was an Ohio bituminous coal. The carbon was injected upstream of the ESP, with an approximate in-flight particle residence time of 1 second. The injection temperature was approximately 204 °C (400 °F) and the ESP inlet temperature was about 174 °C (345 °F). The carbon flow rate was approximately 14 lb/hr, which is equivalent to a C:Hg mass ratio of 9,000:1. Both particulate and gaseous Hg species were measured at the inlet and outlet of the ESP during the carbon injection test. The test results are presented in Figure 7-4. Also shown in this figure are baseline Hg concentrations measured before any injection tests. Compared to the baseline condition, injection of the activated carbon resulted in a total Hg removal of 53 percent. Carbon injection at the test conditions had no effect on the removal of gaseous Hg^0, suggesting that Hg removal appears to be a result of the capture

Table 7-4. Effect of flue gas temperature on fly ash Hg adsorption measured across PCM at PSCO Comanche power plant burning PRB subbituminous coal (source: Reference 10).

Test Condition	Flue Gas Temperature (°C)	Gaseous Hg Removal (%)
Baseline	135	20 to 40
Heated flue gas	152	0
Cooled flue gas	110	60

Table 7-5. Hg removal by activated carbon injection measured at PSE&G Hudson Station burning low-sulfur bituminous coal and using ESP (source: Reference 13).

| Sorbent Tested	ESP Operating Temperature (°F)	Sorbent Injection Ratio (C:Hg)	Total Hg Removal Range (%)
Baseline (no sorbent injection)	255	0	3
	268 –278	0	0
Darco FGD™ Activated Carbon	240 – 255	11,500:1	13 to 17
	240 – 255	20,000:1	41 to 42
	220 –235	45,000:1	76 to 83
	275 –280	27,000:1	14 to 38
	270 –275	45,000:1	28 to 45
Experimental Activated Carbon AC-1	240 –250	18,000:1	33 to 45
	240 – 250	45,000:1	56 to 58
	280	29,000:1	28
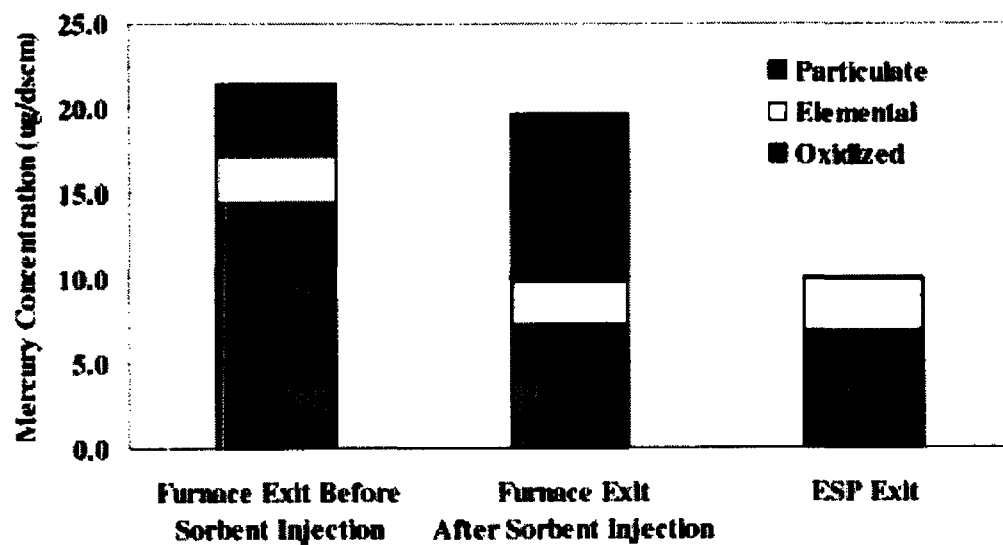
Figure 7-4. Hg removal by activated carbon injection measured at AECDP test facility burning Ohio bituminous coal and using ESP (source: Reference 9).

of gaseous Hg^{2+} (onto or into the particulate phase) and then the subsequent removal of the particulate in the ESP.

The DOE/NETL also tested injecting Darco FGD™ carbon for Hg control using the DOE/NETL in-house coal combustion test facility.[11] For these tests, low-sulfur bituminous coal was burned based on the rationale that this is a coal-type likely be burned in utility power plants that do not have flue gas desulfurization systems. Throughout testing, the furnace was operated to achieve high combustion efficiency with low levels of unburned carbon in the fly ash. Unburned carbon levels in the fly ash under baseline conditions were generally less than two percent. Flue gas measurements of Hg were conducted at the FF inlet using the OH Method, and a Modified Ontario-Hydro Method (MOH Method). The modified method samples the flue gas non-isokinetically whereas the former samples the flue gas isokinetically. Stack measurements downstream of the FF were made for speciated Hg using the OH Method and total Hg using EPA Method 101A. Analysis of coal and ash deposits was made using ASTM D3684. The MOH Method was used at the inlet to minimize PM collection during sampling. Eliminating entrained PM in the sample flue gas allowed researchers to determine in-duct Hg removals. In addition, the effect of filtered solids on Hg speciation was deduced by comparison with the Hg speciation measured with the OH Method.

Test results measured using the DOE/NETL test facility for sorbent injection upstream of a FF using the Darco FGD™ carbon are presented in Table 7-6. Total Hg removals measured ranged from 39 to 86 percent at injection C:Hg ratios of 2, 600:1 to 10, 300:1. The test results show a general trend where the total Hg removal increased with increasing C:Hg ratios. A second commercially available activated carbon has also been tested for possible Hg control using the NETL test facility.[12] Mercury removals of 30 to 40 percent were measured injecting Calgon FluePac™ activated carbon at C:Hg injection ratios of 2,500:1 to 5,100:1. The DOE/NETL in-house research also shows no significant in-duct removals of Hg under the test conditions, and Hg^0 appears to be oxidized by the filter cake. On-going research on activated carbon injection using the DOE/NETL test facility includes tests to quantify the effects of humidification and FF pressure drop on Hg removal, evaluating novel sorbents, determining sorbent effectiveness downstream of a FF with and without recycle, and comparing Hg removals using sorbent injection with ESP versus FF.[12]

A multiple-site, full-scale field test program is currently being conducted under a DOE/NETL cooperative agreement to obtain performance and cost data for using activated carbon injection to reduce Hg emissions from existing coal-fired electric utility power plants equipped only with an ESP or FF for post-combustion air pollution controls.[14] The DOE/NETL is working in partnership with ADA-ES, PG&E National Energy Group (NEG), Wisconsin Electric, a subsidiary of Wisconsin Energy Corp., Alabama Power Company, a subsidiary of Southern Company, EPRI, and Ontario Power Generation on a field evaluation program at four power plant facilities. Other organizations participating in this test program as team members include EPRI, Apogee Scientific, URS Radian, Energy & Environmental Strategies, Physical Sciences, Inc., Southern Research Institute, Hamon Research-Cottrell, Environmental Elements Corporation, Norit Americas, and EnviroCare International. The first test site is a boiler unit at the Alabama Power Gaston facility that burns various low-sulfur bituminous coals and is

Table 7-6. Hg removal by activated carbon injection measured at DOE/NETL in-house test facility burning low-sulfur bituminous coal and using FF (Source: Reference 11).

Test Run ID	Fabric Filter Temperature (°F)	Sorbent Injection Ratio (C:Hg)	Total Hg Removal (%)	Mass Balance (%)	
				Fabric Filter	Overall
9907-1 (baseline)	294	0	2.7	103.2	79.4
9907-2	294	9,500:1	86.0	77.4	78.6
9907-3	265	10,300:1	82.3	130.1	76.7
9907-4	268	6,200:1	75.1	80.0	98.1
9908-1 (baseline)	296	0	35.0	84.4	67.1
9908-2	296	2,600:1	38.8	100.6	90.8
9908-3	296	5,400:1	64.0	94.7	89.1
9908-4	270	2,900:1	54.2	103.2	86.8

equipped with a hot-side ESP followed by a COHPAC FF. Testing at this site was conducted in the spring of 2001.[15] The next test site being tested is a boiler unit at the Wisconsin Electric Pleasant Prairie facility that burns PRB subbituminous coal and uses a cold-side ESP for PM control. The other two sites are scheduled to be tested in 2002, and are the PG&E NEG Salem Harbor and Brayton Point facilities that burn low-sulfur bituminous coals and are equipped with cold-side ESPs.

7.5.3.3 Calcium-based Sorbent Injection

An alternative to using activated carbon is to use a calcium-based sorbent. Laboratory studies conducted by the EPA and Acurex Environmental Corporation (funded by the State of Illinois, ICCI) indicated that the injection of calcium-based sorbents into flue gas could result in significant removal of Hg (discussed in Section 5.3). Other benefits associated with the use of limestone injection for Hg control include an incremental amount of SO_2 removal and a high probability for SO_3 removal. Flue gas Hg removal using furnace limestone injection was evaluated as part of a study conducted by McDermott Technology, Inc. titled Combustion 2000 Project/Low Emission Boiler System Program.[16] In this study, limestone was injected into the upper furnace firing Ohio bituminous coal at a temperature of about 1,204 °C (2,200 °F). The Ca:S ratio was set at 1.40 mol/mol. An 80 percent efficient cyclone was then used to collect the fly ash and calcined lime. At this location the flue gas temperature was approximately 163 °C (325 °F). The Hg concentration in the flue gas was measured downstream of the cyclone using the OH Method. The measured Hg concentrations for the baseline (no limestone injection) and the six limestone injection tests are shown in Figure 7-5. The data show that the Hg concentration in the flue gas was significant lower when limestone was injected compared to the baseline. The overall average Hg reduction for the six limestone injection runs was 82 percent. The researchers note that using more efficient ESP or FF PM control devices with collection efficiencies of greater than 99 percent in place of a cyclone (see Table 3-3) is expected to provide an additional increase in Hg removal.

Based on the test results from the EPA/Acurex ICCI studies and the Combustion 2000 Project/Low Emission Boiler System Program, McDermott Technology, Inc. conducted additional limestone injection tests during Phase III of the AECDP.[9] The same limestone previously tested in the Combustion 2000 program was used for the Phase III tests. Two limestone flow rates were tested. The flow rates chosen for the limestone injection tests were 200 lb/hr (Ca:S = 0.35 mol/mol) and 25 lb/hr (Ca:S = 0.04 mol/mol). An injection temperature target of 1,149 °C to 1260 °C (2,100 °F to 2,300 °F) was chosen as the optimum range to calcine the limestone ($CaCO_3$) into lime (CaO). It was assumed that CaO would be more reactive with Hg, as it is with SO_2, because of the increased surface area and reactivity. Limestone was injected upstream of an ESP. The ESP inlet flue gas temperature was 177 °C (350 °F). Mercury concentrations were determined at the inlet and outlet of the ESP with triplicate Ontario Hydro measurements. One set of triplicate measurements was performed prior to sorbent injection to provide a baseline set of comparison data.

Figure 7-6 shows the Hg partitioning and speciation for three sets of Hg measurement locations: 1) at the ESP inlet without limestone injection (baseline); 2) at the ESP inlet with
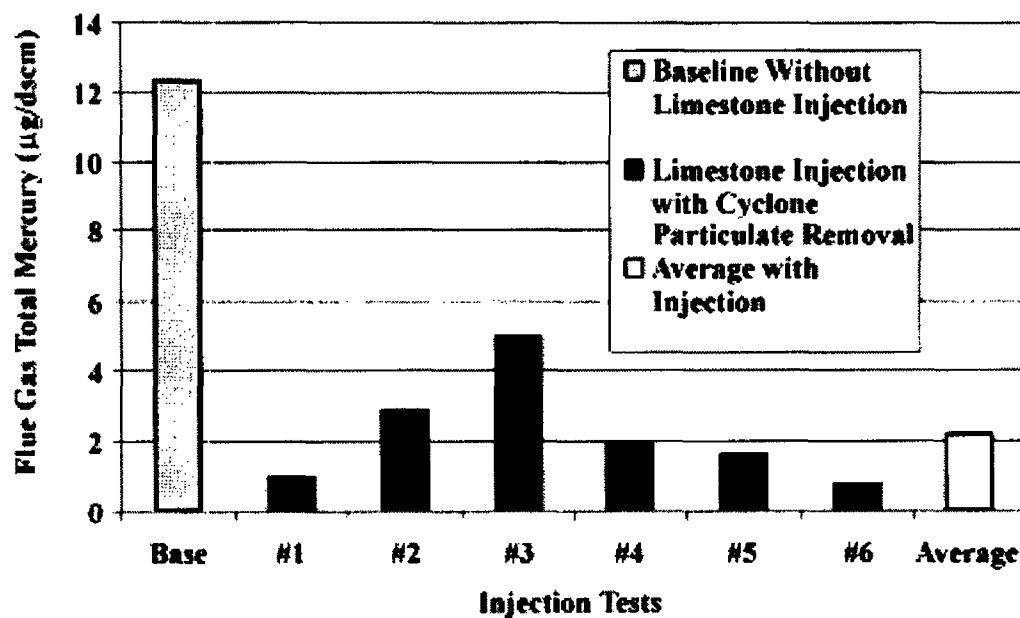
Figure 7-5. Hg removal by limestone injection measured in Combustion 2000 furnace using mechanical cyclone separator (source: Reference 9).
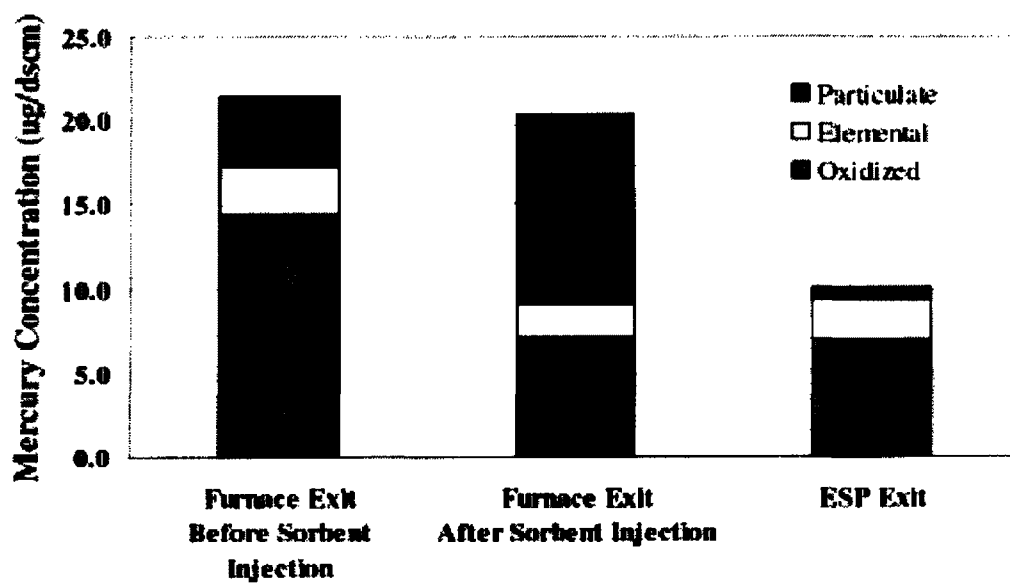
Figure 7-6. Hg removal by limestone injection measured at AECDP test facility burning Ohio bituminous coal and using ESP (Source: Reference 9)

limestone injection of 200 lb/hr; and 3) at the ESP outlet with limestone injection of 200 lb/hr. As shown in Figure 7-6, the total Hg in the flue gas at the ESP inlet with and without limestone injection is about the same. Limestone injection substantially increases the Hg_p, thereby substantially reducing gaseous Hg^{2+}. The Hg_p is then removed by the ESP, providing an overall Hg removal of 53 percent compared to the baseline condition. Reducing the limestone feed rate to 25 lb/hr showed the same Hg partitioning trends observed for 200 lb/hr but with a reduction in total Hg removal. An overall Hg removal of 41 percent compared to the baseline condition was measured. The increased removal provided by limestone injection compared to the baseline appears to be a result of the capture of Hg^{2+} by the CaO particulate (onto or into the particulate phase) and the subsequent removal of the particulate in the ESP. Limestone injection had no apparent effect on the Hg^0.

Table 7-7 presents a summary comparison of limestone sorbent injection test results with the activated carbon injection results from the AECDP Phase III studies (discussed in Section 7.5.3.2). The table shows that limestone sorbent injection at 200 lb/hr achieved an equivalent level of total Hg removal with activated carbon injection. The difference in sorbent-to-Hg ratios for these two tests is about a factor of 15. Based on the test results, the researchers concluded that activated carbon is a more effective sorbent than limestone on a mass basis; however, because the cost of activated carbon typically is an order of magnitude more than the cost for limestone, limestone is more effective on a sorbent cost basis.

7.5.3.4 Multipollutant Sorbent Injection

The EPRI/PSE&G Hudson sorbent injection study discussed in section 7.5.3.2 included measurement of Hg removal by coinjection of activated carbon with calcium-based sorbents for SO_2 control.[13] The calcium-based sorbents tested were sodium bicarbonate and hydrated lime. With the coinjection of either of the calcium-based sorbents, the researchers reported improvement in the adsorption of gaseous Hg by the activated carbon.

A study of the coinjection of a sodium-based sorbent with activated carbon showed that the removal of gaseous Hg by the native fly ash and the activated carbon was impeded when the sodium sesquicarbonate was coinjected. As part of the AECDP Phase III studies using the PCM at the PSCO Comanche Station, tests were conducted to investigate whether any synergistic removal of Hg or impairment of SO_2 removal occurs when injecting both activated carbon for Hg control and sodium sesquicarbonate for SO_2 control into the flue gas and collected in a FF.[17,18] The activated carbon tested was Darco FGD^{TM}.

When no sorbent (carbon or sodium) was injected into the flue gas, the measured Hg removal across the PCM by the native fly ash ranged from 41 to 76 percent at the respective temperatures of 162 °C (324 °F) and 138 °C (280 °F). When activated carbon was injected into the flue gas with no sodium sesquicarbonate, measured Hg removal across the PCM was 74 percent at 162 °C (324 °F). When sodium sesquicarbonate was injected into the flue gas with no activated carbon injection, gaseous Hg removal percentages were in the negative range (i.e., test measurements indicated an increase in Hg concentrations at the PCM outlet compared to the inlet). When both activated carbon and sodium sesquicarbonate were injected into the flue gas,

Table 7-7. Comparison of Hg removals for activated carbon injection versus limestone injection measured at AECDP test facility burning Ohio bituminous coal and using ESP (Source: Reference 9).

Parameter	Sorbent Injected Upstream of ESP		
	Activated Carbon	Limestone	
		0.35 Ca:S mass ratio	0.04 Ca:S mass ratio
Sorbent injection rate	14 lb/hr	200 lb/hr	25 lb/hr
Sorbent:Hg mass ratio	9,000:1	125,000:1	16,000:1
Sorbent injection temperature (^{0}F)	400	2,200	2,200
ESP operating temperature (^{0}F)	345	350	350
Total Hg removal (%)	53	53	41

Hg removal percentages ranged from -104 to 22 percent. The SO$_2$ removal percentages did not appear to be either impeded or improved with the coinjection of the activated carbon.

Based on the limited data, the researchers speculated that the impediment of Hg capture occurred either because of inhibition of the sorbent mechanism or because the addition of sodium increased the level of NO$_2$ in the flue gas. During the sodium sesquicarbonate tests, NO$_2$ in the flue gas increased from 5 to 41 ppmv, with the higher values associated with the higher temperatures tested. If the increase in the NO$_2$ levels was real, researchers are questioning whether NO$_2$ had a negative impact on Hg removal and subsequent Hg desorption in the flue gas. Nitrogen dioxide is a strong oxidizer, which may have stripped Hg from the internal surfaces of the PCM, resulting in higher Hg measured at the outlet than the inlet (thus explaining the negative removal efficiencies for Hg). If this were the case, the effect would diminish over time as the Hg on the walls of the pilot unit came into equilibrium with the flue gas. No tests were run with sufficient time to observe this effect, and credible Hg data were not available in real time.

The negative impact of the sodium sesquicarbonate injection on Hg removal by activated carbon injection is contrary to the results reported for the Hudson Station power plant tests where injecting either sodium bicarbonate or hydrated lime with activated carbon improved the activated carbon's Hg adsorption capability. The Hudson data were taken over a single test day, and the two power plants tested burned different coal types with different fly ash properties and flue gas compositions (eastern bituminous coal at Hudson versus PRB subbituminous at Comanche). Drawing any definite conclusions regarding coinjection of alkaline materials and activated carbon based on these two tests would be conjecture.

7.5.3.5 Noble-metal-based Sorbent in Fixed-bed Configuration

ADA Technologies Inc. (ADA) has patented a sorbent process for Hg control in coal combustion flue gas, trade name Mercu-RE^{TM}. Unlike the dry sorbent injection processes previously discussed, the Mercu-RE^{TM} process is based on the adsorption of the Hg by noble metals in a fixed-bed, regeneration of the sorbents by thermal means, and recovering the desorbed Hg for commercial recycle or disposal.[19, 20] Laboratory testing of the noble-metal sorbent showed that the sorbent captured virtually all of the Hg^0 and mercuric chloride injected into a simulated coal combustion flue gas. During 1999, the noble-metal sorbent was tested for 6 months using a flue gas slipstream from the PSE&G Hudson Station. The acid gases in the flue gas degraded the performance of the noble-metal sorbent. The field data suggested that there are limitations on the commercial application of using noble-metal sorbents for removal of Hg from coal combustion flue gas without upstream acid gas controls installed. Laboratory testing indicated that sorbent capacity can be recovered by scrubbing acid gases from flue gas prior to the sorbent bed. Additional testing is being conducted to determine if noble-metal sorbents can be used effectively on scrubbed flue gas.

7.6 Mercury Control Retrofits for Existing Coal-fired Electric Utility Boilers Using Semi-Dry Absorbers

7.6.1 Retrofit Options

Spray dryer absorber systems are the most common semi-dry scrubbers currently being used at electric utility coal-fired electric utility power plants. With this control technology, a slurry of hydrated or slaked lime is sprayed into an absorber vessel where the flue gas reacts with the drying slurry droplets. The resulting particle-laden dry flue gas then flows to an ESP or an FF where fly ash and SO_2 reaction products are collected. In some cases, water-soluble sodium-based sorbents are used instead of calcium-based sorbents. SDA systems can also provide opportunities for injection of other dry sorbents for Hg or multipollutant control schemes.

In a dry sorbent injection (DSI) system, a sorbent is injected into a flue gas duct upstream of the PM collector. In many cases water is injected upstream of the sorbent injection location to increase flue gas moisture content. This water spray, called spray humidification, reduces the flue gas temperature and increases the sorbent reactivity. DSI systems can also provide opportunities for injection of Hg or multipollutant sorbents. A circulating fluid-bed absorber (CFA) is effectively a "vertical duct absorber" that allow simultaneous gas cooling, sorbent injection and recycle, and gas sorption by flash drying of wet lime reagents. It is believed that CFAs can potentially control Hg emissions at costs lower than those associated with use of spray dryers. With these absorbers, opportunities for use of advanced sorbents appear to be more favorable than for DSI, due to the improved sorbent utilization by re-circulation, recycle, and flash evaporative cooling.

7.6.2 Pilot-scale and Full-scale Research and Development Status

Full-scale tests on eastern bituminous coals (i.e., a 180 MWe boiler with a SDA-FF control system and a 55 MWe boiler with CFA-FF controls) were conducted in September 2000.[21] The EPA Method 101A was used for absorber inlet Hg measurements and the OH Method for the boiler stacks. Both units averaged over 97 percent Hg removal in the respective control systems based on outlet and inlet flue gas measurements. Using the raw coal analysis and the stack OH Method measurements, each system removed about 95 percent of total Hg. Further Hg/multipollutant testing of SDA and CFA units are planned in DOE-EPRI-EPA pilot and field test programs.

7.7 Mercury Control Retrofits for Existing Coal-fired Electric Utility Boilers Using Wet FGD Scrubbers

7.7.1 Retrofit Options

Wet FGD scrubbers are typically installed downstream of an ESP or FF. Removal of PM from the flue gas before it enters the wet scrubber reduces solids in the scrubbing solution and avoids chemistry problems that may be associated with fly ash. In the United States, plants that use wet limestone scrubbers for SO_2 control generally capture more than 90 percent of the Hg^{2+}

in the flue gas entering the scrubber. Consequently these FGD scrubbers may lower Hg emissions by about 20 to more than 80 percent, depending on the speciation of Hg in the inlet flue gas.

Improvements in wet scrubber performance in capturing Hg depend primarily on the oxidation of Hg^0 to Hg^{2+}. This may be accomplished by the injection of appropriate oxidizing agents or installation of fixed oxidizing catalysts to promote oxidization of Hg^0 to soluble species. Oxidation of gaseous Hg^0 to gaseous Hg^{2+} can potentially increase the total Hg removed by wet scrubbing and sorbent systems since gaseous Hg^{2+} is more readily captured by these systems than gaseous Hg^0. Several flue gas additives and scrubbing additives are being developed for this purpose. Flue gas and scrubber additives are also being developed for use in preventing the conversion of absorbed Hg^{2+} to gaseous Hg^0 in wet FGD systems.

An alternative strategy for controlling Hg emissions from wet FGD scrubbing systems is to inject sorbents upstream of the PM control device. In units equipped with FFs this allows for increased Hg capture and oxidization of Hg^0 as the flue gas flows through the filter cake. Increased oxidization afforded by FFs results in increased Hg removal in the downstream scrubber. In FGD units equipped with ESPs, performance gains are limited by sorbent injection and Hg adsorption rates.

7.7.2 Mercury Absorption Theory

Gaseous Hg^0 is insoluble in water and therefore does not absorb in the aqueous slurry of a wet FGD system. Gaseous compounds of Hg^{2+} are water-soluble and do absorb in such slurries. When gaseous compounds of Hg^{2+} are absorbed in the liquid slurry of a wet FGD system, the dissolved species are believed to react with dissolved sulfides to form mercuric sulfide (HgS); the mercuric sulfide precipitates from the liquid solution as a sludge. In the absence of sufficient sulfides in the liquid solution, a competing reaction that reduces/converts dissolved Hg^{2+} to Hg^0 is believed to take place. When this conversion takes place, the newly formed (insoluble) Hg^0 is transferred to the flue gas passing through the wet FGD unit. The transferred Hg^0 increases the concentration of Hg^0 in the flue gas passing through the wet FGD unit (since the incoming Hg^0 is not absorbed) giving rise to a higher concentration of gaseous Hg^0 in the flue gas exiting the wet FGD than entering it. Transition metals in the slurry (originating from the flue gas) are suspected to play an active role in the conversion reaction since they can act as catalysts and/or reactants for reducing oxidized species

7.7.3 Pilot-scale and Full-scale Research and Development Status

7.7.3.1 Oxidation Additives

As part of the AECDP Phase III studies, tests were conducted to investigate two potential chemical additives for controlling the conversion of oxidized Hg to the elemental form, and enhancing the control of Hg in a pilot-scale wet FGD system.[9] The first additive was gaseous H_2S. The selection of H_2S as a potential additive was based on the possibility that a sulfide-donating species could assist in capturing Hg^{2+}. A H_2S gas stream at a concentration of about 2

ppm was injected into the flue gas entering the scrubber. The Hg concentrations of gaseous Hg^{2+} and gaseous Hg^0 measured at the wet scrubber inlet and outlet for the baseline and H_2S injection tests are shown in Figure 7-7. Gaseous Hg removal by the wet scrubber increased with the addition of H_2S (at about 2 ppm) from 46 to 71 percent. This increase was attributed mainly to a decrease in the conversion of Hg^{2+} to gaseous Hg^0.

The second additive tested was ethylenediaminetetraacetic acid (abbreviated EDTA). This chemical was selected because EDTA is strong chelating agent. Chelating agents react with metallic ions to form soluble nonionic compounds. Because, transition metals may act as a catalyst in the conversion of Hg^{2+} to gaseous Hg^0 in wet FGD scrubbers, their chemical binding may reduce the conversion. For the test, EDTA was added to the scrubbing slurry. The Hg concentration of gaseous Hg^{2+} and gaseous Hg^0 measured at the wet scrubber inlet and outlet for the ESP baseline and EDTA additive tests is shown in Figure 7-8. The total Hg removal increased to 73 percent with the addition of EDTA. Under a new cooperative agreement with DOE/NERL, McDermott Technologies, Inc. is conducting a full-scale test program of using scrubber additives to achieve increased Hg removal at two power plants burning high-sulfur Ohio bituminous coal: 1) Michigan South Central Power Agency's (MSCPA) 55-MWe Endicott Station located in Litchfield, MI, and 2) Cinergy's 1300-MWe Zimmer Station located near Cincinnati, OH.[22]

7.7.3.2 Mercury Oxidation Catalysts

Under a DOE/NETL cooperative agreement, laboratory and field tests were conducted to investigate catalytic oxidation of gaseous Hg^0 in coal-fired electric utility boiler flue gas.[23] The project tested the actual rate to convert gaseous Hg^0 to a soluble form using different candidate catalysts under simulated and actual coal combustion flue gas conditions. The results of the bench-scale studies are discussed in Chapter 5. Additional extended tests with the most-active catalysts and fly ash were conducted in the field to assess their adsorption and/or oxidation of Hg in an actual coal-fired boiler flue gas.[24] These tests were conducted in a fixed-catalyst-bed test rig using a flue gas slipstream from a electric utility boiler firing a Texas lignite. Total Hg concentrations in the flue gas slipstream varied from 7 to 35 $\mu g/Nm^3$, with the gaseous Hg^0 concentrations varying from 4 to 18 $\mu g/Nm^3$. The inlet gaseous Hg^{2+} also was variable, ranging from 30 to 80 percent of the total, and the concentrations of SO_2 and NO_X varied considerably during the testing period. The catalysts and fly ash were exposed to flue over periods ranging from 3,480 to 3,490 hours. Table 7-8 presents the oxidation results over the 5-month-plus period of testing. For the values of the catalyst field measurements shown in the table, the Hg^0 oxidation measured across the sand "blank" was subtracted from the actual measured Hg^0 oxidation for each catalyst. In general, the field test results indicate that while the initial Hg^0 oxidation percentages achieved by the catalysts matched the percentages measured in the laboratory tests, the metal-based and some carbon-based catalysts were deactivated after a relatively short time exposure to the actual coal combustion flue gas. The researchers identified sulfur trioxide and selenium (or selenium compounds) as possible flue gas constituents that rapidly deactivate the iron-based and other metal catalysts. Additional bench-scale laboratory tests conducted as part of the study indicate that regeneration of spent catalysts should be possible.
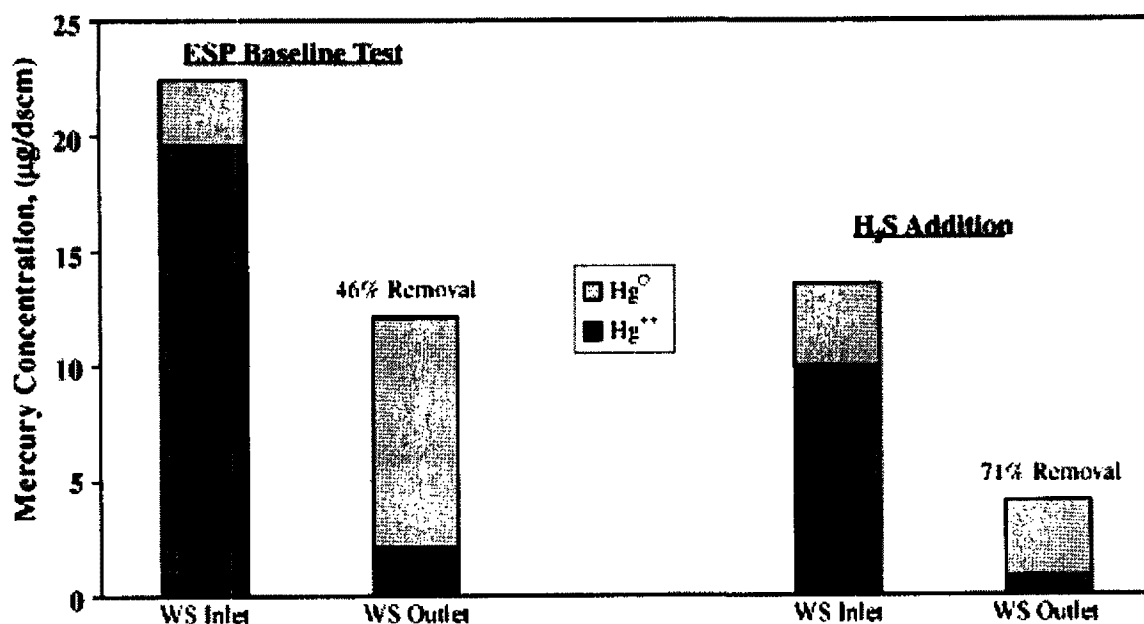
7-33

Figure 7-7. Effect of using H₂S as an oxidation additive on wet FGD scrubber Hg removal measured at AECDP test facility burning Ohio bituminous coal (source: Reference 9).
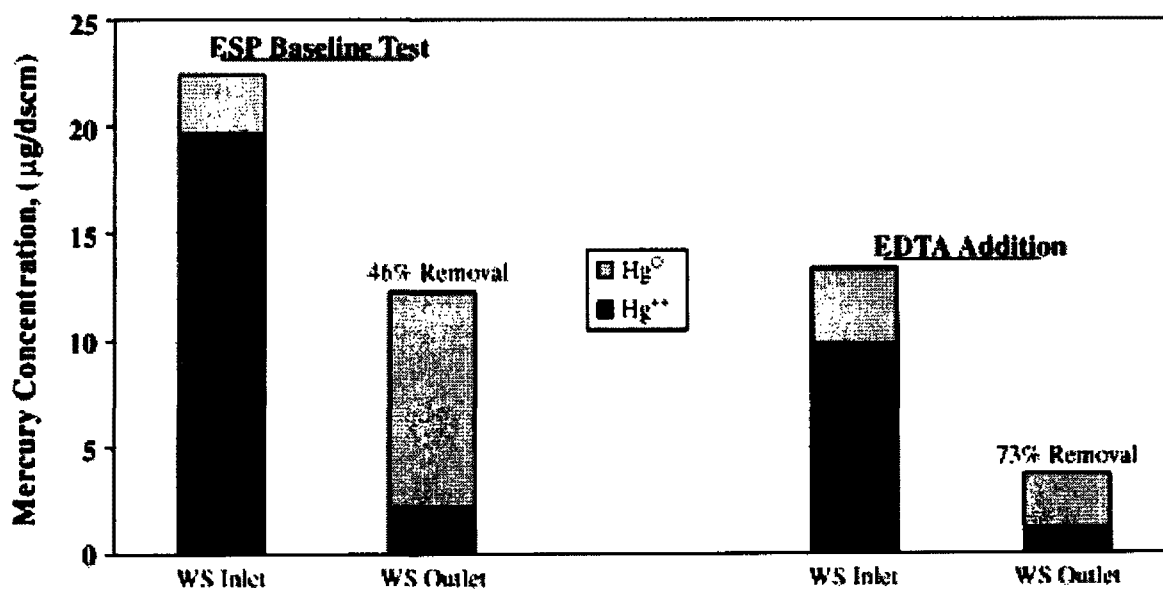
Figure 7-8. Effect of using EDTA as an oxidation additive on wet FGD scrubber Hg removal measured at AECDP test facility burning Ohio bituminous coal (source: Reference 9).

Table 7-8. Comparison of field test results using flue gas from electric utility boiler firing Texas lignite versus bench-scale results using simulated flue gas for selected candidate Hg oxidation catalysts (Source: adapted from Reference 24).

Test Parameters	Laboratory Bench-Scale Results	Field Test Results [a,b]				
		at hour 24	at hour 1,000	at hour 2,400	at hour 3,055	at hour 3,477
Catalyst Type	Percent of Hg^0 Oxidized Across Catalyst Bed					
Sand (non-catalyst blank)	3 %	3.3 - 8.1%	7 %	9 – 12 %	23 %	0 %
Activated carbon #1 (1ˢᵗ Bed)	100 %	100 %	66 %	45 %	0 %	89 %
Activated carbon #1(2ⁿᵈ Bed)	100 %	100 %	81 %	42 – 59 %	0 %	0 %
Activated carbon #2	96 %	97 %	not recorded	76 %	0 %	76 %
Pd#1	91 %	90 %	not recorded	82 %	0 %	0 %
SB #5 (fly ash)	4/70 % [c]	100 %	36 %	82 %	73 %	0 %
Test Conditions						
Catalyst Bed Temp. °C (°F)	149 (300)	149 (300)	149 (300)	149 (300)	104 (220)	149 (300)
Inlet Hg^0 (μg/Nm^3)	50	3.7 - 16.2	5.4	8.3 - 9.3	17.8	3.7
Total Hg (μg/Nm^3)	50	7.0 - 26.1	9.8	15 - 27	31 - 35	27

[a] All catalyst oxidation values corrected for the sand blank oxidation values.
[b] Number of hours passing flue gas through the catalyst materials
[c] Laboratory tests using SB#5 (fly ash) were conducted in a simulated flue gas with HCl (70 percent oxidation with 1 ppmv of HCl) and without HCl (4 percent oxidation).

A pilot-scale field test program is currently being conducted under a DOE/NETL cooperative agreement to obtain addition data on the potential commercial application of Hg oxidation catalysts to enhance Hg capture by an existing wet FGD system downstream of high-efficiency ESP.[25] This study is testing selected catalysts previously identified as being effective by the DOE-sponsored studies in a commercial form in larger pilot-scale units for longer periods. The DOE/NETL is working in partnership with URS Group, Inc., EPRI, and two electric utility companies, Great River Energy and City Public Service of San Antonio, TX. The first test site is the Great River Energy Coal Creek Station, which fires North Dakota lignite. The second site the City Public Service of San Antonio's J.K. Spruce Plant, which fires a PRB subbituminous coal. The pilot-scale tests will continue for over a year at each of two sites.

7.7.3.3 Wet FGD Scrubber Design and Operating Modifications

Several studies of pilot-scale wet FGD scrubbers suggest that modifying the operation and design of the scrubber unit as well as the upstream ESP may improve the capture of gaseous Hg^{2+} and reduce the conversion of absorbed Hg^{2+} to Hg^0. Specifically, these studies have found that the liquid-to-gas ratio and tower design of a wet FGD unit affect the absorption of gaseous Hg^{2+}, while the oxidation air influences the conversion of absorbed Hg^{2+}. The operating voltage of ESPs upstream of wet FGD systems has also been shown to influence the latter. The remainder of this section summarizes these findings.

Scrubber Liquid-to-gas Ratio. The liquid-to-gas ratio (L/G ratio) of a wet FGD system is dictated by the desired removal efficiency to control SO_2 emissions. The selected L/G ratio also can impact the removal efficiency of gaseous Hg^{2+}. In general, high efficiency FGD systems (95+ percent SO_2 removal) are designed with L/G ratios in the range of 120 to 150 gallons (gal.) of aqueous slurry per 1,000 actual cubic feet (acf) of gas flow. In two separate pilot-scale studies[26] increasing the L/G ratio from approximately 40 to 125 gal./1,000 acf increased the removal efficiency of gaseous Hg^{2+} from 90 to 99 percent. However, increasing the L/G ratio did not affect the removal of gaseous Hg^0, which was close to zero percent. Similar studies were conducted prior to these studies and produced similar findings.[23,27]

Scrubber Tower Design. Most of the existing wet FGD systems in the United States use either an open-spray tower or tray tower design. In one study of wet FGD systems, where the composition of the flue gas was mostly gaseous Hg^{2+}, the tray tower design removed from 85 to 95 percent of the total Hg, whereas the open spray tower design removed from 70 to 85 percent of the total Hg.[28] This study suggests that a tray tower design is more effective in removing gaseous Hg^{2+} from boiler flue gas than an open spray tower design for a given SO_2 removal level.

Scrubber Oxidation Air. When SO_2 is absorbed in the scrubbing slurry of a wet FGD system, the dissolved SO_2 reacts with lime or limestone to form insoluble sulfate/sulfite sludge; the sulfate reaction consumes oxygen, which is present in the flue gas. Some wet FGD systems add air to the system to increase the amount of oxygen available for the reaction; the additional oxygen accelerates the reaction between SO_2 and lime or limestone.

The effect of oxidation air on FGD Hg removal was investigated as part of the AECDP Phase III studies by conducting test runs at baseline, intermediate and low levels of oxidation air.[9] Figure 7-9 compares wet scrubber inlet and outlet Hg concentration measured for the base case and the runs at a mid- and low-level of oxidation air. The bars include the elemental and oxidized fractions of the total gaseous Hg. The relative amounts of Hg^0 at the inlet and outlet did not change significantly for the three tests. However, the amount of absorbed Hg^{2+} converted to Hg^0 decreased as the oxidation air decreased. This point is further illustrated in Figure 7-10 that shows only the gaseous Hg^0 for the three tests. For the baseline test, gaseous Hg^0 increased by 265 percent across the wet scrubber. This improved to a 76 percent increase for the second test, and only two percent for the low oxidation air test. Total gaseous-phase Hg removal improved from 46 percent for the base case to 80 percent for the low oxidation air case. These normalized oxidation air stoichiometry results show a strong relationship between oxidation air and wet scrubber Hg removal for a wet FGD system. The researchers of this study hypothesize that low oxidation air must somehow inhibit the reduction of absorbed Hg^{2+}, or provide a species needed to sequester the absorbed Hg^{2+} in the slurry. The researchers also note that the level to which the scrubber oxidation air can be reduced at a given coal-fired electric utility power plant is highly site-specific specific and depends on several factors such as scaling considerations and gypsum purity requirements.

Voltage of ESP Upstream of Scrubber. The effect of ESP operating power on wet scrubber Hg removal was investigated as part of the AECDP Phase III studies.[9] Concentrations of gaseous Hg^{2+} and gaseous Hg^0 were measured at the inlet and outlet of the wet FGD system for three different ESP operating conditions. For the first operating condition (the baseline operation), the pilot-scale ESP was operated with three of its four fields in service, and the power was set to maintain an outlet particulate loading of 0.02 to 0.03 lb/MBtu (below the PM limit of the New Source Performance Standard for utility boilers). In the second operating condition, the ESP voltage was increased by 60 percent above the baseline voltage. In the third operating condition, the ESP power was turned off and an FF was used for PM control upstream of the wet FGD system. For all three operating conditions, triplicate measurements of Hg were made at the inlet and outlet of the pilot-scale wet FGD system.

Figure 7-11 compares the concentrations of gaseous Hg^{2+} and gaseous Hg^0 measured at the inlet and outlet of the wet FGD system for the three different ESP operating conditions. Since the Hg measurements were taken downstream of the ESP and FF, very little Hg_p was measured; thus, Hg_p measurements are not shown in the Figure 7-11. Figure 7-12 presents only gaseous Hg^0 for the same three ESP conditions as those in Figure 7-11. The figures clearly show that the operating voltage of the ESP has a direct, negative impact on the wet scrubber Hg control performance. The proportion of gaseous Hg^{2+} and gaseous Hg^0 at the wet scrubber inlet is the same for all three tests. However, for the high-power test, the amount of gaseous Hg^0 significantly increased across the wet scrubber. The gaseous Hg^0 remains constant for the no-power test, which is the observed behavior when the scrubber is preceded by the FF. This indicates that the electric field affects some component of the flue gas, which, in turn, has a negative impact on wet scrubber chemistry.
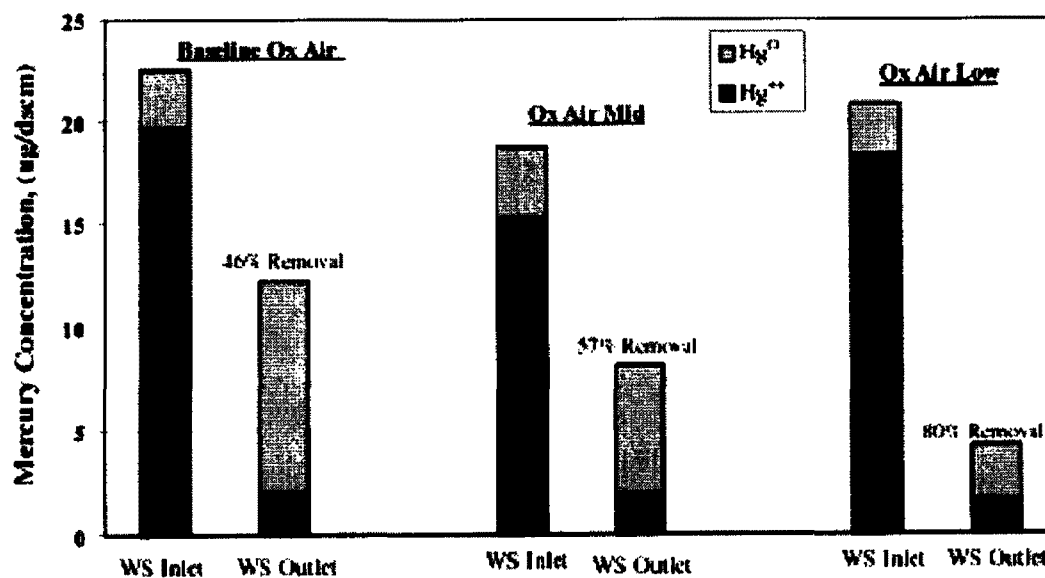
Figure 7-9. Effect of oxidation air on wet FGD scrubber Hg removal as measured at AECDP test facility burning Ohio bituminous coal (source: Reference 9).
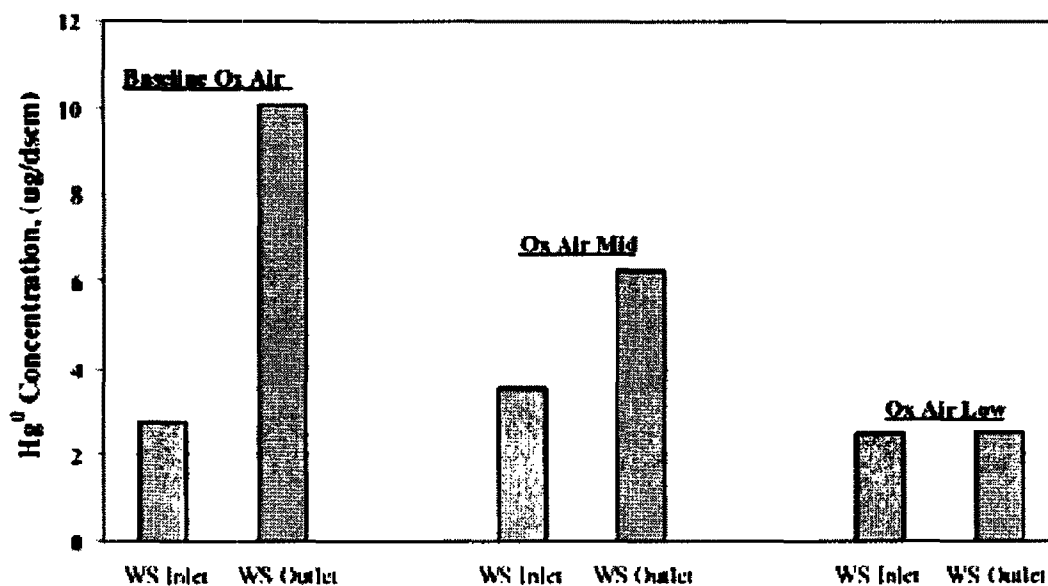
Figure 7-10. Effect of oxidation air on Hg^0 in wet FGD scrubber flue gas as measured at AECDP test facility burning Ohio bituminous coal (source: Reference 9) .
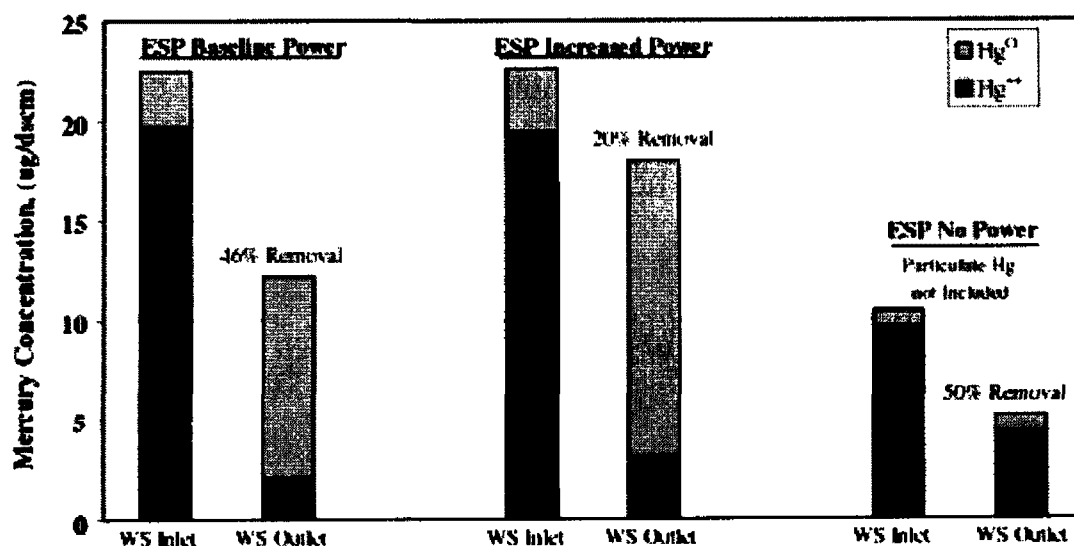
Figure 7-11. Effect of ESP operating voltage on wet FGD scrubber Hg removal as measured at AECDP test facility burning Ohio bituminous coal (source: Reference 9).
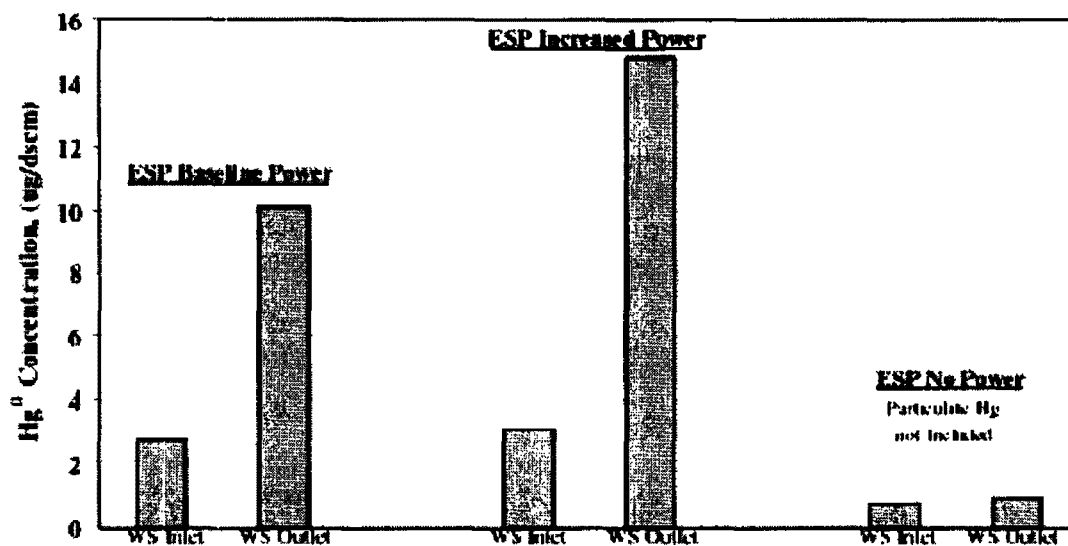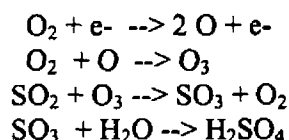
Figure 7-12. Effect of ESP operating voltage on Hg^0 in wet FGD scrubber flue gas as measured at AECDP test facility burning Ohio bituminous coal (Source: Reference 9).
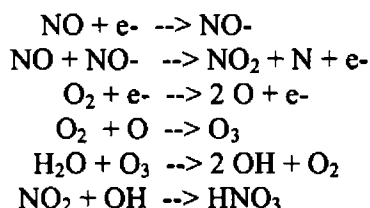
7.8 Multipollutant Control Technologies

This section presents a summary of control systems being commercially offered or developed for multipollutant emissions control. The current status of many systems is based upon reports that targeted one or two pollutants. A caution here is that, when evaluating the best system for a specific application, it is important to consider both: 1) how a given system affects the emissions of all pollutants, and 2) how that system affects the long-term performance, operation, and cost of other downstream systems, including ductwork, heat exchangers, stacks, and other emission control equipment. To date no comprehensive long-term evaluations of the multipollutant systems described below have been conducted.

7.8.1 Corona Discharge

Generation of an intense corona discharge (ionization of air by a high voltage electrical discharge) in the boiler flue gas upstream of an ESP and wet scrubber is being investigated with respect to improving PM control by oxidation of a portion of the entering SO_2 to SO_3.[29] The corona discharge creates oxygen-carrying reactive species, which, in turn, oxidize the Hg^0 in the flue gas (i.e., convert Hg^0 to Hg^{2+}). The increased SO_3 both improves ESP collection of PM and acts to convert Hg^0 to Hg^{2+} which may then be captured by an alkaline FGD scrubber downstream. Representative reactions for SO_2 oxidation by corona discharge include:

$$O_2 + e\text{-} \text{ --> } 2\,O + e\text{-}$$
$$O_2 + O \text{ --> } O_3$$
$$SO_2 + O_3 \text{ --> } SO_3 + O_2$$
$$SO_3 + H_2O \text{ --> } H_2SO_4$$

Similarly, for NO,

$$NO + e\text{-} \text{ --> } NO\text{-}$$
$$NO + NO\text{-} \text{ --> } NO_2 + N + e\text{-}$$
$$O_2 + e\text{-} \text{ --> } 2\,O + e\text{-}$$
$$O_2 + O \text{ --> } O_3$$
$$H_2O + O_3 \text{ --> } 2\,OH + O_2$$
$$NO_2 + OH \text{ --> } HNO_3$$

Environmental Elements Corporation is developing a process based on corona discharge that recovers the oxidized sulfur and nitrogen compounds as marketable sulfuric and nitric acids in wet ESP sections and or/absorbers. A slipstream pilot plant has been installed at Alabama Power Miller Plant (Unit 3). Initial tests indicated 80 percent Hg removal and complete oxidation of Hg^0 at 10 and 20 W/cfm, respectively.

Powerspan Corporation is developing a single, integrated pollution control device that uses a proprietary technology called Electro-Catalytic Oxidation™ or ECO™ to control SO_2, NO_X, Hg, and fine PM in coal-fired boiler flue gas.[30] The first stage of the device uses a dielectric barrier discharge to convert NO_X and SO_2 to acids and to oxidize Hg^0. A condensing,

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wet ESP is used to collect acid mists, fine PM, and Hg. The effluent from the wet ESP is processed to produce salable byproducts (e.g., concentrated acids, gypsum for wallboard manufacture, and ammonia for fertilizer). Before entering the ECO™ unit, flue gas passes through a conventional ESP to remove the majority of the ash particles. In partnership with FirstEnergy Corporation, Powerspan has built a pilot-scale ECO test facility at FirstEnergy's R.E. Burger Plant near Shadyside, OH.[31] This test facility processes a slipstream of flue gas from a 150-MW boiler unit burning high-sulfur eastern bituminous coal. The test results showed a Hg emission reduction of 68 percent. Under a new DOE cooperative agreement, Powerspan and FirstEnergy are conducting a research project using the ECO™ pilot test facility to optimize the technology's Hg removal capability while maintaining the performance of the ECO™ unit for removal of nitrogen oxides, sulfur dioxide, and fine PM.[32] In addition, Powerspan and FirstEnergy are currently constructing an $11.9 million ECO commercial demonstration unit at FirstEnergy's Eastlake Plant near Cleveland, OH. The project is being cofunded by a $3.5 million grant from the Ohio Coal Development Office.
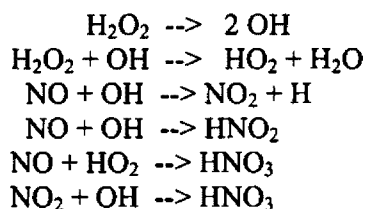
7.8.2 Electron Beam Irradiation

The E-Beam Process has been offered commercially since the 1980s and is now used in Japan and China.[33] The chemical reactions are identical to corona discharge, except that the power source is a battery of irradiating electron "guns" and the oxidation products then enter a semi-dry absorption system with ammonia reagent and are converted to ammonium sulfate and nitrate salts suitable for use as a fertilizer. It is presumed that the Hg solids would also be present in the fertilizer as contaminants. The polishing reactions for E-Beam are:

$$NH_4OH + HNO_3 \longrightarrow NH_4NO_3 + H_2O$$

$$2\ NH_4OH + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2\ H_2O$$
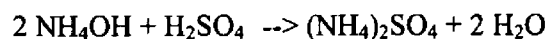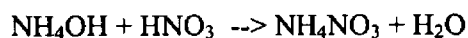
7.8.3 Oxidant Injection in Flue Gas

A number of proposed schemes would add an oxidant such as chlorine, peroxide, or ozone to the flue gas upstream of an absorber. Again the reaction products would be similar to corona or electron beam, and the recovered products could range from weak acids to sulfate/nitrate fertilizers or lower-value soil amendments; trace Hg salts would likely be contained within these products. An example of ozone injection is the Lo-TOx.[34] The ISCA is a chlorine-based system producing byproduct acids. Hydrogen peroxide and other chlorine-based oxidation schemes have been investigated but have not been proposed for commercial use.[35] Typical oxidation reactions are:

Hydrogen Peroxide: Ozone:

$$H_2O_2 \rightarrow 2\,OH$$
$$H_2O_2 + OH \rightarrow HO_2 + H_2O$$
$$NO + OH \rightarrow NO_2 + H$$
$$NO + OH \rightarrow HNO_2$$
$$NO + HO_2 \rightarrow HNO_3$$
$$NO_2 + OH \rightarrow HNO_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$2\,NO_2 + O_3 \rightarrow N_2O_5 + O_2$$
$$SO_2 + O_3 \rightarrow SO_3 + O_2$$
$$N_2O_5 + H_2O \rightarrow 2\,HNO_3$$
$$SO_2 + N_2O_5 \rightarrow SO_3 + 2\,NO_2$$
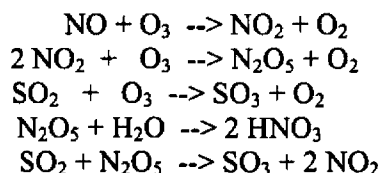
7.8.4 Catalytic Oxidation

Catalysts can be employed in higher temperature regimes to speed up oxidation of SO_2 and NO_X, but not Hg^0. However, increasing the SO_3 and $NO_2/N_2O_4/N_2O_5$ concentrations will likely result in increased conversion of Hg^0 to Hg^{2+} downstream, as acid gases and PM are removed in control devices. Lower temperature catalysis (less than 500 °F) would likely directly oxidize Hg^0 to Hg^{2+}. Thus, any number of catalytic oxidation schemes that produce byproduct acids would likely remove a substantial portion of total Hg with the acids as a Hg salt -- chloride, sulfate, or nitrate. A number of catalytic technologies are under commercial development; an example of this class - SNOx - has been evaluated under DOE's Clean Coal Technology Program. At least one current DOE-sponsored project is examining the effectiveness of an oxidation catalyst upstream of wet FGD scrubber to decrease total Hg emissions.[36]

7.8.5 Oxidant Addition to Scrubber

One current DOE test program is measuring the effectiveness of a Hg oxidant added to the liquor of commercial wet scrubbers. The EPA is sponsoring similar research, which will culminate in a pilot-scale slipstream evaluation of oxidant addition.[37] Another DOE-sponsored project is investigating the use of oxidated-lime and lime-silica sorbents to a semi-dry circulating bed absorber for combined SO_2, NO_X, and Hg control.[38] Other combinations of sorbents injected upstream of an efficient PM collector such as the EPRI Toxecon™ process may be used for a multiple pollutant control strategy centered around PM control.

7.8.6 Catalytic Fabric Filters

Some pilot-scale efforts have reported substantial oxidation of Hg within a FF, presumably by catalytic action of certain fibers or residual fly ash imbedded within the fabric.[39] Several investigations are being made into woven carbon fibers or other catalytic materials integrated into the bag filters for a combined Hg/PM control device.

7.8.7 Carbon-fiber FFs and ESPs

Carbon-fiber FFs are commercially available. Carbon-fiber ESP plates are being investigated under a study sponsored the Ohio Coal Development Office. While combined Hg/PM control using this approach would be initially effective, the Hg capacity would be

realized in a relatively short time period; therefore, means of regenerating the carbon active sites without replacing the fabric filter bags or ESP plates have to be devised.

7.9 Summary

A practical approach to controlling Hg emissions at existing utility plants is to minimize capital costs by adapting or retrofitting existing equipment to capture Hg. Potential retrofit options for control of Hg were investigated for units that currently use the following post combustion emission control methods: (1) ESPs or FFs for control of PM, (2) dry FGD scrubbers for control of PM and SO_2, and (3) wet FGD scrubbers for the control of PM and SO_2.

Hg Control Retrofits for ESP and FF

ESPs and FFs are either cold-side or hot-side devices. Hot-side devices are installed upstream of the air heater while cold-side devices are installed downstream. Flue gas temperatures in hot-side devices typically range from 350 to 450 °C while cold-side devices typically operate at temperatures ranging from 140 to 160 °C. Based on current information, it appears that little Hg can be captured in hot-side ESPs or FFs.

Least-cost retrofit options for the control of Hg emissions from units with ESP or FF are believed to include:

- Injection of a sorbent upstream of the ESP or FF. Cooling of the stack gas or modifications to the ducting may be needed to keep sorbent requirements at acceptable levels.

- Injection of a sorbent between the ESP and a pulsejet FF retrofitted downstream of the ESP. This approach will increase capital costs but reduce sorbent costs.

- Installation of a semi-dry CFA upstream of an existing ESP used in conjunction with sorbent injection. The CFA recirculates both fly ash and sorbent to create an entrained bed with a large number of reaction sites. This leads to higher sorbent utilization and enhanced fly ash capture of Hg and other pollutants.

Units equipped with a FF require less sorbent than units equipped with an ESP. ESP systems depend on in-flight adsorption of Hg by entrained fly ash or sorbent particles. The FFs obtain in-flight capture and capture as the flue gas passes through the FF.

In general, the successful application of cost-effective sorbent injection technologies for ESP and FF units will depend on: (1) the development of lower cost and/or higher performing sorbents, and (2) appropriate modifications to the operating conditions or equipment being currently used to control emission of PM, NO_x, and SO_2.

Mercury Control Retrofits for Wet FGD Scrubbers

Wet FGD scrubbers are typically installed downstream of an ESP or FF. Wet limestone FGD scrubbers are the most commonly used scrubbers on coal-fired electric utility boilers. These FGD units generally capture more than 90 percent of the Hg^{2+} in the flue gas entering the scrubber. Consequently, existing wet FGD scrubbers may lower Hg emissions by about 20 percent to more than 80 percent, depending on the speciation of Hg in the inlet flue gas.

Improvements in wet scrubber performance in capturing mercury depend primarily on the oxidation of $Hg°$ to Hg^{2+}. This may be accomplished by 1) the injection of appropriate oxidizing agents, or 2) the installation of fixed oxidizing catalysts upstream of the scrubber to promote oxidization of Hg^0 to soluble species.

An alternative strategy for controlling Hg emissions from wet FGD scrubbers is to inject sorbents upstream of the PM control device. In wet FGD systems equipped with ESPs, performance gains are limited by the in-flight oxidization of Hg^0, and the in-flight capture of Hg^{2+} and $Hg°$. In systems equipped with FFs, increased oxidization and capture of Hg can be achieved as the flue gas flows through the FF. Increased oxidization of $Hg°$ in the FF will result in increased Hg removal in the downstream scrubber.

Mercury Control Retrofits for Semi-dry FGD Systems

SDA systems that use calcium-based sorbents are the most common dry FGD systems used in the utility industry. An aqueous slurry containing the sorbent is sprayed into an absorber vessel where the flue gas reacts with the drying slurry droplets. The resulting, particle-laden, dry flue gas then flows to an ESP or a FF where fly ash and SO_2 reaction products are collected.

CFAs are "vertical duct absorbers" that allow simultaneous gas cooling, sorbent injection and recycle, and gas absorption by flash drying of wet lime reagents. It is believed that CFAs can potentially control Hg emissions at costs lower than those associated with use of spray dryers.

Dry FGD systems are already equipped to control emissions of SO_2 and PM. The modification of these units by the use of appropriate sorbents for the capture of Hg and other air toxics is considered to be the easiest retrofit problem to solve.

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Chapter 8
Cost Evaluation of Retrofit Mercury Controls for
Coal-fired Electric Utility Boilers

8.1 Introduction

A practical approach to controlling Hg emissions at existing coal-fired electric utility power plants is to minimize control costs by adapting or retrofitting existing air pollution control equipment to capture Hg. As discussed in Chapter 3, coal-fired electric utility power plants currently use a wide variety of technologies to control the emission of criteria air pollutants (e.g., PM, SO_2, and NO_x emissions). Generally, the air pollution control methods and configurations used for a given coal-fired electric utility boiler depend on the type of coal burned, age and size of the boiler unit, and the power plant location.

Potential retrofit technologies for the control of Hg emissions from existing coal-fired electric utility boilers are discussed in Chapter 7. Control technologies using injection of powdered activated carbon (PAC) into the flue gas have been applied successfully on municipal waste combustors to reduce Hg emissions. Pilot-scale testing indicates that these technologies offer the potential to provide significant Hg removal from the flue gas of coal-fired electric utility boilers. This chapter discusses an initial evaluation of annual Hg control costs based on the retrofit of PAC injection-based control technologies to a series of model plant scenarios (not actual full-scale applications) representative of the coal-fired electric utility power plants operating in the United States. It is worth noting that, while performance and cost of only PAC-related technologies were evaluated, other non-PAC-based Hg control technologies are expected to be available in the future. For example, enhanced Hg oxidation using oxidants or catalysts followed by wet scrubbing may become available. Also, the role of an SCR-FGD combination may become more cost effective and attractive. The information presented in this chapter was used in the EPA's recent regulatory determination regarding Hg and other air toxics.

The cost estimates of the PAC injection-based Hg control technologies presented in this chapter are based on relatively few data points from pilot-scale tests and, therefore, are considered to be preliminary estimates. As discussed in Section 8.2, factors that are known to affect adsorption of Hg on activated carbon include speciation of Hg in the flue gas, flue gas and ash characteristics, and the degree of mixing between the flue gas and activated carbon. The effects of these factors may not be entirely accounted for in the relatively few pilot-scale data points available for this evaluation. Successful testing of a control approach at small pilot plants

does not necessarily guarantee successful implementation of the approach in full-scale systems. Temporary wall effects at small scale will generally not be realized at full scale. Appropriate mass transfer associated with mixing and the number, placement, and design of reagent and sorbent injection equipment may also need to be determined. Further, potential longer-term problems such as deposits, fouling, and corrosion of the control equipment are frequently not addressed by pilot-scale tests because of shorter-term, non-continuous operation. Ongoing research is expected to address these issues to improve the potential of using sorbents for Hg control in coal-fired boilers.

Coal-fired electric utility power plants are currently required to reduce emissions of NO_x, SO_2, and PM. The EPA has also revised the National Ambient Air Quality Standards (NAAQS) for PM and ozone. These revisions may require electric utility sources to adopt control measures aimed at reducing concentrations of fine PM in the atmosphere. In addition, as discussed above, the EPA has recently expressed its intent to regulate Hg emissions from these sources. Adding to these environmental requirements and activities, Congress is introducing bills aimed at developing legislation requiring simultaneous reductions in emissions of multiple emissions. Improved sorbents and other methods for controlling Hg and multipollutant (e.g., Hg and NO_x) emissions are also under development by DOE, EPA, EPRI, the electric industry, and equipment vendors. These development activities include large demonstration programs that are underway under the sponsorship of DOE/NETL and industrial participants. The demonstrations are focused on full-scale testing of powdered activated carbon injection and modifications to flue gas cleaning systems aimed at improving Hg capture.

It is expected that, when the research and development activities being conducted by DOE, EPA, EPRI, and others are completed, there will be many more control options for Hg and multipollutants with attendant benefits in improved cost effectiveness.

8.2 Cost Estimate Methodology

The methodology used for the Hg control cost evaluation consists of the following six steps:

- First step, a set of model plant and Hg control scenarios was defined;
- Second step, cost estimates were made for selected scenarios using a cost model developed collaboratively by the DOE and the EPA;
- Third step, the cost impacts of selected variables were examined;
- Fourth step, the cost model results were used to develop indications of costs for those model plant scenarios for which data on PAC use are currently not available;
- Fifth step, potential future improvements in the cost estimates were examined; and
- Sixth step, in order to place Hg control costs in perspective, these costs were compared to current costs of applying NO_x controls to coal-fired electric utility boilers.

8.2.1 Mercury Control Technologies Evaluated

The cost evaluation is based primarily on the application of potential PAC injection-based control technologies. These technologies were selected because sufficient pilot-scale data are available to make reasonable estimates of the Hg capture efficiency of the technologies. Mercury capture performance data are currently not available for other potential Hg control technologies (e.g., use of catalysts to oxidize Hg^0 in wet scrubber systems) that conceivably could be applied to coal-fired electric utility boilers at this time. Table 8-1 lists the PAC injection-based Hg control technologies defined for this study. Pilot-scale applications of most of these technologies have been reported in published literature.[1,2,3,4,5,6]

PAC injection-based retrofit control technologies ESP-1, ESP-3, ESP-4, ESP-6, and ESP-7 are applicable to coal-fired electric utility boilers equipped with a cold-side ESP.

In ESP-1, PAC is injected between the air preheater and the cold-side ESP (CS-ESP, i.e., an ESP located downstream of the boiler's air preheater). This configuration is the simplest to install, requiring only PAC injection equipment upstream of the ESP. Activated carbon consumption is expected to be relatively high because the high temperature of the flue gas would inhibit adsorption of Hg onto PAC.

In ESP-3, PAC is injected downstream of the CS-ESP and is collected using a polishing fabric filter (PFF). This technology permits recycling of the PAC sorbent to increase its utilization. Typically, this recycling is achieved by transferring a portion of used sorbent from the PM control device (e.g., PFF) to the sorbent injection location using a chain or a belt conveyor, mixing the used sorbent with fresh sorbent, and injecting the resulting sorbent mixture into the flue gas. Further, the technology provides a contact bed (i.e., filter cake on PFF) for increased adsorption of Hg.

ESP-4 is similar to ESP-1, but adds spray cooling (SC) upstream of the PAC injection location. Cooling the flue gas aids adsorption and reduces PAC injection requirements. However, adding too much water to the flue gas could cause acid condensation, which would corrode ductwork and equipment. In the cost modeling conducted for this work, flue-gas temperatures are not allowed to reach the acid dewpoint (i.e., the temperature at which the acidic components in the flue gas would condense).

ESP-6 is similar to ESP-3, but provides SC upstream of PAC injection. Cooling the flue gas aids adsorption and reduces PAC injection requirements. Also, use of PFF permits sorbent recycling, leading to improved sorbent utilization.

ESP-7 is the same as ESP-6 except for the addition of a second sorbent, lime. In addition to Hg removal, this technology would remove acid gases from the flue gas. Pilot-scale results have indicated that this may result in significant lowering of PAC injection rates.

Table 8-1. Mercury control technologies.

Existing Post-combustion Control Devices Used for Coal-fired Boiler Unit [a,b]	Mercury Control Technologies [b]	
	Identification Code	Additional Control Equipment Installed
CS-ESP	ESP-1	PAC injection
	ESP-3	PAC injection + PFF
	ESP-4	SC + PAC injection
	ESP-6	SC + PAC injection + PFF
	ESP-7	SC + PAC injection + lime injection + PFF
HS-ESP	HESP-1	SC + PAC injection + PFF
FF	FF-1	PAC injection
	FF-2	SC + PAC injection
SDA + FF	SD/FF-1	PAC injection
SDA + CS-ESP	SD/ESP-1	PAC injection

(a) Existing controls may include wet FGD scrubber system or post-combustion NO_x controls such as selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR).
(b) CS-ESP = cold-side electrostatic precipitator
   HS-ESP = hot-side electrostatic precipitator
   FF = fabric filter
   PAC = powdered activated carbon
   PFF = polishing fabric filter
   SC = spray cooling
   SDA = spray dryer adsorber system

In HESP-1, SC, PAC injection, and a PFF are added downstream from a hot-side ESP (an ESP located upstream of the boiler's air preheater). This configuration is identical to ESP-6, only the location of the ESP is different.

Two PAC injection-based retrofit controls are applicable to coal-fired electric utility boilers equipped with a fabric filter. FF-1 is the fabric filter analogue of ESP-1. However, Hg collection should be better than that in ESP-1 because the FF provides added residence time and a contact bed (filter cake on the bags) for increased adsorption of Hg. FF-2 is the fabric filter analogue of ESP-4; spray cooling and PAC injection are installed upstream of an existing fabric filter. As with ESP-4, cooling reduces PAC requirements, which reduces total annual PAC costs for FF-2 compared to FF-1.

Finally, use of a PAC injection in combination with an existing spray dryer adsorber system for SO_2 control was evaluated. In SD/FF-1, PAC is injected into the flue gas of a boiler that uses a SDA + FF combination. In this configuration, only PAC injection equipment is added to the existing air pollution control system, with the SDA providing flue gas cooling. SD/ESP-1 is similar to SD/FF-1 except that an ESP is used in place of an FF for particulate collection. The advantages are similar to those of SD/FF-1; however, larger amounts of PAC may be needed to achieve performance levels comparable to those achieved by SD/FF-1.

8.2.2 Model Plant Descriptions

Costs for installing and operating the Hg control technologies described in Table 8-1 are estimated by combining these control configurations with appropriate model plant descriptions representing plants firing different types of coal on varying boiler sizes. Eighteen different model plant descriptions or "scenarios" were defined for the cost evaluation. Table 8-2 lists these scenarios.

Approximately 75 percent of the existing coal-fired electric utility boilers in the United States are equipped with an ESP for the control of PM.[7] The remaining boilers employ fabric filters, particulate scrubbers, or other equipment for control of PM. Additionally, units firing medium-to-high sulfur coals may use FGD technologies to meet their SO_2 control requirements. Generally, larger units firing high-sulfur coals employ wet FGD, and smaller units firing medium-sulfur coals use SDAs. While developing the model plant scenarios, these PM and SO_2 control possibilities were taken into account. It may be worth noting that, since the majority of boilers use an ESP for PM control, most Hg control technology applications would likely take place on such boilers and would reflect pertinent performance and costs.

The two coal-fired boiler sizes (expressed as gross electricity output), used for the model plant scenarios listed in Table 8-2, were selected to approximately span the range of typical electric utility boiler sizes, and to be consistent with the model plant sizes used in previous cost studies.[1] It was also envisioned that the use of post-combustion NO_X controls (i.e., SCR or SNCR) may enhance oxidation of Hg in flue gas and result in the "cobenefit" of

Table 8-2. Matrix of model plant scenarios.

Model Plant Scenario	Gross Electricity Output	Coal Burned		Existing Post-combustion PM and SO$_2$ Control Devices	Applicable Mercury Control Retrofit Configuration(s) (see Table 8-1)	Co-benefit Cases with SCR
		Type	Sulfur content			
1	975 MWe	Bituminous	3 %	CS-ESP + wet FGD	ESP-1, ESP-3	SCR
2	975 MWe	Bituminous	3 %	FF + wet FGD	FF-1	SCR
3	975 MWe	Bituminous	3 %	HS-ESP + wet FGD	HESP-1	SCR
4	975 MWe	Bituminous	0.6 %	CS-ESP	ESP-4, ESP-6	
5	975 MWe	Bituminous	0.6 %	FF	FF-2	
6	975 MWe	Bituminous	0.6 %	HS-ESP	HESP-1	
7	975 MWe	Subbituminous	0.5 %	CS-ESP	ESP-4, ESP-6	
8	975 MWe	Subbituminous	0.5 %	FF	FF-2	
9	975 MWe	Subbituminous	0.5 %	HS-ESP	HESP-1	
10	100 MWe	Bituminous	3 %	SDA + CS-ESP	SD/ESP-1	
11	100 MWe	Bituminous	3 %	SDA + FF	SD/FF-1	
12	100 MWe	Bituminous	3 %	HS-ESP + wet FGD	HESP-1	
13	100 MWe	Bituminous	0.6 %	CS-ESP	ESP-4, ESP-6	
14	100 MWe	Bituminous	0.6 %	FF	FF-2	
15	100 MWe	Bituminous	0.6 %	HS-ESP	HESP-1	
16	100 MWe	Subbituminous	0.5 %	CS-ESP	ESP-4, ESP-6	
17	100 MWe	Subbituminous	0.5 %	FF	FF-2	
18	100 MWe	Subbituminous	0.5 %	HS-ESP	HESP-1	

increased Hg removal in wet FGD systems. This is especially relevant since many SCR applications are expected to take place in the next few years and, in response to SO_2 reduction requirements, more wet FGD systems may be installed. However, at the time of this study, some data on this co-benefit were available for SCR applications only. Since SCR is a capital-intensive technology, generally its use is more cost-effective for larger boilers. Accordingly, in this work, the Hg co-benefit resulting from SCR use was evaluated for model plant scenarios 1, 2, and 3, utilizing large (975 MWe) boilers and wet FGD.

8.2.3 Computer Cost Model

The DOE/NETL developed a cost model for estimating the costs of Hg control options for coal-fired electric utility boilers. This cost model, called the NETL Mercury Control Cost Model, can provide capital and operating and maintenance (O&M) costs estimated in year 2000 constant dollars for the application of selected Hg control configurations to coal-fired electric utility boilers. The model has been used for other studies conducted to characterize the costs associated with using PAC injection on coal-fired electric utility boilers.[8] For this evaluation, the EPA collaborated with the DOE to modify this cost model to incorporate the PAC injection rate algorithms described in the following section. An overview of the modified version of the NETL Mercury Control Cost Model used for this cost evaluation is presented in Appendix D to this report. This model is hereafter referred to simply as the cost model.

8.2.4 PAC Injection Rate Algorithms

The current understanding is that Hg_p is well collected in PM or SO_2 control systems, Hg^0 is not so well collected, and Hg^{2+} is collected to a greater or lesser degree depending on characteristics of the control device and conditions within it. Therefore, for a specified Hg removal requirement, the rate of PAC injection needed will depend, in part, on the ability of existing controls to remove the three forms of Hg. The major factor affecting the cost of PAC injection-based technologies is the rate of PAC injection needed for the required Hg removal efficiency. In general, this rate depends on the time of contact between carbon particle and flue gas, the properties of the carbon (particle size, micropore surface area, pore size distribution, and Hg adsorption capacity), the temperature of the flue gas, and the type of coal-fired in the boiler. For this work, PAC injection rates at specific flue gas temperatures and Hg removal efficiencies achieved in pilot-scale tests were fitted to the form of Equation (8-1) with curve-fit parameters a, b, and c (see Attachment 2 in Appendix D). For each technology for which pilot-scale test data are available, separate correlations of Hg removal efficiency and PAC injection rate were determined for bituminous and subbituminous coals. These coals are predominantly used at electric utility boilers and, therefore, were chosen for this work.

$$Mercury\ Removal\ Efficiency\ (\%) = 100 - \frac{a}{\left[PAC\ Injection\ Rate\ \left(lb/10^6 acf\right) + b\right]^c} \quad (Eq.\ 8-1)$$

Equation 8-1 can be used to calculate the PAC injection rate (lb/10^6 acf) needed to achieve a specified Hg removal efficiency (percent) for the control technology of interest. Note that Hg removal efficiency (percent) is based on total Hg (the sum of Hg^0, Hg^{2+}, and Hg_p) removed from the flue gas and is defined as

$$Mercury\ Removal\ Efficiency\ (\%) = 100 \times \frac{\left(Emission_{in} - Emission_{out}\right)}{Emission_{in}} \qquad \text{(Eq.8-2)}$$

where: $Emission_{in}$ = total flue gas Hg concentration at the inlet to the first air pollution control device; and
$Emission_{out}$ = total flue gas Hg concentration at the outlet of the last air pollution control device.

Preliminary analysis of the Pat III EPA ICR data [9] reflected that, at boilers firing bituminous coals and using a CS-ESP for PM capture, higher levels (more than 50 percent) of Hg were being removed with fly ash than were found in earlier pilot-scale tests (see Attachment 2 in Appendix D). Accordingly, for each of technologies ESP-1, ESP-3, ESP-4, and ESP-6, two separate sets of correlations, relating PAC injection rate (lb/10^6 acf) to Hg removal efficiency (percent), were created for use with bituminous-coal-fired boilers. The first of these sets, hereafter referred to as the pilot-scale PAC injection rate, was derived using presently available pilot-scale test data. The other set, hereafter referred to as the ICR/pilot-scale PAC injection rate, was derived using preliminary ICR results for fly ash capture of Hg (i.e., no PAC injection) and pilot-scale results for PAC injection.

Note that the above data-fitting procedure resulted in correlations of PAC injection rate (lb/10^6 acf) versus Hg removal efficiency (percent), as a function of flue gas temperature, for all of the technologies except: (1) FF-1, FF-2, and SD/FF-1, applied on boilers firing bituminous coals, for which no data are available; (2) HESP-1, applied on boilers firing either bituminous or subbituminous coals, for which no data are available; and (3) ESP-7, applied on boilers firing either bituminous or subbituminous coals. The only available data on ESP-7 are from a pilot-scale application on a boiler firing a bituminous coal.[10] Since these data reflect that more than 90 percent of the Hg can be removed by injecting relatively small amounts of PAC with lime, in this work, application of ESP-7 was evaluated at 90 percent Hg removal efficiency in a sensitivity analysis.

The algorithms describing sorbent injection rates for various technologies can be found in Attachment 2 in Appendix D. The PAC injection rate algorithms could not be determined for the retrofit configurations defined for model plant scenarios 2, 3, 5, 6, 9, 11, 12, 14, 15, and 18. As such, costs for these model plant configurations cannot be estimated using the cost model.

8.2.5 Cost Estimate Assumptions

To estimate the costs for the model plant configurations using the cost model, the following specifications were used.

(1) Mercury concentration in the flue gas for each model plant scenario is 10 $\mu g/Nm^3$. This concentration has been used in previous cost studies[1,8] and is in the range of mean concentrations (1.7-50.1 $\mu g/dscm$) determined from ICR data for pulverized-coal-fired electric utility boilers equipped with different air pollution controls.[9] Note also that the corresponding median and mean concentrations are 9.1 and 11.4 $\mu g/dscm$, respectively.

(2) For each of retrofit configurations ESP-1, ESP-3, ESP-4, and ESP-6, two separate sets of correlations, relating PAC injection rate (lb/10^6 acf) to Hg removal efficiency (percent), were created for use with bituminous-coal-fired boilers. The first of these sets, hereafter referred to as the pilot-scale PAC injection rate, was derived using presently available pilot-scale test data. The other set, hereafter referred to as the ICR/pilot-scale PAC injection rate, was derived using preliminary EPA ICR results for fly ash capture of Hg (i.e., no PAC injection) and pilot-scale results for PAC injection. Accordingly, two sets of cost estimates for applying retrofit configurations ESP-1, ESP-3, ESP-4, and ESP-6 were made: one estimate used the pilot-scale PAC injection rate, and the other used the ICR/pilot-scale PAC injection rate.

(3) PAC injection rate correlations generally reflect that PAC injection requirements increase nonlinearly with increases in Hg removal efficiency. To characterize the impact of this behavior, wherever possible, model plant costs were estimated for Hg removal efficiencies of 60, 70, 80, and 90 percent.

(4) In general, for any given Hg removal requirement, the PAC injection rate decreases if the temperature of the flue gas is lowered. For this reason, the flue gas is cooled by water injection in some of the retrofit configurations (see Table 8-1). However, injecting water into an acidic flue gas can lead potentially to corrosion of downstream equipment. To avoid this corrosion, an approach to acid dew point (ADP) of 18 °F was used for the retrofit configurations with spray cooling (i.e., ESP-4, ESP-6, ESP-7, and FF-2).[11] For these retrofit configurations, the extent of SC provided was determined based on the temperature of the flue gas before cooling and the temperature nearest to the above approach to ADP for which a PAC injection rate correlation was available. Note that, in the high-sulfur coal applications with relatively high ADPs, this constraint resulted in no SC if the SO_2 control technology was wet FGD. However, in applications using SDAs for SO_2 control, SC is inherent and acid gases are removed prior to PAC injection; therefore, this constraint was not applied.

(5) No data are currently available for recycling of sorbent in technology applications utilizing PAC injection and PFF. Accordingly, no sorbent recycle was used in retrofit configurations ESP-3 and ESP-6.

(6) Mercury speciation in the flue gas from bituminous-coal-fired boilers is assumed to be 70 percent of the total Hg being oxidized, with 30 percent being Hg^0. The corresponding assumption for boilers firing subbituminous coals is 25 percent oxidized with 75 percent Hg^0. These Hg speciation percentages were determined from a preliminary analysis of ICR data (see Attachment 2 in Appendix D).

(7) Wet FGD systems are assumed to remove 100 percent of Hg^{2+} and no Hg^0. This is based on the fact that mercuric chloride (the assumed major oxidized species) is soluble in water, while Hg^0 is insoluble. It is anticipated that ongoing research on wet scrubbers will result in improved performance through the use of reagents or catalysts to convert Hg to chemical compounds that are soluble in aqueous-based scrubbers.

(8) Use of SCR is assumed to increase Hg^{2+} content in flue gas by 35 percent for both bituminous- and subbituminous-coal-fired boilers. This increase in mercury oxidation was determined from a preliminary analysis of ICR data as follows. As explained above, oxidized mercury content in flue gas from bituminous-coal-fired boilers is assumed to be 70 percent. Also, ICR data revealed that SCR application with SDA at one plant firing bituminous coal resulted in greater than 95 percent mercury removal. It is hypothesized that virtually all of the mercury removed at this plant was oxidized mercury. Based on these considerations, it is assumed that SCR increases oxidized mercury content by 35 percent (also see Attachment 2 in Appendix D). Currently, research and development efforts are underway to investigate the effects of SCR on Hg oxidation. A more mature set of findings regarding SCR impacts are expected from these efforts.

(9) For each of the model plant scenarios, a plant capacity factor of 65 percent was used.

(10) The cost of PAC is assumed to be $1.00 per kilogram.[12]

Other specifications are described in Attachments 1, 2, and 3 in Appendix D.

8.3 Estimated Costs of Reducing Mercury Emissions

This section describes the estimates of total annual cost determined using the cost model for application of Hg controls to those model plant scenarios for which PAC injection rate algorithms could be determined (i.e., model plant scenarios 1, 4, 7, 8, 10, 13, 16, and 17). It is important to note that cost estimates presented in this section are based on currently available data and, as explained later, may be improved with R&D efforts and as long-term operating data from full-scale demonstrations become available.

In general, capital costs of PAC injection-based Hg control technologies comprise a relatively minor fraction of the total annual costs of these technologies; the major fraction is associated with the costs related to the use of PAC.[12] As an example, for application of SC+PAC injection (ESP-4) to achieve 80 percent Hg reduction on a 975-MWe boiler firing bituminous

coal and using an ESP, the capital cost contributes about 23 percent of the total annual cost. Therefore, for such technologies, the cost assessment should be based on total annual costs. Accordingly, total annual costs of controlling Hg emissions from coal-fired electric utility boilers are examined in this section. These costs include annualized capital charge, annual fixed operation and maintenance (O&M) costs, and annual variable O&M costs. Note that Reference 12 provides an examination of the contribution of various cost elements, including cost of PAC, to total annual cost of Hg controls.

8.3.1 Bituminous-coal-fired Boiler Using CS-ESP

Several of the Hg control technologies listed in Table 8-1 are potential options for reducing Hg emissions from a electric utility boiler that fires bituminous coal and already is using an ESP for PM control. For boilers firing low-sulfur bituminous coals, these options include configurations ESP-4 (SC + PAC injection) and ESP-6 (SC + PAC injection + PFF). For large boilers firing high-sulfur bituminous coals, the options include configurations ESP-1 (PAC injection + wet FGD) and ESP-3 (PAC injection + PFF + wet FGD). For smaller boilers (typically less than 300 MW), these options include configuration SD/ESP-1 (SDA + PAC injection + ESP). For each of these cases, cost estimates were determined using the cost model.

Table 8-3 presents the estimated total annual Hg control costs for a bituminous-coal-fired boiler with existing CS-ESP. The table presents two sets of cost estimates. The first set of estimates was made based on levels of Hg capture on fly ash using PAC injection rates derived from the available pilot-scale test data. A subsequent review of the Part III EPA ICR data (discussed in Section 6.2), however, suggests that levels of Hg capture higher than those measured in the pilot-scale tests may be occurring. Consequently, the cost estimates based solely on pilot test data for Hg control technologies applied to bituminous-coal-fired boilers using ESP may be overstating the costs. Therefore, a second set of estimates is presented based on the preliminary ICR results for fly ash capture of Hg (i.e., no PAC injection) in combination with the pilot-scale results for PAC injection.

For ESP-4 applied to low-sulfur (0.6 percent) bituminous coal and using pilot-scale PAC injection rates, the estimated total annual cost ranges from 2.81 mills/kWh for a 100-MWe boiler removing 90 percent of the total Hg to 0.53 mill/kWh for a 975-MWe boiler removing 60 percent of the total Hg. The corresponding costs with ICR/pilot-scale PAC injection rates are 1.65 mills/kWh for the 100-MWe boiler and 0.24 mill/kWh for the 975-MWe boiler.

In general, these results reflect that, for a given boiler, the total annual cost increases non-linearly with increases in the Hg reduction requirement in concert with the behavior of the PAC injection rate algorithms (see Attachment 2 in Appendix D). A comparison of results obtained with pilot-scale and ICR/pilot-scale PAC injection rates also indicates that research and development efforts aimed at ensuring broad availability of relatively high levels of fly ash capture of Hg have the potential of providing significant reductions in Hg control costs.