A Study of Hazardous Air Pollutants at the Tidd PFBC Demonstration Plant

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EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE) Clean Coal Technology (CCT) Program is a joint effort between government and industry to develop a new generation of coal utilization processes. In 1986, the Ohio Power Company, a subsidiary of the American Electric Power Service Corporation (AEP), was awarded cofunding through the CCT program for the Tidd Pressurized Fluidized Bed Combustor (PFBC) Demonstration Plant located in Brilliant, Ohio. The Tidd PFBC unit began operation in 1990 and was later selected as a test site for an advanced particle filtration (APF) system designed for hot gas particulate removal. The APF system was sponsored by the DOE Morgantown Energy Technology Center (METC) through their Hot Gas Cleanup Research and Development Program.

A complementary goal of the DOE CCT and METC R&D programs has always been to demonstrate the environmental acceptability of these emerging technologies. The Clean Air Act Amendments of 1990 (CAAA) have focused that commitment toward evaluating the fate of hazardous air pollutants (HAPs) associated with advanced coal-based and hot gas cleanup technologies. Radian Corporation was contracted by AEP to perform this assessment of HAPs at the Tidd PFBC demonstration plant with funding from the DOE-METC Hot Gas Cleanup R&D program. The objective of this study is to assess the major input, process, and emission streams at Plant Tidd for the HAPs identified in Title III of the CAAA.

Site Description

The boiler at Plant Tidd is a bubbling bed, pressurized fluidized bed combustor (PFBC) rated at 70 MWe; 55 MW is produced by a steam turbine generator and 15 MW is produced by depressurizing the hot flue gas in a gas turbine generator. Total plant load during the test period was steady at 45 to 46 MW, which is representative of stable, long-term operation. A slurry of Pittsburgh No. 8 bituminous coal (3.4% sulfur) is fed to the PFBC unit along with dolomite sorbent to control SO_2 emissions. Particulate matter is controlled by primary and secondary cyclones in series with an electrostatic precipitator (ESP). Formation of NO_x is minimized because of relatively low combustion temperatures within the PFBC process.

An additional feature of the Plant Tidd facility is a demonstration-scale hot gas clean-up system. Treated gas from one of the seven cyclones is directed to a ceramic barrier, advanced particle filter (APF), and back-up cyclone. The treated gas is then returned to the process upstream of the ESP. The APF operated at approximately 1350°F during the test period. The ceramic candles were backpulsed approximately every 30 minutes to remove particulate matter captured on the outside of the candles.

Sampling Locations

Four flue gas stream locations were tested: ESP inlet, ESP outlet, APF inlet, and APF outlet. Other process streams sampled were raw coal, coal paste, sorbent, bed ash, cyclone ash, individual ESP hopper ash, APF ash, and service water.

Sample Collection

Radian's approach to meeting the test objectives utilized established sampling methods (where possible) and a sampling strategy consistent with that of the DOE-sponsored program, "Comprehensive Assessment of Air Toxics Emissions from Coal-Fired Utility Boilers," and the EPRI-sponsored Field Chemical Emissions Monitoring (FCEM) program. Samples were collected with the boiler operating at steady-state conditions and in triplicate over four days (April 12-15, 1994).

Quality Assurance and Quality Control

During sample collection, quality assurance audits were conducted by Radian's internal QA auditor. Radian's auditor also conducted a performance evaluation audit by submitting "double-blind" (identity and composition unknown) samples to the analytical laboratories. Quality control procedures involved the evaluation of results for field and laboratory blank samples, duplicate field samples, matrix-spiked and surrogate-spiked samples, and laboratory control samples.

Overall, QA/QC data associated with this program indicate that measurement data are acceptable and can be used with confidence. The QA/QC results indicate that the quality control mechanisms were effective in ensuring measurement data reliability within the expected limits of sampling and analytical error.

Plant Operating Conditions

During sample collection, operating conditions were continuously monitored using a computerized data acquisition system which logged process information as five-minute averages. In addition, ESP operating data (voltages and currents for each field) were logged hourly by the on-site Radian engineer. Overall, all processes were very stable, and the key operating parameters were within the targeted range during the entire test period. Continuous emission monitors were operated during the test period, providing data for sulfur dioxide, nitrogen oxides, opacity, and carbon monoxide at the ESP outlet location. These data indicate steady process operation and ESP performance.

Analytical Results

Samples were analyzed for trace elements, minor and major elements, anions, volatile organic compounds, dioxin/furan compounds, ammonia, cyanide, formaldehyde, and semivolatile organic compounds. The particle size distribution in the ESP inlet and outlet gas streams and collected ash from individual ESP hoppers was also determined. Analytical results have been tabulated in detail as mean values with 95% confidence intervals. In the detailed data tabulations, some data have been identified with flags; for example, where background analyte levels in the sampling media exceeded 30% of the uncorrected sample result.

Data Analysis: Mass Balances, Removal Efficiencies, and Emission Factors

Emission factors, removal efficiencies, and other results rely on measurement data that are near the limit of detection or below it for many of the substances of interest. For that reason, uncertainty analyses and the calculation of confidence intervals were performed as part of this program. The method used to determine uncertainties in calculated results is based on "Measurement Uncertainty".[1]

The following observations are results of the data analysis:

- Material balances were calculated for 26 elements. Sixteen of these elements met the target closure objectives of 70-130% for balance around the plant. Nineteen elements met a closure criteria of 50-150 percent. Closures could not be estimated for four species (antimony, cadmium, molybdenum, and silver) because they were not detected in one or more of the outlet ash streams.

- Use of the ICP-MS analytical technique to analyze vapor phase multi-metals train samples at the four gas locations provided superior detection limits and allowed quantification of vapor phase trace metals at low ng/Nm^3 levels—below the detection limits of standard ICP-AES and GFAAS techniques.

- Removal efficiencies for non-volatile metals were generally greater than 95% across the ESP. Less than 10% removal was observed for volatile species such as chloride, fluoride, and mercury.

- The particulate removal efficiency of the APF system was measured at 99.99 percent. Removal efficiencies for most non-volatile metals was greater than 99.5% across the APF. Removals of less than 30% were measured for mercury, selenium, chloride and fluoride. Approximately 40% removal of SO_2 was measured across the APF system as well as some removal for ammonia (25%), cyanide (69%), and formaldehyde (94%).

- High resolution GC/MS analysis of the Modified Method 5 sampling train components provided detection limits for selected polycyclic aromatic hydrocarbons at 2 to 5 orders of magnitude lower than low resolution GC/MS. Quantification of PAHs at these lower levels provides a better estimate of emissions.

- Hexavalent chromium analyses conducted in an on-site laboratory provided measurable results slightly above blank levels. Compared to total chromium results for the ESP outlet stream, chromium (VI) was measured at 37% of the total chromium concentration; however, additional research and validation of this method for coal-fired power plant flue gas is needed.

- Emission factors have been calculated for the target trace species detected in the ESP outlet gas and are presented in Table ES-1.

- Particle size distribution (PSD) results for the ESP inlet and outlet flue gas measurements were consistent and repeatable. PSD results for ash collected from the four ESP hoppers show a progressive shift downward in the mean particle diameter through the ESP. The particle size range collected in the first and second ESP field hoppers is consistent with that of the ESP inlet gas particulate. The mean aerodynamic particle diameter at the ESP inlet was 3.5 μm with less than approximately 8% of the particles below 1 μm.

Recommendations and Considerations

Some technical issues have been identified during this study that may warrant further consideration. Among these are the following sampling, analytical and/or process related issues:

- Contamination of the APF outlet particulate phase samples with chromium, nickel, and molybdenum associated with the Inconel 800 components of the hot gas sampling system was observed;

- Improved detection limits are required for some trace elements in gas stream particulate and process solid samples to facilitate complete material characterizations and balance closures;

- Analysis of multiple reagent blanks is necessary to provide a more representative statistical value for background levels of target analytes in the sampling media when samples are analyzed by highly sensitive analytical techniques;

- Gas sampling methods for semi-volatile organic compounds should be studied to determine if benzoic acid, phthalate esters, and other related compounds are sampling artifacts associated with the reactivity of flue gas components on XAD-2 resin; and

- The hexavalent chromium sampling method has not been validated for application to flue gas from coal-fired combustion systems and should be thoroughly evaluated for sampling bias and precision.

References

1. American Society of Mechanical Engineers. *Measurement Uncertainty: Instruments and Apparatus*. PTC 19.1-1985 (reaffirmed 1990), pp 1-65. United Engineering Center, New York, NY. Published by the American National Standards Institute.

Table ES-1
Emission Factors

	$lb/10^{12}$ Btu	95% CI
Anions		
Chloride	83,000	4,000
Fluoride	5,600	270
Reduced Species		
Ammonia	140	7
Cyanide	610	29
Selected Elements[a]		
Arsenic	1.2	0.06
Barium	0.92	0.04
Beryllium	0.26	0.0012
Cadmium	2.2	0.11
Chromium	4.6	0.22
Chromium (VI)	1.7	0.08
Copper	5.3	0.25
Lead	0.8	0.038
Manganese	8.5	0.41
Mercury	18	1
Molybdenum	0.31	0.015
Nickel	7.4	0.35
Selenium	49	2.3
Silver	0.5	0.024
Vanadium	1.2	0.06
Aldehydes		
Formaldehyde	5.1	0.24
Volatile Organic Species[a,b]		
Benzene	6.6	0.32
Carbon Disulfide	1.0	0.05
PAHs by HRGC/MS[c]		
Acenaphthylene	$1.2x10^{-1}$	$5.8x10^{-3}$
2-Chloronaphthalene	$1.2x10^{-3}$	$5.7x10^{-5}$

Table ES-1 (Continued)

	lb/10^{12} Btu	95% CI
PAHs by Method 8270[c,d]		
Acetophenone	3.9[e]	0.2
Benzoic Acid	160	8
Isophorone	21[e]	1
Phenol	1.2[e]	0.06
Dioxin/furan Species[a,f]		
1,2,3,4,6,7,8-Heptachlorodibenzofuran	6.4×10^{-6}	3.1×10^{-6}
Octachlorodibenzofuran	1.2×10^{-5}	5.8×10^{-7}
Total Heptachlorodibenzo-p-dioxin	1.4×10^{-5}	6.7×10^{-7}
Total Heptachlorodibenzofuran	4.5×10^{-6}	2.1×10^{-7}
Total Hexachlorodibenzofuran	1.4×10^{-5}	6.7×10^{-7}
Total Pentachlorodibenzofuran	4.3×10^{-6}	2.1×10^{-7}

[a] Only those compounds with an average concentration above the detection limit are included.

[b] Methylene chloride, toluene, and other halogenated hydrocarbons are not included because their presence is strongly suspected to be the result of contamination from common field and laboratory reagents.

[c] Substances for which the reagent blank background levels were greater than or equal to 30% of the sample result are not included because their quantification is considered suspect.

[d] Phthalate esters are not included because their presence is suspected to be either the result of resin contamination from plasticizers commonly found in the laboratory environment, or a sampling artifact.

[e] Reported concentration is between the quantitation limit and the method detection limit. Results in this range are considered uncertain.

[f] Result is less than five times the detection limit.

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INTRODUCTION

Background

The U.S. Department of Energy (DOE) Clean Coal Technology (CCT) Program focuses on developing a new generation of coal utilization processes. One objective of the program is to move the most promising of the advanced coal-based technologies into the commercial marketplace through a series of demonstrations cofunded by government and industry. The DOE-Morgantown Energy Technology Center (METC) Hot Gas Cleanup Research and Development Program examines advanced technologies for application to hot gas streams in coal combustion and gasification systems. One objective is to aid in designing hot gas cleanup technologies for second-generation pressurized-fluidized bed combustor (PFBC) units.

In the first round of CCT solicitations in 1986, the Ohio Power Company, a subsidiary of American Electric Power Service Corporation (AEP), was awarded funding for the Tidd PFBC demonstration plant in Brilliant, Ohio. The Tidd PFBC unit began operation in late 1990 and was later selected by the DOE-METC R&D program as a test facility for an advanced particle filtration (APF) system.

Because of continuing concern that the use of coal as an energy source could cause significant environmental impact, a complementary goal of the DOE CCT and METC R&D programs has always been to demonstrate the environmental acceptability of these projects. The Clean Air Act Amendments of 1990 (CAAA) added another focus to DOE's environmental protection commitment; evaluating the fate of hazardous air pollutants (HAPs) associated with the demonstration of advanced coal-based and hot gas cleanup technologies.

The study of HAPs at the Tidd PFBC demonstration plant was funded by the DOE Hot Gas Cleanup R&D program through AEP to assess the major input, process, and emission streams for the HAPs identified in Title III of the CAAA. Included in this assessment were the inlet and outlet gas and solid samples from the APF system and the electrostatic precipitator (ESP). The resulting data from this study are used to generate emission factors for the HAPs so that the environmental acceptability of commercialized PFBC technologies can be assessed.

Radian Corporation was selected to perform the HAPs assessment at the Tidd PFBC demonstration plant with the advanced particle filter in operation. This report presents the results of that assessment.

Objectives

The specific objectives of this project are:

- To collect and analyze representative solid, liquid, and gas samples of all specified input and output streams of the Tidd PFBC Plant, including the advanced particle filtration system, for selected hazardous air pollutants contained in Title III of the CAAA;
- To determine the removal efficiencies of the APF and ESP subsystems for selected pollutants;
- To calculate material balance closures for selected pollutants in specified subsystems of the power plant and for the entire plant;
- To determine the concentrations of the respective pollutants associated with the particulate and vapor-phase fractions of the specified flue gas streams;
- To determine hexavalent chromium stack emissions; and
- To provide data (emission factors) for use in comparing emissions and system data from Plant Tidd with similar studies on conventional coal-fired power plants.

Table 1-1 lists the chemical substances selected for analysis during this project.

Table 1-1
Target Analytes

Trace Elements

Antimony
Arsenic
Barium
Beryllium
Boron
Cadmium
Chromium, total
Cobalt
Copper
Lead
Manganese
Mercury
Molybdenum
Nickel
Selenium
Silver
Vanadium

Radionuclides

Hexavalent Chromium

Anions

Chloride (HCl)
Fluoride (HF)
Sulfate
Phosphate

Reduced Species

Ammonia
Cyanide

Dioxins/Furans

Volatile Organics

Benzene
Bromoform
Carbon Disulfide
Carbon Tetrachloride
Chlorobenzene
Chloroform
1,4-Dichlorobenzene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethyl Benzene
Ethyl Chloride (Chloroethane)
Ethylene Dichloride (1,2-Dichloroethane)
Ethylidene Dichloride (1,1-Dichloroethane)
Formaldehyde
Methyl Bromide (Bromomethane)
Methyl Chloride (Chloromethane)
Methyl Chloroform (1,1,1-Trichloroethane)
Methyl Ethyl Ketone (2-Butanone)
Methylene Chloride (Dichloromethane)
Propylene Dichloride (1,2-Dichloropropane)
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
1,1,2-Trichloroethane
Trichloroethene
Vinyl Acetate
Vinyl Chloride
Vinylidene Chloride (1,1-Dichloroethene)
m,p-Xylene
o-Xylene

Table 1-1 (Continued)

Semivolatile Organics

Acenaphthene
Acenaphthylene
Acetophenone
4-Aminobiphenyl
Aniline
Anthracene
Benzidine
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Benzoic Acid
Benzyl Alcohol
4-Bromophenyl Phenyl Ether
Butylbenzylphthalate
4-Chloro-3-Methylphenol
p-Chloraniline
bis(2-Chloroethoxy)methane
bis(2-Chloroethyl)ether
bis(2-Chloroisopropyl)ether
2-Chloronaphthalene
2-Chlorophenol
4-Chlorophenyl Phenyl Ether
Chrysene
bis(2-Ethylhexyl)phthalate
Fluoranthene
Fluorene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Indeno(1,2,3-cd)pyrene
Isophorone
2-Methylnaphthalene
2-Methylphenol (o-cresol)
4-Methylphenol (p-cresol)
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosopropylamine
Naphthalene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
Nitrobenzene
Di-n-octylphthalate
Dibenz(a,h)anthracene
Dibenzofuran
Dibutylphthalate
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
3,3-Dichlorobenzidine
2,4-Dichlorophenol
Diethylphthalate
p-Dimethylaminoazobenzene
2,4-Dimethylphenol
Dimethylphthalate
4,6-Dinitro-2-methylphenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
2-Nitrophenol
4-Nitrophenol
Pentachloronitrobenzene
Pentachlorophenol
Phenanthrene
Phenol
Pyrene
1,2,4-Trichlorobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol

Additional Elements

Aluminum
Calcium
Iron
Magnesium
Potassium
Sodium
Titanium

Emission factors, removal efficiencies, and other results rely on measurement data that vary and which may be near or below the limit of detection for many of the substances of interest. This report includes uncertainty analysis and confidence intervals to assess the precision of the data.

Auditing

During the field sampling program conducted at Plant Tidd in April 1994, quality assurance (QA) audits were conducted by Radian Corporation's internal QA auditor. Radian's audit provided an objective, independent assessment of the sampling procedures, data gathering, and measurement activities to ensure the production of reliable and useful results. The audit provided a review of calibration documentation, documentation of QC data, completeness of data forms and notebooks, data review/validation procedures, sample logging procedures, and others. Included in this audit was the preparation and analysis of analytical standards as blind samples for assessing the potential bias associated with the analytical methods. The audit results and responses to the auditor's comments are provided in Section 4.

Project Organization

Figure 1-1 shows the organization of this project.

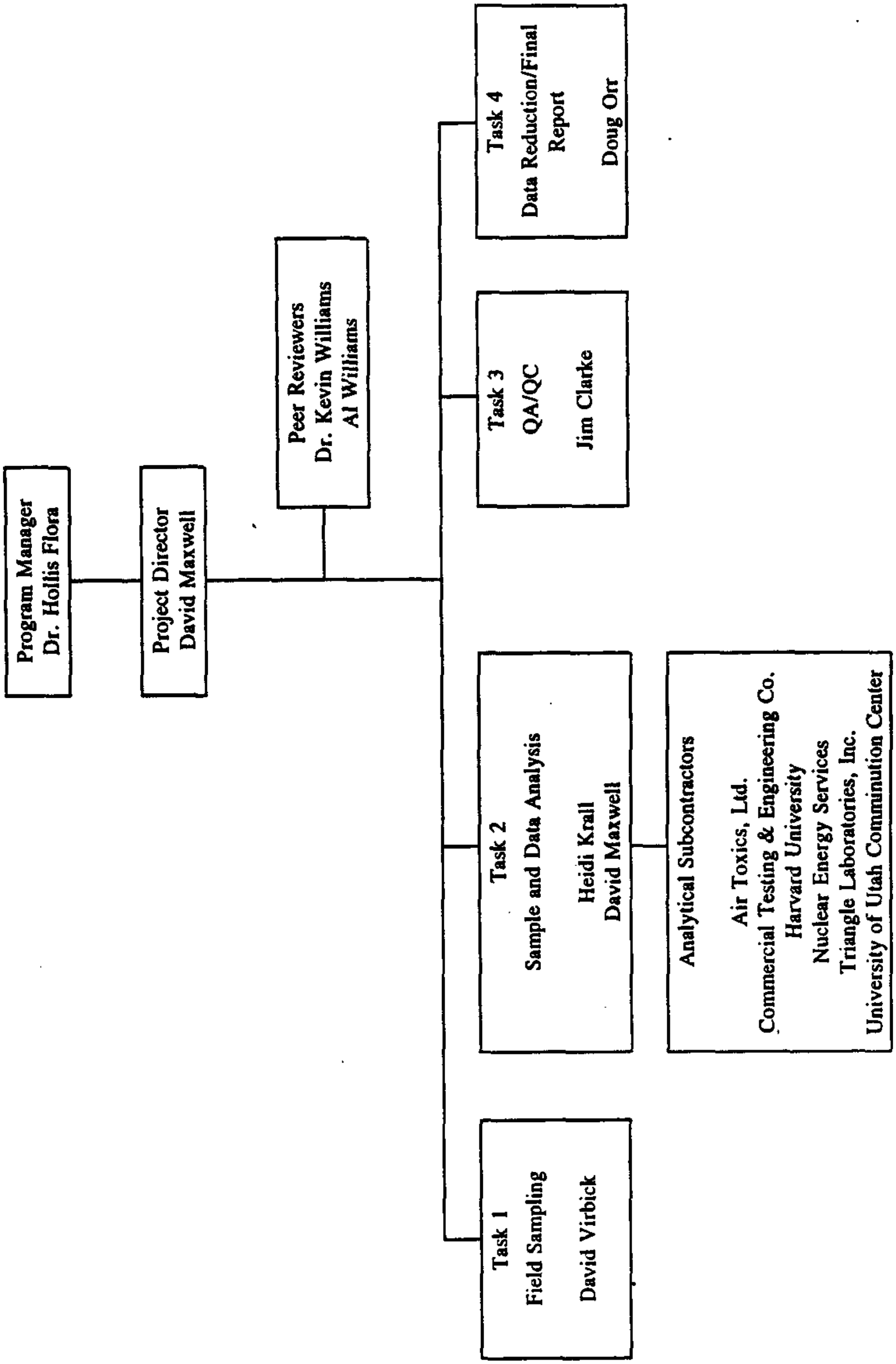


Figure 1-1
Project Organization

2
SITE DESCRIPTION

This section presents a description of the test site and sampling locations used during the test period. Deviations from the sampling locations described in the test plan are also discussed.

Site Description

Plant Tidd, located in Brilliant, Ohio, is operated by Ohio Power Company, a subsidiary of American Electric Power Service Corporation (AEP). The boiler at the Plant Tidd site is a bubbling-bed, pressurized fluidized bed combustor (PFBC) rated at 70 MWe full load. Total plant load during the test period was 45 to 46 MW; 37 MW was produced by a steam turbine generator and 8 MW was produced by depressurizing the hot flue gases through a gas turbine generator. The process operating conditions for the unit were selected by AEP and represent typical long-term operating conditions for the process. A simple schematic of the unit is shown in Figure 2-1.

Crushed coal (Pittsburgh No. 8, bituminous) is combined with water from a nearby river to produce a coal paste which was approximately 25 weight percent moisture. The paste is fed to the combustion chambers along with crushed dolomite. The material is fluidized by high velocity combustion air in the water-cooled boiler. Mean bed temperatures in the combustion chambers were controlled at approximately 1500°F during the test period. As the coal is combusted, the calcium carbonate in the dolomite or limestone is calcined to form quick lime which then reacts with the sulfur dioxide and oxygen in the combustion gases to form solid calcium sulfate. This reaction removes sulfur dioxide from the combustion gases, thus controlling SO_2 emissions. Test data from this program show approximately 88% removal of sulfur dioxide in the combustor. Formation of nitrogen oxides (NO_x) is minimized because of the relatively low combustion temperature of the PFBC process.

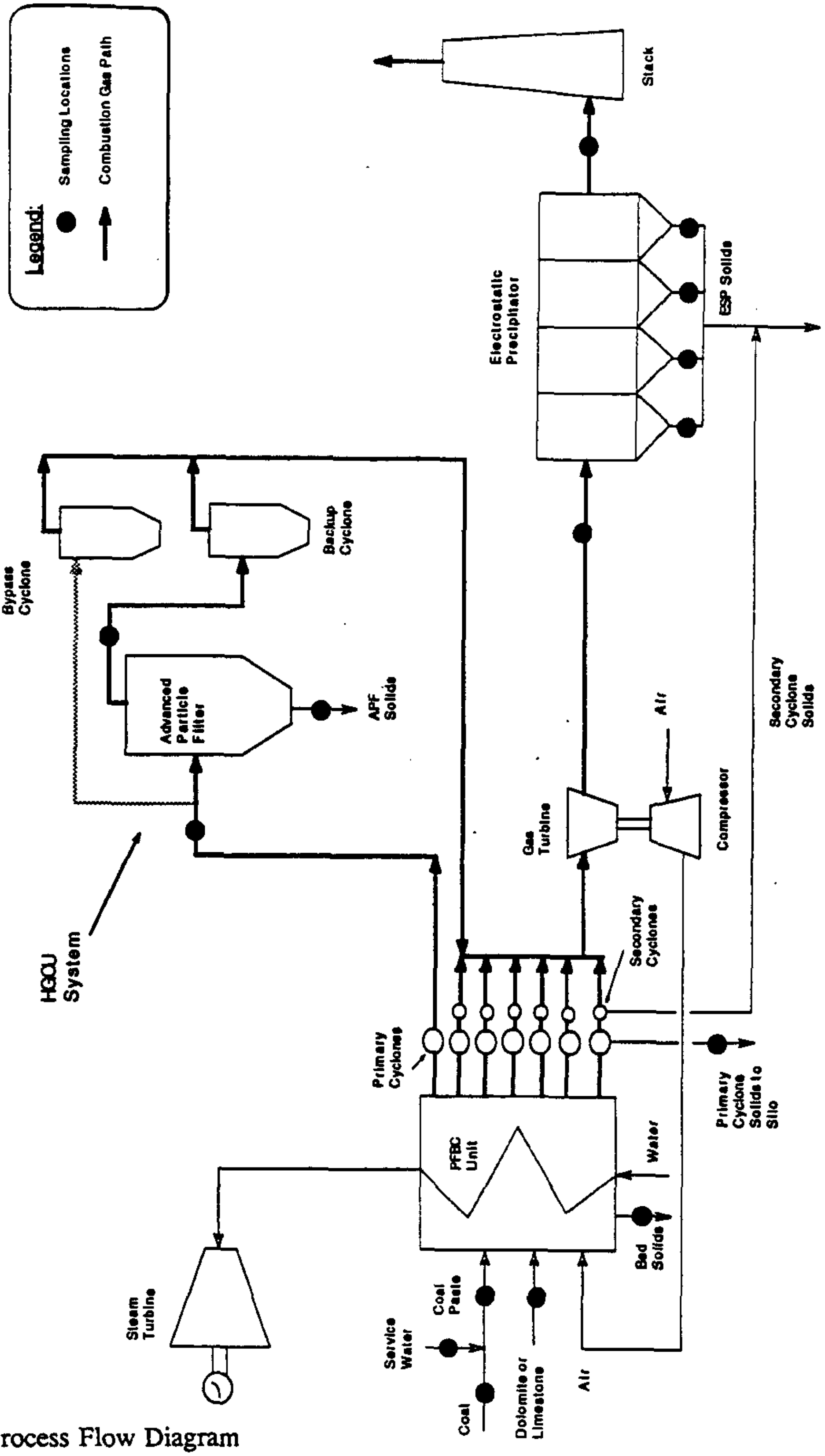


Figure 2-1
Plant Tidd Process Flow Diagram

After releasing heat to the in-bed, water-cooled boiler tubes, the particulate-laden combustion gases flow into seven parallel, two-stage cyclones. These cyclones remove approximately 93% of the entrained solids (primarily sulfated lime, unreacted lime, ash, and unburned carbon) from the gases. The combustion gases then flow to the ASEA Stal GT-35P gas turbine where they are expanded and then exit through the turbine exhaust gas economizer. Final particulate removal from the gases is achieved in an electrostatic precipitator (ESP) before the gases are released to the atmosphere.

Bed ash, which comprises about 45% of the total ash produced, is removed from the bottom of the combustor periodically through a lock hopper system. Solids collected by the primary cyclone are transported to a storage silo using a pressurized pneumatic transport system. Secondary cyclone solids are combined with the material collected in the ESP. All solids are transported by truck off site for disposal.

Hot Gas Cleanup

A research feature of the Plant Tidd facility is a demonstration-scale hot gas cleanup (HGCU) system, as shown in Figure 2-1. Treated gas from one of the seven cyclone systems (approximately one-seventh of the total gas flow from the combustor) is diverted to a ceramic barrier, advanced particle filter (APF) and back-up cyclone, and directed back to the outlet header of the secondary cyclones. The APF uses Schumacher silicon carbide candles in a cluster/ plenum arrangement developed by Westinghouse Corporation to filter the gas. Tempering air was added to the system during the test period to control ash bridging within the APF system, reducing the APF inlet gas temperature from 1500°F to approximately 1350°F.

Each candle element in the APF is a porous ceramic cylinder which is closed on the bottom and open at the top. Hot, particulate-laden gas flows through the outer surface of the candles and the clean gas exits through the inner cylinder of the candles. The candle clusters are back-pulsed sequentially on a continuous cycle by nine pulse injectors to remove particulate matter captured on the outside of the candles. The pulse cycle during the test period was approximately every 30 minutes. Entrained solids removed in the APF system are collected and transported by truck off site for disposal.

Sampling Locations

Process streams that were sampled during the test are listed in Table 2-1 along with a brief description of the planned sampling location and any deviations from the planned location. Solid, liquid, and gas stream sampling locations are illustrated in Figure 2-1. Solid and liquid stream samples were collected at intervals that accounted for the residence times within the system so that solid and liquid samples corresponded to gas sampling periods. The procedures for collecting, preserving, and analyzing samples are presented in Appendix A. Tables 2-2 and 2-3 present an overview of the types of analyses performed on these process streams.

All streams were sampled from the planned locations, with the exception of the sorbent and APF ash streams. A different sample location was used for the sorbent because the gear box on the autosampler at the East sorbent injector became jammed on the first day of testing. An alternate location at the diversion gate upstream of the East and West silos was used to collect sorbent samples on Day 2 and Day 3. This change did not adversely affect sample representativeness. Once on site, the crew identified an improved sampling location for the APF ash. Instead of sampling from the disposal trucks, as planned, a sample point was identified at the bottom of the APF ash collection system.

Table 2-1
Sampling Locations at Plant Tidd

Process Stream	Sampling Location
Coal [a]	Solid automatic sampler on feed belt to crusher.
Coal Paste	Paddle belt feeder to storage tank.
Sorbent (Dolomite)	Automatic sampler on east sorbent injector (planned). Diversion gate upstream of both the East and West sorbent silos (actual).
Bed Ash	Bed ash collector before ash conveyor.
ESP Ash	ESP Hoppers 11 and 12; Hoppers 13 and 14 sampled on last day.
Primary Cyclone Ash	Automatic samplers on ash storage silo.
APF Ash	Sampled upon loading into disposal trucks (planned). Bottom of APF ash collector (actual).
Service Water	Tap on low pressure service water header.
APF Inlet Gas	Single 4-inch-diameter port on APF inlet duct.
APF Outlet Gas	Single 4-inch-diameter port on APF outlet duct.
ESP Inlet Gas	Five 4-inch-diameter ports on ESP inlet duct.
ESP Outlet Gas	Two 4-inch-diameter ports on ESP outlet duct.

[a] Raw coal samples were collected as a backup to the coal paste sample.

Table 2-2
Analyses Performed for Solid and Liquid Streams

Analysis	Coal[a]	Coal Paste	Sorbent (Dolomite)	Service Water	Bed Ash	ESP Ash	Primary Cyclone Ash	APF Ash
Metals		✓	✓	✓	✓	✓	✓	✓
Anions		✓	✓	✓	✓	✓	✓	✓
Semivolatile Organics					✓	✓	✓	✓
Particle Size Distribution						✓		
Ultimate/Proximate		✓						
Radionuclides		✓			✓	✓	✓	✓
Carbon					✓	✓	✓	✓
Dioxins/Furans						✓	✓	✓
Moisture		✓						

[a] Raw coal samples, collected as alternate feedstock samples, were not analyzed.

Table 2-3
Analyses Performed for Gas Streams

Analysis	APF Inlet Gas	APF Outlet Gas	ESP Inlet Gas	ESP Outlet Gas
Particulate Loading	✓	✓	✓	✓
Metals[a]	✓	✓	✓	✓
Anions[a]	✓	✓	✓	✓
Ammonia/Cyanide	✓	✓	✓	✓
Formaldehyde	✓	✓	✓	✓
Volatile Organics	✓	✓	✓	✓
Semivolatile Organics[a]	✓	✓	✓	✓
Dioxins/Furans[b]	✓	✓	✓	✓
Particle Size Distribution			✓	✓
Hexavalent Chromium[a]				✓

[a] Particulate and vapor phases analyzed separately.

[b] Solid- and vapor-phase fractions were combined prior to analysis for all streams except APF outlet.

3

RESULTS

This section summarizes the results of the stream characterization for the Tidd PFBC demonstration plant. Sampling, preparation, and analytical methods are described in Appendix A. Detailed analytical data for each individual sample can be found in Appendix B.

Sampling Schedule

Samples were collected during the week of April 11, 1994. Figures 3-1 and 3-2 show the gas stream sample times for the ESP and APF systems, respectively. Figure 3-3 shows the sample collection periods for solid and liquid process streams. Three valid sample sets for each stream were obtained.

Every attempt was made to collect inlet and outlet gas samples for a given sample type over the same time period so that results would provide a meaningful comparison. All ESP inlet and outlet gas samples were collected simultaneously as shown in Figure 3-1. Run 1 multi-metals and anions train samples at the APF inlet were invalidated because of particulate breakthrough across the filter; these samples were recollected later in the test period. The higher than expected particulate loadings at the APF inlet caused delays in gas sample collection; therefore, the test period was extended one day to allow for collection of all three PAH, dioxin/furan, and volatile organic trains.

Data Treatment

Several conventions have been developed for treating the test data and developing average concentrations of substances in the various streams.

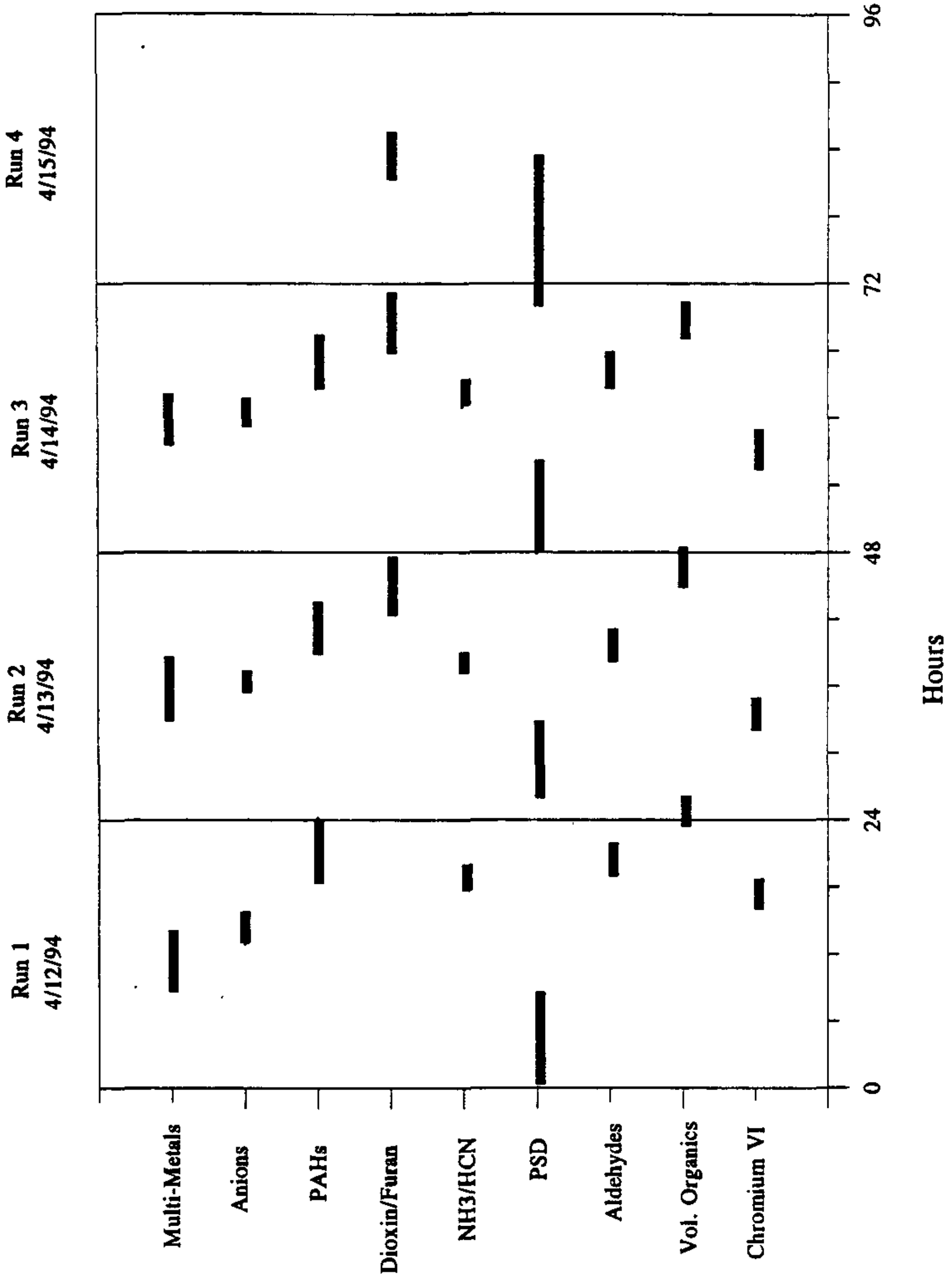


Figure 3-1
ESP Inlet and Outlet Sampling Schedule

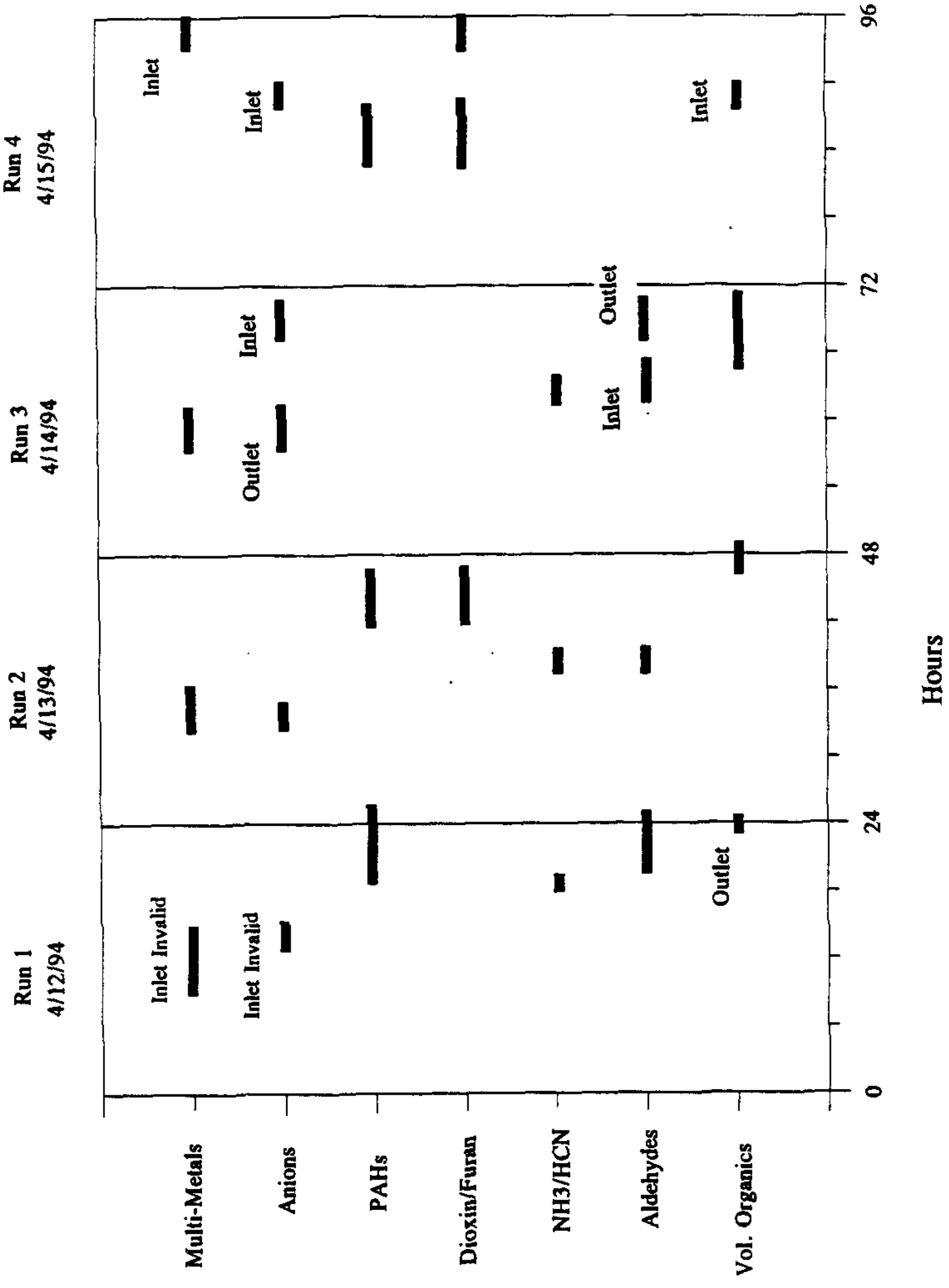


Figure 3-2
APF Inlet and Outlet Sampling Schedule

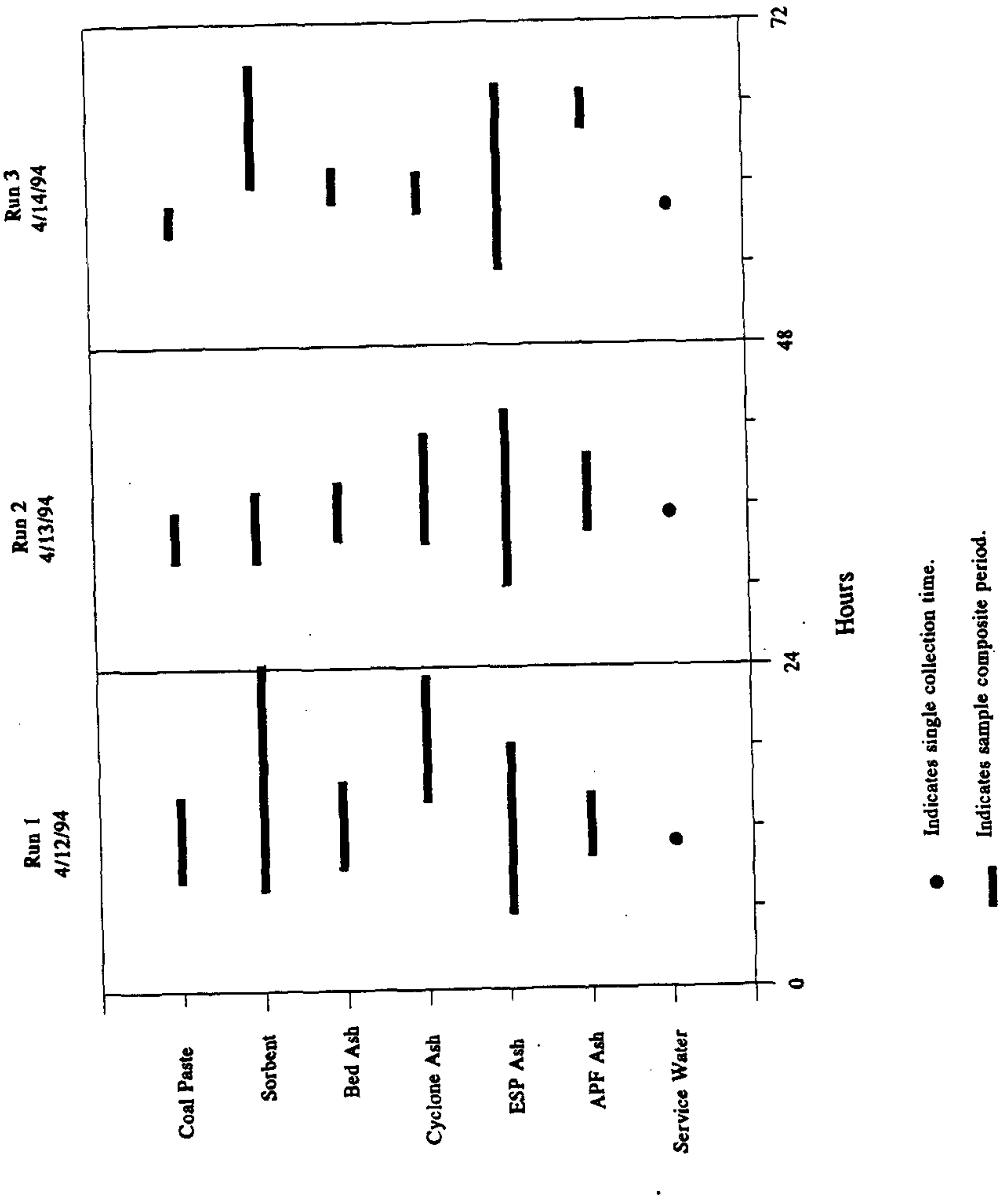


Figure 3-3
Sample Times for Solid and Liquid Process Streams

To determine the total concentration for gas streams within a run, both the solid- and vapor-phase contributions were considered; however, the absence of some detectable concentrations in either (or both) phase(s) required that conventions be developed for dealing with these data. These conventions are summarized below:

Case 1: The concentrations in both the solid and vapor phases are above detection limits.

Case 2: The concentrations in both the solid and vapor phases are below detection limits.

Case 3: The concentration in one phase is above the detection limit, and the concentration in the other phase is below the detection limit.

For inorganic constituents of interest other than HF, HCl, NH_3, HCN, and mercury, the flue gas stream data from previous studies of coal-fired power plants have shown that most of the material is present in the solid phase, and that only a small fraction is generally found in the vapor phase. The opposite is generally true for organic species. Thus, the following conventions were selected for defining the total gas stream concentrations:

- For Case 1, the total concentration is the sum of the concentrations in the vapor and solid phases.

  For example, the total selenium concentration in the ESP inlet gas for Run 1 is calculated as follows:

  Selenium in the solid phase = 52 $\mu g/Nm^3$

  Selenium in the vapor phase = 20 $\mu g/Nm^3$

  Total selenium in the ESP inlet gas = 72 $\mu g/Nm^3$

- For Case 2, the total concentration is considered to be the detection limit in the solid phase.

For example, the total silver concentration in the ESP inlet gas for Run 1 is calculated as follows:

Silver in the solid phase = ND(2.1) μg/Nm^3

Silver in the vapor phase = ND(1.6) μg/Nm^3

Total silver in the ESP inlet gas = ND(2.1) μg/Nm^3

- For Case 3, multiple conventions have been established, depending on the group of substances being considered.

For metals train results, if the substance is not detected in the solid phase and detected in the vapor phase at levels below the detection limit of the solid phase, the total concentration is reported as the detection limit of the solid phase and total is flagged to note that the substance was detected at low levels in the vapor phase.

For example, the total antimony concentration in the ESP inlet gas for Run 1 is calculated as follows:

Antimony in the solid phase = ND(3.2) μg/Nm^3

Antimony in the vapor phase = 0.016 μg/Nm^3

Total antimony in the ESP inlet gas = ND(3.2) μg/Nm^3

For metals train results, if the substance is not detected in the vapor phase and detected in the solid phase, the vapor-phase component is considered to be equal to zero.

For example, the total lead concentration in the ESP inlet gas for Run 1 is calculated as follows:

Lead in the solid phase = 76 μg/Nm^3

Lead in the vapor phase = ND(0.005) $\mu g/Nm^3$

Total lead in the ESP inlet gas = 76 $\mu g/Nm^3$

For semivolatile organic compounds, if the substance is not detected in the solid phase and detected in the vapor phase, the reported total is the concentration in the vapor phase.

For example, the total 2-chloronaphthalene concentration in the APF inlet gas for Run 1 is (refer to Table 3-15) calculated as follows:

2-chloronaphthalene in the solid phase = ND(0.09) ng/Nm^3

2-chloronaphthalene in the vapor phase = 5.9 ng/Nm^3

Total 2-chloronaphthalene in the ESP inlet gas = 5.9 ng/Nm^3

Historical test data for conventional power systems has indicated that HCl, HF, and mercury are present primarily in the vapor phase (although mercury is sometimes also detected in the solid phase). One would also expect that semivolatile organic compounds would be primarily associated with the vapor phase. For Case 2, the total concentration of each of these species is considered to be the detection limit in the vapor phase. For Cases 1 and 3, the methodologies are unchanged from those described above.

The following criteria were used when averaging the results of different runs:

- When all values for a given variable were above the detection limit, the mean concentration was calculated as the true arithmetic mean.

- For results that included values both above and below the detection limit, one-half the detection limit was used to calculate the mean. For example:

Analytical Values	Calculation	Mean Value
10, 12, ND(8)	[10+12+(8/2)]/3	8.7

By convention, the calculated mean is not allowed to be smaller than the largest detection limit value. In the following example, using one-half the detection limit would yield a calculated mean of 2.8. This is less than the highest detection limit obtained; therefore, the reported mean is ND(4).

Analytical Values	Calculation	Mean Value
5, ND(4), ND(3)	[5+(4/2)+(3/2)]/3 = 2.8	ND(4)

- When all analytical results for a given variable are below the detection limit, the mean is reported as ND(x), where the x is the largest detection limit. The bias estimate (used where calculating confidence intervals for other parameters) is one-half of the detection level, and no confidence interval is reported.

Calculations were performed with unrounded numbers, and the results were rounded for presentation in the tables; therefore, slight differences in calculated means and confidence intervals are attributable to round-off errors.

Coal and Dolomite

Tables 3-1 and 3-2 show the analytical results for the coal paste and sorbent samples, respectively. Appendix A describes the analytical methods used for each combination of substance and stream. Measurements of the concentrations reported here were made using what Radian considered to be the best method for each matrix. Typically, the method with the lowest detection limit was chosen, except when QA/QC audit results indicated significant problems with precision or bias for a particular technique. Additional information regarding selection of data is provided in Section 4. For each substance, a mean was calculated, along with the 95% confidence interval about the mean. The confidence interval is the range about the mean wherein the probability is 95% that he true mean lies. For example, according to the three results shown in Table 3-1, it can be said, with 95% certainty, that the true mean

Table 3-1
Coal Paste Composition (μg/g, dry unless noted)

Substance	Analytical Method	Run 1	Run 2	Run 3	Mean	95% CI
Date		4/12/94	4/13/94	4/14/94		
Gross Load (MW)	DAS	46	46	45		
Coal Paste Rate (lb/hr, dry)	DAS	33,750	33,570	33,020	33,500	940
Coal Paste Solids (wt%)	Gravimetric	75.0	74.6	75.1	74.9	0.7
HHV (Btu/lb, dry)	Proximate	12,900	12,700	12,600	12,700	380
Ash (wt%, dry)	Ultimate	11.2	11.8	14.1	12	4
Sulfur (wt%, dry)	Ultimate	3.1	3.4	3.6	3.4	0.6
Major Species						
Aluminum	INAA	14,800	15,300	16,800	15,600	2,600
Calcium	ICP-AES	1,100	1,400	1,400	1,300	430
Iron	INAA	20,200	17,200	23,200	20,200	7,500
Magnesium	ICP-AES	840	820	910	860	120
Potassium	INAA	5,040	4,310	3,540	4,300	1,900
Sodium	INAA	310	407	297	340	150
Titanium	ICP-AES	680	680	720	690	60
Target Species						
Antimony	INAA	0.44	0.47	0.52	0.48	0.10
Arsenic	INAA	38	50	48	45	17
Barium	ICP-AES	49	51	61	54	16
Beryllium	ICP-AES	1.7	1.5	1.6	1.6	0.3
Boron	ICP-AES	79	83	ND (3.0)	55	114
Cadmium	GFAAS	0.080	0.060	0.19	0.11	0.17
Chlorine	SIE	990	1,300	1,200	1,200	390
Chromium	ICP-AES	15	17	17	16	3
Cobalt	INAA	3.7	3.9	4.2	3.9	0.6
Copper	ICP-AES	6.8	6.7	7.4	7.0	0.9
Fluorine	SIE	120	99	120	110	30
Lead	GFAAS	6.0	6.0	7.0	6.3	1.4
Manganese	INAA	22	26	29	26	9
Mercury	CVAAS	0.16	0.16	0.13	0.15	0.04
Molybdenum	INAA	1.2	0.30	ND (0.51)	0.58	1.3
Nickel	INAA	12	8	18	13	12
Phosphorus	ICP-AES	90	97	100	96	13
Selenium	INAA	1.6	1.8	1.9	1.8	0.4
Silver	INAA	0.80	0.44	0.64	0.63	0
Vanadium	INAA	25	21	26	24	6

CI = Confidence interval.
ND = Not detected at the concentration in parentheses.

Table 3-2
Sorbent Composition (μg/g, as fired unless noted)

Substance	Analytical Method	Run 1	Run 2	Run 3	Mean	95% CI
Date		4/12/94	4/13/94	4/14/94		
Flow Rate (lb/hr, as fired)	DAS	18,000	21,000	19,000	19,300	3,800
Major Species						
Aluminum	ICP-AES	659	662	632	651	41
Calcium	ICP-AES	193,000	192,000	193,000	193,000	1,400
Iron	ICP-AES	2,130	2,430	2,160	2,240	410
Magnesium	ICP-AES	106,000	106,000	106,000	106,000	0
Potassium	ICP-AES	240	218	255	238	46
Sodium	ICP-AES	194	198	202	198	10
Titanium	ICP-AES	7.49	10.9	9.65	9.35	4.29
Sulfate	IC	6,420	6,370	6,460	6,420	110
Target Species						
Antimony	ICP-AES	ND (4.9)	ND (5.5)	ND (5.5)	ND (5.5)	--
Arsenic	GFAAS	2.2	2.1	1.2	1.9	1.3
Barium	ICP-AES	3.5	3.5	3.4	3.5	0.09
Beryllium	ICP-AES	0.049	ND (0.031)	ND (0.031)	ND (0.031)	--
Boron	ICP-AES	33	31	34	33	3
Cadmium	GFAAS	0.14	0.17	0.093	0.14	0.10
Chloride	SIE	370	340	250	320	160
Chromium	ICP-AES	2.8	2.9	2.9	2.8	0.1
Cobalt	ICP-AES	0.46	ND (0.5)	ND (0.50)	ND (0.5)	--
Copper	ICP-AES	ND (0.42)	ND (0.47)	ND (0.47)	ND (0.47)	--
Fluoride	SIE	300	210	140	210	200
Lead	GFAAS	7.3	6.2	7.2	6.9	2
Manganese	ICP-AES	72	73	72	72	1
Mercury	CVAAS	ND (0.012)	ND (0.012)	ND (0.012)	ND (0.012)	--
Molybdenum	ICP-AES	1.4	1.3	1.6	1.5	0.4
Nickel	ICP-AES	20	17	1	12	26
Phosphorus	ICP-AES	ND(6.1)	ND(6.8)	ND(6.8)	ND(6.8)	--
Selenium	GFAAS	0.90	0.48	0.98	0.79	0.68
Silver	ICP-AES	ND (0.37)	ND (0.41)	ND (0.41)	ND (0.41)	--
Vanadium	ICP-AES	4.8	4.9	5.2	4.9	0.5

CI = Confidence interval.
ND = Not detected at the concentration in parentheses.

arsenic concentration in the coal paste was between 14 and 40 μg/g. Calculation of this confidence interval is discussed in Section 5.

For those substance which could not be quantified, the notation "ND(x)" is used. This means "not detected at a concentration of x." The detection limit can vary according to sample size, sample preparation, and analytical method. All of the target species were detected in the coal paste. Levels of the target species were generally much lower in the sorbent, with the exception of fluoride, manganese and molybdenum.

Ash Streams

Tables 3-3 and 3-4 show the mean compositions of inorganic and organic species in the bed ash, cyclone ash, APF ash, and ESP ash. The ESP ash sample represents ash collected from the first two hoppers of the ESP. Composite samples were prepared by combining ESP ash collected from Hopper 1 with ash from Hopper 2 in a ratio of 90:10, respectively.

The compositions of the ash streams illustrate the differences and similarities between solid byproducts produced by conventional pulverized coal (PC) and PFBC combustion. The bed ash from the PFBC system is a dense, coarse material consisting primarily of sulfated lime, unreacted lime, magnesite, and char, making it very different from PC byproducts. Trace metals, which can either volatilize in the combustion process or volatilize/recondense on the fine particulate matter, are present at relatively low levels in the bed material compared to the other ash streams. The cyclone ash is comparable to fly ash from a PC unit, with the exception that it contains a significant amount of spent sorbent material. The ESP and APF ashes are very similar to the ash produced in a conventional PC boiler (i.e., higher levels of aluminum, potassium, sodium, and titanium). These ashes contain smaller amounts of spent dolomite and a greater percentage of the fine coal ash particulate; therefore, concentrations of trace metals are highest in these two streams due to the volatilization/condensation mechanism associated with the fine particulate. This is particularly evident for beryllium and lead where the concentrations in the ESP ash are 12 to 17 times higher than the concentration in the bed ash. Concentrations of major coal elements such as aluminum and titanium are

Table 3-3
Ash Stream Compositions - Inorganic Species ($\mu g/g$ unless noted)

Substance	Analytical Method	Bed Ash		Cyclone Ash		APF Ash		ESP Ash	
		Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI
Flow Rate (lb/hr)		9,300	2,100	10,300	3,290	313	61	775	76
Major Species									
Aluminum	ICP-AES	8,990	7,650	31,900	2,800	54,800	5,380	60,400	10,100
Calcium	ICP-AES	164,000	8,600	124,000	8,960	87,500	7,430	89,700	15,000
Iron	ICP-AES	15,300	13,700	50,200	1,940	28,700	1,250	27,400	2,500
Magnesium	ICP-AES	125,000	18,000	79,300	1,490	46,500	4,770	45,600	5,800
Potassium	ICP-AES	1,010	1,000	6,350	960	12,600	1,030	15,400	1,320
Sodium	ICP-AES	219	65	963	217	2,100	240	2,600	90
Titanium	ICP-AES	485	390	1,670	170	2,920	370	3,760	360
Carbon (wt%)	Ultimate	3.5	0.5	5.3	0.4	0.1	0.1	0.23	0.48
Sulfur (wt%)	Ultimate	7.8	0.8	3.9	0.3	16	2.3	9.2	20
Target Species									
Antimony	ICP-AES	ND (54)	--	ND (40)	--	ND (50)	--	ND (59)	--
Arsenic	GFAAS	71	27	93	16	270	71	380	62
Barium	ICP-AES	34	25	150	16	200	31	220	29
Beryllium	ICP-AES	0.65	0.49	3.8	1.2	6.5	2.1	8.0	2.4
Boron	ICP-AES	96	16	110	29	310	630	60	130
Cadmium	GFAAS	ND (1.6)	--	0.35	0.21	1.6	0.1	1.9	0.2
Chloride	SIE	890	380	360	110	110	380	ND (78)	--
Chromium	ICP-AES	19	6	44	4	74	8	94	10
Cobalt	ICP-AES	13	5	13	5	16	7	22	6
Copper	ICP-AES	ND (4.6)	--	ND (3.7)	--	ND(4.2)	--	6.5	12

Table 3-3 (Continued)

Substance	Analytical Method	Bed Ash		Cyclone Ash		APF Ash		ESP Ash	
		Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI
Fluoride[a]	SIE	100	14	110	93	ND (12)	--	110	91
Lead	GFAAS	5.0	3.2	19	6	69	19	84	48
Manganese	ICP-AES	100	32	110	7	100	5	110	9
Mercury	CVAAS	ND (0.010)	--	ND (0.012)	--	ND (0.012)	--	ND (0.012)	--
Molybdenum	ICP-AES	ND (3.5)	--	ND (2.8)	--	ND (3.3)	--	ND (3.8)	--
Nickel	ICP-AES	ND (11)	--	14	36	29	29	50	38
Phosphorus	ICP-AES	ND(70)	--	ND(71)	--	ND(71)	--	ND(71)	--
Selenium	GFAAS	4.6	1.4	4.0	7.6	ND (0.99)	--	4.9	1.2
Silver	ICP-AES	ND (4.1)	--	ND (3.3)	--	ND (3.8)	--	ND (4.4)	--
Vanadium	ICP-AES	20	10	55	12	87	13	120	17

[a] QA/QC results and material balance evaluations indicate that ash stream results are likely biased low.

CI = Confidence interval.

ND = Not detected at the concentration in parentheses.

Table 3-4
Ash Stream Compositions - Organic Species ($\mu g/g$, unless noted)

Substance	Bed Ash		Cyclone Ash		APF Ash		ESP Ash	
	Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI
Flow Rate (lb/hr)	9,300	2,100	10,300	3,290	313	61	775	76
Semivolatile Organic Species								
bis(2-Ethylhexyl)phthalate	ND(0.05)	--	ND(0.05)	--	ND(0.05)	--	0.34	0.91
Dioxin and Furan Species (pg/g)								
1,2,3,4,6,7,8-HpCDD	NS	--	ND(0.9)	--	ND(0.6)	--	1.4	1.0
2,3,4,6,7,8-HxCDF	NS	--	ND(0.4)	--	0.3	0.3	ND(0.8)	--
Total HpCDD	NS	--	ND(0.9)	--	ND(0.6)	--	2.3	1.0
Total HxCDD	NS	--	ND(0.7)	--	ND(0.4)	--	5.8	1.8
Total HxCDF	NS	--	ND(0.4)	--	0.3	0.3	ND(0.8)	--
Total PeCDD	NS	--	ND(0.7)	--	ND(0.4)	--	4.6	1.5
Total TCDD	NS	--	ND(0.4)	--	ND(0.3)	--	3.2	0.9

CI = Confidence interval.
ND = Not detected at the concentration in parentheses.
NS = Not sampled.
HpCDD = Heptachlorodibenzo-p-dioxin.
HxCDF = Hexachlorodibenzofuran.
HxCDD = Hexachlorodibenzo-p-dioxin.
PeCDD = Pentachlorodibenzo-p-dioxin.
TCDD = Tetrachlorodibenzo-p-dioxin.

generally five to seven times higher in the ESP ash than in the bed ash. It is also interesting to note the difference in the carbon content of the various ash streams. The bed ash and cyclone ash contain roughly 4% to 5% carbon, whereas the APF ash and ESP ash contain about 0.1% to 0.2% carbon.

None of the target semivolatile organic compounds were present in the ash stream at levels above the detection limits, with the exception of bis(2-ethylhexyl)phthalate in the ESP ash. Levels of this compound in the three ESP ash samples ranged from 0.06 μg/g to 0.75 μg/g. Phthalate esters are typical plasticizers commonly attributed to plastic bottles, bags, etc., used in the field laboratory environment. Although all samples for organic compound analyses were collected in glass jars, the presence of this phthalate compound is most likely due to contamination.

Results for dioxin and furan compounds indicate that none of the target compounds were detected in the cyclone ash samples. 2,3,4,6,7,8-hexachlorodibenzofuran and total hexachlorodibenzofuran were detected in all three APF ash samples at a mean concentration of 0.3 pg/g (picograms/gram). 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin, total heptachlorodibenzo-p-dioxin, total hexachlorodibenzo-p-dioxin, total pentachlorodibenzo-p-dioxin, and total trichlorodibenzo-p-dioxin were detected in all three ESP ash samples at concentrations in the range of 1.4 to 5.8 pg/g.

Service Water

Characterization data for the plant service water are shown in Table 3-5. Levels of target inorganic species indicate that the service water does not contribute significant amounts of these species to the process.

Table 3-5
Service Water Composition (μg/mL unless noted)

Substance	Analytical Method	Run 1	Run 2	Run 3	Mean	95% CI
Date		4/12/94	4/13/94	4/14/94		
Flow Rate (lb/hr)	DAS	11,250	11,430	10,980	11,220	570
Flow Rate (L/hr)	DAS	5,100	5,200	5,000	5,100	250
Major Species						
Aluminum	ICP-AES	1.3	2.2	1.9	1.8	1.2
Calcium	ICP-AES	24	26	22	24	5
Iron	ICP-AES	3.0	4.7	4.5	4.1	2.3
Magnesium	ICP-AES	6.3	6.7	5.8	6.2	1.2
Potassium	ICP-AES	1.6	1.8	1.8	1.7	0.3
Sodium	ICP-AES	10	11	10	10	1
Sulfate	IC	59	58	47	55	17
Phosphorus	ICP-AES	ND(0.06)	ND(0.06)	ND(0.06)	ND(0.06)	–
Total phosphate (as P)	Colorimetry	ND(0.02)	ND(0.02)	0.03	ND(0.02)	–
Target Species						
Antimony	ICP-AES	ND(0.076)	ND(0.076)	ND(0.076)	ND(0.076)	–
Arsenic	GFAAS	ND(0.00065)	0.0011	0.0017	0.0011	0.0017
Barium	ICP-AES	0.049	0.069	0.066	0.061	0.027
Beryllium	ICP-AES	0.0016	0.00054	0.0046	0.0022	0.0052
Boron	ICP-AES	0.043	0.041	0.042	0.042	0.002
Cadmium	GFAAS	ND(0.00027)	ND(0.00027)	ND(0.00027)	ND(0.00027)	–
Chloride	IC	12	12	12	12	1
Chromium	ICP-AES	ND(0.0052)	ND(0.0052)	0.00788	ND(0.0052)	–
Cobalt	ICP-AES	0.0071	0.0046	ND(0.0041)	0.0046	0.0063
Copper	ICP-AES	0.013	0.017	0.021	0.017	0.010
Lead	GFAAS	0.0063	0.012	0.013	0.010	0.009
Manganese	ICP-AES	0.29	0.44	0.43	0.39	0.21
Mercury	CVAAS	ND(0.00003)	ND(0.00003)	ND(0.00003)	ND(0.00003)	–
Molybdenum	ICP-AES	ND(0.0074)	ND(0.0074)	0.00739	ND(0.0074)	–
Nickel	ICP-AES	ND(0.014)	ND(0.014)	0.0145	ND(0.014)	–
Selenium	GFAAS	ND(0.0018)	ND(0.0018)	ND(0.0018)	ND(0.0018)	–
Silver	ICP-AES	ND(0.0052)	ND(0.0052)	ND(0.0052)	ND(0.0052)	–
Titanium	ICP-AES	0.014	0.023	0.025	0.021	0.015
Vanadium	ICP-AES	0.0053	ND(0.0045)	0.0076	0.0051	0.0066

ESP Inlet and Outlet Gas

Inorganic Species

Tables 3-6 and 3-7 show the concentrations of the target inorganic analytes in the ESP inlet and outlet gas streams, respectively. The data are presented as solid and vapor-phase compositions, along with the mean concentrations and confidence intervals of the combined phases. Although the data are presented as solid- and vapor-phase concentrations, it is important to note that the Method 29 multi-metals train has not been validated by EPA for determination of phase splits. For ease of interpretation, researchers typically assume that the material collected on the filter represents the solid-phase composition, while the material collected in the impiner solutions represent vapor-phase composition. It is possible for extremely fine particulate matter to penetrate the pores of the filter and be collected in the nitric acid/hydrogen peroxide impinger solution. The gas flow rate data represent the average of the flow rate measurements obtained from all the trains which were traversed in the duct for a given run.

The solid-phase multi-metals train data from the ESP outlet have been corrected for the background levels associated with the quartz filters. At the ESP inlet, filtered gas particulate matter was analyzed separately from the filter media, so background corrections were not necessary. Vapor-phase data have been corrected for the background levels present in the nitric acid/hydrogen peroxide impinger reagent due to the lower detection limits provided by ICP-MS and the significance of the background levels compared to the samples.

Reported solid-phase concentrations for antimony, barium, beryllium, chromium, cobalt, copper, manganese, molybdenum, nickel, silver, vanadium, and all major species were determined by ICP-AES. Arsenic, cadmium, lead, and selenium were determined by GFAAS. Mercury was determined by CVAAS. Chloride and sulfate were determined by IC, while fluoride was determined by SIE.

Table 3-6
ESP Inlet Gas Composition - Inorganic Species (µg/Nm^3 unless noted)

Substance	Solid Phase				Vapor Phase				Total	
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Mean	95%CI
Date	4/12/94	4/13/94	4/14/94	4/15/94	4/12/94	4/13/94	4/14/94	4/15/94		
Gas Flow Rate (dscfm)[a]	153,000	151,000	153,000	146,000					151,000	5,300
Gas Flow Rate (Nm^3/hr)[a]	242,000	240,000	242,000	231,000					239,000	8,500
Particulate Matter (lb/hr)	778	809	800						796	39
Particulate Matter (mg/Nm^3)	1,460	1,530	1,500						1,500	96
Major Species										
Aluminum	72,600	55,900	73,500	NS	36	43	66	NS	67,400	24,600
Calcium	107,000	87,900	114,000	NS	180	260	370	NS	103,000	33,000
Iron	32,500	27,900	34,100	NS	31	30	370	NS	31,500	8,200
Magnesium	54,400	44,900	57,600	NS	26	27	58	NS	52,300	16,500
Phosphorus	30	26	30	NS	ND(19)	ND(19)	ND(17)	NS	28	6
Potassium	18,000	13,100	17,800	NS	ND(250)	ND(250)	ND(230)	NS	16,300	6,870
Sodium	3,390	2,460	3,090	NS	207	294	250	NS	3,230	1,060
Sulfate	9,441,000	9,151,000	9,260,000	NS	795,000	756,000	784,000	NS	10,100,000	411,000
Titanium	4,430	3,360	4,340	NS	1.2	1.6	3.0	NS	4,040	1,480
Target Species										
Ammonia	NS	NS	NS	NS	160	95	120	NS	130	87
Antimony	ND(3.2)	ND(2.9)	ND(76)	NS	0.016	0.016	0.017	NS	ND(76)[b]	--
Arsenic	450	380	420	NS	0.34	0.26	0.36	NS	420	79
Barium	260	190	270	NS	ND(0.005)	ND(0.005)	ND(0.005)	NS	240	110
Beryllium	10	6.8	8.7	NS	ND(0.005)	ND(0.005)	0.026	NS	8.6	4.2
Boron	1.2	2.5	4.4	NS	200	210	190	NS	200	23

Table 3-6 (Continued)

Substance	Solid Phase				Vapor Phase				Total	
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Mean	95%CI
Cadmium	3.7	2.3	2.3	NS	1.1	0.22	0.15	NS	3.2	3.3
Chloride	1,600	1,800	860	NS	68,000	67000	74,000	NS	71,000	7,200
Chromium (multi-metals)	150	100	120	NS	3.8	0.76	26	NS	130	60
Cobalt	22	20	26	NS	0.019	0.019	1.1	NS	23	9
Copper	11	17	ND(6.7)	NS	0.63	0.23	2.4	NS	11	19
Cyanide	NS	NS	NS	NS	870	610	390	NS	630	590
Fluoride	4,100	3,200	2,300	NS	7,000	6,300	6,400	NS	9,800	3,100
Lead	76	70	75	NS	ND(0.005)	ND(0.005)	ND(0.005)	NS	73	8
Manganese	130	150	140	NS	1.2	1.2	3.3	NS	140	22
Mercury(total)	0.079	0.050	0.072	NS	15	16	15	NS	16	2
Mercury (nitric impingers)	--	--	--	NS	12	14	13	NS	--	--
Mercury (permanganate impingers)	--	--	--	NS	3.4	2.1	1.7	NS	--	--
Molybdenum	ND(1.6)	ND(3.4)	ND(1.2)	NS	0.14	ND(0.008)	3.3	NS	ND(3.4)[b]	--
Nickel	50	43	49	NS	0.15	0.20	29	NS	57	45
Selenium	52	43	41	NS	20	14	17	NS	62	21
Silver	ND(2.1)	0.45	ND(5.7)	NS	ND(1.6)	ND(1.6)	ND(1.4)	NS	ND(5.7)	--
Vanadium	130	100	130	NS	1.5	0.83	0.94	NS	120	42

[a] Assumed equal to the measured ESP outlet gas flow rate. Measured ESP inlet flow rate are considered non-representative because of the non-ideal sampling location.

[b] Substance detected in the vapor phase at low levels. Reported value is an upper limit.

CI = Confidence interval.

ND = Not detected at the concentration in parentheses.

NS = Not sampled.

Table 3-7
ESP Outlet Gas Composition - Inorganic Species ($\mu g/Nm^3$ unless noted)

Substance	Solid Phase				Vapor Phase				Total	
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Mean	95% CI
Date	4/12/94	4/13/94	4/14/94	4/15/94	4/12/94	4/13/94	4/14/94	4/15/94		
Gas Flow Rate (dscfm)	153,000	151,000	153,000	146,000					151,000	5,300
Gas Flow Rate (Nm^3/hr)	242,000	240,000	242,000	231,000					239,000	8,500
Particulate Matter (lb/hr)	33	4.4	29						22	38
Particulate Matter (mg/Nm^3)	61	8.2	54						41	72
Major Species										
Aluminum	140	56	29	NS	38	42	53	NS	120	126
Calcium	270	227	152	NS	213	256	342	NS	490	14
Iron	220	705	92	NS	42	48	61	NS	392	793
Magnesium	110	94	61	NS	25	16	30	NS	114	55
Phosphorus	3.4	3.8	3.1	NS	ND(16)	ND(19)	ND(16)	NS	3.4	0.8
Potassium	39	24	18	NS	ND(210)	ND(250)	ND(210)	NS	27	26
Sodium	77	48	36	NS	287	310	338	NS	360	23
Sulfate	450	4,940	198	NS	780,000	746,000	--[b]	NS	766,000	188,000
Titanium	16	5.9	4.0	NS	1.2	1.6	1.8	NS	10	16
Target Species										
Ammonia	NS	NS	NS	NS	94	130	93	NS	110	54
Antimony	ND(2.0)	ND(2.1)	ND(2.0)	NS	0.013	0.017	0.023	NS	ND(2.1)[a]	--
Arsenic	0.78	1.1	0.63	NS	0.16	0.24	0.26	NS	1.0	0.5
Barium	1.9	0.19	0.11	NS	ND(0.004)	ND(0.005)	ND(0.004)	NS	0.74	7.5
Beryllium	0.01	ND(0.012)	ND(0.011)	NS	ND(0.004)	ND(0.005)	0.048	NS	0.021	0.17
Boron	NA	NA	NA	NS	170	160	160	NS	170	19

Table 3-7 (Continued)

Substance	Solid Phase				Vapor Phase				Total	
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Mean	95% CI
Cadmium	0.67	0.27	0.38	NS	ND(0.005)	0.55	3.5	NS	1.8	4.5
Chloride	1.3	1.2	3.8	NS	66,000	66,000	69,000	NS	67,000	5,200
Chromium (multi-metals)	1.7	1.8	0.8	NS	1.4	0.89	4.7	NS	3.7	3.7
Cobalt	ND(0.19)	ND(0.19)	ND(0.18)	NS	0.020	0.048	0.065	NS	ND(0.19)[a]	--
Copper	1.6	2.3	0.71	NS	0.46	2.2	4.9	NS	4.1	4.4
Cyanide	NS	NS	NS	NS	810	370	300	NS	490	680
Fluoride	ND(0.12)	0.13	ND(0.12)	NS	5,100	4,100	4,300	NS	4,500	1,400
Lead	1.4	ND(0.027)	ND(0.13)	NS	ND(0.004)	ND(0.005)	0.53	NS	0.65	3.8
Manganese	2.4	7.4	1.0	NS	ND(0.006)	1.0	8.7	NS	6.9	9.8
Mercury (total)	0.0042	0.0045	ND(0.0082)	NS	15	15	14	NS	15	1
Mercury (nitric impingers)	--	--	--	NS	13	14	12	NS	--	--
Mercury (permanganate impingers)	--	--	--	NS	1.8	1.6	1.9	NS	--	--
Molybdenum	0.32	ND(0.13)	0.37	NS	ND(0.007)	ND(0.008)	0.071	NS	0.25	0.57
Nickel	0.98	8.8	1.3	NS	0.72	1.3	4.9	NS	6.0	11
Selenium	19	19	19	NS	13	19	30	NS	39	21
Silver	ND(0.15)	1.0	ND(0.15)	NS	ND(1.3)	ND(1.6)	ND(1.3)	NS	0.40	1.4
Vanadium	0.24	0.18	0.14	NS	0.67	0.85	1.0	NS	1.0	0.33

[a] Substance detected in vapor phase at low levels. Reported concentration is an upper limit.

[b] Value considered suspect. Data were not used in the calculation of the mean total concentration.

CI = Confidence interval.
NA = Not analyzed.
ND = Not detected at the concentration in parentheses.
NS = Not sampled.

QA/QC audit sample results for the following target species did not meet the 75%-125% recovery objective for the filtered particulate matter audit sample: cadmium (919%), cobalt (51%), manganese (69%), molybdenum (129%), and selenium (175%). However, matrix spike results for these elements in the samples indicate good analytical precision and accuracy. These results indicate a potential bias in the reported particulate-phase ESP outlet results for these substances. Refer to Section 4 for a detailed discussion of QA/QC results.

Reported vapor-phase concentrations for the target species were determined by ICP-MS, with the exception of boron (ICP-AES), mercury (CVAAS), and silver (ICP-AES). Other techniques such as GFAAS and ICP-AES were also used for many of the species; however, the ICP-MS data were selected based on their superior detection limits and performance. In most cases, the levels of target species in the vapor phase at the ESP outlet were below detection limits for GFAAS and ICP-AES methods; therefore, the use of the ICP-MS technique provided a means to accurately quantify the very low levels found in the gas streams. All major metal species were determined by ICP-AES.

Boron, chloride, fluoride, mercury and selenium were quantified in the vapor phase at both the ESP inlet and outlet locations because of their high volatility at the temperatures within the ESP (approximately 350°F). Levels of vapor-phase mercury in the nitric acid/hydrogen peroxide and potassium permanganate impinger solutions were similar at both locations. Approximately 10-15% of the total vapor-phase mercury was found in the permanganate impinger solutions, which is believed to capture the elemental species of mercury (Hg^0). Conversely, the nitric acid/hydrogen peroxide impinger solution contained 85-90% of the vapor-phase mercury and is believed to capture ionic mercury species. Essentially 100% of the mercury entering the system exits in the ESP outlet gas. For chloride, fluoride, and selenium, these percentages are somewhat smaller: 80%, 30%, and 24%, respectively. Ammonia and cyanide were quantified in both the ESP inlet and outlet gas at levels well above detection limits.

QA/QC results for ICP-MS analysis of the nitric acid impinger solutions indicate that vapor-phase results for antimony, selenium, and nickel may be biased slightly low based on recovery data for the audit samples (recoveries in the 60-70% range were reported). Matrix-spiked sample results indicate acceptable analytical accuracy for all species except selenium. Major species such as aluminum, calcium, iron, magnesium, sodium, and titanium were detected in the vapor-phase fractions at similar levels at both locations after background corrections were applied. QA/QC audit sample results for calcium, potassium, and sodium indicate a high bias in the ICP-AES method used to measure these species in this matrix near the detection limit. Recovery results for the nitric acid/hydrogen peroxide impinger audit sample indicate recoveries of 151% (calcium), 1420% (potassium), and 321% (sodium). Thus, sample results for these elements may be biased high.

Organic Species

Tables 3-8 and 3-9 show the concentrations of the target organic species in the ESP inlet gas. Tables 3-10 and 3-11 show results for organic species in the ESP outlet gas. Since the number of volatile and semivolatile organic compounds analyzed was quite large and very few compounds were detected, only those species which were present at levels above the detection limit in one or more samples are reported. Complete results for substances which were not detected are provided in Appendix B.

The following volatile organic compounds were detected in VOST samples collected at the ESP inlet: 1,2-dichloroethane, benzene, carbon disulfide, chloromethane, methylene chloride, and toluene. None of these substances were detected in the reagent blanks which are used to assess background levels in the sampling media; however; chloromethane, methylene chloride, and toluene were detected in the field blank samples, indicating potential field contamination for these three substances. The presence of toluene and methylene chloride are not unexpected, since these solvents are routinely used to rinse probes after sample collection and were present at all four gas sampling locations. 1,2-dichloroethane and carbon disulfide were present at levels which were less than five times the detection limit (0.5 $\mu g/Nm^3$); therefore, the presence of these species in the ESP inlet gas is uncertain. Benzene was not present in the reagent blank and was the only species consistently detected in the samples at levels greater than five times the detection limit; therefore, it is considered

Table 3-8
ESP Inlet Gas Composition - VOST and Method 23 Species (μg/Nm^3 unless noted)

Substance	Run 1	Run 2	Run 3	Run 4	Mean	95% CI	Mean Blank Level[a]
Date	4/12/94	4/13/94	4/14/94	4/15/94			
Gas Flow Rate (dscfm)	153,000	151,000	153,000	146,000	152,000	5,300	
Gas Flow Rate (Nm^3/hr)	242,000	240,000	242,000	231,000	241,000	8,500	
VOST							
1,2-Dichloroethane	2.0	ND(0.5)	ND(0.6)	NS	0.84	2.4	ND(0.5)
Benzene	6.5	11	6.7	NS	8.0	6.0	ND(0.5)
Carbon Disulfide	0.83	1.3	1.0	NS	1.0	0.59	ND(0.5)
Chloromethane	1.3[b]	1.4[b]	1.1[b]	NS	1.3[b]	0.34	ND(0.5)
Methylene Chloride	ND(0.8)	14[b]	3.5[b]	NS	6.0[b]	18	ND(0.5)
Toluene	ND(0.8)	1.8[b]	1.1[b]	NS	1.1[b]	1.7	ND(0.5)
Dioxin/Furan (pg/Nm^3)							
1,2,3,4,6,7,8-HpCDD	NS	6.4	3.3 E	6.4	5.3	4.5	ND(2.8)
1,2,3,4,6,7,8-HpCDF	NS	0.32 E	1.6 E	2.0	1.3	2.2	ND(1.4)
1,2,3,4,7,8-HxCDD	NS	ND(4.1)	ND(2.7)	ND(4.4)	ND(4.4)	--	ND(2.8)
1,2,3,4,7,8-HxCDF	NS	6.4 E	1.6 E	2.0 B	3.3	6.6	1.4 E
1,2,3,6,7,8-HxCDF	NS	2.2	ND(1.7)	ND(2.0)	ND(2.0)	--	ND(1.0)
1,2,3,7,8-PeCDF	NS	0.96 E	ND(0.99)	ND(1.7)	ND(1.7)	--	ND(1.0)
2,3,4,6,7,8-HxCDF	NS	3.2 E,B	3.3 E,B	2.9 B	3.1	0.40	2.1
2,3,7,8-TCDF	NS	ND(1.7)	1.7 E	ND(1.5)	ND(1.7)	--	ND(1.0)
OCDD	NS	57	34	43	44	28	3.4 E
OCDF	NS	8.4	ND(4.3)	5.2	5.2	7.7	ND(3.4)

Table 3-8 (Continued)

Substance	Run 1	Run 2	Run 3	Run 4	Mean	95% CI	Mean Blank Level[a]
Total HpCDD	NS	6.4	3.6	11	6.8	8.6	ND(2.8)
Total HpCDF	NS	2.6 E	3.3 E	2.6	2.8	0.98	ND(1.7)
Total HxCDD	NS	1.6 E	2.4	2.5 E	2.2	1.2	ND(2.1)
Total HxCDF	NS	7.2 B	6.5 E,B	6.3	6.7	1.1	2.1
Total PeCDD	NS	3.2	2.0 E	2.2	2.4	1.7	ND(1.4)
Total PeCDF	NS	5.4	0.98 E	2.2	2.8	5.6	ND(1.0)
Total TCDD	NS	ND(1.7)	1.6	1.7 E	ND(1.7)	--	ND(1.4)
Total TCDF	NS	ND(1.7)	1.6 E	ND(1.5)	ND(1.7)	--	ND(1.0)
Aldehydes							
Formaldehyde	8.7	4.5	3.0	NS	5.4	7.4	ND

[a] Calculated based on the mean level in the reagent blank divided by the mean gas sample volume.

[b] Levels in the field blanks are ≥30% of the sample value.

B indicates the substance was detected in the reagent blanks at ≥30% of the sample value.
E indicates value is an estimated upper limit.
CI = Confidence interval
ND = Not detected at the concentration in parentheses.
NS = Not sampled.
HpCDD = Heptachlorodibenzo-p-dioxin.
HpCDF = Heptachlorodibenzofuran.
HxCDD = Hexachlorodibenzo-p-dioxin.
HxCDF = Hexachlorodibenzofuran.
PeCDD = Pentachlorodibenzo-p-dioxin.
PeCDF = Pentachlorodibenzofuran.
TCDD = Tetrachlorodibenzo-p-dioxin.
TCDF = Tetrachlorodibenzofuran.
OCDD = Octachlorodibenzo-p-dioxin.
OCDF = Octachlorodibenzofuran.

Table 3-9
Results for Semivolatile Organic Species at the ESP Inlet

Substance	Particulate Phase			Vapor Phase			Total	
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Mean	95% CI
PAHs by HRGC/MS (ng/Nm^3)								
Acenaphthene	1.8 B	3.5 B	2.2 B	35 B	12 B	7.9 B	21 B	35
Acenaphthylene	0.53 B	0.54 B	0.45 B	6.5	19	43	23	46
Anthracene	1.1 B	0.90 B	0.47 B	11	1.1 B	0.94 B	5.1 B	15
Benzo(a)anthracene	1.6 B	0.37 B	1.0 B	0.86	0.32 B	0.63	1.6 B	2.2
Benzo(a)pyrene	2.2 B	0.62 B	1.1 B	1.3	0.37 B	0.56 B	2.1 B	3.2
Benzo(b)fluoranthene	5.0 B	0.98 B	2.8 B	2.4	1.1 B	1.5 B	4.6 B	6.6
Benzo(g,h,i)perylene	5.2 B	2.9 B	5.3 B	2.5 B	1.4 B	1.4 B	6.3 B	4.3
Benzo(k)fluoranthene	1.7 B	0.29 B	1.3 B	0.93	0.32 B	0.45 B	1.7 B	2.5
2-Chloronaphthalene	0.064	0.12	0.058	0.59	1.1	1.9	1.3	1.6
Chrysene	3.5 B	1.6 B	2.2 B	2.3	1.4	1.5	4.2 B	3.6
Dibenz(a,h)anthracene	0.64 B	ND(0.51)	3.4	0.45 B	ND(0.23)	0.41 B	1.7 B	4.2
Fluoranthene	7.4 B	4.4 B	3.7 B	18	10 B	11	18 B	16
Fluorene	4.1 B	3.3 B	2.9 B	10 B	6.8 B	7.4 B	12 B	6.0
Indeno(1,2,3-cd)pyrene	2.5 B	0.75 B	2.7 B	1.4	0.56 B	0.78 B	2.9 B	3.5
2-Methylnaphthalene	16 B	14 B	13 B	46 B	32 B	43 B	55 B	19
Naphthalene	140 B	370 B	150 B	180 B	200 B	73 B	370 B	440
Phenanthrene	24 B	13 B	15 B	68	32 B	27 B	59 B	69
Pyrene	5.0 B	9.9 B	4.1 B	16	3.5 B	4.0 B	14 B	17

Table 3-9 (Continued)

Substance	Particulate Phase			Vapor Phase			Total	
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Mean	95% CI
Semivolatile Organic Compounds by 8270 ($\mu g/Nm^3$)								
Acetophenone	ND(2.9)	ND(2.3)	ND(2.6)	4.1 J	4.7 J	2.5 J	3.8 J	2.9
Benzoic acid	ND(11)	ND(9.0)	ND(9.8)	120 E	220 d	120 d	150 d	140
Butylbenzylphthalate	ND(1.4)	ND(1.2)	ND(1.3)	0.70 J	ND(0.44)	ND(0.48)	ND(0.48)	--
Di-n-butylphthalate	110 d	5.1 J,B	2.3 J,B	11 B	2.0 J,B	29	52 d,J,B	150
Di-n-octylphthalate	ND(0.69)	ND(0.56)	ND(0.64)	ND(0.30)	0.19 J	ND(0.70)	ND(0.70)	--
Diethylphthalate	ND(1.5)	ND(1.2)	ND(1.3)	0.77 J	0.97 J	ND(0.35)	0.64 J	0.78
bis(2-Ethylhexyl)phthalate	8.5 B	4.7 J,B	5.5 J,B	470 d	9.0	1.2 J,B	170 d,J,B	670
Hexachlorobenzene	ND(3.8)	ND(3.3)	ND(3.4)	34	ND(1.3)	ND(1.4)	12	47
Isophorone	ND(1.7)	ND(1.5)	ND(1.6)	ND(0.39)	6.8 J	11	6.1 J	14
Naphthalene	5.3 J,B	ND(0.92)	ND(1.0)	0.67 J,B	0.73 J,B	ND(0.34)	2.3 J,B	8.0
4-Nitrophenol	ND(12)	ND(10)	ND(11)	ND(1.7)	0.47	ND(2.0)	ND(1.4)	--
Phenol	ND(2.4)	ND(2.0)	ND(2.2)	2.8 J	3.0 J	1.7 J	2.5 J	1.8

B indicates the substance was detected in the reagent blank at levels greater than or equal to 30% of the sample value.

J indicates that the concentration was less than the quantitation limit of the method but above the detection limit.

d indicates that the undiluted sample exceeded the calibration range of the instrument; result shown is for the diluted sample.

CI = Confidence interval.

ND = Not detected at the concentration in parentheses.

Table 3-10
ESP Outlet Gas Composition - VOST and Method 23 Species

Substance	Run 1	Run 2	Run 3	Run 4	Mean	95% CI	Mean Blank Level[a]
Date	4/12/94	4/13/94	4/14/94	4/15/94			
Gas Flow Rate (dscfm)	153,000	151,000	153,000	146,000	152,000	5,300	
Gas Flow Rate (Nm^3/hr)	242,000	240,000	242,000	231,000	241,000	8,500	
VOST (μg/Nm^3)							
Bromodichloromethane	0.6	ND(0.5)	ND(0.5)	NS	ND(0.5)	--	ND(2.5)
Bromoform	ND(0.5)	ND(0.5)	ND(0.5)	NS	ND(0.5)	--	ND(2.5)
Bromomethane	0.7	ND(0.5)	ND(0.5)	NS	ND(0.5)	--	ND(0.5)
Chloroethane	1.1	ND(0.5)	ND(0.5)	NS	ND(0.5)	--	ND(0.5)
Chloroform	ND(0.5)	0.5	ND(0.5)	NS	ND(0.5)	--	ND(0.5)
1,1,1-Trichloroethane	0.7	0.60	37	NS	13	52	ND(0.5)
1,2-Dichloroethane	16	2.5	2.5	NS	7.0	20	ND(0.5)
Benzene	3.8	5.4	6.8	NS	5.4	3.7	ND(0.5)
Carbon Disulfide	1.0	0.7	0.74	NS	0.83	0.42	ND(0.5)
Chloromethane	6.7	ND(0.5)	3.7	NS	3.5	8.0	ND(0.5)
Methylene Chloride	2.1[b]	0.82[b]	5.8[b]	NS	2.9[b]	6.4	ND(0.5)
Toluene	0.95[b]	1.7[b]	0.89[b]	NS	1.2[b]	1.1	ND(0.5)
Dioxin/Furan (pg/Nm^3)							
1,2,3,4,6,7,8-HpCDD	NS	5.3	11	1.9 E	5.9	11	ND(2.8)
1,2,3,4,6,7,8-HpCDF	NS	ND(1.6)	7.3 E	7.5 E	5.2	9.5	ND(1.4)
1,2,3,4,7,8-HxCDD	NS	ND(3.1)	ND(3.9)	ND(3.6)	ND(3.9)	--	ND(2.8)
1,2,3,4,7,8-HxCDF	NS	1.9 E	1.5 E,B	10	4.5	12	1.4 E
1,2,3,4,7,8,9-HpCDF	NS	ND(2.8)	ND(3.9)	ND(4.0)	ND(4.01)	--	ND(2.4)
1,2,3,6,7,8-HxCDD	NS	ND(2.5)	ND(3.2)	ND(2.9)	ND(3.2)	--	ND(2.1)
1,2,3,6,7,8-HxCDF	NS	ND(1.2)	ND(1.8)	2.4	ND(1.77)	--	ND(1.0)

Table 3-10 (Continued)

Substance	Run 1	Run 2	Run 3	Run 4	Mean	95% CI	Mean Blank Level[a]
1,2,3,7,8-PeCDF	NS	ND(1.2)	ND(1.8)	2.3 E	ND(1.77)	--	ND(1.0)
2,3,4,6,7,8-HxCDF	NS	2.9 E,B	3.9 B	4.0 B	3.58	1.6	2.1
2,3,4,7,8-PeCDF	NS	ND(1.2)	ND(1.8)	1.5 E	ND(1.77)	--	ND(1.0)
2,3,7,8-TCDF	NS	ND(1.2)	ND(1.6)	1.8	ND(1.59)	--	ND(1.0)
OCDD	NS	48	110	30 E	62	100	3.4 E
OCDF	NS	6.1	20	ND(6.2)	9.90	23	ND(3.4)
Total HpCDD	NS	11	20	3.9	11	20	ND(2.8)
Total HpCDF	NS	ND(1.9)	7.5	2.4	3.60	8.6	ND(1.7)
Total HxCDD	NS	ND(2.8)	2.9 E	ND(3.3)	ND(3.28)	--	ND(2.1)
Total HxCDF	NS	6.3 E,B	6.4 B	22	11	22	2.1
Total PeCDD	NS	1.3 E	ND(2.8)	ND(1.8)	ND(2.83)	--	ND(1.4)
Total PeCDF	NS	ND(1.2)	3.2	6.7	3.49	7.5	ND(1.0)
Total TCDD	NS	ND(1.2)	8.0E-07	ND(1.5)	ND(1.46)	--	ND(1.4)
Total TCDF	NS	ND(6.2E-07)	ND(1.6)	1.8	ND(1.59)	--	ND(1.0)
Aldehydes ($\mu g/Nm^3$)							
Formaldehyde	5.1	3.5	3.6	NS	4.1	2.3	ND

[a] Calculated based on the mean level in the reagent blank divided by the mean gas sample volume.
[b] Levels in the field blanks are ≥30% of the sample value.
B indicates the substance was detected in the reagent blanks at ≥30% of the sample value.
E indicates value is an estimated upper limit.
CI = Confidence interval.
ND = Not detected at the concentration in parentheses.
NS = Not sampled.
HpCDD = Heptachlorodibenzo-p-dioxin.
HpCDF = Heptachlorodibenzofuran.
HxCDD = Hexachlorodibenzo-p-dioxin.
HxCDF = Hexachlorpdibenzofuran.
PeCDD = Pentachlorodibenzo-p-dioxin.
PeCDF = Pentachloorodibenzofuran.
TCDD = Tetrachlorodibenzo-p-dioxin.
TCDF = Tetrachlorodibenzofuran.
OCDD = Octachlorodibenzo-p-dioxin.
OCDF = Octachlorodibenzofuran.

Table 3-11
Results for Semivolatile Organic Species at the ESP Outlet

Substance	Particulate Phase			Vapor Phase			Total	
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Mean	95% CI
PAHs by HRGC/MS (ng/Nm^3)								
Acenaphthene	1.9 B	2.6 B	0.92 B	15 B	23 B	180	75 B	230
Acenaphthylene	0.54 B	0.75 B	0.24 B	84 B	4.4	210	98	250
Anthracene	1.1 B	1.6 B	0.33 B	1.0 B	0.82 B	1.5 B	2.1 B	0.71
Benzo(a)anthracene	0.33 B	0.15 B	0.26 B	0.61 B	0.46 B	0.87	0.89 B	0.66
Benzo(a)pyrene	0.48 B	0.17 B	0.16 B	1.3	0.62 B	NR	0.90 B	2.0
Benzo(b)fluoranthene	0.83 B	0.56 B	0.50 B	1.7	1.4 B	1.1 B	2.0 B	1.1
Benzo(g,h,i)perylene	2.2 B	0.86 B	1.2 B	1.6 B	1.6 B	180	62 B	250
Benzo(k)fluoranthene	0.25 B	0.14 B	0.13 B	0.70	0.44 B	0.59	0.75 B	0.46
2-Chloronaphthalene	ND(0.019)	ND(0.024)	ND(0.10)	1.9	0.72	0.32	0.97	2.0
Chrysene	0.56	0.51 B	0.94 B	1.6	0.72 B	0.98	1.8 B	1.2
Dibenz(a,h)anthracene	ND(0.066)	ND(0.037)	ND(0.24)	0.54 B	ND(0.65)	0.35 B	ND(0.65)	--
Fluoranthene	4.2 B	5.6 B	2.0 B	12	5.0 B	6.4 B	12 B	9.9
Fluorene	5.6 B	11 B	2.3 B	8.4 B	5.0 B	7.9 B	13 B	7.2
Indeno(1,2,3-cd)pyrene	0.79 B	0.36 B	0.33 B	0.92 B	0.69 B	5.7	2.9 B	6.8
2-Methylnaphthalene	10 B	14 B	5.3 B	110 B	59 B	61 B	85 B	67
Naphthalene	15 B	19 B	17 B	94 B	170 B	62 B	130 B	150
Phenanthrene	33 B	48 B	11 B	35 B	22 B	25 B	58 B	48
Pyrene	2.1 B	2.6 B	1.5 B	2.0 B	3.0 B	1.2 B	4.1 B	3.7

Table 3-11 (Continued)

Substance	Particulate Phase			Vapor Phase			Total	
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Mean	95% CI
Semivolatile Organic Compounds by 8270 ($\mu g/Nm^3$)								
Acetophenone	ND(1.6)	ND(1.7)	ND(2.4)	3.0 J	2.7 J	3.8 J	3.1 J	1.4
Benzoic acid	ND(6.2)	ND(6.4)	ND(11)	110 d	150 d	140 d	130 d	43
Dibenzofuran	ND(0.72)	ND(0.72)	ND(1.1)	0.079 J	ND(0.30)	ND(1.5)	ND(1.5)	--
Di-n-butylphthalate	ND(0.39)	2.4 J,B	32	19	6.3 B	14	25	48
Diethylphthalate	ND(0.85)	ND(0.86)	ND(1.2)	3.3 J	ND(0.30)	ND(1.4)	ND(3.3)	--
bis(2-Ethylhexyl)phthalate	1.4 J,B	ND(0.61)	0.64 J,B	22	1.6 J,B	14	13 J,B	27
Isophorone	ND(1.0)	ND(1.0)	ND(1.4)	20	ND(0.39)	31	17	39
Naphthalene	ND(0.65)	ND(0.67)	ND(0.94)	0.78 J,B	0.44 J,B	0.92 J,B	0.71 J,B	0.61
Phenol	ND(1.3)	ND(1.4)	ND(2.0)	1.2 J	1.2 J	ND(0.74)	0.95 J	1.2

B indicates the substance was detected in the reagent blank at levels greater than or equal to 30% of the sample value.

J indicates that the concentration was less than the quantitation limit of the method but above the detection limit.

d indicates that the undiluted sample result exceeded the calibration range of the instrument; results are shown for the diluted samples.

CI = Confidence interval.

ND = Not detected at the concentration in parentheses.

NR = Not reported. Internal standard was not detected; therefore, substance could not be quantified.

a process-generated compound. Mean benzene concentrations were 8 $\mu g/Nm^3$ at the ESP inlet and 5.4 $\mu g/Nm^3$ at the ESP outlet.

A similar set of volatile organic compounds were detected at the ESP outlet in one or more samples: bromodichloromethance, bromoethane, chloroethane, 1,1,1-trichloroethane, 1,2-dichloroethane, benzene, carbon disulfide, chloromethane, methylene chloride, and toluene. Bromodichloromethane, bromoethane, and chloroethane were detected at levels less than five times the detection limit in only one of the three samples and are not considered to be present in the ESP outlet gas. The presence of chloromethane, methylene chloride, and toluene is due to field contamination. 1,1,1-trichloroethane levels were less than five times the detection limit in two of the three samples; therefore, its presence in the ESP outlet gas is uncertain. The presence of the halogenated hydrocarbon species in the ESP inlet and outlet gas is attributed to an unknown source of solvents or refrigerants in the field environment and they are not considered to be process-generated compounds.

Method 23 results for dioxin and furan compounds and congeners indicate some species were detected in both the ESP inlet and outlet gas at pg/Nm^3 levels (near the detection limit). For many of the compounds detected, background levels associated with the reagent blank were similar to the levels found in the samples (refer to Section 4 for a detailed discussion of the blank results for organic compounds); these results are flagged with the "B" symbol. Compounds or congeners detected in one or more ESP outlet samples, but not detected in the reagent blank include: 1,2,3,4,6,7,8-heptachlorodibenzofuran, octachlorodibenzofuran, total heptachlorodibenzo-p-dioxin, total heptachlorodibenzofuran, total hexachlorodibenzofuran, and total pentachlorodibenzofuran.

Data for semivolatile organic compounds at the ESP inlet and outlet are summarized in Tables 3-9 and 3-11, respectively. Samples were analyzed by standard GC/MS as specified in Method 8270 and by high resolution HRGC/MS as specified in CARB Method 29 for a selected subset of the species listed in Method 8270. The high resolution GC/MS technique provided detection limits which were three to four orders of magnitude lower than those obtained with the conventional GC/MS technique.

All of the 18 compounds analyzed by HRGC/MS were detected in the samples collected at the ESP inlet and outlet, with the exception of dibenz(a,h)anthracene at the ESP outlet. However, because of the extremely low detection limits for the HRGC/MS method, most substances were also detected in the reagent and field blanks at levels similar to those found in the samples. The "B" flag is used in Tables 3-9 and 3-11 to denote cases where the background levels in the blanks were greater than or equal to 30% of the levels found in the samples. Acenaphthylene and 2-chloronaphthalene were the only substances detected in the ESP inlet and outlet gas samples and not present in the blanks at significant levels. For those substances flagged with a "B" symbol, accurate quantification by HRGC/MS is not possible; however, the reported results do provide an indication of the maximum possible concentration of these substances present in the gas streams and, as such, should provide useful information for use in health risk assessments.

Six semivolatile organic compounds routinely detected in ESP inlet and outlet samples analyzed by conventional GC/MS include: acetophenone, benzoic acid, di-n-butylphthalate, diethylphthalate, bis(2-ethylhexyl)phthalate, hexachlorobenzene, isophorone, naphthalene, and phenol. The phthalate esters detected in these samples are typical plasticizers commonly attributed to plastic bottles, bags, etc. used in the field laboratory environment. Sample and blank concentrations are comparable; since phthalates are ubiquitous in the laboratory environment, their presence is most likely due to contamination. Although, acetophenone, isophorone, hexachlorobenzene, phenols, and benzene (discussed previously) are potential products of coal devolatilization, their presence is more likely attributed to oxidation of the XAD resin. Concentrations of these substances (on the order of 1-6 $\mu g/Nm^3$) were also between the quantification limit and detection limits of the method, thus increasing the uncertainty in these results. Levels of naphthalene in the blanks were greater than 30% of the samples values.

Benzoic acid was measured in the ESP inlet and outlet gas samples at mean concentrations of 150 $\mu g/Nm^3$ and 130 $\mu g/Nm^3$, respectively.

Benzoic acid is not on the CAAA of 1990 list of 189 toxic substances, but it is noteworthy that all of the detected organic compounds are aromatic and share a common toluene, benzene, or substituted-benzene structure. Benzoic acid may be a degradation product of XAD resin in the acidic environment that exists while sampling flue gas streams with high moisture, SO_2, and NO_x levels. However, Radian knows of no scientific studies that have been conducted to determine if this compound, and possibly other compounds, are generated as a sampling artifact.

APF Inlet and Outlet Gas

The elevated temperature (1350°F) and pressure (135 psig) at the APF inlet and outlet locations made it necessary to design a unique sampling system to extract gas samples at these locations. The capacity of the system was also designed to allow quantification of the extremely low particulate loadings in the APF outlet gas. Particulate matter was filtered outside the duct and filter temperatures were maintained at approximately 500-600°F. A detailed discussion of the APF sampling system is provided in Appendix A. Unlike the moveable, glass-lined probes used at the ESP inlet and outlet, the APF sampling system used a fixed probe made of Inconel 800 (a chromium/nickel alloy material). The fixed probe design did not allow the APF inlet or outlet ducts to be traversed; therefore, the particulate-phase data are subject to this limitation. The use of the chromium/nickel alloy introduced the potential for chromium and nickel contamination in the sampling system; however, both the fixed probe and Inconel 800 material were necessary to meet the safety requirements for the plant and ensure safe operation of the system.

Laboratory tests were conducted at Radian before the on-site testing to evaluate the potential for chromium and nickel contamination from the APF sampling system. These tests consisted of heating a section of the Inconel 800 tubing to 1600°F in a muffle furnace and passing 100 dscf of ambient air through the tubing over a period of approximately two hours. The air was bubbled through a series of impingers containing the nitric acid/hydrogen peroxide reagent used in the metals train. The impinger solutions were subsequently analyzed for chromium, nickel, and iron by ICP-AES. Following these tests, the Inconel

800 tubing was examined and exfoliation on the surface of the tubing was noted. In addition, small flecks of this exfoliated material were also found in the impinger solutions. Chromium, nickel, and iron were detected in the impinger solutions when analyzed by ICP-AES and the presence of these species is attributed to the presence of the exfoliated material. Results of these laboratory tests indicated that chromium and nickel contamination may occur during field sampling at the APF locations and the contamination was expected to be significant at the APF outlet location because of the extremely low particulate loading.

Inorganic Species

Tables 3-12 and 3-13 show the concentrations of the target inorganic analytes in the APF inlet and outlet gas streams, respectively. The analytical methods chosen for each substance were identical to those chosen for the ESP inlet and outlet gas streams.

The solid-phase multi-metals train data from the APF outlet have been corrected for the background levels associated with the quartz filters. Vapor-phase data have been corrected for the background levels present in the nitric impinger reagent. No corrections were necessary at the APF inlet since the particulate matter was analyzed separately from the ceramic filter media. The potential biases discussed above for the ESP inlet and outlet gas streams also apply to the APF gas stream results.

The measured particulate loadings at the APF inlet are approximately three times larger than those measured at the ESP inlet. This is the expected result, since unlike the ESP inlet gas, the gas fed to the APF system is not treated in a secondary cyclone. The levels of particulate-phase metals measured at the APF inlet are consistent with the higher particulate loading relative to the ESP inlet.

Concentrations of target species in the vapor phase at the APF inlet were generally higher than levels measured at the ESP inlet, presumably because of the increased volatility at the elevated temperatures of the APF gas stream (1350°F versus 350°F at the ESP locations). It is interesting to note that the distribution of mercury between the nitric acid/hydrogen

Table 3-12
APF Inlet Gas Composition - Inorganic Species ($\mu g/Nm^3$ unless noted)

Substance	Solid Phase				Vapor Phase				Total	
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Mean	95% CI
Date	4/12/94	4/13/94	4/14/94	4/15/94	4/12/94	4/13/94	4/14/94	4/15/94		
Gas Flow Rate (dscfm)[a]	21,800	21,600	21,800	20,800					21,500	760
Gas Flow Rate (Nm^3/hr)[a]	34,600	34,200	34,600	33,000					34,100	1,200
Particulate Matter (lb/hr)	274	359	290	327					312	60
Particulate Matter (mg/Nm^3)	3,590	4,760	3,810	4,500					4,170	880
Major Species										
Aluminum	NS	271,000	235,000	210,000	NS	1,190	395	263	239,000	78,100
Calcium	NS	474,000	356,000	323,000	NS	2,500	1,220	700	386,000	199,000
Iron	NS	153,000	120,000	114,000	NS	332	173	136	129,000	51,900
Magnesium	NS	249,000	187,000	170,000	NS	1,070	817	214	203,000	104,000
Phosphorus	NS	ND(310)	ND(260)	ND(240)	NS	ND(19)	ND(16)	ND(17)	ND(310)	--
Potassium	NS	62,600	54,000	44,300	NS	280	ND(220)	ND(230)	53,700	23,100
Sodium	NS	10,100	8,880	7,750	NS	123	135	148	9,100	2,930
Sulfate	NS	3,850,000	4,589,000	2,682,000	NS	954,000	811,000	791,000	4,560,000	2,450,000
Titanium	NS	14200	12,600	10,500	NS	63	19	13	12,500	4,530
Target Species										
Ammonia	NS	NS	NS	NS	250	180	170	NS	200	120
Antimony	NS	ND(270)	ND(220)	ND(190)	NS	0.085	2.8	0.043	0.96	3.9
Arsenic	NS	1,400	1,000	830	NS	7.9	2.2	ND(0.005)	1,100	750
Barium	NS	970	890	710	NS	4.8	1.5	2.3	860	330
Beryllium	NS	28	27	24	NS	0.23	0.063	0.053	27	5
Boron	NS	NA	NA	NA	NS	210	200	250	220[b]	56

Table 3-12 (Continued)

Substance	Solid Phase				Vapor Phase				Total	
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Mean	95% CI
Cadmium	NS	6.9	8.2	5.0	NS	ND(0.006)	ND(0.006)	0.31	6.8	3.7
Chloride	NS	1100	5,300	1,100	NS	72,000	65,000	79,000	75,000	12,000
Chromium (multi-metals)	NS	490	400	620	NS	3.0	13	41	520	310
Cobalt	NS	88	73	48	NS	0.22	0.15	0.43	70	50
Copper	NS	95	63	170	NS	7.7	44	68	150	190
Cyanide	NS	NS	NS	NS	1,600	1,600	960	NA	1,400	920
Fluoride	NS	770	1,800	640	NS	6,900	6,000	72,000	7,800	310
Lead	NS	290	240	200	NS	2.9	1.1	1.2	240	120
Manganese	NS	520	440	380	NS	8.7	3.2	33	460	160
Mercury (total)	NS	ND(0.050)	ND(0.046)	ND(0.042)	NS	16	16	17	16	2
Mercury (nitric impingers)	NS	--	--	--	NS	16	15	16	--	--
Mercury (permanganate impingers)	NS	--	--	--	NS	0.30	0.53	0.28	--	--
Molybdenum	NS	ND(18)	ND(14)	66	NS	0.71	1.2	5.9	25	100
Nickel	NS	110	160	300	NS	19	25	58	220	300
Selenium	NS	54	49	51	NS	18	15	14	67	12
Silver	NS	ND(20)	ND(16)	ND(14)	NS	ND(1.6)	ND(1.4)	ND(1.4)	ND(20)	--
Vanadium	NS	450	380	330	NS	3.1	1.7	1.9	390	150

[a] Assumed equal to 1/7th of the measured ESP outlet gas flow rates.
[b] Vapor phase only.
CI = Confidence interval.
NA = Not analyzed.
ND = Not detected at the concentration in parentheses.
NS = Not sampled.

Table 3-13
APF Outlet Gas Composition - Inorganic Species ($\mu g/Nm^3$ unless noted)

Substance	Solid Phase				Vapor Phase				Total	
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Mean	95% CI
Date	4/12/94	4/13/94	4/14/94	4/15/94	4/12/94	4/13/94	4/14/94	4/15/94		
Gas Flow Rate (dscfm)	21,800	21,600	21,800	20,800					21,500	760
Gas Flow Rate (Nm^3/hr)	34,600	34,200	34,600	33,000					34,100	1,200
Particulate Matter (lb/hr)	0.0056	0.024	0.014	0.049					0.023	0.030
Particulate Matter (mg/Nm^3)	0.074	0.31	0.18	0.68					0.31	0.42
Major Species										
Aluminum	0.87	4.8	2.4	NS	NS	55	59	53	58	10
Calcium	0.092	5.8	2.7	NS	NS	280	360	210	290	181
Iron	1.4	7.3	2.8	NS	NS	37	810	58	310	1,100
Magnesium	ND(0.53)	2.8	1.3	NS	NS	23	15	20	26	9
Phosphorus	ND(0.40)	ND(0.45)	ND(0.32)	NS	NS	ND(21)	ND(17)	ND(18)	ND(0.45)	--
Potassium	ND(2.4)	ND(2.7)	ND(2.0)	NS	NS	ND(280)	ND(230)	ND(250)	ND(2.7)	--
Sodium	ND(0.17)	1.4	ND(0.14)	NS	NS	360	410	260	359	190
Sulfate	38	84	52	NS	NS	532,000	470,000	474,000	492,000	85,426
Titanium	0.061	0.409	0.232	NS	NS	2.1	2.1	1.9	2.2	0.7
Target Species										
Ammonia	NS	NS	NS	NS	170	150	120	NS	150	55
Antimony	ND(0.33)	ND(0.36)	ND(0.26)	NS	NS	0.023	0.033	0.022	ND(0.36)[a]	--
Arsenic	0.21	0.36	0.27	NS	NS	3.9	4.1	3.0	3.9	1.7
Barium	0.091	0.017	0.0049	NS	NS	ND(0.006)	ND(0.005)	ND(0.005)	0.038	0.12
Beryllium	ND(0.0018)	ND(0.0020)	ND(0.0015)	NS	NS	0.028	0.013	0.018	0.020	0.019
Boron	NA	NA	NA	NS	NS	390	320	380	360[c]	84

Table 3-13 (Continued)

Substance	Solid Phase				Vapor Phase				Total	
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Mean	95% CI
Cadmium	ND(0.0043)	ND(0.0048)	ND(0.0035)	NS	NS	ND(0.007)	ND(0.006)	ND(0.006)	ND(0.005)	--
Chloride	0.19	0.16	ND(0.11)	NS	NS	73,000	50,000	60,000	61,000	28,000
Chromium (multi-metals)	8.0[d]	13[d]	8.9[d]	NS	NS	1.7	150	3.2	60	200
Cobalt	ND(0.030)	ND(0.033)	ND(0.024)	NS	NS	0.020	0.83	0.061	0.30	1.1
Copper	ND(0.028)	ND(0.031)	ND(0.022)	NS	NS	0.77	0.88	0.75	0.80	0.2
Cyanide	NS	NS	NS	NS	510	430	360	NS	430	190
Fluoride	0.046	0.22	0.12	NS	NS	9,400	8,900	8,500	8,900	1,200
Lead	0.019	0.035	0.033	NS	NS	ND(0.006)	ND(0.005)	ND(0.005)	0.029	0.022
Manganese	0.21	0.62	0.14	NS	NS	0.72	22	0.56	8.1	30
Mercury (total)	ND(0.00027)	ND(0.00030)	ND(0.00021)	NS	NS	16	14	14	15	2.6
Mercury (nitric impingers)	--	--	--	NS	NS	13	9.4	9.3	--	--
Mercury (permanganate impingers)	--	--	--	NS	NS	2.9	4.9	4.8	--	--
Molybdenum	3.4[d]	6.5[d]	2.9[d]	NS	NS	3.4	3.4	7.7	9.1	6.1
Nickel	ND(0.26)	1.3[d]	0.34[d]	NS	NS	6.7	89	54	51	100
Selenium	ND(0.0044)	ND(0.0050)	ND(0.0036)	NS	NS	46	41	58	49	22
Silver	0.31	0.37	0.14	NS	NS	ND(1.8)	ND(1.5)	ND(1.6)	0.27	0.3
Vanadium	0.96	0.81	0.85	NS	NS	1.0	1.4	1.0	2.0	0.5

[a] Detected in the vapor phase at low levels. Reported value is an upper limit.

[b] *Assumed equal to 1/7th of the ESP outlet gas flow rate.*

[c] Vapor phase only.

[d] Results indicate the presence of Inconel 800 residue in the particulate matter. Data are considered biased high.

CI = Confidence interval.

NA = Not analyzed.

ND = Not detected at the concentration in parentheses.

NS = *Not sampled.*

peroxide and permanganate impinger solutions at the APF outlet is distinctly different than the distribution observed at the ESP locations and the APF inlet location. Approximately 1-2% of the total vapor-phase mercury was captured in the permanganate impinger solution at the APF outlet compared to 10-15% at the other three gas sampling locations. This indicates that the form of mercury may change as the gas passes through the APF system.

Organic Species

Tables 3-14 and 3-15 show the concentrations of the target organic compounds in the APF inlet gas. Tables 3-16 and 3-17 show the results for organic compounds in the APF outlet gas. For volatile and semivolatile organic compounds, only those species which were present at levels above the detection limit in one or more samples are reported.

Levels of volatile organic compounds at the APF inlet and outlet were similar to the levels observed at the ESP locations. Methylene chloride and toluene are likely present due to field contamination. With the exception of carbon disulfide at the APF outlet (mean concentration = 25 $\mu g/Nm^3$), most of these species were detected at levels less than five times the detection limit; therefore, their presence in the APF gas samples is uncertain. Benzene was quantified in two of the three APF inlet samples at levels greater than five times the detection limit. At the APF outlet, benzene was found at levels greater than five times the detection limit in only one of the three samples. Mean concentrations of benzene were 3.0 and 3.1 $\mu g/Nm^3$ at the APF inlet and outlet, respectively.

Dioxin and furan results for the APF inlet indicate all of the species were present in the gas at levels which are 2 to 3 orders of magnitude greater than detection limits. Concentrations of the various dioxin/furan compounds or congeners ranged from 8.1 pg/Nm^3 for 2,3,7,8-tetrachlorodibenzo-p-dioxin to 2300 pg/Nm^3 for total pentachlorodibenzo-p-dioxin. Levels in the reagent blank were insignificant compared to the sample results at the APF inlet.

At the APF outlet, the front (filter) and back (resin) half of the Method 23 train were analyzed separately. None of the dioxin and furan species were detected in the front half

Table 3-14
APF Inlet Gas Composition - VOST and Method 23 Species

Substance	Run 1	Run 2	Run 3	Run 4	Mean	95% CI	Mean Blank Level[a]
Date	4/12/94	4/13/94	4/14/94	4/15/94			
Gas Flow Rate (dscfm)	21,800	21,600	21,800	20,800	21,500	760	
Gas Flow Rate (Nm^3/hr)	34,600	34,200	34,600	33,000	34,100	1,200	
VOST ($\mu g/Nm^3$)							
Benzene	NS	1.2	4.1	3.7	3.0	3.9	ND(0.5)
Carbon Disulfide	NS	1.8	5.2	4.1	3.7	4.3	ND(0.5)
Chloroethane	NS	ND(0.6)	ND(0.6)	19	6.5	27	ND(0.5)
Chloroform	NS	ND(0.6)	ND(0.6)	1.6	0.7	1.9	ND(0.5)
Chloromethane	NS	ND(0.5)	2.9	4.9	2.7	5.8	ND(0.5)
Methylene Chloride	NS	0.8[b]	11[b]	55	22[b]	71	ND(0.5)
Toluene	NS	ND(0.6)	ND(0.6)	1.4[b]	0.6[b]	1.7	ND(0.5)
Dioxin/Furan (Method 23, pg/Nm^3)							
1,2,3,4,6,7,8-HpCDD	NS	460	650	270	460	470	ND(2.8)
1,2,3,4,6,7,8-HpCDF	NS	210	440	190	280	350	ND(1.4)
1,2,3,4,7,8-HxCDD	NS	110	170	51	110	150	ND(2.8)
1,2,3,4,7,8-HxCDF	NS	210	500	160	290	460	1.4 E
1,2,3,4,7,8,9-HpCDF	NS	49	67	39	52	35	ND(2.4)
1,2,3,6,7,8-HxCDD	NS	130	170	72	120	120	ND(2.1)
1,2,3,6,7,8-HxCDF	NS	76	160	53	95	140	ND(1.0)
1,2,3,7,8-PeCDD	NS	81	100	47	78	73	ND(1.4)
1,2,3,7,8-PeCDF	NS	65 E	93	230 E	130	230	ND(1.0)
1,2,3,7,8,9-HxCDD	NS	170	220	83	160	170	ND(2.1)

Table 3-14 (Continued)

Substance	Run 1	Run 2	Run 3	Run 4	Mean	95% CI	Mean Blank Level[a]
1,2,3,7,8,9-HxCDF	NS	18	42	9.3	23	42	ND(1.7)
2,3,4,6,7,8-HxCDF	NS	90	160	53	100	140	2.1
2,3,4,7,8-PeCDF	NS	110 E	150	53	100	120	ND(1.0)
2,3,7,8-TCDD	NS	6.5 B	12	5.8	8.1	8.7	ND(1.4)
2,3,7,8-TCDF	NS	170	400	93	220	390	ND(1.0)
OCDD	NS	490	800	330	540	590	3.4 E
OCDF	NS	160	250	240	210	130	ND(3.4)
Total HpCDD	NS	940	1,400	560	970	1,000	ND(2.8)
Total HpCDF	NS	340	690	310	450	530	ND(1.7)
Total HxCDD	NS	1,900	2,400	1,100	1,800	1,600	ND(2.1)
Total HxCDF	NS	700	1,600	510	930	1,400	2.1
Total PeCDD	NS	2,600	3,000	1,400	2,300	2,100	ND(1.4)
Total PeCDF	NS	610	2,000	540	1,000	2,000	ND(1.0)
Total TCDD	NS	2,600	2,900	1,200	2,200	2,300	ND(1.4)
Total TCDF	NS	1,600	3,200	740	1,800	3,100	ND(1.0)
Aldehydes ($\mu g/Nm^3$)							
Formaldehyde	40	150	17	NS	68	170	

[a] Calculated based on the mean of the levels in the reagent blanks divided by the mean gas sample volume for the three sample runs.

[b] Levels in the field blanks are ≥30% of the sample value.

E indicates value is an estimated upper limit.

CI = Confidence interval.

ND = Not detected at the concentration in parentheses.

NS = *Not sampled.*

HpCDD = Heptachlorodibenzo-p-dioxin.

HpCDF = Heptachlorodibenzofuran.

HxCDD = Hexachlorodibenzo-p-dioxin.

HxCDF = Hexachlorodibenzofuran.

PeCDD = Pentachlorodibenzo-p-dioxin.

PeCDF = Pentachlorodibenzofuran.

TCDD = Tetrachlorodibenzo-p-dioxin.

TCDF = Tetrachlorodibenzofuran.

OCDD = Octachlorodibenzo-p-dioxin.

OCDF = Octachlorodibenzofuran.

Table 3-15
Results for Semivolatile Organic Species at the APF Inlet ($\mu g/Nm^3$)

Substance	Particulate Phase			Vapor Phase			Total	
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Mean	95% CI
PAHs by HR GC/MS (ng/Nm^3)								
Acenaphthene	0.87 B	0.96 B	1.4 B	21 B	44 B	10 B	26 B	43
Acenaphthylene	0.18 B	0.27 B	0.37 B	4.3	10	4.0	6.5 B	8.9
Anthracene	0.68 B	1.9 B	3.2	ND(0.96)	0.97 B	0.76 B	2.5 B	4.1
Benzo(a)anthracene	0.27 B	1.3	1.8	0.69	0.25 B	0.50 B	1.6 B	1.7
Benzo(a)pyrene	0.43 B	1.7	2.8	0.91	ND(0.42)	0.46 B	2.1 B	2.5
Benzo(b)fluoranthene	0.65 B	2.3	5.4	1.5 B	0.68 B	1.0 B	3.9 B	5.6
Benzo(g,h,i)perylene	2.4 B	8.3	12	6.1	0.99 B	1.2 B	10 B	5.6
Benzo(k)fluoranthene	0.22 B	0.65	3.1	0.91	0.19 B	0.31 B	1.8 B	3.5
2-Chloronaphthalene	ND(0.089)	ND(0.12)	ND(0.18)	5.9	4.5	7.3	5.9	3.5
Chrysene	1.5 B	3.1	6.5	0.87 B	0.52 B	0.92 B	4.4 B	6.5
Dibenz(a,h)anthracene	ND(0.25)	ND(1.2)	2.2	ND(1.1)	ND(0.23)	0.17 B	ND(1.1) B	--
Fluoranthene	3.1 B	8.5	14	7.3 B	8.3 B	5.7 B	16	12
Fluorene	3.3 B	6.3 B	10	5.9 B	8.7 B	10 B	15 B	14
Indeno(1,2,3-cd)pyrene	0.59 B	2.0	3.6	1.8	0.49 B	0.63 B	3.0 B	2.7
2-Methylnaphthalene	5.4 B	5.8 B	7.6 B	79 B	140	200	150 B	150
Naphthalene	17 B	17 B	24 B	700	150 B	190 B	370 B	760
Phenanthrene	17 B	27 B	46	26 B	43 B	41 B	67 B	56
Pyrene	3.2 B	7.2	10	4.0 B	3.5 B	2.8 B	10 B	7.3

Table 3-15
Results for Semivolatile Organic Species at the APF Inlet ($\mu g/Nm^3$)

Substance	Particulate Phase			Vapor Phase			Total	
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Mean	95% CI
Semivolatile Organic Compounds by 8270 ($\mu g/Nm^3$)								
Acetophenone	ND(2.8)	ND(2.7)	ND(2.9)	1.4 J	1.7 J	2.6 J	1.9 J	1.6
Benzoic acid	ND(10)	ND(10)	ND(11)	88	120 d	110	110	45
Di-n-butylphthalate	3.1 J,B	20	11	1.3 J,B	5.4 J,B	55	32 B	77
bis(2-Ethylhexyl)phthalate	1.2 J,B	ND(1.1)	ND(1.2)	1.1 J,B	ND(0.62)	1.5 J,B	1.4 B	2.5
2-Methylnaphthalene	ND(1.7)	ND(1.6)	ND(1.7)	ND(1.3)	ND(0.70)	0.082 J	ND(1.3)	--
Naphthalene	ND(1.1)	ND(1.1)	ND(1.1)	ND(0.81)	ND(0.45)	0.73 J,B	ND(0.81)	--
2-Nitrophenol	ND(5.1)	ND(5.1)	ND(5.3)	ND(3.8)	ND(2.7)	0.28 J	ND(3.8)	--
4-Nitrophenol	ND(12)	ND(12)	ND(13)	ND(8.5)	0.65 J	0.54 J	ND(8.5)	--
Phenol	ND(2.3)	ND(2.3)	ND(2.4)	ND(1.7)	ND(1.4)	0.66 J	ND(1.7)	--
Benzo(a)anthracene	ND(0.84)	0.82	ND(0.89)	ND(0.51)	ND(0.50)	ND(0.33)	ND(0.51)	--
bis(2-Chloroethoxy)methane	ND(2.5)	ND(2.5)	ND(2.5)	ND(2.6)	ND(1.9)	1.5	ND(0.70)	ND(1.9)

B indicates the substance was detected in the reagent blank at levels greater than or equal to 30% of the sample value.

J indicates that the concentration was less than the quantitation limit of the method but above the detection limit.

d indicates that the undiluted sample results exceeded the calibration range of the instrument. The sample was diluted and the results for the diluted samples are shown.

Table 3-16
APF Outlet Gas Composition - VOST and Method 23 Species

Substance	Run 1	Run 2	Run 3	Run 4	Mean	95% CI	Mean Blank Level[a]
Date	4/12/94	4/13/94	4/14/94	4/15/94			
Gas Flow Rate (dscfm)	21,800	21,600	21,800	20,800	21,500	760	
Gas Flow Rate (Nm^3/hr)	34,600	34,200	34,600	33,000	34,100	1,200	
VOST (μg/Nm^3)							
Chloroform	0.7	ND(0.5)	0.5	NS	ND(0.5)	--	ND(0.5)
Benzene	8.0	0.5	0.8	NS	3.1	7.7	ND(0.5)
Bromomethane	ND(0.4)	ND(0.5)	2.2	NS	0.89	2.9	ND(0.5)
Carbon Disulfide	21	31	23	NS	25	62	ND(0.5)
Chloromethane	5.1	ND(0.5)	2.3	NS	2.6	3.5	ND(0.5)
Methylene Chloride	1,500	280	330	NS	720	1,800	ND(0.5)
Toluene	2.6^b	ND(0.4)	0.6^b	NS	1.2^b	3.2	ND(0.5)
Dioxin/Furan (pg/Nm^3)							
1,2,3,4,6,7,8-HpCDD	NS	22	10	8.8	14	18	ND(2.8)
1,2,3,4,6,7,8-HpCDF	NS	17	13	11	14 B	7.8	ND(1.4)
1,2,3,4,7,8-HxCDD	NS	2.3 E	ND(5.6)	ND(7.1)	ND(7.1)	0.0	ND(2.8)
1,2,3,4,7,8-HxCDF	NS	24	15	9.1	16 B	19	1.4 E
1,2,3,4,7,8,9-HpCDF	NS	3.3 E	5.2	ND(7.1)	ND(7.1)	--	ND(2.4)
1,2,3,6,7,8-HxCDD	NS	5.7	ND(4.5)	ND(6.0)	ND(6.0)	--	ND(2.1)
1,2,3,6,7,8-HxCDF	NS	5.5	3.5	ND(3.0)	3.5	4.9	ND(1.0)
1,2,3,7,8-PeCDD	NS	2.7 E	ND(5.3)	ND(6.0)	ND(6.0)	--	ND(1.4)
1,2,3,7,8-PeCDF	NS	6.8	ND(3.0)	ND(3.0)	3.1	0.61	ND(1.0)
1,2,3,7,8,9-HxCDD	NS	5.7	5.3	ND(6.3)	ND(6.3)	--	ND(2.1)

Table 3-16 (Continued)

Substance	Run 1	Run 2	Run 3	Run 4	Mean	95% CI	Mean Blank Level[a]
1,2,3,7,8,9-HxCDF	NS	2.5	ND(3.4)	ND(4.1)	ND(4.1)	--	ND(1.7)
2,3,4,6,7,8-HxCDF	NS	6.0 B	3.8 B,E	3.4 E,B	4.4	3.5	2.1
2,3,4,7,8-PeCDF	NS	3.3 E	ND(3.0)	ND(3.0)	ND(3.0)	--	ND(1.0)
2,3,7,8-TCDD	NS	1.0 E	ND(3.4)	ND(3.0)	ND(3.4)	--	ND(1.4)
2,3,7,8-TCDF	NS	12	4.5	ND(1.1)	5.7	14	ND(1.0)
OCDD	NS	43 E	34 E	35	37	13	3.4 E
OCDF	NS	66	42	34 E	47	42	ND(3.4)
Total HpCDD	NS	22	10	8.8	14	18	ND(2.8)
Total HpCDF	NS	24	20	14	19	13	ND(1.7)
Total HxCDD	NS	46	3.8 E	5.2	18	59	ND(2.1)
Total HxCDF	NS	51	18	8.6 B	26	56	2.1
Total PeCDD	NS	41	11 E	ND(6.0)	19	50	ND(1.4)
Total PeCDF	NS	53	7.5 E	4.0	21	68	ND(1.0)
Total TCDD	NS	130	14	ND(3.0)	47	170	ND(1.4)
Total TCDF	NS	99	12	2.8	38	130	ND(1.0)
Aldehydes							
Formaldehyde	3.6	4.1	3.8	NS	3.9	0.6	

[a] Calculated based on the mean level in the reagent blank divided by the mean gas sample volume.
[b] Levels in the field blanks are ≥30% of the sample value.
B indicates the substance was detected in the reagent blanks at ≥30% of the sample value.
E indicates value is an estimated upper limit.
CI = Confidence interval.
ND = Not detected at the concentration in parentheses.
NS = Not sampled.
HpCDD = Heptachlorodibenzo-p-dioxin.
HpCDF = Heptachlorodibenzofuran.
HxCDD = Hexachlorodibenzo-p-dioxin.
HxCDF = Hexachlorodibenzofuran.
PeCDD = Pentachlorodibenzo-p-dioxin.
PeCDF = Pentachlorodibenzofuran.
TCDD = Tetrachlorodibenzo-p-dioxin.
TCDF = Tetrachlorodibenzofuran.
OCDD = Octachlorodibenzo-p-dioxin.
OCDF = Octachlorodibenzofuran.

Table 3-17
Results for Semivolatile Organic Species at the APF Outlet

Substance	Particulate Phase			Vapor Phase			Total	
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Mean	95% CI
PAHs by HR GC/MS (ng/Nm^3)								
Acenaphthene	0.1 B	0.080 B	0.28 B	70 B	9.5 B	31 B	37 B	76
Acenaphthylene	0.027 B	0.017 B	0.078 B	27	1.3 B	3.5 B	10 B	35
Anthracene	0.16 B	0.097 B	0.34 B	0.25 B	0.53 B	0.78 B	0.72 B	0.92
Benzo(a)anthracene	0.070	0.077	0.043 B	0.26 B	0.26 B	0.38 B	0.36 B	0.13
Benzo(a)pyrene	0.090	0.044 B	0.078 B	NR	0.28 B	0.31 B	0.27 B	0.39
Benzo(b)fluoranthene	0.15 B	0.17 B	0.11 B	0.80 B	0.71 B	0.87 B	0.93 B	0.13
Benzo(g,h,i)perylene	0.48	0.79	0.30	53	1.2 B	1.1 B	19 B	74
Benzo(k)fluoranthene	0.033 B	0.027 B	0.032 B	0.41 B	0.32 B	0.28 B	0.37 B	0.17
2-Chloronaphthalene	ND(0.028)	ND(0.015)	ND(0.019)	ND(0.070)	ND(0.13)	0.40	0.17	0.50
Chrysene	0.13 B	0.27	0.23	0.73 B	0.38 B	0.77 B	0.83 B	0.43
Dibenz(a,h)anthracene	ND(0.073)	ND(0.018)	ND(0.026)	0.41 B	ND(0.24)	0.23 B	0.25 B	0.33
Fluoranthene	0.61 B	0.37 B	1.0 B	4.7 B	3.9 B	7.2 B	5.9 B	5.1
Fluorene	0.71 B	0.47 B	1.7 B	6.0 B	3.8 B	9.2 B	7.3 B	8.2
Indeno(1,2,3-cd)pyrene	0.092 B	0.17	0.092 B	0.65 B	0.58 B	0.48 B	0.69 B	0.25
2-Methylnaphthalene	1.1 B	0.99 B	2.4 B	51 B	24 B	22 B	34 B	39
Naphthalene	2.9 B	2.8 B	3.2 B	140 B	380 B	380 B	300 B	350
Phenanthrene	3.4 B	3.1 B	8.3 B	24 B	19 B	39 B	32 B	33
Pyrene	1.1	0.30 B	0.63 B	1.1 B	1.8 B	3.4 B	2.8 B	2.7

Table 3-17 (Continued)

Substance	Particulate Phase			Vapor Phase			Total	
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Mean	95% CI
Semivolatile Organic Compounds by 8270 ($\mu g/Nm^3$)								
Acetophenone	ND(0.44)	ND(0.36)	ND(0.40)	2.0 J	1.6 J	2.8 J	2.1 J	1.5
Benzoic acid	ND(1.6)	ND(1.4)	ND(1.5)	130 d	110	23 d	84 d	140
Di-n-butylphthalate	18	1.2	10	3.7 J,B	1.0 J,B	100	45	150
bis(2-Ethylhexyl)phthalate	0.094 J,B	0.10 J,B	0.070 J,B	1.0 J,B	0.52 J,B	9.9	3.9	13
Isophorone	ND(0.26)	ND(0.22)	ND(0.25)	1.7 J	ND(0.38)	ND(0.40)	0.70 J	2.2
Phenol	ND(0.37)	ND(0.30)	ND(0.33)	1.3 J	0.65 J	1.2 J	1.0 J	0.85

B indicates the substance was detected in the reagent blank at levels greater than or equal to 30% of the sample.

J indicates that the concentration was less than the quantitation limit of the method but above the detection limit.

d indicates that the undiluted sample result *exceeded the calibration range of the instrument; results are shown* for the diluted sample.

CI = Confidence interval.

ND = Not detected at the concentration in parentheses.

NR = Not reported. Internal standard was not detected; therefore, substance could not be quantified.

sample. The results presented in Table 3-15 are the back half results only; the front half concentrations were assumed to be zero for the purpose of calculating a total concentration. Detection limits for the front-half samples can be found in Appendix B. Levels of dioxin/furan compounds and congeners at the APF outlet were much lower than those observed at the APF inlet. Mean concentrations for those species which were detected in the samples but not detected at significant levels in the reagent blanks (i.e., less than 30% of the sample value) ranged from 3.5×10^{-6} $\mu g/Nm^3$ for 1,2,3,6,7,8-hexachlorodibenzofuran to 4.7×10^{-5} $\mu g/Nm^3$ octachlorodibenzofuran. The apparent reduction of dioxin/furan concentrations across the APF system may be due to condensation of these species on the particulate matter in the APF gas. Data for the APF and ESP ash (Table 3-4) indicate the presence of some dioxin/furan compounds at pg/g levels.

Results for semivolatile organic compounds measured in the APF inlet and outlet gas are presented in Tables 3-15 and 3-17, respectively. Results are very similar to those discussed above for the ESP inlet and outlet gas steams. The same compounds were detected at similar concentrations at both the ESP and APF locations. The discussion presented previously also applies to the results for the APF gas streams.

ESP System Control Efficiency

Table 3-18 presents the removal efficiencies for the ESP system, listed by species. The average particulate removal efficiency was calculated to be 97.2% based on the data collected during the three Method 29 train tests. Little or no removal is indicated for chloride (6%), mercury (4%) and SO_2 (2%). Modest removal was measured for cadmium (44%), copper (62%), fluoride (54%), selenium (37%), ammonia (16%), cyanide (21%), and formaldehyde (24%). Removal of other target species is much higher, ranging from 90% (nickel) to 99.8% (arsenic).

Table 3-18
ESP and APF Control Efficiencies

Substance	ESP		APF	
	Mean Removal (%)	95% CI	Mean Removal (%)	95% CI
Particulate	97.2	4.8	99.99	0.01
Antimony	NC	--	>65	--
Arsenic	99.8	0.1	99.6	0.2
Barium	99.7	3.1	99.996	0.014
Beryllium	99.8	4.0	>99.9	--
Boron	NC	--	NC	--
Cadmium	44	150	>99.9	--
Chloride (total)	6.0	7.7	18	39
HCl[a]	4	10	11	33
Chromium	97.2	2.2	89	40
Cobalt	>99.2	--	99.6	1.6
Copper	62	41	99.5	0.7
Fluoride (total)	54	13	-15	16
HF[a]	32	16	-33	25
Lead	99.1	5.1	99.99	0.01
Manganese	95.2	6.8	98.2	6.6
Mercury	4	40	9	39
Molybdenum	NC	43	63	82
Nickel	90	15	77	38
Selenium	37	29	27	26
Silver	NC	--	NC	--
Vanadium	99.2	0.2	99.5	0.2
Aluminum	99.8	0.2	99.98	0.01
Calcium	99.5	0.2	99.9	0.04
Iron	98.8	2.5	99.8	0.9
Magnesium	99.8	0.1	99.99	0.005
Potassium	99.8	0.1	>99.995	--
Sodium	88.9	3.5	96.2	1.8
Titanium	99.7	0.4	99.98	0.01
Ammonia	16	42	25	31
Cyanide	21	92	69	15
Formaldehyde	24	66	94	20
Sulfur (total)	92	--	89	4
SO_2	2	--	42	11

[a] Assumes that the vapor-phase concentration of the anion is present as HCl or HF.

NC = Not calculated. Substance was not detected in the inlet gas stream.

> indicates the reported removal efficiency is a lower limit. The substance was not detected in the device outlet gas. Detection limit was used to estimate a lower limit for the removal efficiency.

CI = Confidence interval.

APF System Control Efficiency

Estimates of the APF system control efficiency are also shown in Table 3-18. Over 1300 dscf of gas was collected during each test run at the APF outlet to quantify the particulate loading. The mean measured particulate removal efficiency was 99.993 percent. Low removals are indicated for chloride (18%), fluoride (-15%), and mercury (9%). Modest removals were observed for molybdenum (63%), nickel (77%), selenium (27%), ammonia (25%), and cyanide (69%). Removals for major elements (Al, Ca, Ti, etc.) were comparable to the removal observed for particulate matter.

The relatively low removal efficiencies for chromium, molybdenum, and nickel, relative to the total particulate removal, suggests either 1) a significant fraction of these elements exists in the vapor phase and is not removed; or 2) that contamination from the Inconel 800 sampling probe or elsewhere in the process equipment may have occurred within the APF outlet particulate matter. Examination of the data in Tables 3-12 and 3-13 shows high levels of these substances in the vapor phase at both the APF inlet and outlet compared to the ESP gas locations. A comparison of the mean particulate-phase composition on a μg/g basis at all four gas locations and collected ash from these systems is shown below:

	ESP Inlet	ESP Ash	ESP Outlet	APF Inlet	APF Ash	APF Outlet
Chromium (μg/g)	82	94	35	110	74	66,500
Molybdenum (μg/g)	<2	<3.8	6	7	<3.3	27,700
Nickel (μg/g)	32	29	270	130	50	2,600

The abnormally high concentrations of chromium, nickel, and molybdenum in the APF outlet particulate matter shown above strongly suggest that residue from the Inconel 800 components of the sampling system is present in the particulate matter collected at the APF outlet; however, the impact on the overall calculated removal across the APF system is insignificant because of the high levels of these substances found in the vapor phase. The particulate-phase concentrations of these species reported for the APF outlet should be considered biased high, but the reported overall removal efficiencies are considered representative of the APF high, but the reported overall removal efficiencies are considered representative of the APF performance. If the ESP outlet particulate composition is used to estimate the particulate-phase removal of these species across the APF, values of 99.997% (chromium), 99.993% (molybdenum), and 99.98% (nickel) are obtained. These values are more consistent with the overall particulate removal measured across the APF system.

Data from the anions train indicate approximately 40% removal of SO_2 across the APF system, presumably because of reaction of the SO_2 with the sorbent material on the surface of the ceramic candles. The SO_2 measurements made during the three tests were consistent with the levels of SO_2 measured by the plant's CEM system at both the APF inlet and outlet; both data sets suggest SO_2 removal occurs across the APF unit.

Emission Factors

Table 3-19 provides calculated ESP outlet emissions factors for all of the target species. Emissions factors are presented on a lb/10^{12} Btu heat input basis. Emissions factors for inorganic substances detected in the ESP outlet gas range from 83,000 lb/trillion Btu (chloride) to 0.31 lb/trillion Btu (molybdenum). The range of emission factors for organic species is 4.3×10^{-6} lb/trillion Btu (pentachlorodibenzofuran) to 6.6 lb/trillion Btu (benzene).

Particle Size Distribution Data

Particle size distributions (PSDs) were determined for the ash material collected at the ESP inlet, ESP outlet, and the each of the four ESP hoppers. PSDs for the gas stream particulate matter were determined using an "in-stack" cascade impactor which separated the entrained particulate matter into 11 fractions according to aerodynamic particle size. ESP hopper ash samples were analyzed by laser diffraction to determine the physical diameter of the particles. Results from the laser diffraction analyses of the ESP hopper ash were converted from physical particle diameters to aerodynamic particle diameters so that they could be compared to the cascade impactor results from the ESP inlet location. Physical and aerodynamic particle sizes are related by the following equation:

Table 3-19
Emission Factors for ESP Outlet Gas (lb/10^{12} Btu, unless noted)

Substance	Emission Factor	95% CI
Particulate (lb/10^6 Btu)	0.051	0.09
Inorganic Species		
Ammonia	140	7
Antimony	ND(2.6)	--
Arsenic	1.2	0.06
Barium	0.92	0.044
Beryllium	0.026	0.0012
Boron	210	10
Cadmium	2.2	0.11
Chloride (total)	83,000	4,000
Chromium	4.6	0.22
Cobalt	ND(2.4)	--
Copper	5.3	0.25
Cyanide	610	29
Fluoride (total)	5600	270
Lead	0.80	0.038
Manganese	8.5	0.41
Mercury (total)	18	1
Molybdenum	0.31	0.015
Nickel	7.4	0.35
Selenium	49	2.3
Silver	0.50	0.024
Vanadium	1.2	0.06
Chromium (VI)	1.7	0.08
Organic Species		
Formaldehyde	5.1	0.24
1,1,2,2-Tetrachloroethane	ND(0.7)	--
1,1,2-Trichloroethane	ND(0.7)	--
1,1-Dichloroethane	ND(0.7)	--
1,1-Dichloroethene	ND(0.7)	--
1,2-Dichlorobenzene	ND(0.7)	--
1,2-Dichloropropane	ND(0.7)	--
1,3-Dichlorobenzene	ND(0.7)	--
1,4-Dichlorobenzene	ND(0.7)	--

Table 3-19 (Continued)

Substance	Emission Factor	95% CI
2-Butanone	ND(3.3)	–
2-Hexanone	ND(3.3)	–
4-Methyl-2-Pentanone	ND(3.3)	–
Acetone	ND(3.3)	–
Bromodichloromethane	ND(0.7)	–
Bromoform	ND(0.7)	–
Bromomethane	ND(0.7)	–
Carbon Tetrachloride	ND(0.7)	–
Chlorobenzene	ND(0.7)	–
Chloroethane	ND(0.7)	–
Chloroform	ND(0.7)	–
cis-1,3-Dichloropropene	ND(0.7)	–
Dibromochloromethane	ND(0.7)	–
Ethyl Benzene	ND(0.7)	–
m,p-Xylene	ND(0.7)	–
o-Xylene	ND(0.7)	–
Styrene	ND(0.7)	–
Tetrachloroethene	ND(0.7)	–
trans-1,2-Dichloroethene	ND(0.7)	–
trans-1,3-Dichloropropene	ND(0.7)	–
Trichloroethene	ND(0.7)	–
Trichlorofluoromethane	ND(0.7)	–
Vinyl Acetate	ND(3.3)	–
Vinyl Chloride	ND(0.7)	–
1,1,1-Trichloroethane	16[a]	1
1,2-Dichloroethane	8.7[a]	0.41
Benzene	6.6	0.32
Carbon Disulfide	1.0	0.05
Chloromethane	4.4[a]	0.21
Methylene Chloride	3.6[a]	0.17
Toluene	1.4[a]	0.07

Table 3-19 (Continued)

Substance	Emission Factor	95% CI
1,2,3,4,6,7,8-HpCDD	7.3E-06[b,c]	3.5E-07
1,2,3,4,6,7,8-HpCDF	6.4E-06[c]	3.1E-07
1,2,3,4,7,8-HxCDD	ND(4.8E-6)	--
1,2,3,4,7,8-HxCDF	5.6E-06[b,c]	2.7E-07
1,2,3,4,7,8,9-HpCDF	ND(5.0E-6)	--
1,2,3,6,7,8-HxCDD	ND(3.9E-6)	--
1,2,3,6,7,8-HxCDF	ND(2.2E-6)	--
1,2,3,7,8-PeCDD	ND(3.5E-6)	--
1,2,3,7,8-PeCDF	ND(2.2E-6)	--
1,2,3,7,8,9-HxCDD	ND(4.4E-6)	--
1,2,3,7,8,9-HxCDF	ND(3.5E-6)	--
2,3,4,6,7,8-HxCDF	4.4E-06[b,c]	2.1E-07
2,3,4,7,8-PeCDF	ND(2.2E-6)	--
2,3,7,8-TCDD	ND(2.0E-6)	--
2,3,7,8-TCDF	ND(2.0E-6)	--
OCDD	7.7E-05[b,c]	3.7E-06
OCDF	1.2E-05[c]	5.8E-07
TOTAL HpCDD	1.4E-05[c]	6.7E-07
TOTAL HpCDF	4.5E-06[c]	2.1E-07
TOTAL HxCDD	ND(4.1E-6)	--
TOTAL HxCDF	1.4E-05[c]	6.7E-07
TOTAL PeCDD	ND(3.5E-6)	--
TOTAL PeCDF	4.3E-06[c]	2.1E-07
TOTAL TCDD	ND(1.8E-6)	--
TOTAL TCDF	ND(2.0-E-6)	--

[a] Methylene chloride, toluene, and other halogenated hydrocarbons are suspected to be present as a result of contamination.

[b] Substance was detected in the reagent blank at greater than or equal to 30% of the sample result. Results are considered to be bias high. Quantification is suspect.

[c] Substance was quantified at less than five times the detection limit.

CI = Confidence interval.
HpCDD = Heptachlorodibenzo-p-dioxin.
HpCDF = Heptachlorodibenzofuran.
HxCDD = Hexachlorodibenzo-p-dioxin.
HxCDF = Hexachlorodibenzofuran.
PeCDD = Pentachlorodibenzo-p-dioxin.
PeCDF = Pentachlorodibenzofuran.
TCDD = Tetrachlorodibenzo-p-dioxin.
TCDF = Tetrachlorodibenzofuran.
OCDD = Octachlorodibenzo-p-dioxin.
OCDF = Octachlorodibenzofuran.

$$D_a = D_p / (\rho)^{0.5}$$

where

D_a = aerodynamic particle size (μm)

D_p = physical particle size (μm)

ρ = particle density (assumed to be 2.0 g/cm^3)

In this case, the specific gravity of the material collected at the ESP outlet was assumed to be equal to that of typical fly ash (2.0 g/cm^3).

Results for each of the three runs at the gas stream locations were combined to obtain the average PSD plots shown in Figures 3-4 and 3-5 for the ESP inlet and outlet, respectively. Similarly, the results for the samples collected from each of the four ESP hoppers were combined to obtain the average PSD plots shown in Figures 3-6 and 3-7. PSD plots for individual samples and hoppers are provided at the end of Appendix C along with the detailed PSD results. Weight gains from the initial precutter fraction of the impactor were not included in the PSD analysis, since these weight gains caused the total particulate loadings to become abnormally high. The large weight gains associated with right angle precutter fractions are believed to be caused by collection of large rust/ash particles from the walls of the sample ports as the impactors were inserted into the duct. Rust flakes and a reddish-brown discoloration were noted in the precutter fractions.

As expected, data for the ESP hoppers show a downward shift in the particle size distribution from the first to the last hopper (i.e., Hopper #1 to Hopper #4) since the largest particles are easily collected in the first field of the ESP. One would also expect that the PSD data for the ESP inlet and the first ESP hopper to be similar, since these samples represent the same material. Comparison of the data shown in Figures 3-4 and 3-6 show that this is generally true. ESP inlet PSDs indicate particle diameters range from approximately 0.3 μm to 10 μm with a median diameter of about 3.5 μm. Data for ESP Hopper #1 indicate particle sizes in approximately the 0.2 μm to 30 μm range with a median diameter of about 3 μm. The lack

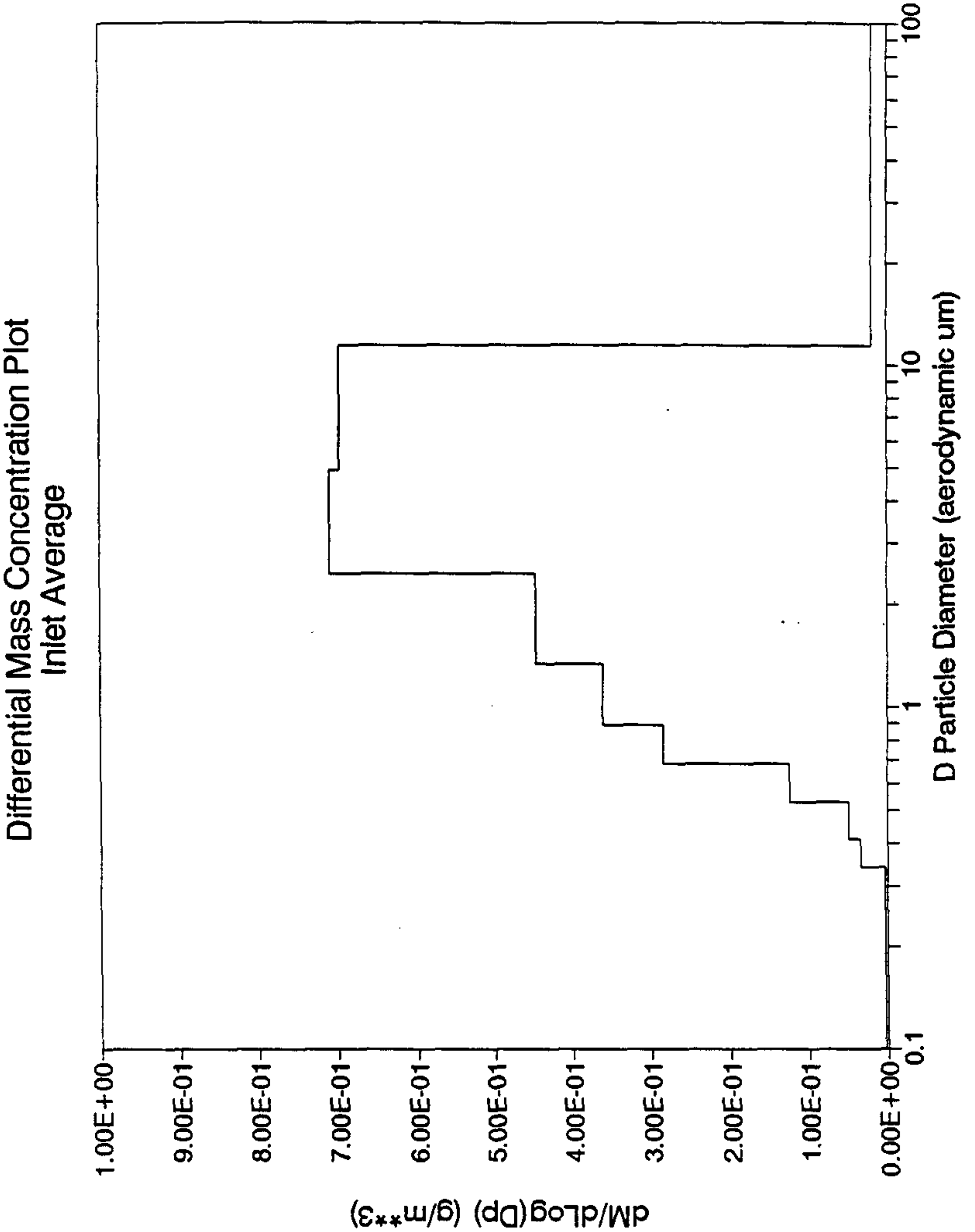


Figure 3-4
ESP Inlet PSD

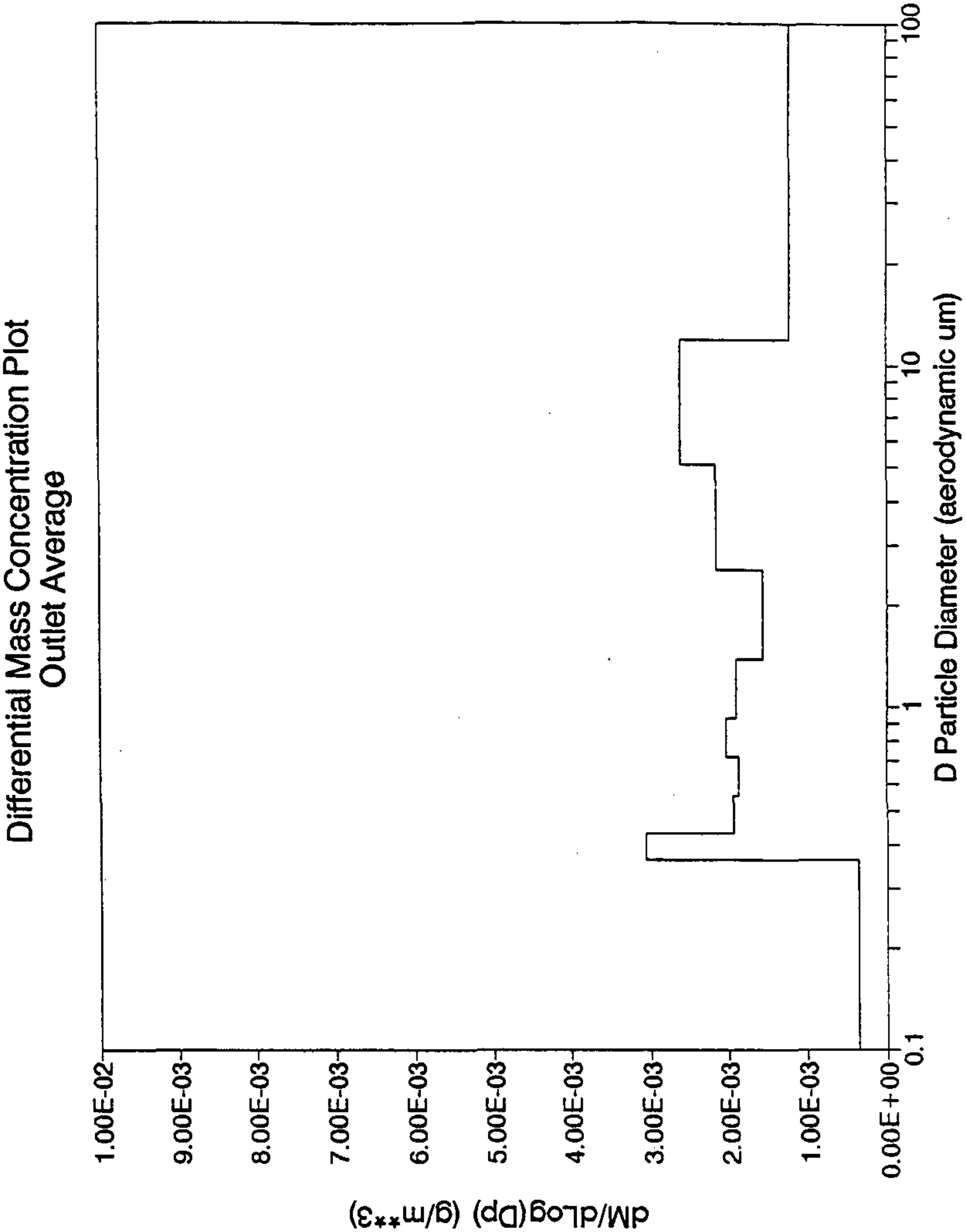


Figure 3-5
ESP Outlet PSD

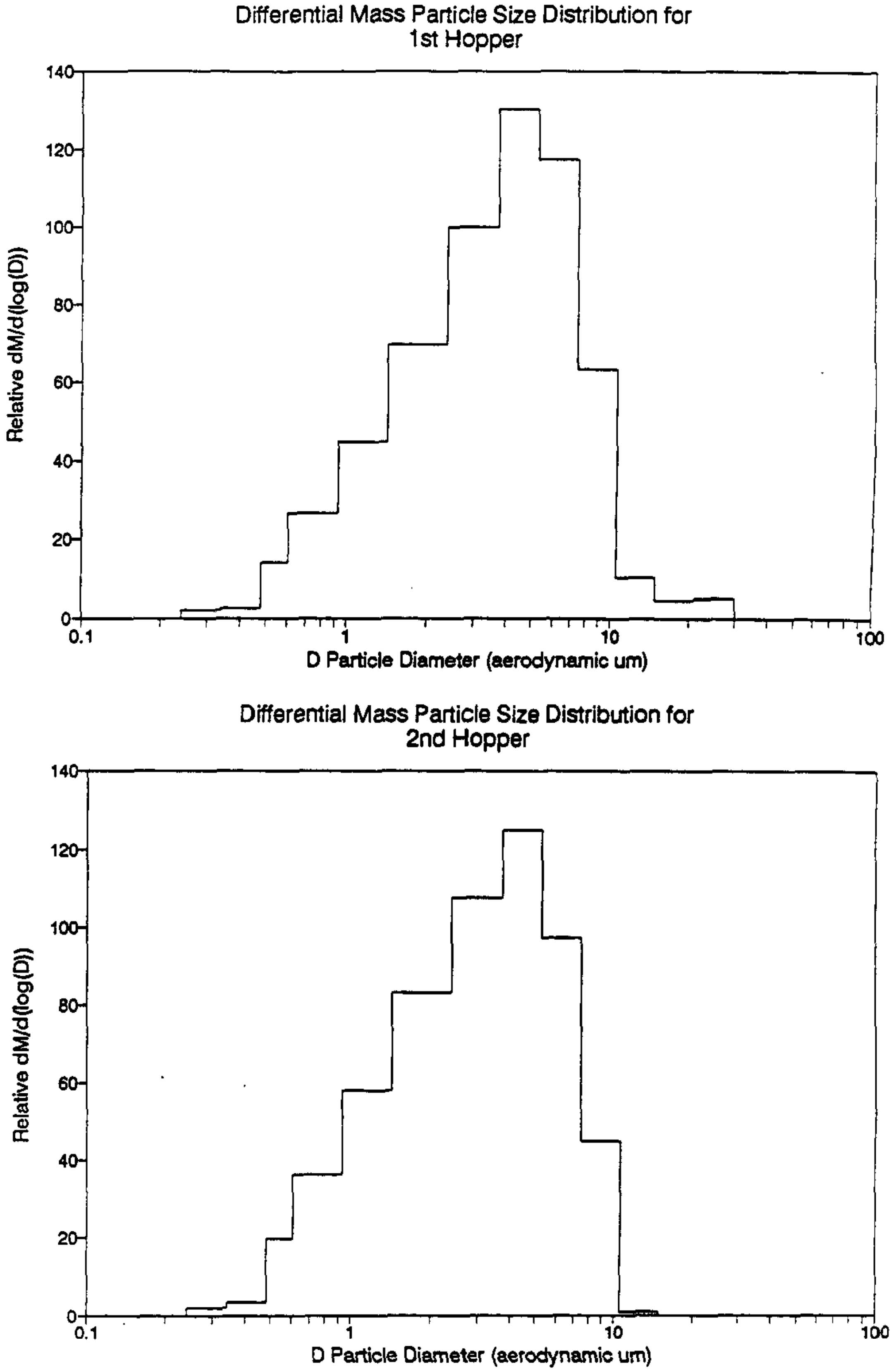
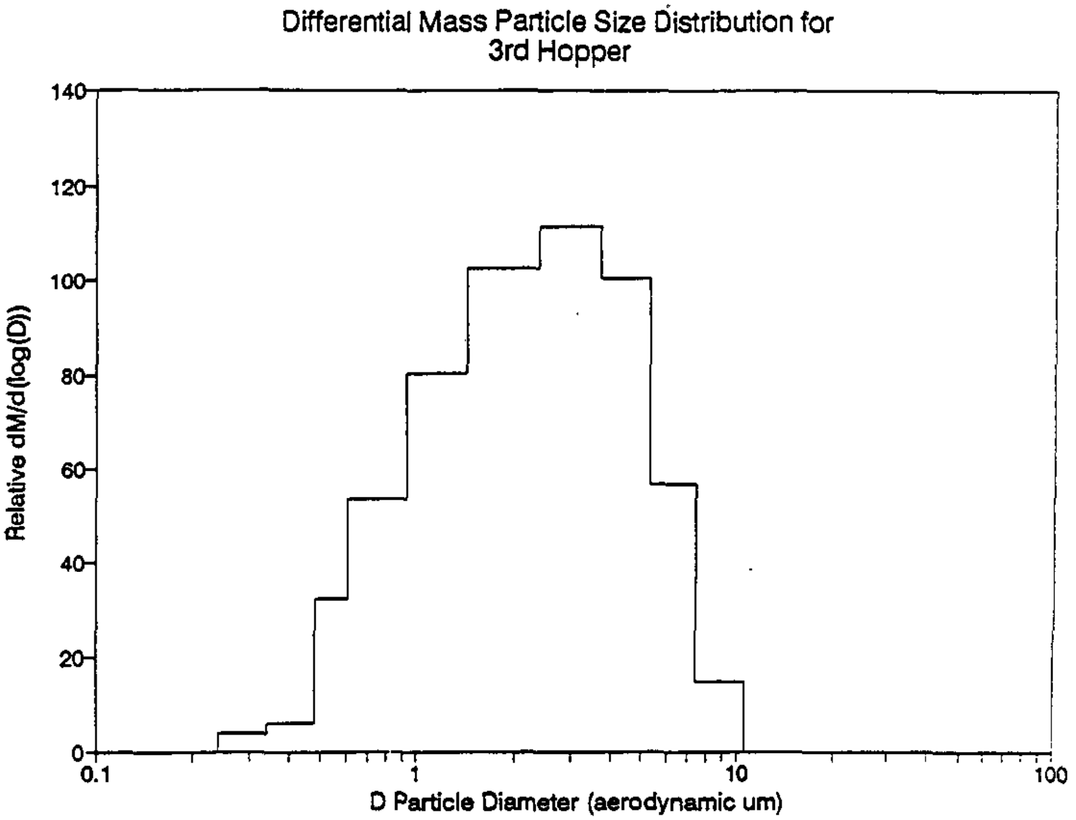
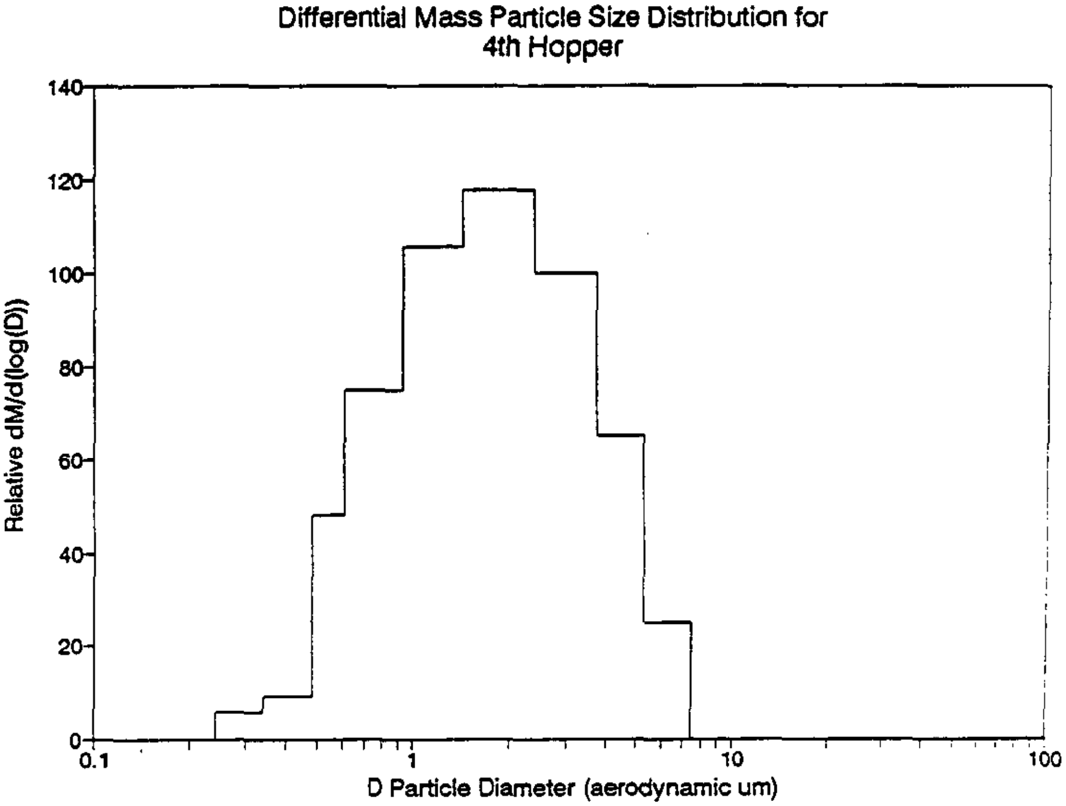


Figure 3-6
ESP Hoppers 1 and 2 PSD



Differential Mass Particle Size Distribution for 3rd Hopper



Differential Mass Particle Size Distribution for 4th Hopper

Figure 3-7
ESP Hoppers 3 and 4 PSD

of particles in the 10 μm to 30 μm range at the ESP inlet reflects the exclusion of the cyclone precutter fraction from the PSD analysis.

Radionuclide Data

Results of the radionuclide analyses performed on the coal and ash streams, expressed in activity units of picocuries per gram of sample, are summarized in Tables 3-20 and 3-21, respectively. The highest levels of radionuclides were found in the APF and ESP ash samples, both of which show very similar results. All of the ash results are consistent with the relative amount found in the coal (i.e., species with the largest levels in the coal also show the largest levels in the ash streams).

Chromium (VI) Measurements

Results for the chromium (VI) samples collected at the ESP outlet are shown in Table 3-22. Background levels in the reagent blank accounted for greater than 65% of the chromium (VI) detected in the samples; therefore, the data presented in Table 3-22 have been corrected for background contributions. The samples were analyzed on site by IC to determine chromium (VI) concentrations and, subsequently, analyzed by ICP-AES to determine the total chromium concentrations. Total chromium results for the nitric acid rinses indicated all of the chromium was accounted for in the impinger solutions. The mean chromium (VI) concentrations represent about 27% of the total chromium concentrations measured in the ESP outlet gas.

Experience has shown that measurement of hexavalent chromium can be very difficult in electric utility flue gas. A brief discussion of the technical implications of determination of chromium (CI) in stack gas and, in particular, in combustion sources and utility sources is included here. Additional details regarding chromium (VI) sampling are included in Appendix A.

Table 3-20
Coal Radionuclide (pCi/g)

Substance	Run 1	Run 2	Run 3	Mean	95% CI
Date					
Actinium-228 @338 KeV	ND(0.01)	0.15	0.21	0.12	0.26
Actinium-228 @911 KeV	0.15	0.15	0.07	0.12	0.11
Actinium-228 @968 KeV	0.16	ND(0.02)	0.22	0.13	0.27
Bismuth-212 @727 KeV	0.48	ND(0.31)	0.11	ND(0.31)	–
Bismuth-214 @1120.4 KeV	0.02	0.09	0.39	0.17	0.50
Bismuth-214 @1764.7 KeV	0.28	0.05	0.01	0.11	0.17
Bismuth-214 @609.4 KeV	0.22	0.27	0.28	0.26	0.24
K-40 @1460 KeV	1.3	1.6	2.0	1.6	1.6
Lead-210 @46 KeV	0.88	0.09	0.49	0.49	0.54
Lead-212 @238 KeV	0.08	0.12	0.3	0.17	0.33
Lead-214 @295.2 KeV	0.17	0.23	0.14	0.18	0.18
Lead-214 @352.0 KeV	0.34	0.32	0.15	0.27	0.23
Radium-226 @186.0 KeV	0.19	0.62	ND(0.1)	0.27	0.75
Thallium-208 @583 KeV	0.04	0.05	0.04	0.04	0.04
Thallium-208 @860 KeV	ND(0.14)	0.1	0.05	0.09	0.15
Thorium-234 @63.3 KeV	0.02	ND(0.1)	0.61	0.23	0.83
Thorium-234 @92.6 KeV	ND(0.1)	0.22	ND(0.08)	0.10	0.25
Uranium-235 @143.8 KeV	0.01	0.04	ND(0.01)	0.02	0.05

CI = Confidence interval.

ND = Not detected at the concentration in parentheses.

Table 3-21
Ash Stream Radionuclide (pCi/g, unless noted)

Substance	Bed Ash		Cyclone Ash		APF Ash		ESP Ash	
	Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI
Actinium-228 @338 KeV	0.23	0.20	0.68	0.27	1.1	0.80	1.2	0.14
Actinium-228 @911 KeV	0.06	0.10	0.56	0.10	1.1	0.90	0.99	0.26
Actinium-228 @968 KeV	0.05	0.09	0.60	0.53	0.62	0.52	1.1	0.56
Bismuth-212 @727 KeV	0.21	0.08	0.71	1.5	1.2	1.9	1.3	0.74
Bismuth-214 @1120.4 KeV	0.47	0.65	1.1	0.25	2.1	2.4	1.8	0.52
Bismuth-214 @1764.7 KeV	0.42	0.29	0.97	0.38	2.1	2.8	1.6	0.14
Bismuth-214 @609.4 KeV	0.59	0.32	0.99	0.06	1.9	1.2	1.8	0.25
K-40 @1460 KeV	1.0	0.26	6.6	1.9	14	12	11	1.4
Lead-210 @46 KeV	0.28	0.63	1.3	1.4	4.0	3.0	4.8	8.9
Lead-212 @238 KeV	0.19	0.29	0.63	0.09	1.8	1.8	0.97	0.07
Lead-214 @295.2 KeV	0.51	0.20	1.0	0.15	1.7	1.4	1.8	0.38
Lead-214 @352.0 KeV	0.59	0.17	1.1	0.25	2.2	1.8	1.9	0.29
Radium-226 @186.0 KeV	1.0	1.3	2.0	1.3	3.3	4.0	2.6	1.1
Thallium-208 @583 KeV	0.06	0.07	0.22	0.07	0.42	0.33	0.36	0.14
Thallium-208 @860 KeV	ND(0.28)	--	ND(0.44)	--	0.25	0.78	0.28	0.29
Thorium-234 @63.3 KeV	0.99	1.6	1.0	1.8	3.5	3.9	1.6	1.7
Thorium-234 @92.6 KeV	0.14	0.27	0.48	1.0	0.50	1.5	0.70	0.88
Uranium-235 @143.8 KeV	0.07	0.08	0.12	0.07	0.21	0.24	0.16	0.07

Table 3-22
Chromium (VI) and Total Chromium Results for the ESP Outlet ($\mu g/Nm^3$)

Substance	Method	Run 1 4/12/94	Run 2 4/13/94	Run 3 4/14/94	Mean	95% CI
Chromium (VI) (impinger)	IC	2.2[a]	0.96[a]	1.0[a]	1.4	1.7
Total Chromium (impinger solution)	ICP-AES	5.1	ND(1.1)	9.8	5.2	11
Total Chromium (nitric acid rinse)	ICP-AES	ND(0.2)	ND(0.2)	ND(0.4)	ND(0.4)	--
Total Chromium (Method 29)	ICP-AES ICP/MS	3.1	2.7	5.5	3.7	3.7

[a] Background concentrations in the reagent blank were ≥65% of the sample values. Results have been corrected for background levels.

CI = Confidence interval.

ND = Not detected at the concentration in parentheses.

The chromium (VI) method depends on the solubility and stability of chromium (VI) in basic aqueous solution. The method calls for the use of a strong base in a solution contained in the impingers and recycled to the probe tip for early gas contact and flushing to the probe walls. The method is theoretically sound but has some limitations when applied to combustion sources in general and utility flue gases specifically.

As mentioned above, chromium (VI) is stable in a strong alkaline solution ($pH > \sim 9$), but all combustion gas streams contain large amounts of CO_2 (10-20%), which is an acid gas, and serves to lower the pH of the impinger solution. As a result, the pH may dip lower than desirable during sampling. As a further complication, utility flue gas contains significant levels of SO_2 (100 ppm or more). SO_2 is also an acid gas but is a reductant as well, so the impinger solution designed to absorb chromium (VI) also absorbs CO_2 and SO_2. The result of this is a lowered pH and a solution which contains an oxidant [chromium (VI)] and a reductant (SO_2/HSO_3^-). As the pH falls, the redox couple becomes more favorable, and any chromium (VI) present may be reduced by SO_2/HSO_3^- and not detected as chromium (VI).

4

DATA EVALUATION

Three methods were used to evaluate the quality of data obtained from the tests at Plant Tidd. First, the process data were examined to determine if the unit was operating at normal, steady-state conditions during the test periods. Second, the QA/QC protocol for sampling and analytical procedures (i.e., equipment calibration and leak checks, duplicate analyses, blanks, spikes, standards, etc.) was evaluated. In addition, QC sample results (presented in Appendix D) were compared with project objectives. Third, material balances were calculated for various systems within the plant. Material balances involve the summation and comparison of mass flow rates in several streams, often sampled and analyzed by different methods. Closure within an acceptable range can be used as an indicator of accurate results for streams that contribute significantly to the overall inlet or outlet mass rates.

Process Operation During Testing

Process operating data were examined to ensure that operation was stable during the sampling periods. Measurements were available in five-minute intervals from the plant computerized data acquisition system. Table 4-1 shows the mean value and coefficient of variation (CV, standard deviation divided by the mean) for key process parameters associated with the combustor, ESP, and APF systems. In addition, process data trend plots are included in Appendix E.

The CVs were calculated to evaluate process stability. Steady combustor operation was maintained during each of the test runs, as indicated by the low CVs for the total load, the coal paste feed rate, the mean bed temperature, and the bed outlet oxygen levels (see Table 4-1). The sorbent feed rate (CVs of 18 to 24%) showed greater variability than the other combustor parameters. However, this amount of variability is typical of normal operation

Table 4-1
Summary of Process Monitoring Data

		Run 1		Run 2		Run 3		Run 4	
		04-12-94		04-13-94		04-14-94		04-15-94	
Combustor Parameters	**Units of Measure**	**Mean**	**CV (%)**	**Mean**	**CV (%)**	**Mean**	**CV (%)**	**Mean**	**CV (%)**
Total Load	MW	46	2.1	46	1.9	45	1.9	46	2.7
Steam Turbine Load	MW	38	2.2	37	2.1	37	2.1	38	2.5
Gas Turbine Load	MW	8.3	4.2	9.0	3.6	8.0	3.4	8.0	6.0
Coal Paste Feed Rate	10^3 lb/hr[a]	45	1.5	45	1.5	44	1.8	45	2.2
Sorbent Feed Rate	10^3 lb/hr[a]	18	18	21	21	19	19	18	24
Mean Bed Temperature	°F	1499	0.3	1497	0.3	1497	0.3	1497	0.3
Bed Level	inches	122	1.3	115	0.5	113	0.4	112	0.9
Bed Outlet Oxygen	% vol.	6.9	4.0	7.0	4.1	6.9	4.3	6.5	6.0
ESP Parameters									
ESP Outlet Opacity	%	10	7.5	10	4.3	10	8.6	11	6.0
ESP Outlet CO	ppmv	33	30	35	15	34	23	36	16
ESP Outlet SO_2	ppmv	182	10	178	12	179	11	181	13
ESP Outlet NO_x	ppmv	143	9	145	10	138	10	137	10
ESP Outlet Oxygen	% vol.	7.0	1.7	7.0	2.2	7.0	2.8	6.6	2.7
ESP Outlet Temperature	°F	404	0.2	403	0.3	405	0.3	403	0.4
APF Parameters									
APF Inlet Temperature	°F	1352	0.8	1364	0.8	1347	1.7	1359	1.1
APF Outlet Temperature	°F	1322	0.6	1328	0.9	1329	1.8	1322	1.0
APF Differential Pressure	inches H_2O	116	5	117	5	116	6	118	6

[a] Feed rate reported on an "as fired" basis.

CV = Coefficient of variation (standard deviation divided by the mean).

since the sorbent feed system cycles between the east and west feeder systems approximately every 2 1/2 hours. The total load was controlled at approximately 46 MW throughout the test period which is representative of stable, long-term operation.

Stable ESP operations were also indicated by the low CVs for ESP outlet opacity. ESP outlet CO (CVs of 15 to 30%) and SO_2 levels (CVs of 10 to 13%) were typically more variable than other parameters. ESP outlet SO_2 levels increased for a short period each time the sorbent feed system switched from the east feeder to the west feeder. These fluctuations are typical of normal operation.

Data for APF system parameters indicate stable operation of this system during all test periods. APF differential pressure measurements indicate that the APF pulse-cleaning cycle was approximately 30 minutes during all tests. APF inlet gas temperatures were approximately 200°F cooler than design (1350°F versus 1550°F) because tempering air was added to the system during the test period. The cooler gas temperature and reduced load during the tests made it necessary to adjust the gas sampling rate through the gas cooling apparatus at both the APF inlet and outlet. Since the gas cooling system was designed for an inlet gas temperature of 1550°F and a unit load of 85 MW; a reduction in the gas sampling rate was necessary to ensure that an isokinetic sampling rate was maintained at these locations.

Sample Collection

Appendix A describes the sampling procedures used at Plant Tidd. Several factors indicate representative sample collection. First, the key components of the sampling equipment—pitot tubes, thermocouples, orifice meters, dry gas meters, and sampling nozzles—had been calibrated before use in the field; the calibrations are on file at Radian Corporation. Second, the sampling runs were well documented. Third, all flue gas samples (except one) were collected at rates between 90 and 110% of the isokinetic rates. Fourth, sufficient data were collected using standard sampling and analytical methods to ensure acceptable data completeness and the comparability of the measurements.

Following are some significant observations about sample collection:

- The multi-metals and anions samples collected at the APF inlet during Run 1 (4/12/94) were voided because of breakthrough of particulate matter across the thimble filter into the impinger solutions. The higher than expected particulate loading exceeded the capacity of the filter, resulting in filter gasket failure and particle penetration. During subsequent runs, additional filters were added in series to prevent breakthrough. The completeness objective of three valid runs was met despite this problem.
- The sampling systems at the APF inlet and outlet were designed to allow gas samples to cool only after the gas entered the recoverable quartz tubing portion of the sampling train. However, the quartz tubing broke repeatedly during the initial test runs because the quartz tube ball joint could not withstand the thermal stresses at 600°F. To solve this problem, the heat tracing tape was removed from the sample line downstream of the orifice meter to allow the gas to cool slightly. Skin temperatures at the header sample valves were typically 250-350°F after this modification. Because most of the quartz tubes were broken during the initial test, subsequent tests at the APF locations were conducted by connecting the Teflon® tubing directly to the sample valves. This modification should have no measurable affect on the results.

Analytical Quality Control Results

Quality control (QC) information obtained for the Tidd PFBC HAPs project is related to measurement precision, accuracy (which includes precision and bias), and blank effects, determined using various types of replicate, spiked, and blank samples. The specific characteristics evaluated depend on the type of QC checks performed. For example, blanks may be prepared at different stages in the sampling and analysis process to isolate the source of a blank effect. Table 4-2 summarizes the QC measures used as part of the data evaluation protocol and the characteristic information obtained. The absence of any of these types of quality QC checks does not necessarily reflect poorly on the quality of the data but does limit the ability to estimate the magnitude of the measurement error and, hence, prevents placing an estimate of confidence in the results.

Different QC checks provide different types of information, particularly pertaining to the sources of inaccuracy, imprecision, and blank effects, as shown in Table 4-2. As part of the Tidd PFBC HAPs project, measurement precision and accuracy are typically estimated from

Table 4-2
Types of Quality Control Samples

QC Activity	Characteristic Measured
Precision	
Replicate samples collected over time under the same conditions	Total variability, including process or temporal, sampling, and analytical, but not bias.
Duplicate field samples collected simultaneously	Sampling plus analytical variability at the actual sample concentrations.
Duplicate analyses of a single sample	Analytical variability at the actual sample concentrations.
Matrix- or media-spiked duplicates	Sampling plus analytical variability at an established concentration.
Laboratory control sample duplicates	Analytical variability in the absence of sample matrix effects.
Surrogate-spiked sample sets	Analytical variability in the sample matrix but at an established concentration.
Accuracy (including bias and precision)	
Matrix-spiked samples	Analyte recovery in the sample matrix, indicating possible matrix interferences and other effects. In a single sample, includes both random error (imprecision) and systematic error (bias).
Media-spiked samples	Similar to matrix-spiked samples. Used where a matrix-spiked sample is not feasible, such as certain stack sampling methods.
Surrogate-spiked samples	Analyte recovery in the sample matrix, to the extent that the surrogate compounds are chemically similar to the compounds of interest. Primarily used as indicator of analytical efficacy.
Laboratory control samples (LCS)	Analyte recovery in the absence of actual sample matrix effects. Used as an indicator of analytical control.
Standard reference material	Analyte recovery in a matrix similar to the actual samples.
Blank Effects	
Field blank	Total sampling plus analytical blank effect, including sampling equipment and reagents, sample transport and storage, and analytical reagents and equipment.
Trip blank	Blank effects arising from sample transport and storage. Typically used only for organic compound analyses.
Method blank	Blank effects inherent in the analytical method, including reagents and equipment.
Reagent blank	Blank effects from reagents used.

QC indicators that cover as much of the total sampling and analytical process as feasible. Precision and accuracy measurements are based primarily on the actual sample matrix. The precision and accuracy estimates obtained experimentally during the test programs are compared with data quality objectives (DQOs) established for this project.

The DQOs are not intended to be used as validation criteria but as empirical estimates of the precision and accuracy that would be expected from existing reference measurement methods that are considered acceptable. Although analytical precision and accuracy are relatively easy to quantify and control, sampling precision and accuracy are unique to each site and each sample matrix. Data that do not meet these objectives are not necessarily unacceptable. Rather, the intent is to document the precision and accuracy actually obtained, and the objectives serve as benchmarks for comparison. The effects of not meeting the objectives should be considered in light of the intended use of the data.

A summary of the types of QC data evaluated for this project is presented in Table 4-3. The individual results for blank samples, matrix spike, and surrogate spike recoveries can be found in Appendix D. Table D-1 presents a summary of blank sample results. Table D-2 presents a summary of the precision and accuracy estimates. Table D-3 presents surrogate spike data reported for the project. Most of the QC results met the project objectives.

A performance audit was conducted as an independent check to evaluate the data produced. The performance audit addressed the chemical analysis of the samples collected and the physical measurements supporting the field sampling effort. The laboratories conducting the analyses were given performance audit samples prepared by spiking representative sample matrices with target analytes at representative concentration levels. Results for the audit samples for the field and laboratory activities were compiled and discussed in an audit report submitted to the project team on July 15, 1994. Table 4-4 presents a summary of analytical results for the audit samples. A list of concerns was presented as a part of that report. The concerns, as stated in the report, are listed below followed by the response from the project team (in italics).

Table 4-3
Types of Quality Control Data

Analysis (Grouped by Source/Matrix)	Precision				Accuracy				Blank			
	Dup Field Samples	Dup Lab Analysis	Matrix or *Media* Spiked Dup	Lab Control Sample Dup	Matrix *or* Media Spike	Surrogate Spike	*Lab* Control Sample	*Standard* Reference Material	Field Blank	Trip Blank	Method Blank	Reagent Blank
Gas Streams												
Metals - Vapor Phase			✓	✓	✓		✓		✓		✓	✓
Metals - Solid Phase			✓	✓	✓		✓	✓	✓		✓	✓
Anions - Vapor Phase			✓	✓	✓		✓		✓		✓	✓
Anions - Solid Phase			✓	✓	✓		✓		✓		✓	✓
Chromium (VI)			✓		✓		✓		✓			✓
Total Chromium			✓		✓		✓		✓		✓	✓
Volatile Organics						✓	✓		✓	✓	✓	
Semivolatile Organics						✓			✓	✓	✓	
Formaldehyde		✓			✓				✓		✓	✓
Ammonia			✓		✓		✓		✓		✓	✓
Cyanide			✓		✓		✓		✓		✓	✓
PAHs						✓			✓	✓	✓	
PCDD/PCDF						✓			✓	✓	✓	
Coal												
Metals	✓	✓						✓				
Radionuclides	✓											
Anions	✓	✓						✓				
Ultimate/Proximate	✓							✓				

Table 4-3 (Continued)

Analysis (Grouped by *Source/Matrix*)	Precision				Accuracy				Blank			
	Dup Field Samples	Dup Lab Analysis	*Matrix or Media Spiked Dup*	Lab Control Sample Dup	*Matrix or Media Spike*	*Surrogate Spike*	*Lab Control Sample*	*Standard Reference Material*	*Field Blank*	*Trip Blank*	*Method Blank*	*Reagent Blank*
Bed Ash and Fly Ash												
Metals	✓		✓		✓			✓			✓	
Anions	✓		✓		✓			✓			✓	
Radionuclides	✓											
Semivolatile Organics	✓		✓		✓	✓	✓				✓	
PCDD/PCDF	✓					✓					✓	
Carbon	✓											
Particle Size Dist.	✓											
Service Water												
Metals	✓		✓		✓		✓				✓	
Anions	✓		✓		✓		✓				✓	
Dolomite Sorbent												
Metals	✓		✓		✓		✓				✓	
Anions	✓		✓		✓		✓				✓	

Table 4-4
Analytical Results for Audit Samples

Lab[a]	Sample ID	Matrix	Analyte	Units	Lab Result	Reference Value	Percent Recovery	Audit Objective
Multi-Metals Trains								
Radian	AEP-QD02MMFD AEP-QD02MMAP	Filter Acetone PNR	Particulate Weight	gram	0.0601	0.1198	50	NS
Radian	AEP-QD02MMAP	Acetone PNR	Aluminum	µg/g	97,715	140,000	70 Q	75-125
	AEP-QD02MMNR	HNO_3 PNR	Antimony	µg/g	ND	7	NA	75-125
	AEP-QD02MMFD	Filter	Arsenic	µg/g	180	145	124	75-125
			Barium	µg/g	854	1,500	57 Q	75-125
			Beryllium	µg/g	9.9	12	82	75-125
			Cadmium	µg/g	9.19	1	919 Q	75-125
			Calcium	µg/g	14,147	11,100	127 Q	75-125
			Chromium	µg/g	149	196	76	75-125
			Cobalt	µg/g	23.4	46	51 Q	75-125
			Copper	µg/g	123	118	104	75-125
			Iron	µg/g	46,995	94,000	50 Q	75-125
			Lead	µg/g	60.2	72.4	83	75-125
			Magnesium	µg/g	5,033	4,550	111	75-125
			Manganese	µg/g	131	190	69 Q	75-125
			Mercury	µg/g	0.192	0.16	120	75-125
			Molybdenum	µg/g	37.3	29	129 Q	75-125
			Nickel	µg/g	111	127	87	75-125
			Phosphorus	µg/g	ND	NA	NA	75-125
			Potassium	µg/g	13,463	18,800	72 Q	75-125
			Selenium	µg/g	18.1	10.3	175 Q	75-125
			Silver	µg/g	ND	NA	NA	75-125
			Sodium	µg/g	1,586	1,700	93	75-125
			Titanium	µg/g	5,808	8,000	73 Q	75-125
			Vanadium	µg/g	229	300	76	75-125
Radian	AEP-QD01MMHT	HNO_3 Impingers	Aluminum	mg/L	0.0101	NA	NA	75-125
			Antimony	mg/L	0.183	0.20	91	75-125
			Arsenic	mg/L	1.85[a]	2.00	92	75-125
			Barium	mg/L	0.190	0.20	95	75-125
			Beryllium	mg/L	0.210	0.20	105	75-125
			Boron	mg/L	0.0385	NA	NA	75-125
			Cadmium	mg/L	0.296[a]	0.20	148 Q	75-125
			Calcium	mg/L	0.302	0.20	151 Q	75-125
			Chromium	mg/L	1.72	2.00	86	75-125
			Cobalt	mg/L	0.191	0.20	95	75-125
			Copper	mg/L	0.437	0.50	87	75-125
			Iron	mg/L	ND	NA	NA	75-125

Table 4-4 (Continued)

Lab	Sample ID	Matrix	Analyte	Units	Lab Result	Reference Value	Percent Recovery	Audit Objective
Radian	AEP-QD01MMHT	HNO_3 Impingers	Lead	mg/L	1.91[a]	2.00	95	75-125
			Magnesium	mg/L	0.186	0.20	93	75-125
			Manganese	mg/L	0.221	0.20	110	75-125
			Mercury	mg/L	4.36	5.00	87	75-125
			Molybdenum	mg/L	0.154	0.20	77	75-125
			Nickel	mg/L	0.444	0.50	89	75-125
			Phosphorus	mg/L	ND	NA	NA	75-125
			Potassium	mg/L	2.85	0.20	1,425 Q	75-125
			Selenium	mg/L	0.175[a]	0.20	87	75-125
			Silver	mg/L	0.0269	0.20[b]	NA[b]	75-125
			Sodium	mg/L	0.642	0.20	321 Q	75-125
			Titanium	mg/L	0.00294	NA	NA	75-125
			Vanadium	mg/L	0.443	0.5	89	75-125
Harvard ICP/MS	AEP-QD02MMHT	HNO_3 Impingers	Antimony	µg/L	3.48	5.0	70 Q	75-125
			Arsenic	µg/L	8.97	10.0	90	75-125
			Barium	µg/L	10.66	10.0	107	75-125
			Beryllium	µg/L	11.45	10.0	114	75-125
			Cadmium	µg/L	9.40	10.0	94	75-125
			Chromium	µg/L	9.37	10.0	94	75-125
			Cobalt	µg/L	8.80	10.0	88	75-125
			Copper	µg/L	8.80	10.0	88	75-125
			Lead	µg/L	9.49	10.0	95	75-125
			Manganese	µg/L	9.23	10.0	92	75-125
			Mercury	µg/L	10.78	10.0	108	75-125
			Molybdenum	µg/L	5.26	5.0	105	75-125
			Nickel	µg/L	6.97	10.0	70 Q	75-125
			Selenium	µg/L	6.20	10.0	62 Q	75-125
			Vanadium	µg/L	9.41	10.0	94	75-125
Radian	AEP-QD01MMHI	$KMnO_4$ Impingers	Mercury	mg/L	0.479	0.400	120	75-125
Anions Train								
Radian	AEP-QD01ANIT	$Na_2CO_3/NaHCO_3$ Impingers	Chloride	mg/L	284	297	96	80-120
			Fluoride	mg/L	9.22	9.8	94	80-120
			Sulfate	mg/L	8,680	10,000	86	80-120

Table 4-4 (Continued)

Lab	Sample ID	Matrix	Analyte	Units	Lab Result	Reference Value	Percent Recovery	Audit Objective
Ammonia/Cyanide Train								
Radian	AEP-QD01NHIP	H_2SO_4 Impinger	Ammonia	mg/L	1.31	0.27	485 Q	80-120
Radian	AEP-QD01NHIP	ZnOAc Impinger	Cyanide	mg/L	0.0257	0.10	26 Q	75-125
Chromium (VI) Trains								
Radian	AEP-QD01CRIP	KOH Impinger	Chromium(VI)	µg/L	19.35	16	121	75-125
Radian	AEP-QD01CRIP	KOH Impinger	Tot. Chrome	µg/L	22	16	138 Q	75-125
Service Water								
Radian	AEP-QD01SWMM	Service Water	Aluminum	mg/L	0.126	NA	NA	75-125
			Antimony	mg/L	1.06	0.99	107	75-125
			Arsenic	mg/L	0.870[a]	1.00	87	75-125
			Barium	mg/L	0.0021	NA	NA	75-125
			Beryllium	mg/L	0.97	0.96	101	75-125
			Boron	mg/L	0.314	NA	NA	75-125
			Cadmium	mg/L	0.853[a]	0.94	91	75-125
			Calcium	mg/L	1.12	1.00	112	75-125
			Chromium	mg/L	0.976	1.03	95	75-125
			Cobalt	mg/L	0.954	1.00	95	75-125
			Copper	mg/L	0.996	1.03	97	75-125
			Iron	mg/L	1.02	1.02	100	75-125
			Lead	mg/L	0.934[a]	1.01	92	75-125
			Magnesium	mg/L	0.968	1.06	91	75-125
			Manganese	mg/L	0.978	1.02	96	75-125
			Molybdenum	mg/L	1.00	1.06	94	75-125
			Nickel	mg/L	0.979	1.02	96	75-125
			Phosphorus	mg/L	ND	NA	NA	75-125
			Potassium	mg/L	0.0968	NA	NA	75-125
			Selenium	mg/L	0.936[a]	0.99	94	75-125
			Silver	mg/L	ND	NA	NA	75-125
			Sodium	mg/L	0.286	NA	NA	75-125
			Titanium	mg/L	0.936	1.01	93	75-125
			Vanadium	mg/L	0.966	1.01	96	75-125
Radian	AEP-QD02SWMM	Service Water	Mercury	mg/L	0.0724	0.08	90	75-125
Radian	AEP-QD01SWAN	Service Water	Chloride	mg/L	31.0	33.0	94	80-120
			Fluoride	mg/L	1.91	1.7	112	80-120
			Sulfate	mg/L	44.4	50.0	89	80-120
			Phosphate	mg/L	ND	NA	NA	80-120

Table 4-4 (Continued)

Lab	Sample ID	Matrix	Analyte	Units	Lab Result	Reference Value	Percent Recovery	Audit Objective
Dolomite Sorbent								
Radian	AEP-QD00SOAN	Sorbent	Aluminum	μg/g	60.4	1,193	5 Q	75-125
			Antimony	μg/g	ND	NA	NA	75-125
			Arsenic	μg/g	3.48[a]	NA	NA	75-125
			Barium	μg/g	1.89	NA	NA	75-125
			Beryllium	μg/g	0.0108	NA	NA	75-125
			Boron	μg/g	ND	NA	NA	75-125
			Cadmium	μg/g	0.587	NA	NA	75-125
			Calcium	μg/g	191,000	215,000	89	75-125
			Chromium	μg/g	1.51	NA	NA	75-125
			Cobalt	μg/g	ND	NA	NA	75-125
			Copper	μg/g	0.900	NA	NA	75-125
			Iron	μg/g	1,400	1,960	71 Q	75-125
			Lead	μg/g	0.220[a]	NA	NA	75-125
			Magnesium	μg/g	108,000	127,800	85	75-125
			Manganese	μg/g	161	232	69 Q	75-125
			Mercury	μg/g	ND	NA	NA	75-125
			Molybdenum	μg/g	0.0676	NA	NA	75-125
			Nickel	μg/g	0.0186	NA	NA	75-125
			Phosphorus	μg/g	ND	43	NA	75-125
			Potassium	μg/g	60.8	996	6 Q	75-125
			Selenium	μg/g	1.81[a]	NA	NA	75-125
			Silver	μg/g	ND	NA	NA	75-125
			Sodium	μg/g	50.6	74	68 Q	75-125
			Titanium	μg/g	7.41	120	6 Q	75-125
			Vanadium	μg/g	3.63	NA	NA	75-125
			Chloride	μg/g	0	NA	NA	75-125
			Fluoride	μg/g	14.9	NA	NA	75-125
Coal Paste								
CT&E	AEP-QD00GCCM	Coal	Arsenic	μg/g	8.5	10.3	82	75-125
			Barium	μg/g	32	32.76	98	75-125
			Beryllium	μg/g	1.2	1.33	90	75-125
			Boron	μg/g	71	72.3	98	75-125
			Cadmium	μg/g	0.10/0.08	0.11	91	75-125
			Calcium	μg/g	900	861	104	75-125
			Chromium	μg/g	17	16.3	104	75-125
			Copper	μg/g	7.5	8.47	88	75-125

Table 4-4 (Continued)

Lab	Sample ID	Matrix	Analyte	Units	Lab Result	Reference Value	Percent Recovery	Audit Objective
CT&E	AEP-QDOOGCCM	Coal	Lead	μg/g	7	6.00	117	75-125
			Magnesium	μg/g	470	420	112	75-125
			Mercury	μg/g	0.20	0.14	143 Q	75-125
			Molybdenum	μg/g	<3	2.19	NA	75-125
			Phosphorus	μg/g	38	NA	NA	75-125
			Selenium	μg/g	0.8	1.83	44 Q	75-125
			Titanium	μg/g	660	690	96	75-125
			Chloride	μg/g	1,230	860	143	75-125
			Fluoride	μg/g	70	58	121	75-125
			Carbon	%	72.33	72.08	100	75-125
			Hydrogen	%	4.76	4.96	96	75-125
			Nitrogen	%	1.43	1.39	103	75-125
			Sulfur	%	3.28	3.26	101	75-125
			Ash	%	11.94	11.56	103	75-125
			HHV	Btu/lb	12,923	12,888	100	75-125
NC State	AEP-QD00GCCM	Coal	Aluminum	μg/g	14,734	13,075	113	75-125
			Antimony	μg/g	0.543	0.64	85	75-125
			Arsenic	μg/g	18.97	10.33	184 Q	75-125
			Barium	μg/g	57.9	32.76	177 Q	75-125
			Cadmium	μg/g	2.087	0.11	1,897 Q	75-125
			Calcium	μg/g	1785	861	207 Q	75-125
			Chromium	μg/g	20.6	16.30	126 Q	75-125
			Cobalt	μg/g	5.75	5.50	104	75-125
			Copper	μg/g	12.2	8.47	144 Q	75-125
			Iron	μg/g	22,314	20,031	111	75-125
			Magnesium	μg/g	631	420	150 Q	75-125
			Manganese	μg/g	20.9	18.35	114	75-125
			Mercury	μg/g	0.058	0.14	41 Q	75-125
			Molybdenum	μg/g	0.628	2.19	29 Q	75-125
			Nickel	μg/g	16.2	14.07	115	75-125
			Potassium	μg/g	1,859	1,762	105	75-125
			Selenium	μg/g	1.96	1.83	107	75-125
			Silver	μg/g	0.303	NA	NA	75-125
			Sodium	μg/g	344	367	94	75-125
			Titanium	μg/g	1013	690	147 Q	75-125
			Vanadium	μg/g	35.8	31.01	115	75-125

Table 4-4 (Continued)

Lab	Sample ID	Matrix	Analyte	Units	Lab Result	Reference Value	Percent Recovery	Audit Objective
ESP Ash, APF Ash, Bed Ash, Cyclone Ash								
Radian	AEP-QD00FAMM	Ash	Aluminum	µg/g	107,000	140,000	76	75-125
			Antimony	µg/g	ND	7	NA	75-125
			Arsenic	µg/g	174[a]	145	120	75-125
			Barium	µg/g	1,120	1,500	75	75-125
			Beryllium	µg/g	10.3	12	86	75-125
			Cadmium	µg/g	1.06[a]	1.0	106	75-125
			Calcium	µg/g	8,090	11,100	73 Q	75-125
			Chromium	µg/g	171	196	87	75-125
			Cobalt	µg/g	44.4	46	96	75-125
			Copper	µg/g	88.8	118	75	75-125
			Iron	µg/g	78,200	94,000	83	75-125
			Lead	µg/g	71.0[a]	72.4	78	75-125
			Magnesium	µg/g	3,020	4,550	66	75-125
			Manganese	µg/g	138	190	73 Q	75-125
			Mercury	µg/g	0.180	0.16	112	75-125
			Molybdenum	µg/g	20.7	29	71 Q	75-125
			Nickel	µg/g	110	127	87	75-125
			Phosphorus	µg/g	ND	NA	NA	75-125
			Potassium	µg/g	16,000	18,800	85	75-125
			Selenium	µg/g	11.7[a]	10.3	114	75-125
			Silver	µg/g	0.147	NA	NA	75-125
			Sodium	µg/g	1,430	1,700	84	75-125
			Titanium	µg/g	726,0	8,000	91	75-125
			Vanadium	µg/g	269	300	90	75-125
Radian	AEP-QD00FAAN	Ash	Chloride	µg/g	0.0	NA	NA	80-120
			Fluoride	µg/g	38.2	NA	NA	80-120

[a] Analytical result from GFAAS method.

[b] Silver precipitated in the solution during audit sample preparation; this result should be used for qualitative assessment only.

NA = Not applicable or not able to be calculated.

ND = Not detected.

NS = None specified.

Q = Outside of audit objective for recovery.

- Particulate matter collection efficiency in the QC audit sample at the ESP inlet was 50 percent.

  Incomplete rinsing or recovery of solids deposited in the probe and/or filter losses during disassembly of the filter holder are likely contributors to low sample recovery. In this sample, the unrecovered mass was approximately 0.05 gram. At the ESP inlet where the recovered particulate mass for actual samples was approximately 5 grams, this amount of sample loss is not significant. However, at the ESP outlet where the recovered particulate mass was much lower, sample losses or incomplete particulate recovery may be more significant. Since a particulate audit sample was not collected by the sampling team at the ESP outlet, their recovery technique cannot be assessed.

- Ammonia QC audit sample recovery was 485% at 0.27 mg/L, outside the accuracy objective of 80-120 percent. Cyanide QC audit sample recovery was 26% at 0.10 mg/L, also outside the accuracy objective of 80-120 percent.

  The ammonia audit sample was prepared in fresh impinger solution and required a five-fold dilution to reduce acidity prior to distillation and analysis. Since the audit sample concentration was prepared near the method detection limit, sample dilution lowered the concentration to a level where there is a greater degree of uncertainty in the analytical result. Actual field samples did not require dilution and the QC results for matrix spikes and matrix spike duplicates indicate excellent analytical precision and recovery.

  The cyanide audit sample was prepared using an EPA water quality standard as the source material. An investigation of possible causes for low recovery revealed that a complex form of cyanide (iron ferricyanide) was used in the EPA standard which is susceptible to photodegradation. In the event the source material was exposed to sunlight prior to audit sample preparation, photodegradation may explain the low recovery, although there is no evidence to confirm this. In the laboratory, field samples were spiked with a cyanide salt solution (free cyanide) which more closely simulates the dissociation of HCN in solution. The recovery results for these matrix spike samples indicate excellent analytical precision and accuracy. However, firm conclusions regarding the accuracy of the cyanide analysis cannot be made based on the audit sample results.

- Eleven target metals (Al, Ba, Ca, Cd, Co, Fe, Mn, Mo, K, Se, and Ti) did not meet the recovery objective for the particulate matter audit sample.

  Quartz filter blanks are analyzed along with the samples to determine the background metal concentrations contributed by the filter media. Blank results equilibrated to the tare weight of the sample filters are subtracted from the samples to determine the filtered particulate metal concentrations. In some cases, the result is the difference between two relatively high, or similarly low concentrations thereby increasing the uncertainty of the background-corrected result.

- Four target metals (Ca, Cd, K, and Na) did not meet the recovery objective for the vapor-phase metals impinger audit sample analyzed by ICP-AES and GFAAS.

  Audit sample concentrations were near the ICP-AES detection limit for sodium and potassium. The reasons for high recovery of calcium and cadmium are unknown; however, the matrix spike recoveries for these elements were within the recovery objective range. The metal concentrations in the audit sample prepared for ICP-AES and GFAAS analysis were between 200 and 5000 parts per billion (ppb). These concentrations were significantly higher than the actual sample concentrations, but were made that way to provide detectable concentrations for these techniques. Cadmium results by ICP/MS were selected for reporting since audit results for cadmium by ICP/MS met the data quality objectives.

- Three target metals (Sb, Ni, and Se) did not meet the recovery objective for the vapor-phase metals impinger audit sample submitted to Harvard for ICP/MS analysis.

  The metal concentrations prepared in the audit sample for ICP/MS analysis were 5 and 10 ppb, much closer to the actual sample concentrations and therefore more representative of the technique's performance on the gas impinger samples. Antimony and nickel were recovered at 70%, slightly lower than the 80% recovery objective; however, matrix spike recoveries for these elements were within the desired range and demonstrate acceptable accuracy in the sample matrix.

  The quantitation of selenium is subject to interferences from the argon plasma in ICP/MS. Low recovery (62%) is caused by incomplete resolution of the selenium mass peak at 79 atomic mass units (amu) from the much larger Ar-Ar mass peak at 80 amu. Selenium recovery in the matrix spike was also low at 71 percent. These results indicate that vapor-phase selenium results may be biased low.

- Six target metals (Al, Fe, Mn, K, Na, and Ti) did not meet the recovery objective for the dolomite sorbent audit sample.

  Dolomite samples were digested with nitric acid and hydrogen peroxide by EPA Method SW-3050. This procedure is generally adequate for the digestion of calcium and magnesium, which accounts for 99% of the sample matrix. The amounts of major coal ash minerals (silica, alumina, titania, etc.) are relatively small and do not affect the material balances for these elements. The digestion procedure applied here does not use hydrofluoric acid (HF) which is required to dissolve the oxides of aluminum, silicon, titanium, and others that may be bound in the inert matrix. A mixed acid digestion which includes HF should be considered for future laboratory analyses if the level of inert substances is thought to be a significant contributor to the mass flow rates of these materials.

- Two target metals (Hg and Se) did not meet the recovery objective for the coal audit sample submitted to CT&E.

The coal audit sample selected for this project was taken from coal collected at the Ohio Power Cardinal Station as part of a recent round robin coal study sponsored by the Department of Energy.[1] *This coal audit sample is not a standard reference material; however, it has been well characterized for all of the target analytes, and it is representative of the Pittsburgh #8 bituminous coal feedstock at Plant Tidd.*

The variability inherent in coal mercury measurements was demonstrated in the DOE round robin study and has been the subject of studies sponsored by the Electric Power Research Institute (EPRI) and others.[2] *Although the recovery of mercury by the double gold amalgamation technique was 143% of the mean value reported, it is within two standard deviations of the mean for all results reported in the round robin study. These results reflect the variability and uncertainty typically encountered with coal mercury determinations.*

Selenium values by GFAAS were not selected for reporting as a result of the audit sample recovery. The INAA results for selenium were selected since the audit sample recovery by INAA was within the recovery objective at 107 percent.

- Ten target metals (As, Ba, Ca, Cd, Cr, Cu, Mg, Hg, Mo and Ti) did not meet the recovery objective for the coal audit sample submitted to NC State.

  All elements not meeting the audit sample recovery objectives for INAA were analyzed by alternative analytical procedures. The results reported from the alternative procedures were within the recovery objectives and were reported in lieu of the INAA results with the exception of arsenic.

  INAA results for arsenic were selected for reporting over those determined by GFAAS in spite of the apparent failure of INAA to meet the desired recovery objectives. Based on the audit sample recovery data, GFAAS results were initially selected for calculating material balance closures. However, the use of GFAAS arsenic values resulted in a closure of 213%, while a closure of 129% was obtained using INAA arsenic values. Since audit sample recovery results were used to select the most accurate data for reporting, the individual results used to determine the mean arsenic value of the coal audit sample were reviewed for consistency and accuracy. Twenty-two results for arsenic were averaged to obtain a mean concentration of 10.3 µg/g (CV = 0.33). The analytical methods used to measure arsenic in the round robin study included GFAAS, ICP/MS, INAA, and cold vapor atomic fluorescence (CVAF). Based on arsenic results obtained for an SRM coal sample analyzed with the round robin samples, ICP/MS results were the most accurate and consistent, followed by INAA results. The average arsenic result of the audit sample as determined by ICP/MS in the round robin study was 13.28 µg/g. The arsenic result by INAA in the audit sample was 18.97 µg/g or 143% of the ICP/MS average. Although this result still suggests a high analytical bias, supporting information indicates that the INAA result for arsenic is more accurate than the GFAAS result. It is also reasonable to expect that the direct analysis of coal by INAA would provide more complete quantitation of arsenic. This is based on the volatile nature of this element and the potential for losses during sample digestion for GFAAS analysis.

- Three target metals (Ca, Mn, and Mo) did not meet the recovery objective for the fly ash audit sample.

  The recovery percentages for Ca, Mn, and Mo are 73%, 73%, and 71%, respectively. These are very close to the recovery objective of 75% and indicate a possible analytical bias. Sample digestion is assumed complete based on the 91% recovery of titanium. Measurement results for Ca, Mn, and Mo may be biased slightly low in ash streams.

Detailed QC Results

Precision is a measure of the reproducibility of measurements under a given set of conditions. It reflects the distribution or scatter of the data and is expressed as the standard deviation or coefficient of variation (CV, standard deviation divided by the mean). For duplicates, precision is expressed as the relative percent difference (RPD).

Accuracy is a measure of agreement between a value generated by a specific procedure and the assumed or accepted known value and includes both bias and precision. Bias is the persistent positive or negative deviation of the method average value from the assumed or accepted known value.

The efficiency of the analytical procedure for a given sample matrix is quantified by the analysis of spiked samples containing target or indicator analytes or other quality assurance measures, as necessary. However, all spikes, unless made to the flowing stream ahead of sampling, produce only estimates of the recovery of the analyte through all of the measurement steps occurring after the addition of the spike. A good spike recovery tells little about the concentration of the analyte in the sample before spiking, but it does provide an indication of a method's ability to accurately measure an analyte in a given sample matrix.

Representativeness expresses the degree to which the sampling data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition. Representativeness is improved by making certain that sampling locations are properly selected and that a sufficient number of samples are collected.

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. Sampling data should be comparable to other measurement data for similar samples collected under similar conditions. This goal is achieved using standard techniques (wherever possible) to collect and analyze representative samples and by reporting analytical results in appropriate units. Data sets can be compared with confidence when the precision and accuracy are known.

Completeness is an expression of the number of valid measurements obtained compared with the number planned for a given study. The goal to generate three valid sample results for each measurement parameter was met.

A discussion of the overall measurement precision, accuracy, and blank effects is presented below for each set of analytes. The individual QC sample results used to assess these analytical measurements are presented in Appendix D. This assessment of data quality is limited to the analytical techniques used to determine the results selected for reporting.

Metals

Precision. The analysis of matrix spike/matrix spike duplicate (MS/MSD) samples, or analytical duplicate samples provided the basis for assessing analytical precision. The precision objective for metals in all samples was 20% RPD.

In general, good analytical precision is indicated for almost all of the target metals in all sample matrices. Noteworthy exceptions include cadmium in coal by GFAAS (22% RPD), calcium in dolomite (45% RPD), silver in ash (70% RPD), and selenium in both gas particulate- and vapor-phase samples by GFAAS. Poor analytical precision for these metals in these streams increases the uncertainty associated with the measured value.

Other metals failing to meet the precision objective include aluminum (71% RPD), calcium (34% RPD), and magnesium (63% RPD) in an acetone probe/nozzle rinse (PNR) sample, and phosphorus (43% RPD) in a filter sample. The impact of imprecise analytical measurements for these samples is less because they each represent only a fraction of the total gas particulate samples specific to the ESP.

Accuracy. Recovery data for matrix spikes, analytical spikes, and standard reference materials (SRMs) provided the basis for assessing analytical accuracy. For most of the analytical techniques, the accuracy objective was 75-125% spike, or standard recovery. Performance audit samples submitted to the laboratory as blind samples also served as indicators of analytical accuracy in the coal, dolomite sorbent, and ash matrices. Audit sample results not meeting program objectives were discussed earlier in this section.

Matrix spiked samples and performance audit samples were used to estimate the accuracy of the flue gas vapor-phase metals analyses. Six of the metals analyzed recorded audit sample recoveries outside the specified objective: antimony, calcium, nickel, potassium, selenium, and sodium. Only selenium failed to meet recovery objectives in both the audit and matrix spike samples.

Poor selenium recovery was experienced in the vapor-phase samples analyzed by GFAAS (4-61%) and ICP/MS (62-71%). In response to the poor recovery by direct GFAAS analysis, the method of standard additions (MSA) was used to reanalyze the impinger samples for selenium. The GFAAS-MSA result for selenium in the audit standard was 87% and the remaining sample results were in close agreement with the ICP/MS results. Based on this recovery data, ICP/MS results were selected for reporting, although they may be biased low.

Gas particulate-phase samples were characterized in two different batches depending on the particulate loading of the sample. Matrix spikes and a standard reference fly ash material (NIST 1633a) were used to estimate the accuracy of the particulate-phase metals analyses for the APF and ESP inlet samples. Six of the metals analyzed recorded spike recoveries outside the specified objective: aluminum, calcium, lead, magnesium, selenium, and silver. Matrix spike recoveries for all of these elements were in the range of 58-72% except silver (15-18%) and may indicate a low bias in the results.

The analytical accuracy of gas particulate samples analyzed in conjunction with filters (APF and ESP outlet) was estimated using analytical spikes and a standard reference fly ash material aspirated onto a filter as an audit sample. The audit sample results were discussed earlier in this section. Analytical spike recoveries below the desired recovery range were experienced for aluminum, calcium, magnesium, selenium, silver, and titanium in an acetone PNR sample from the ESP inlet. Matrix spike recoveries for all target metals associated with filter samples met the recovery objective except for one phosphorus spike (153%).

Matrix spikes and SRMs were used to estimate the accuracy of the fly ash, bed ash, and dolomite sorbent metals analyses. In the ash matrices, matrix spike recoveries for aluminum (70%), calcium (73%), magnesium (64%), and silver (27%) did not meet the program objective. Fly ash SRM recovery results for calcium (73%), manganese (73%), and molybdenum (71%) were also reported slightly below the objective range. Matrix spike recoveries outside the program objectives were experienced in the dolomite sorbent for calcium (286%), cobalt (74%), and iron (74%).

All matrix spike and audit sample results for metals in service water were between 93 and 108%, well within the specified recovery range.

Blank Effects. The field blank impinger samples analyzed by ICP-AES, GFAAS, CVAAS, and ICP/MS showed no significant levels of field contamination when compared to the reagent blank analyses. Relative to the actual gas impinger samples, the background levels detected in the reagent blank are significant (greater than 30% of the sample result), especially at the trace levels detected by ICP/MS. Significant concentrations of calcium, iron, magnesium, manganese, and sodium were also detected by ICP-AES in the blanks. All sample results for vapor-phase metals have therefore been corrected to account for the background concentrations found in the reagents.

Filter media blanks were also analyzed to determine the levels of target metals present in the quartz filters. Significant levels of aluminum, barium, calcium, chromium, magnesium, molybdenum, and sodium were reported. Arsenic, cadmium, lead, mercury, and selenium were also detected in the filter media at levels more than five times the detection limit. Background corrections were also performed for gas-particulate samples analyzed in the presence of filter media (APF and ESP outlet).

Anions

Precision. The precision of anion analyses in coal and ash samples was estimated using duplicate analyses. The precision estimates for chloride and sulfur in the ash and dolomite samples met the objective of 20% RPD, as did the precision estimates for chloride, fluoride, and sulfur in the coal. Analytical results for chloride, fluoride, and sulfate in the flue gas particulate- and vapor-phase samples, as well as the service water samples, all met the precision objectives. Precision estimates for fluoride in ash and dolomite were between 25 and 33% RPD, slightly outside the objective.

Accuracy. Matrix spikes were used to estimate the accuracy of anion analyses in ash and flue gas samples. All anions met the recovery objective for flue gas analysis accuracy. All anions in ash met the accuracy objective with the exception of fluoride. The recovery of fluoride in the ash was below the project objective (32% compared to 75-125%). A performance audit sample and a standard reference material were analyzed to provide accuracy estimates for coal. Chloride recovery was 143% and fluoride recovery was 121% in the performance audit sample (objective of 80-120%). For the standard reference materials, chloride recovery was 101% for NBS SRM 1632-b and 87% for a coal standard from a recent laboratory round-robin study. Fluoride recovery in the standard reference material was 110 percent.

No reference values were available for the dolomite sorbent audit sample; therefore, no estimate of accuracy was obtained. However, anions in the sorbent material are minor constituents that are not expected to play a major role in material balance calculations. For service water, a single matrix spike recovery of 62% for fluoride was the only result outside the expected range of recovery.

Low fluoride spike recoveries were experienced in many of the sample matrices analyzed. Fluoride results, particularly in ash samples, are likely biased low. An investigation into the possible causes has identified aluminum and iron as potential interferents with the specific ion electrode analysis method. This is particularly significant in the analysis of fluoride in ash samples which are prepared by fusion with sodium hydroxide. Separation of fluoride by distillation from the ash fusion matrix is suggested as a means to provide an interference-free analytical matrix.

Blank Effects. Field blank impinger solutions and probe/nozzle rinses were analyzed for chloride, fluoride, and sulfate. The concentrations of these anions were above reporting limits in many of the blanks but well below the levels observed in the samples. The levels of chloride, fluoride, and sulfate found in the field blank for the flue gas solid phase were 4%, 3%, and 2% of the concentrations in the samples, respectively; therefore, these data should not be affected by the blank levels. The field blank associated with the vapor-phase samples contained all of the anions at levels much lower than those found in the vapor-phase samples. The method blanks associated with the stack gas samples showed fluoride at levels less than five times the detection limit; much higher levels of fluoride were observed in the associated samples. Sulfur was also observed in the method blank associated with the sorbent samples at a level near the detection limit, but at a higher concentration than those observed in the samples. Therefore, the results for sulfur in the sorbent samples may be overestimated.

Chromium (VI) and Total Chromium

Precision. The precision of the chromium (VI) and total chromium analyses was assessed by matrix spike duplicate analyses. All results met the RPD objective of 20 percent.

Accuracy. The accuracy of the analyses was estimated using performance audit spike recoveries. Recovery of chromium (VI) was within the 75-125% objective, and recovery of total chromium was slightly outside the objective at 138 percent. Total chromium sample data may be slightly overestimated.

Blank Effects. Low concentrations of total chromium were reported in the field and reagent blanks, but none of the values were more than five times the expected detection limit. Chromium (VI) concentrations in the field and reagent blanks were significant when compared to the gas impinger samples. Background concentrations in the reagent blank accounted for over 65% of the chromium (VI) concentration measured in the samples. Chromium (VI) results were background corrected for reporting and emission factor calculations.

Volatile Organic Compounds

Precision. The precision of the volatile organic compounds measured for this project was not assessed.

Accuracy. The accuracy of the analyses was estimated using surrogate spike recoveries. Recovery of all surrogates (1,2-dichloroethane-d4, toluene-d8, and 4-bromofluorobenzene) was within the compound specific objective.

Blank Effects. The trip and method blanks show no results above the detection limit for the target compounds. Concentrations of chloromethane, methylene chloride, and toluene were reported in the field blank, but only methylene chloride is present at more than five times the expected detection limit. Methylene chloride and toluene are common contaminants from field laboratory operations. The range of results (48 to 230 ng) for methylene chloride suggests that no specific, consistent source of the contamination was present.

Semivolatile Organic Compounds

Precision. The precision of the semivolatile organic compounds measured for this project was not assessed.

Accuracy. The accuracy of the analyses was estimated using surrogate spike recoveries. All vapor-phase sample surrogate spikes were recovered within the accuracy expectations.

Recovery of several surrogates in the cyclone ash and gas particulate-phase samples were outside the compound specific objectives.

Blank Effects. The trip and method blanks show no results above the expected detection limit for the target compounds, except for a single naphthalene result of 4.77 µg. Concentrations of bis(2-ethylhexyl)phthalate and naphthalene were reported in the field blank, but only naphthalene is present at more than five times the expected detection limit. Reported results for naphthalene have the potential to be overestimated at low levels.

Polycyclic Aromatic Hydrocarbons (PAHs) by HRGC/MS

Precision. The precision of the PAH analytical results was not evaluated.

Accuracy. The accuracy of the PAH analytical results was evaluated using surrogate spike recoveries. All recoveries were within the project objective of 50-150 percent.

Blank Effects. Many low-level measurements were reported for the trip, field, and method blanks. Concentrations ranged from 0.13-309 ng for the compounds in the method blank and 0.19-129 ng for the compounds in the trip blank. Field blank results ranged from 0.06-1050 ng. For compounds found in the samples, the results have been flagged if trip blank results for PAHs exceed 30% of the sample value.

Formaldehyde

Precision. The precision of formaldehyde measurements was assessed from duplicate analyses. Results for formaldehyde at two different concentration levels was excellent, with both RPDs within 5 percent.

Accuracy. The accuracy of the analyses was estimated using matrix spike recoveries. Both spikes were recovered within the accuracy objective of 50-150 percent.

Blank Effects. The reagent and method blanks show no results above the expected detection limit for formaldehyde. Significant concentrations of formaldehyde were reported in the field blank, at more than ten times the expected detection limit. Reported results for formaldehyde in the APF outlet and ESP inlet and outlet gas streams have the potential to be overestimated at low levels.

Ammonia

Precision. The precision of ammonia measurements was assessed from matrix spike duplicate analyses. Results for ammonia met the 20% RPD objective.

Accuracy. The accuracy of the analyses was estimated using matrix spike recoveries and a performance audit sample. The audit sample recovery was 485% at a theoretical concentration of 0.27 mg/L. A laboratory flag was attached to the audit sample result stating that the acidity of the sample was so high that an unusually small sample aliquot was taken for analysis. Since it appears that the audit sample was not distilled and analyzed in exactly the same manner as routine field samples, no firm conclusions about the accuracy of ammonia analysis can be made based on the performance audit. Both matrix spikes were recovered within the accuracy objective of 80-120 percent.

Blank Effects. The field, reagent, and method blanks all show results above the expected detection limit for ammonia. None of these blank results is greater than five times the expected detection limit.

Cyanide

Precision. The precision of cyanide measurements was assessed from matrix spike duplicate analyses. Results for cyanide met the 20% RPD objective.

Accuracy. The accuracy of the analyses was estimated using matrix spike recoveries and a performance audit sample. Both matrix spikes were recovered within the accuracy objective of 75-125 percent. The audit sample recovery was 26% of a prepared concentration of 0.1 mg/L. For the audit sample, an EPA water quality standard was used which may have degraded as discussed previously in this section. The EPA standard material was not analyzed, so no data are available to confirm the standard's theoretical value.

Blank Effects. The field, reagent, and method blanks all show results below the expected detection limit for cyanide.

Dioxins and Furans (PCDD/PCDF)

Precision. The precision of the PCDD/PCDF analyses was not assessed.

Accuracy. The accuracy of the analyses was estimated using surrogate spike recoveries. Nearly all spike recoveries were within the project objective. The four recoveries outside the objective were within 10% of the lower limit of the objective.

Blank Effects. Low concentrations of eight compounds in the method, trip, and field blanks associated with these samples were observed. All concentrations reported for the blank results were near the analytical detection limits. Sample concentrations, which were also near the detection limits of many compounds, may be slightly overestimated for these compounds.

Ultimate/Proximate

Precision. The precision of ultimate/proximate analyses was not assessed.

Accuracy. The accuracy of the ultimate/proximate analyses for coal was estimated using performance audit sample recoveries. All recoveries were within the accuracy objective of 75-125% recovery.

Blank Effects. Ultimate/proximate test parameters are generally not subject to blank or background assessments.

Material Balances

Evaluating data consistency can be another overall data quality evaluation tool. Material balances for major elements can be used to verify the internal consistency of stream flow rates. Material balance closures for trace species can be used to indicate whether the samples collected were representative with respect to the trace element concentrations and can help identify analytical biases in one or more types of samples.

Table 4-5 shows the results of the material balances around the entire plant, the ESP system and the APF system. Closure is defined as the ratio of outlet to inlet mass rates for a particular substance. A 100% closure indicates perfect agreement. When trace substances are analyzed, a closure of between 70% and 130% has been set as a goal for the Tidd PFBC HAPs project. This range reflects the typical level of uncertainty in the measurements and, therefore, allows one to interpret the inlet and outlet mass flow rates as being equivalent. The 95% confidence intervals about the closures have been calculated using error propagation analysis, which is discussed in Appendix G. Inlet streams and their associated flow rates for each material balance system are provided in Table 4-6. Flow rates are presented in units consistent with the reported stream concentrations to facilitate mass flow rate determinations. A brief description of the methods for determining flow rates is also provided in Table 4-6.

Entire Plant

As shown in Table 4-5, 10 of the 19 target elements have closures around the entire plant that meet the project goal. The target elements that do not meet the closure goal are copper (<37%), fluorine (58%), mercury (155%), nickel (<45%), and selenium (148%). Closures could not be determined for antimony, cadmium, molybdenum, and silver because these elements were not detected in the major outlet ash streams. Closures for the other major

Table 4-5
Material Balance Results

	Entire Plant		ESP System		APF System	
Substance	**Closure (%)**	**95% CI**	**Closure (%)**	**95% CI**	**Closure (%)**	**95% CI**
Target Species						
Antimony	NC	--	NC	--	NC	--
Arsenic	129	36	134	21	101	59
Barium	111	27	134	63	97	29
Beryllium	101	22	137	59	101	27
Boron	91	140	126	95	NC	--
Cadmium	NC	--	140	124	95	43
Chlorine	105	24	94	8	83	29
Chromium	122	21	107	51	70	36
Cobalt	119	49	137	44	97	55
Copper	<37	--	129	184	<12	--
Fluorine	58	22	47	13	120	16
Lead	95	3	167	97	120	44
Manganese	102	2	119	14	92	25
Mercury	155	33	96	9	91	13
Molybdenum	NC	--	NC	--	<92	--
Nickel	<45	--	138	95	77	80
Selenium	148	87	74	27	<79	--
Silver	NC	--	NC	--	NC	--
Vanadium	97	4	136	38	95	29
Other Species						
Aluminum	89	17	131	40	95	25
Calcium	78	0.1	128	35	94	42
Iron	96	27	128	27	93	30
Magnesium	99	0.1	127	33	95	42
Potassium	61	20	138	60	98	33
Sodium	99	25	128	42	93	30
Titanium	109	19	136	53	98	28

Closure goal for the Tidd PFBC HAPs project is 70-130 percent.

CI = Confidence interval.

Table 4-6
Material Balance Stream Flow Rates

Stream	Mean Flow Rate	95% CI	Units of Measure	How Calculated
Entire Plant				
Coal Paste (inlet)	15,170	430	kg/hr, dry	Five-minute averages from the plants data acquisition system and coal paste moisture determinations.
Sorbent (inlet)	8,620	1,020	kg/hr, as fired	Five-minute averages from the plants data acquisition system.
Bed Ash (outlet)	4,220	970	kg/hr, dry	Data from AEP bed ash generation test on 4/9/94. Test conditions: Coal paste = 45 KPPH (as fired), MW = 46, sorbent = 19.8 KPPH.
Cyclone Ash (outlet)	4,690	1,490	kg/hr, dry	Average of the cyclone ash rate determined from material balances for magnesium, titanium, and sodium.
APF Ash (outlet)	142	28	kg/hr, dry	Measured particulate loading data collected at the APF inlet and outlet.
ESP Ash (outlet)	352	35	kg/hr, dry	Measured particulate loading data collected at the ESP inlet and outlet.
ESP Outlet Gas (outlet)	238,700	8,500	Nm^3/hr	Direct measurement at the ESP outlet location.
APF System				
APF Inlet Gas (inlet)	34,100	1,200	Nm^3/hr	Assumed equal to 1/7th of the ESP outlet gas rate.
APF Outlet Gas (outlet)	34,100	1,200	Nm^3/hr	Assumed equal to 1/7th of the ESP outlet gas rate.
APF Ash (outlet)	142	28	kg/hr, dry	Measured particulate loading data collected at the APF inlet and outlet.
ESP System				
ESP Inlet Gas (inlet)	264,900	44,400	Nm^3/hr	Direct measurement at the ESP inlet location. ESP outlet rate used in the material balance.
ESP Outlet Gas (outlet)	238,700	8,500	Nm^3/hr	Direct measurement at the ESP outlet location.
ESP Ash (outlet)	352	35	kg/hr, dry	Measured particulate loading data collected at the ESP inlet and outlet.

CI = Confidence interval.

species met the project goal, with the exception of potassium (61%). For mercury and selenium, the closures are slightly above the desired range and the wide 95% confidence intervals indicate that imprecision may be partially responsible for the high closures. For copper, fluorine, and nickel, the results may indicate an analytical bias in one or more of the process streams.

ESP System

Closures for the ESP system were typically in the 125-135% range, which is slightly outside the project goal. This indicates that the ESP ash rate, calculated from the measured particulate loadings at the ESP inlet and outlet, may be biased slightly high. Concentrations of antimony, molybdenum, and silver were below detection limits in one or more of the inlet or outlet streams; therefore, closures could not be calculated around the ESP.

APF System

All closures around the APF system met the project goal except copper (<12%). Closures could not be determined for antimony, boron, and silver because substances were not detected in the inlet and outlet streams. Again, the low closure for copper indicates an analytical bias in one or more of the process streams. The relatively wide 95% confidence intervals for most of the target and other major elements in the ESP and APF material balances reflect the inherent variability in the gas stream measurements.

Recommendations and Considerations

Some technical issues have been identified during this study that may warrant further consideration. Some significant sampling, analytical and/or process related issues are discussed below.

APF Outlet Particu

Comparison of the c
the ESP outlet, ESP
um, nickel, and mol
may be present in th
becomes significant
tude lower than thos

statistical average for estimating background concentrations in the sampling media and performing reliable background corrections.

Gas Sampling Methods for Semivolatile Organic Compounds

The gas sampling method for semivolatile organic compounds should be studied to confirm the suspicion that benzoic acid and phthalate esters detected in the flue gas samples are sampling artifacts. The presence of benzoic acid, and other intermediate oxidation products of naphthalene could possibly arise from the reaction of flue gas components with the XAD-2 resin matrix. Sulfur and nitrogen oxides in the flue gas combine with condensed moisture in the resin traps to form acids. These acids may be contributing to the breakdown of the resin into the by-products detected most frequently in the vapor-phase sample fraction.

Hexavalent Chromium Sampling and Analysis

The hexavalent chromium sampling method has not been validated for application to flue gas from coal-fired combustion systems and should be thoroughly evaluated for sampling bias and precision. The analytical method is relatively sound, but the fate of Cr(VI) during sampling in a recirculating caustic impinger solution with constant exposure to CO_2 and SO_2 is not well defined. Multiple sampling trains should be used in parallel to obtain duplicate spiked and duplicate unspiked samples simultaneously from the same location in the process duct. Multiple samples providing spike recovery and duplicate sample results will provide an indication of method accuracy and precision.

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2. J. Lengyel, Jr., M.S. DeVito, and R.A. Bilonick, "Interlaboratory and Intralaboratory Variability in the Analyses of Mercury in Coal," paper presented at the Air & Waste Management Association Annual Meeting. Cincinnati, OH (1994).

5

EXAMPLE CALCULATIONS

This section describes the methodology and sample calculations used to develop the results discussed in Section 3. Specifically, the calculation of stream flow rates, emission factors, mean values, and confidence intervals are presented.

Stream Flow Rates

Table 4-6 in Section 4 contains information about the stream flow rates used in the material balance calculations. Coal paste and sorbent feed rates were determined from five-minute averages from the plant's data acquisition system. The bed ash rate was determined from data supplied by the Plant Tidd personnel. This data was from a bed ash generation test conducted on April 9, 1994, during operating conditions very similar to those used during the air toxics test period (ash generation test conditions: 46 MW, coal paste rate = 45,000 lb/hr, sorbent rate = 19,800 lb/hr). Therefore, the bed ash rate is considered representative of plant operation during the air toxics tests. The APF and ESP ash rates were calculated using measured particulate loading data and gas flow rate data for each run as follows:

Ash rate = (inlet loading x inlet gas rate) - (outlet loading x outlet gas rate)

For the ESP ash rate, the ESP inlet and outlet gas rates were assumed equal to the measured ESP outlet gas rate. The ESP outlet gas rate was selected because that sampling point is configured to minimize flow disturbances upstream and downstream of the sample ports, thus providing more reliable flow rate measurements. For the APF ash rate, the inlet and outlet gas rates were assumed equal to 1/7th of the measured ESP outlet gas flow rate. The cyclone ash rate was determined by calculating overall plant material balances for magnesium, titanium and sodium as follows:

Cyclone ash rate = [(coal rate x concentration of element) + (sorbent rate x concentration of element) - (ESP ash rate x concentration of element) - (APF ash rate x concentration of element) - (bed ash rate x concentration of element) - (ESP outlet gas rate x concentration of element)] ÷ concentration of element in cyclone ash

These elements were selected on the basis of the superior quality of the analytical data for the coal, sorbent, and major ash streams, as indicated by QA/QC data. The final cyclone ash rate used in the material balance calculations was the average of the cyclone ash rates determined for each element.

The flow rates in the ESP inlet and outlet were measured directly during sampling. The flow rate of the APF inlet and outlet were assumed to be equal to 1/7th of the measured ESP outlet gas flow rates. This assumption was based on plant design information supplied by Plant Tidd personnel.

Means and Confidence Intervals for Stream Concentrations

The mean concentration and 95% confidence interval (CI) about the mean were calculated for each target substance in the coal, sorbent, ash streams, and gas streams. The means were calculated according to the conventions listed in Section 3. Equations used to calculate 95% confidence intervals are presented in Appendix G. Example calculations are presented here for arsenic in the ESP inlet gas; these results were shown in Table 3-6.

The concentration data (in $\mu g/Nm^3$) given for arsenic are:

	Run 1	Run 2	Run 3
Solid Phase	450	380	420
Vapor Phase	0.34	0.26	0.36
Total	450.3	380.3	420.4

The mean is calculated from the individual run totals:

$$\text{Mean} = (450 + 380.3 + 420.4)/3$$
$$= 417$$

The sample standard deviation of the individual run totals is calculated:

$$S_p = \sqrt{[(450.3-417)^2 + (380.3-417)^2 + (420.4-417)^2]/2}$$
$$= 35.1$$

The standard deviation of the mean is calculated according to Equation 6 in Appendix G for N = 3:

$$S_{\bar{p}} = \frac{35.1}{\sqrt{3}}$$

$$= 20.3$$

The bias error is found by root-sum-squaring the product of the bias error and the sensitivity from each run (see Equation 2 in Appendix G). According to the conventions listed in Section 3, no bias error is assigned to values above detection limits, whereas a bias error of one-half the detection limit is assigned to values below detection limits. The sensitivity of the mean to each run in this case is one-third.

$$\beta_r = \sqrt{(1/3 \times 0)^2 + (1/3 \times 0)^2 + (1/3 \times 0)^2}$$
$$= 0$$

The total uncertainty in the result is found from Equation 1 in Appendix G:

$$U_r = \sqrt{\beta_r^2 + (t \times S_{\bar{p}})^2}$$

$$= \sqrt{0^2 + (4.3 \times 20.3)^2}$$

$$= 87$$

Thus, the result is reported as 420 ± 87 μg/Nm^3.

Unit Energy Emission Factors

In addition to the gas-phase concentrations, unit-energy-based emission factors have been developed for each target substance. These values were determined by calculating the mass flow of a substance in the ESP outlet gas (mean concentration times mean flow rate) and dividing by the mean heat input to the boiler during testing. The mean heat input is the product of the mean coal flow rate and the mean higher heating value (HHV) of the coal.

As an example, the calculation of the emission factor for arsenic is presented. The mean coal paste flow rate is 33,450 lb/hr on a dry basis. The mean HHV of the coal is 12,700 Btu/lb on a dry basis. Multiplying the coal flow rate by the HHV gives a mean heat input of 425 million Btu/hr. The mean arsenic mass flow through the stack (the product of the mean concentration, 1.0 μg/Nm^3, and the mean gas flow rate, 239,000 Nm^3/hr) is 0.239 g/hr or 0.000526 lb/hr. When the mean mass flow rate is divided by the mean heat input, an emission factor of 1.2 lb/10^{12} Btu is obtained, as shown in Table 3-19.

The 95% confidence intervals for emission factors were calculated according to the equations presented in Appendix G. For each parameter (ESP outlet gas flow rate, concentration, coal flow rate, and HHV) the mean, standard deviation, number of points, and bias estimates were used to calculate the combined uncertainty in the mean emission factors.

6

GLOSSARY

AAS	Atomic absorption spectrophotometry
acfm	Actual cubic foot (feet) per minute
AEP	American Electric Power Service Corporation
APF	Advanced particle filter
AS	Analytical standard
ASTM	American Society for Testing and Materials
Btu	British thermal unit
CARB	California Air Resources Board
CEM	Continuous emission monitor
CEMS	Continuous emission monitoring system
CI	Confidence interval
C_p	Pitot tube coefficient
CT&E	Commercial Testing & Engineering
CVAAS	Cold vapor atomic absorption spectrophotometry
DAS	Data acquisition system
ΔP	"Delta P"; pressure drop; pressure difference (measured in inches of water column)
DGA	Double gold amalgamation
DL	Detection limit
DNPH	Dinitrophenylhydrazine
DQO	Data quality objective
dscfm	Dry standard (1 atm. 68°F) cubic foot (feet) per minute
EPA	U.S. Environmental Protection Agency
ESP	Electrostatic Precipitator
FPAs	Analytical services laboratory of Radian Corporation

GC/MS	Gas chromatography/mass spectrometry (low resolution)
GFAAS	Graphite furnace atomic absorption spectrophotometry
HAP	Hazardous Air Pollutant
HGCU	Hot Gas Clean Up (System)
HHV	Higher heating value
HR GCMS	High-resolution gas chromatography/mass spectrometry
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
ICP-MS	Inductively coupled plasma-mass spectrometry
INAA	Instrumental neutron activation analysis
IS	Internal standard
MS/MSD	Matrix spike/matrix spike duplicate
NA	Not applicable
NC	Not calculated
ND	Not detected (below detection limit)
Nm^3	Normal cubic meter(s): 1 m^3 @ 0°C and 1.0 atm (equivalent to 37.44 ft^3 @ 68°F and 1.0 atm)
NO_x	Nitrogen oxides
Orsat	Method of fixed-gas (O_2, CO_2, CO) analysis
PAH	Polycyclic aromatic hydrocarbon
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzofuran
PFBC	Pressurized fluidized bed combustion
PNR	Probe and nozzle rinse
POM	Polycyclic organic matter
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
PSD	Particle size distribution
RS	Recovery standard
RSF	Relative sensitivity factor (used in mass spectrometry)

scf	Standard cubic foot (feet): 1 ft^3 @ 68°F and 1.0 atm (equivalent to 0.02671 m^3 @ 0°C and 1.0 atm)
scfm	Standard cubic foot (feet) per minute
SIE	Specific ion electrode
SVOC	Semivolatile organic compound; semivolatile organic chemical
SW-846	Publication number of "Test Methods for Evaluating Solid Waste"
SS	Surrogate spike
TCLP	Toxicity characteristic leaching procedure
Tenax	An organic resin used for sample collection
UV-Vis	Ultraviolet-visible
VOC	Volatile organic compound; volatile organic chemical
VOST	Volatile organic sampling train
XAD	An organic resin used for sample collection