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EPRI

Preliminary Draft

FIELD CHEMICAL EMISSIONS MONITORING PROJECT:

SITE 10 EMISSIONS MONITORING

EPRI Project RP3177-1

October 1992

Prepared by:
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P.O. Box 201088
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Prepared For:

Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, California 94304

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DCN 92-213-152-25

FIELD CHEMICAL EMISSIONS MONITORING PROJECT: SITE 10 EMISSIONS REPORT

PRELIMINARY DRAFT REPORT

Prepared for:

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6 October 1992

EPRI
Electric Power
Research Institute *Leadership in Science and Technology*

October 15, 1992

Mr. William H. Maxwell, P.E. (MD13)
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Mr. Maxwell:

In response to the Clean Air Act Amendments of 1990, the Electric Power Research Institute (EPRI) initiated the PISCES (Power Plant Integrated Systems: Chemical Emissions Studies) program to better characterize the source, distribution, and fate of trace elements from utility fossil-fuel-fired power plants. As part of the PISCES program, the Field Chemical Emissions Monitoring (FCEM) program has sampled extensively at a number of utility sites, encompassing a range of fuels, boiler configurations, and particulate, SO_2, and NO_x control technologies. EPRI is actively pursuing additional FCEM sampling programs, with at least 22 sites either completed or planned.

This site report presents a preliminary summary of data gathered during a sampling program conducted at one of the FCEM sampling programs - Site 10. Site 10 consists of a fluidized bed boiler burning sub-bituminous coal and a fabric filter. The sampling protocol is to obtain three sets of measurements for chemical analysis of each process stream. However, for Site 10, only one set of samples was collected for each stream due to a forced unit outage. **It should be noted that the results presented in this report are considered PRELIMINARY.** The results are believed to be essentially correct except as noted. As additional data from other sites are collected and evaluated, however, EPRI may conduct verification tests at this site. If this is done, the new data will be made available to the Environmental Protection Agency (EPA).

The primary objective of this report is to transmit the preliminary results from Site 10 to the EPA for use in evaluating select trace chemical emissions from fossil-fuel-fired steam generating plants. In addition to the raw data in the Appendix, the report provides an assessment of the trace metals material balances, discusses the data quality, identifies suspect data, and offers possible explanations for the questionable data. Because the discussion only focuses upon the suspect or invalidated data, please keep in mind that most of the data meet the standards of quality established for this study. This report does not compare the results from Site 10 with the results from previous utility

sites. Generic conclusions and recommendations were not drawn concerning the effectiveness of the fabric filter as a potential control technology for trace elements; however, removal efficiencies were calculated where possible. Nor does this site report attempt to address the environmental and health risk impacts associated with the trace chemical emissions.

A thorough evaluation of the results from Site 10 revealed that some sampling and analytical errors may have occurred. The data have been qualified to note potential sampling or analytical errors, and where significant biases or inconsistencies were substantiated, the data were discarded. The two most notable examples were the flue gas measurements of the volatile organic compounds (VOCs) and mercury.

At Site 10, a teflon-lined probe, instead of the glass-lined probe specified in the EPA sampling protocol, was used to sample for the VOCs. EPRI later retested using the canister technique. This retest confirmed that the results from the teflon-lined probe were contaminated and were invalid, and thus excluded. Only the results using the canister technique are included in this site report.

The Site 10 mercury measurements in flue gas are believed to be biased low due to incomplete recovery of mercury from the impinger solution prior to analysis. The mercury data are included in the report, even though the data are suspect, because they do provide an approximation for mercury emissions. The reader is strongly advised to exercise good scientific judgment in using the flue gas mercury concentrations in any further evaluations.

EPRI hopes that this site report is of assistance to the EPA in evaluating utility trace chemical emissions as well as the associated environmental and health risk impacts.

Sincerely,

Paul Chu
Manager, Toxic Substances Control
Environment Division

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Section 1

INTRODUCTION

This report presents a summary of data gathered during a sampling program sponsored by the Electric Power Research Institute (EPRI). The data have been prepared in a manner suitable for use by the Environmental Protection Agency to study emissions from fossil-fuel-fired power plants as mandated by the Clean Air Act Amendments (CAAA) of 1990. The plants studied during this project were chosen to reflect a cross section of the existing technologies for controlling air emissions. They were not chosen to represent "typical" fossil-fuel-fired power plant operation per se, nor should the solid or aqueous waste treatment systems used or discharge levels achieved be deemed representative of the industry as a whole.

The project examined the fate of selected substances found in the process streams at the host site. All of the analytical data generated during the project are presented in the appendices. The body of the report presents information relative to the coal, limestone and gas stream compositions. Information for the gas streams is presented on both a concentration and unit energy basis.

This report is one of a series being produced under the Field Chemical Emissions Monitoring (FCEM) project (RP 3177-1) sponsored by EPRI. The objective of this project has been to measure selected inorganic and organic substances in the process and discharge streams of power plants. Table 1-1 presents the list of substances which are of interest to the program. Data on additional substances reported by the analytical methods employed are presented in Appendix B. By characterizing all streams of interest, information regarding the control and fate of these substances can be developed.

This report presents summarized information about stack emissions from the operation of a fluidized bed boiler burning low sulfur subbituminous coal. Sampling was conducted during May of 1990. **Note that the results presented in this report should be considered preliminary.** At the present time, they are believed to be correct; however, as information is obtained at other sites, we may reanalyze samples to obtain additional information. We have also resampled plants when the initial results do not appear to be reasonable indicators of process performance.

The results reported in this document are of generally good quality and meet the objectives of the FCEM study. They provide a more accurate and comprehensive characterization of a power plant system than is often found in the published literature. The samples upon which the reported results are based have been collected in a careful manner using accepted and appropriate sampling and analytical methods. The sampling

Table 1-1

FCEM Substances

Elements	Organic Compounds
Arsenic	Benzene
Barium	Toluene
Beryllium	Formaldehyde
Cadmium	Polycyclic Organic Matter (POM)*
Chlorine (as chloride)	
Chromium	
Cobalt	
Copper	
Fluorine (as fluoride)	
Lead	
Manganese	
Mercury	
Molybdenum	
Nickel	
Phosphorus	
Selenium	
Vanadium	

*Also referred to as semivolatile organic compounds. Includes polynuclear aromatic hydrocarbons (PAHs).

and analytical results have been subjected to an extensive QA/QC evaluation (a separate QA/QC report is provided in Appendix E). In this report, the data which are of satisfactory quality are simply reported and not extensively discussed. The focus of the discussions is, instead, on those results which are questionable, uncertain, or known to be of poor quality.

The technical approach used at each plant has been to use "standard" sampling and analytical procedures to the extent possible, i.e., the FCEM program is not a methods development or research program designed to measure extremely low levels of emissions. The target reporting level for the selected substances in gas streams was initially chosen as 20 $\mu g/Nm^3$ (as the FCEM project has progressed, lower levels of reporting for some species have been sought to provide more information). The sampling protocol is to obtain three sets of measurements for chemical analysis of each process stream. However, for this site, because of a forced unit outage, only one set of samples was collected from each stream.

Section 2 of this report presents a brief description of the plant and sample locations. Section 3 presents the chemical analyses of the coal, limestone, and the two gas streams sampled at the plant. (Results of the analysis of other sampled streams are presented in Appendix B.) Section 4 discusses the results in terms of both analytical and engineering considerations. Section 5 presents example calculations, and a glossary is provided in Section 6. The appendices present sampling and analytical methods, stream concentrations, measured and calculated stream flows, particulate measurement results, QA/QC information, and blank correction data.

Section 2

SITE DESCRIPTION

The boiler at this site is a fluidized bed combustor (FBC) capable of producing approximately 100 MW (gross) of power at full load. A simple schematic of the unit is shown in Figure 2-1. Crushed coal and limestone enter the combustion chambers and are fluidized by high-velocity air in the water-cooled boiler. Temperatures in the combustion chambers are typically about 1650° F. As the coal is combusted, the limestone is calcined to form lime which then reacts with the sulfur dioxide in the combustion gases to form solid calcium sulfate. This reaction removes sulfur dioxide from the combustion gases, thus controlling emissions. The calcium-to-sulfur ratio during the test was approximately 4.0 (coal plus sorbent).

After releasing heat to the water-cooled boiler jacket and radiant superheater, the particulate-laden combustion gas flows into the hot cyclones. The cyclones separate the entrained solids (primarily sulfated lime, lime, ash, and carbon) from the hot combustion gas. The combustion gas leaving the cyclones flows through the economizer and air heater before entering the fabric filter system. Some entrained particles are collected in the economizer and air heater. Ash from the economizer and air heater are combined with the ash collected in the fabric filters and conveyed to a storage silo. The fly ash is periodically removed from the silo and trucked to a landfill for disposal. This collected fly ash constitutes the largest solid waste stream produced at the plant. (The ratio of fly ash to bottom ash is approximately 15 to 1 on a mass basis.)

Combustion gases from the combustion chambers are combined and treated in four parallel reverse gas fabric filters to remove fly ash before the gas is discharged to the atmosphere through a single stack. Fabric filters 1, 2, and 3 treat approximately 45% of the gas flow. The remaining 55% passes through baghouse #4 which has an air-to-cloth ratio of approximately 2.5 acfm/ft^2. Filter bags in baghouse #4 are constructed of a Teflon bead material (Model No. 427-615) manufactured by BGF Industries.

Bottom ash (bed material) is periodically removed from the combustion chambers to control the amount of solids in the chambers. This bottom ash is discharged to ash coolers before it is conveyed to an ash hopper. The bottom ash is periodically trucked to a local landfill for disposal.

Sampling Locations

Solid and gas sampling locations are illustrated in Figure 2-1 and are briefly described in this section.

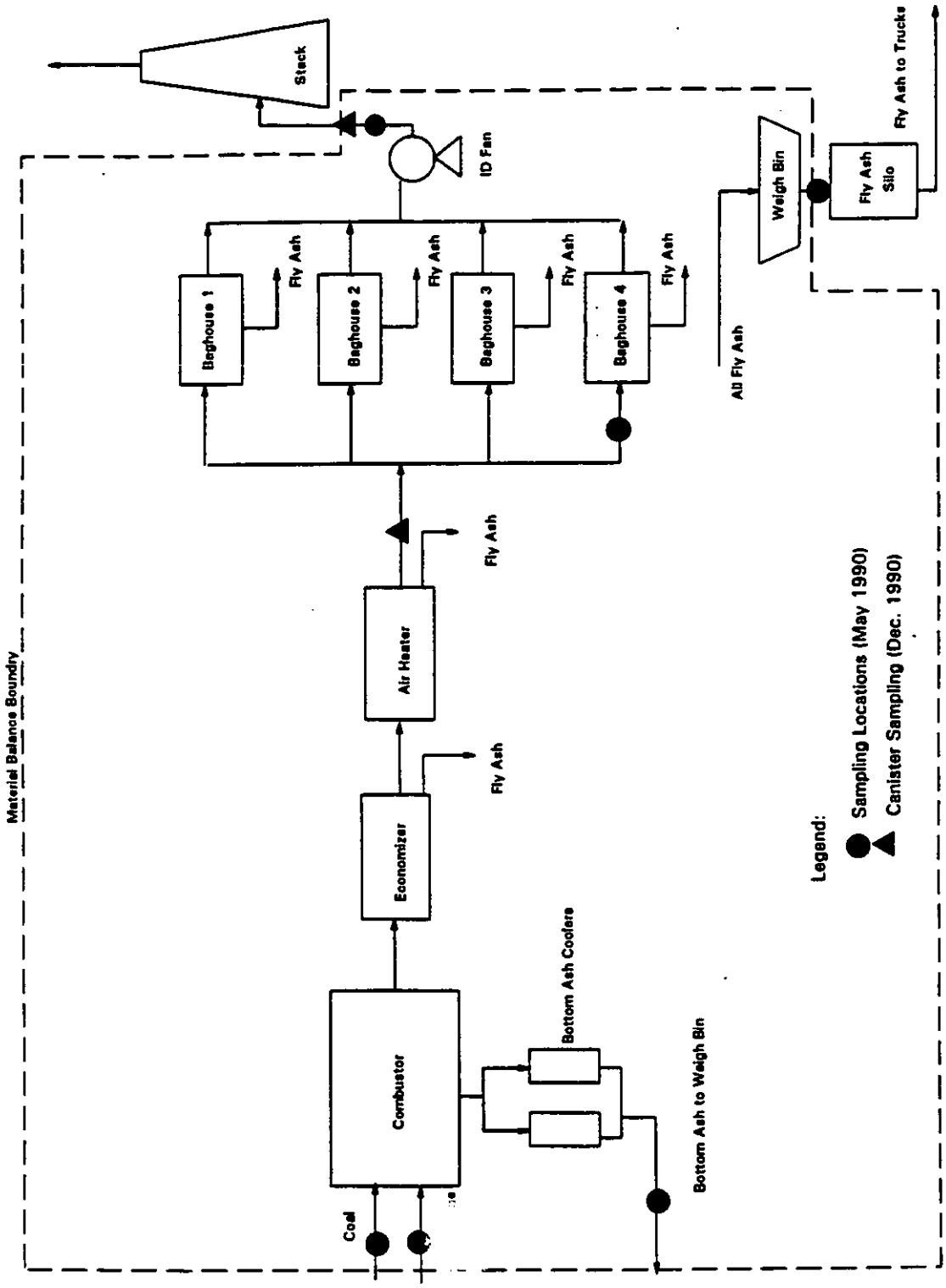

Figure 2-1. Schematic Flow Diagram of the Site 10 FBC Process

Representative coal samples were collected from each of the full-cut automatic samplers, located downstream of the final crusher, at the six coal feeders.

Representative limestone samples were collected manually from the sample ports on each of the two limestone weigh bins.

Samples of the bottom ash (bed drain material from the combustors) were manually collected from each of the four bottom ash drains. The drains were located in the ash basin between the ash coolers and the ash hoppers. Fly ash samples (consisting of economizer ash, air heater ash, and fabric filter ash) were collected at the top of the fly ash silo using a full-cut auto sampler.

Samples of the flue gas entering baghouse #4 were collected from nine dedicated ports located in a horizontal run of duct immediately upstream of fabric filter number four. These ports are located downstream of the point where the gas from the two combustors combined and subsequently splits to feed the four fabric filters. Sampling for multi-metals and semivolatiles was conducted at isokinetic conditions.

Flue gas leaving the fabric filter system was sampled from three ports located between the induced draft (ID) fan and the stack. This location is downstream of the point where gas from all four fabric filters is recombined.

Section 3

RESULTS

This section presents a summary of results from coal and limestone characterization and gas stream analyses. Supplemental data are presented in the appendices.

Sampling Schedule

Site 10 was sampled at the beginning of May in 1990. To obtain samples for the analytes in Table 1-1, seven sampling trains were used for sampling the fabric filter inlet and the stack. The multi-metals, PSD, and semivolatile trains require full traversing of the ducts. The other four trains (VOST, anions, nitrosamines, and aldehydes) were sampled at single points. Because of suspected contamination problems with the VOST sample (a Teflon®-lined probe was used instead of a glass-lined probe), a follow-up sampling effort was conducted in December 1990 to collect canister samples. During this latter test, the process was operated at the same conditions as those of the May 1990 testing.

Because of a forced outage of the boiler (due to a tube leak), only one day of sampling was completed in May, and only one run of each of the sampling trains was completed. Figure 3-1 shows when the various samples were collected. Three fabric filter inlet and five outlet canister samples were collected in the December sampling effort. To our knowledge, there is no reason to suspect that the operation of the plant during testing was irregular and would therefore be a reason to discard a data set because of non-representative operating conditions. However, because only one set of samples (except for the canister samples) was collected, the quality of the results from this site cannot be described statistically.

Data Treatment

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

To determine the total gas concentration and the emission factors, both the solid and vapor phase contributions were considered. However, the absence of some reportable concentrations in either (or both) phases required that conventions be developed for dealing with these data and formulating emission factors. These conventions are summarized below.

For each substance, there are three possible combinations of vapor and solid phase concentrations in the gas streams. These are:

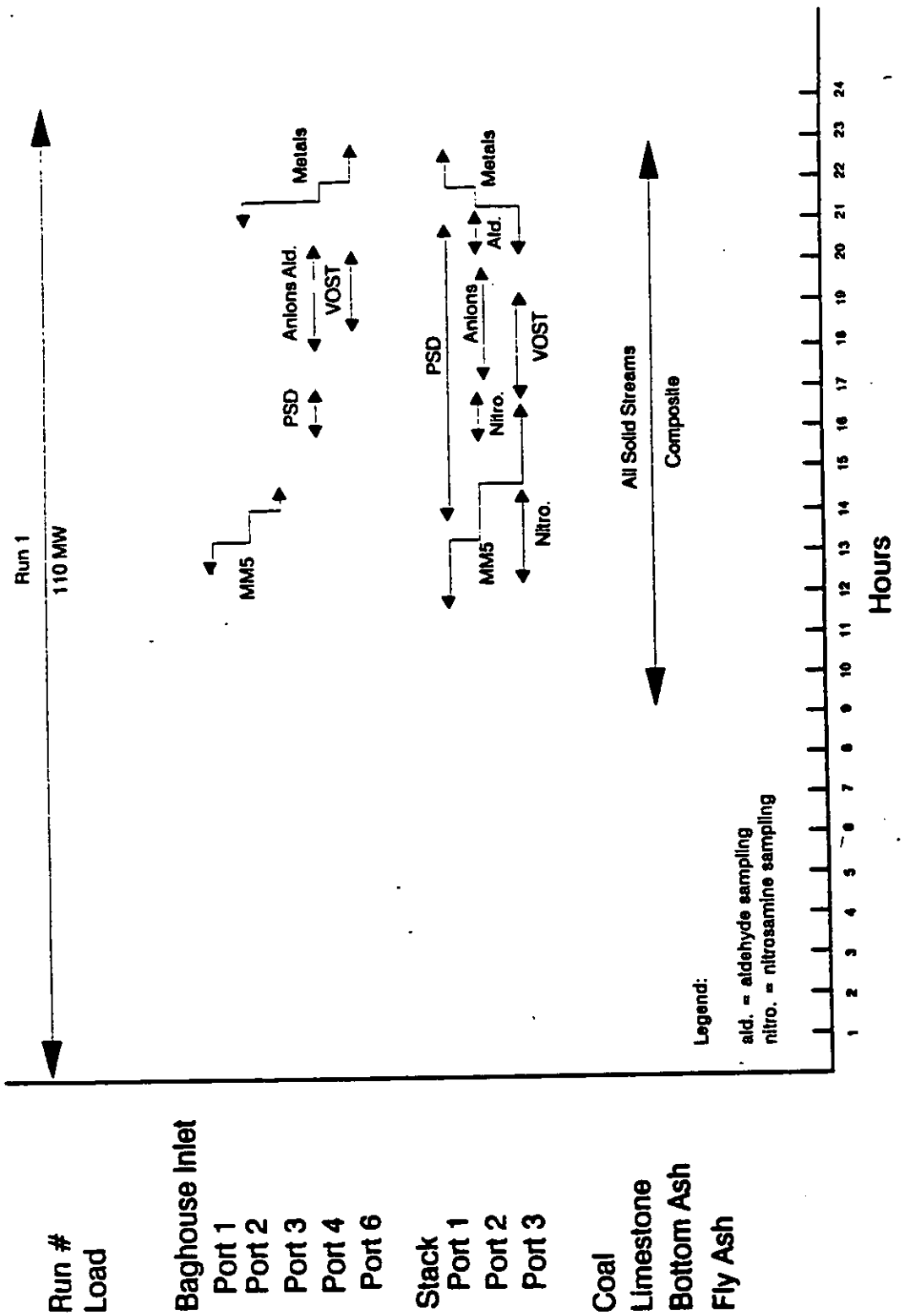

Figure 3-1. Sequence of Sampling Activities on 1 May 1990

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

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

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

For those inorganic constituents of interest other than mercury, HCl, and HF, the stack gas stream data from coal-fired power plants have indicated that most of the material is present in the solid phase, and only a minor fraction is generally found in the vapor phase. Thus, the following conventions were selected for defining total gas stream concentrations:

Case 1: The total concentration is the sum of the concentrations in the vapor and solid phases.

For example, the total nickel concentration in the fabric filter inlet gas is calculated as follows:

Ni in solid phase = 1,300 μg/Nm^3

Ni in vapor phase = 30 μg/Nm^3

Total Ni in fabric filter inlet gas = 1,330 μg/Nm^3

Case 2: The total concentration is considered to be the reporting limit in the solid phase.

For example, the cadmium concentration in the fabric filter inlet gas is calculated as follows:

Cd in solid phase = NR(1.5 μg/Nm^3)

Cd in vapor phase = NR(8 μg/Nm^3)

where NR(1.5) indicates that the analytical result was below the reporting limit of 1.5 μg/Nm^3 (see footnote in Table 3-1 for additional details)

Total Cd in fabric filter inlet gas = NR(1.5 μg/Nm^3)

Case 3: The total concentration is considered to be the level measured above the reporting limit, regardless of which phase this represents.

For example, the total chromium concentration in the stack gas is calculated as follows:

Cr in solid phase = 2.2 $\mu g/Nm^3$

Cr in vapor phase = NR(1 $\mu g/Nm^3$)

Total Cr in stack gas = 2.2 $\mu g/Nm^3$

The above conventions are also in general agreement with guidance provided by EPA (Technical Implementation Document for EPA's Boiler and Furnace Regulations, U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., March 1992).

Testing at several sites has indicated that mercury, HCl, and HF are present primarily in the vapor phase. For Case 2, then, the total concentration in the gas stream is considered to be the reporting limit in the vapor phase. For Cases 1 and 3, the methodologies are unchanged from those described above.

Questionable analytical data have been excluded from all summary calculations. These include results that indicate a sampling bias, analytical interference, or the presence of organic compounds known to be laboratory contaminants.

Concentrations were corrected against blank sample concentrations, where appropriate (i.e., where blank concentrations were reported). Details of the blank corrections are provided in Appendix E.

Coal and Limestone

Analyses of the coal and limestone samples are presented in Tables 3-1 and 3-2, respectively. The reported results for the coal represent an average of four duplicate samples except where noted. The limestone results are the average of one pair of duplicate samples. Because only one independent sample was available, no confidence intervals are reported for either coal or limestone. Appendix A presents the analytical method reported for each combination of substance and stream. The results reported here were obtained using the analytical methods felt to be the most applicable to each matrix.

Fabric Filter Inlet Gas

Table 3-3 summarizes the results of the measurements made on the gas exiting the air preheaters and entering the fabric filter at Site 10. In addition to the species shown on this table, toluene was also analyzed; however, none was reported. The metals and anions concentrations for both solid and vapor phase fractions are presented in Table 3-3. For the multi-metals train, the particulate filter and probe and nozzle rinse fractions

Table 3-1

Analytical Results for Coal [a]

Substance	Measure	Units
Mass Flow Rate (dry)	110	klb/hr
HHV [b] (dry)	11,000	Btu/lb
Moisture	7.3	wt%
Ash	17	wt%
Sulfur	0.53	wt%
Arsenic	1.6	ppm
Barium	180	ppm
Beryllium [c]	0.6	ppm
Cadmium	NR(2) [d]	ppm
Chloride	60	ppm
Chromium	7.5	ppm
Cobalt	1.7	ppm
Copper	NR(30)	ppm
Fluoride [c]	140	ppm
Lead [c]	6.1	ppm
Manganese	11	ppm
Mercury	0.08	ppm
Molybdenum	NR(1.5)	ppm
Nickel	NR(10)	ppm
Phosphorus [c]	200	ppm
Selenium	1.5	ppm
Vanadium	19	ppm

[a] As received, except where otherwise noted.

[b] HHV = higher heating value.

[c] Result of one sample analysis.

[d] NR = Below reporting limit; the reporting limit is shown in parentheses. The "reporting limit" is the concentration below which results are not routinely reported. The reporting limit is set at a concentration representing an upper tolerance for the method reporting limit (MRL). As described in Appendix B to 40 CFR 136, the MDL is a value that is calculated from a series of measurements made at a particular point in time under a particular set of conditions; it is not an intrinsic characteristic of a method. Thus, for a given method, the numerical value of the MDL will vary somewhat with each determination. Likewise, MDLs would be expected to vary somewhat between instruments, between analysts, and between laboratories all using the same method. Thus, the reporting limit, as the upper tolerance for the MDL, represents a laboratory-specific value below which the MDL would be expected to fall for any determination in that particular laboratory, regardless of instrument, analyst, etc. The reporting limit does not necessarily have utility in regulatory application.

Table 3-2

Analytical Results for Limestone

Substance	Measure	Units
Mass Flow Rate (dry)	8.2	klb/hr
Moisture	0.10	wt%
Arsenic	19	ppm
Barium	23	ppm
Beryllium	NR(0.2) [a]	ppm
Cadmium	NR(0.4)	ppm
Chloride	77	ppm
Chromium	2.3 [b]	ppm
Cobalt	0.88 [b]	ppm
Copper	NR(2)	ppm
Fluoride	50	ppm
Lead	7.1	ppm
Manganese	280	ppm
Mercury	NR(0.04)	ppm
Molybdenum	NR(4)	ppm
Nickel	2.1 [b]	ppm
Phosphorus	NR(25)	ppm
Selenium	NR(0.4)	ppm
Vanadium	4.6 [b]	ppm

[a] NR = Below reporting limit; the reporting limit is shown in parentheses.

[b] Concentration is less than five times the reporting limit.

Table 3-3a

Fabric Filter Inlet

Substance	Vapor Phase µg/dNm³ [a]	Solid Phase µg/dNm³ [a]
Arsenic	3.0	870
Barium	NR(3.0) [b]	5,700
Beryllium	1.5	56
Cadmium	NR(1.5)	NR(7) [c]
Chloride	1,200	1,050
Chromium	NR(3) [c]	370
Cobalt	7.4	230
Copper	7.6	740
Fluoride	68	410
Lead	15	380
Manganese	220,000	2,300
Mercury	NR(3) [d]	NR(3)
Molybdenum	18	140
Nickel	30	1,300
Phosphorus	170	30,000
Selenium	NR(2)	290
Vanadium	18	1,300
Stream Flow Rate		15,500,000 dscfh [e]
Particulate Loading		10.83 gr/dscf [e]

[a] Standard conditions 0 °C, 1 atm.

[b] NR = Below reporting limit; the reporting limit is shown in parentheses.

[c] Blank correction was greater than 50% of the measured concentration.

[d] The reported vapor phase mercury data are suspected to be low. Problems were encountered in analyzing these samples (see discussion in Section 4).

[e] Standard conditions 68 °F, 1 atm; represents total flow to all fabric filters.

Table 3-3b

Fabric Filter Inlet

Parameter	Vapor Phase $\mu g/dNm^3$	Solid Phase $\mu g/dNm^3$
Polycyclic Organic Matter [a]	NR [b]	NR
Volatile Organic Compounds		
Formaldehyde	NR(17) [c]	NA [d]
Benzene	4.48 ± 2.1 [e]	NA

[a] Solid and vapor phase fractions were analyzed together; no polycyclic organic matter (POM) was reported in the combined sample.

[b] NR = Below reporting limits; see Appendix B for specific laboratory reporting limits of the analyzed substances.

[c] Blank correction was greater than 50% of the measured value.

[d] NA = Not analyzed.

[e] Confidence interval represents product of standard error from scatter in canister results and student "t" at 95% confidence.

reported in the blank), this weight was blank corrected. This total weight was divided by the total mass of particulate collected to obtain an elemental composition of the suspended ash. The suspended ash (collected particulate) composition was also compared to the collected ash composition (ash removed by the fabric filter) as an additional verification of the consistency of the measured solids composition.

The suspended ash flow rate was multiplied by the elemental analysis to obtain a solid phase substance mass rate. When divided by the gas flow, this value becomes the solid phase portion of the gas concentration. The multi-metals train impingers were analyzed directly for total elemental mass and divided by the sampled gas volume to obtain the vapor phase concentration.

Examination of Table 3-3 shows that the measured concentration of manganese in the fabric filter inlet vapor phase is unexpectedly and extraordinarily high. The limited volatility of this element would suggest that the result is in error. This conclusion is supported by the fact that the manganese concentration in the stack gas vapor was much lower and consistent with those of the other metals. Furthermore, the amount of manganese in the fabric filter inlet gas, at the reported concentrations, is much greater than the quantity entering the system in the coal and limestone. It should also be noted that these observations are based on a single sample, so some caution should be used in interpreting the results.

Stack Gas

Tables 3-4 and 3-5 present the concentration and unit-energy basis results of stack gas emission measurements from Site 10. Again, the data are presented as solid and vapor phase components. The concentrations of many of the measured substances are very low. In addition, some concentrations were blank corrected, i.e., analysis of the filter blank and/or impinger solution blanks showed some reportable concentration of the substance. The blank concentration was subtracted from the sample concentration of these substances.

Fabric Filter Performance

Table 3-6 presents the removal efficiency calculated for the fabric filter for various substances. The average particulate removal is 99.95 percent. Most of the selected elements are also removed quite effectively. As expected, the tests showed that the acid gases (HCl) and volatile organic compounds are not effectively controlled by a particulate removal device. The high concentration of lime in the fabric filter solids may have been responsible for the observed removal of the acid gases (particularly HF).

Other Species of Interest

Some compounds which were not on the FCEM substance list (Table 1-1) but which are listed in Title III of the CAAA of 1990 were also measured. Those substances for which concentrations were reported are shown in Table 3-7. Two of these compounds, dibutyl

Table 3-4a

Stack Gas

Substance	Vapor Phase µg/dNm³ [a]	Solid Phase µg/dNm³ [a]
Arsenic	NR(0.5) [b]	NR(1) [c]
Barium	1.4	14.9
Beryllium	NR(0.2)	NR(0.2)
Cadmium	NR(0.6)	NR(0.5) [c]
Chloride	1200	86.2
Chromium	NR(1) [c]	2.2
Cobalt	NR(1)	NR(1)
Copper	NR(2)	NR(2)
Fluoride	NR(24)	NR(4) [c]
Lead	0.77	NR(0.3) [c]
Manganese	22	19.0
Mercury	NR(0.6) [d]	NR(0.2)
Molybdenum	NR(6)	NR(5) [c]
Nickel	NR(2)	NR(2) [c]
Phosphorus	NR(36)	NR(32) [c]
Selenium	NR(0.6)	NR(21)
Vanadium	NR(2)	NR(2)
Stream Flow		15,500,000 dscfh [e]
Particulate Loading		0.00517 gr/dscf [e]

[a] Standard conditions 0 °C, 1 atm.

[b] NR = Below reporting limits; laboratory reporting limits are shown in parentheses.

[c] Blank correction was greater than 50% of the measured concentration.

[d] The reported vapor phase mercury data are suspected to be low. Problems were encountered in analyzing these samples (see discussion in Section 4).

[e] Standard conditions 68 °F, 1 atm.

Table 3-4b

Stack Gas

Substance	Vapor Phase $\mu g/dNm^3$	Solid Phase $\mu g/dNm^3$
Semivolatile Organic Compounds [a]	NR [b]	NR
Volatile Organic Compounds		
Formaldehyde	NR(15) [c]	NA [d]
Benzene	2.69 ± 2.46 [e]	NA

[a] Solid and vapor phase fractions were analyzed together; no semivolatile compounds were found in the combined sample.

[b] NR = Below reporting limit; specific laboratory reporting limits of the analyzed substances are presented in Appendix B.

[c] Blank correction was greater than 50% of the measured value.

[d] NA = Not analyzed.

[e] Confidence interval represents product of standard error and student "t" at 95% confidence.

Table 3-5

Stack Emissions (lb/10^{12} Btu)

Substance	(lb/10^{12} Btu)
Arsenic	NR(1) [a,b]
Barium	12.1
Beryllium	NR(0.2)
Cadmium	NR(0.4) [b]
Chloride	958
Chromium	1.6
Cobalt	NR(0.8)
Copper	NR(2)
Fluoride	NR(18)
Lead	0.6
Manganese	31
Mercury	-- [c]
Molybdenum	NR(4) [b]
Nickel	NR(2) [b]
Phosphorus	NR(24) [b]
Selenium	NR(16)
Vanadium	NR(2)
Semivolatile Organic Compounds	NR [d]
Volatile Organic Compounds	
Formaldehyde	NR(15) [b]
Benzene	2.0 ± 1.8 [e]

[a]NR = Below reporting limits; values based on reporting limits are shown in parentheses.

[b]Concentrations in the blank samples were greater than 50% of the measured concentration.

[c]The reported vapor phase mercury data are suspected to be low. Problems were encountered in analyzing these samples (see discussion in Section 4).

[d]Specific reporting limits for each of the analyzed substances are provided in Appendix B.

[e]Confidence interval is product of standard error from scatter in canister results and student "t" at 95% confidence.

Table 3-6

Fabric Filter Removal Efficiency

Substance	Removal (%)
Particulate Control	99.95
Arsenic	>99.9
Barium	99.7
Beryllium	>99.6
Cadmium	NC[a]
Chloride	42.8
Chromium	99.4
Cobalt	>99.6
Copper	>99.7
Fluoride	>95.0
Lead	99.8
Manganese	98.2[b]
Mercury	NC[c]
Molybdenum	>96.8
Nickel	>99.8
Phosphorus	>99.9
Selenium	>92.8
Vanadium	>99.8
Benzene	40

[a]NC = Not calculated. Element was not measured above reporting limits in the inlet to the fabric filter.

[b]Manganese removal was calculated without including the reported vapor phase concentration of manganese in the inlet to the fabric filter. The inlet concentration is thought to be erroneous.

[c] NC = Not calculated. Analytical difficulties resulted in vapor phase mercury concentrations which are suspected to be low (see Section 4 for additional information.)

Table 3-7

Other Species of Interest

Substance	Baghouse Inlet Concentration, $\mu g/Nm^3$	Stack Gas Concentration, $\mu g/Nm^3$
Dibutyl phthalate	195	3.1
bis(2-Ethylhexyl) phthalate	75	6.0
N-nitrosodiethylamine	NS [a]	15
Acetaldehyde	0.5 [b]	0.5 [b]

[a] NS = Not sampled.

[b] Blank corrections were greater than 50% of the sample concentration (see Appendix E).

phthalate and bis(2-ethylhexyl) phthalate are known to be common laboratory contaminants contributed from sampling and analytical components such as plastics and rubber materials (M.A. Mazurek, et. al., Environmental Science and Technology, Volume 25, No. 4, 1991).

Section 4

DATA ASSESSMENT

Several procedures can be used to evaluate the information developed during a field sampling program. Within the overall FCEM program, three methods are used to assess data quality. The first is the use of material balances. If closure of a substance material balance can be made within an acceptable percentage, the measurements of the major contributors to the balance should be representative of the process operation. Since material balances involve the summation and comparison of mass flow rates in several streams, often sampled by different procedures and analyzed by different methods, good agreement indicates either a statistically improbable degree of luck or accurate results. However, the validity of measured stack emission rates of most elements can seldom be validated by material balances. The amount of these elements which are emitted in the stack gas are too low to be of much significance in the material balance closure. The second data assessment method involves the traditional QA/QC protocols of laboratory analysis, i.e., duplicates, blanks, spike recovery, etc. The use of QA/QC data becomes more effective as more sites are sampled and trends are defined. For some substances, closing a material balance is difficult, perhaps because of low concentration levels, so that QA/QC results are the only means of substantiating that the measurements were performed correctly. Finally, we can compare current results with literature information, where available.

Material Balance Results

At Site 10, five streams define the plant overall material balance: coal, limestone, bottom ash, collected fly ash, and stack gas. For substances of interest, the material balance closures were calculated. Closure is defined as the ratio of outlet to inlet mass. A 100% closure indicates perfect agreement. When trace substances are analyzed, closures between 70 and 130% have been set as a goal of the FCEM project. This range reflects the typical level of uncertainty in the measurements and, therefore, permits one to interpret the inlet and outlet stream mass rates as being statistically equivalent. Poor closures usually indicate measurement problems in one or more sample matrices. However, poor closures do not necessarily mean that the emissions measurements are in error. Since the emission rate of many substances is less than 1% of the mass entering with the coal, the material balance closure is controlled by measurements of the solids streams.

Table 4-1 presents the results of the material balance calculations. All of the substances present at fairly high concentrations in the coal and limestone have closures in the desirable range (aluminum, calcium, iron, magnesium, potassium, and titanium). This

Table 4-1

Material Balance

	Substance	Closure (%)
Major Elements:	Aluminum	96
	Calcium	117
	Iron	101
	Magnesium	76
	Potassium	NC [a]
	Sodium	87
	Titanium	104
Minor/Trace Elements:	Arsenic	NC
	Barium	72
	Beryllium	177
	Cadmium	NC
	Chloride [b]	84
	Chromium	119
	Cobalt	227
	Copper	NC
	Fluoride [b]	56
	Lead	156
	Manganese	140
	Mercury	NC
	Molybdenum	NC
	Nickel	NC
	Phosphorus	125
	Selenium	75
	Vanadium	103

[a]NC = Not calculated; not found above reporting limit in one or more of the major inlet or outlet streams.

[b]Chlorine and fluorine are assumed to be in the form of chloride and fluoride, respectively, in the combustion gas stream.

indicates that the flow rates for the streams and the chemical analysis for these substances in the input and ash streams are probably reasonably accurate.

Concentrations of cadmium, copper, potassium, mercury, molybdenum, and nickel were below reporting limits in the coal; therefore, material balances could not be developed for these substances. A material balance was not determined for arsenic, because arsenic was not reported in any of the outlet streams. For those substances with closure values between 70 and 130%, we consider the data to be valid and no further discussion is presented. Substances that did not or could not achieve acceptable closures are discussed below. Material balances were not attempted for organic species since these substances may not be conserved in the plant (i.e., they can be created or destroyed by reaction as they pass through the plant).

Substance Discussion

In general, the material balance closure for most substances indicates the flow rate data and major element analysis are adequate in terms of describing the operation of Site 10. However, because only one sample set was collected at this site, very little interpretation can be attempted when a material balance does not close. Also, since the measured elements exit the system primarily with the fly ash and bottom ash, material balances provide little information about the accuracy of stack emissions results.

Beryllium

The material balance closure for beryllium was 178 percent. Most of the beryllium enters the system in the coal and exits in the fly ash. The poor material balance indicates a high result in the fly ash analyses, a low result in the coal analysis, or both.

Cobalt

The material balance closure for cobalt was 227 percent. Most of the cobalt enters the system in the coal and exits in the fly ash. The poor material balance indicates a high result in the fly ash sample, a low result in the coal analysis, or both.

Fluorine

It is assumed that fluorine is present as fluoride in the combustion gas. The overall fluorine/fluoride material balance closure was 56 percent. The low recovery is probably due to a low result in the ash analysis. The sodium hydroxide fusion digestion method used has been shown to be biased low by about 50 percent. There may also be a high result from the coal analysis.

Lead

The material balance closure for lead was 156 percent. Most of the lead enters the system in the coal and exits in the fly ash. The poor material balance indicates a high result in the fly ash sample, a low result in the coal analysis, or both.

Mercury

Very sensitive analytical measurement techniques were used to measure mercury concentrations in coal, ashes, and impinger solutions to provide the best information possible. Even with these methods, however, mercury was not reported in any of the sampled materials, except for the coal. It was discovered during later sampling efforts that a large portion of mercury present in a gas stream was trapped in the nitric acid impingers. However, these impingers were not analyzed properly because insufficient permanganate (which reacts with H_2O_2 in the solution) was added prior to analysis by CVAAS. Thus, the vapor phase mercury results are believed to be lower than actual concentrations.

Manganese

The material balance closure for manganese was 140 percent. Most of the manganese enters the system in the coal and exits in the fly ash. The high material closure was, in part, caused by a high result in the ash analysis by ICP-AES. The stack emissions of manganese may also be biased high.

Molybdenum

In testing at sites subsequent to Site 10, it has been found that internally consistent analytical results could not be obtained for molybdenum in any of the ash streams prepared by microwave digestion and analyzed by ICP-AES. Molybdenum recoveries from analyses of NBS reference coal fly ash have been consistently biased high. This bias can be attributed to spectral interference from aluminum and iron in the ash matrix. Thus, reported molybdenum levels in ash streams should be considered questionable.

Volatile Organics

The VOST sample collected during May indicated unexpectedly high concentrations of benzene in the fabric filter inlet and stack gas streams. It is believed that the VOST train was contaminated during sampling because of the use of a Teflon® probe. The sampling method specifies the use of a glass-lined probe, but a Teflon probe was used at some sites in an effort to overcome some sampling problems (i.e., breaking probes and sampling with vertical probe orientation). However, it was later discovered that aromatics (benzene, toluene) were apparently being released from the insulation surrounding the probe. These aromatics were diffusing through the Teflon probe and contaminating the samples. (In subsequent testing at another site, VOST results with Teflon® were confirmed to be higher while results of VOST with a glass probe were in agreement with canister results). For this reason, none of the VOST results are reported. During

subsequent sampling, canister samples were analyzed for benzene and total non-methane hydrocarbons. The results of the canister sample analyses are reported. The inlet and outlet concentrations agree within the standard error limits of the results. Since a change in vapor phase benzene levels would not be expected across a fabric filter, this result is reasonable.

The formaldehyde results should be considered questionable. Only one sample was collected, and QA/QC results suggest a possible contamination in the field blank train. Formaldehyde levels in the field blanks were as much as five times higher than those found in the test samples.

POMs

No polycyclic organic material was identified in any gas stream. Reporting limits for POMs were in the range of 0.08 - 3.2 $\mu g/Nm^3$.

Overview of Vapor Phase Metals

Impinger results indicate substantial amounts of the major elements in the vapor phase. Since these substances are not volatile, it is possible that there was a breakthrough of particulates through the sampling train filter and into the impingers. Therefore, the reported levels of any of the metals measured above the reporting limit (barium, chromium, lead, and manganese) in the vapor phase could be high.

Overview of Solid Phase Metals

A comparison of the collected fly ash and fabric filter inlet solid phase analysis shows that the fabric filter inlet solids generally have lower concentrations than found in the collected fly ash. Since the gas solid phase material was prepared using a microwave digestion, and the collected ash was prepared by lithium metaborate fusion or perchloric acid digestion, it is possible that the reported concentrations in the gas solids may be biased low because of an incomplete digestion. This bias would affect both the fabric filter inlet and stack gas solid phase results.

Section 5

EXAMPLE CALCULATIONS

This section presents the methodology and sample calculations used to develop the results presented in Sections 3 and 4. Specifically, the calculation of stream flow rates and unit-energy basis results are presented.

Stream Flows

Appendix C presents information about the stream flows that were measured or calculated at Site 10 during the sampling trip. The coal feed rate, limestone feed rate, flue gas flow, and the fabric filter inlet and outlet particulate loadings were measured directly. The collected fly ash flow rate was calculated by an on-site material balance program which performs a balance on inert substances around the system. The calculated fly ash flow rate and the measured fabric filter inlet particulate rate compared well. The stack flue gas flow rate was used for material balance calculations around the fabric filter (to calculate removal efficiency). The measured flue gas flow rate agreed with the site flue gas flow sensors.

Unit Energy Calculation

In addition to the gas phase concentrations, a unit-energy basis emission factor has also been developed for each substance. These values were determined by using the mass flow of a substance and dividing by the heat input to the boiler during testing rather than the resulting gas flow. The heat input was obtained from the coal flow rate and the HHV of the fuel for the sampling period.

The coal mass rate was 110,000 (dry) lbs/hr with a HHV of 11,000 Btu/lb, for a heat input of 0.00121×10^{12} Btu/hr. As an example, the solid phase barium mass flow rate out of the fabric filters is calculated by multiplying the gas concentration in Table 3-4 by the stack gas flow rate of 409,155 dNm^3/hr ($14.9\ \mu g/dNm^3$ * 409,155 dNm^3/hr * 10^{-3} $mg/\mu g$ = 6,096.4 mg/hr). The same is done for the vapor phase, producing a rate of 572.8 mg/hr. These two rates are added using the rules presented in Section 3. In this case, since both values are above the reporting limit, the values can simply be added. (If, however, one of the values had been less than a reporting limit, that value would have been assumed to be zero. For the case of both the vapor and solid phase being below the reporting limit only, the reporting limit of the particulate phase would have been used to calculate the emission rate. The result would be reported as less than the reporting limit.) In this case the total emission rate is 6,669.2 mg/hr (0.0147 lb/hr) of barium. This value is divided by the energy input (0.0147/0.00121) to get the emission rate of 12.1 $lb/10^{12}$ Btu reported in Table 3-5.

Section 6

GLOSSARY

Btu	British Thermal Unit
CFBC	Circulating Fluidized Bed Combustion
dNm^3	Dry Normal Cubic Meter
DQO	Data Quality Objectives
dscfh	Dry Standard Cubic Feet per Hour
FCEM	Field Chemical Emissions Monitoring
GFAAS	Graphite Furnace Atomic Adsorption Spectroscopy
HHV	Higher Heating Value
IC	Ion Chromatography
ICP (ICAP, ICAPES, ICP-AES)	Inductively Coupled Argon Plasma Emissions Spectroscopy
ID	Induced Draft
klb/hr	Thousand Pounds per Hour
MSD	Matrix Spike Duplicate
NAA	Neutron Activation Analysis
NBS	National Bureau of Standards
PAH	Polynuclear Aromatic Hydrocarbons
POM	Polycyclic Organic Matter
PSD	Particle Size Distribution
QA/QC	Quality Assurance/Quality Control
RPD	Relative Percent Difference
SIE	Selective Ion Electrode
TNMHC	Total Non-Methane Hydrocarbons
VOC	Volatile Organic Compound
VOST	Volatile Organic Sampling Train

Appendix A

Detailed Sample Collection/Preparation/Analysis Tables

Table A-1

Reference Table for Analytical Methods Section - By Sample Stream

Sampling Stream	Collection Method	Fraction Description	Sample Handling	Comments
Gases:				
Fabric Filter Inlet	SW 0030	VOST	Cooled to 4°C	
	EPA TO-14	Canister		Sample volume was limited to an increase in pressure of 3 inches mercury.
	SW 0010	MM5-Thimble	Cooled to 4°C	
		MM5-XAD Resin	Cooled to 4°C	
		MM5-PNR/Condensate	Cooled to 4°C	
	EPA Draft Method	Metals-Probe and Nozzle Rinse	Acetone portion dried and weighed; nitric acid portion cooled.	Subsamples of the acetone probe and nozzle rinse and filter catch were digested and combined with the digested nitric acid probe and nozzle rinse.
		Metals-Filter	Dried at 105°C to constant weight.	See above.
		Metals-Impinger 1 & 2		For mercury analysis only.
		Metals-Impinger 3 & 4		
	SW 0011	Formaldehyde Impinger	Rinsed with water and MeCl2.	
	Radian Method	Anion Train		
Stack	SW 0030	VOST	Cooled to 4°C	
	EPA TO-14	Canister		Sample volume was limited to an increase in pressure of 3 inches mercury.
	SW 0010	MM5-Filter	Cooled to 4°C	
		MM5-XAD Resin	Cooled to 4°C	
		MM5-PNR/Condensate	Cooled to 4°C	
	EPA Draft Method*	Metals-Probe and Nozzle Rinse	Acetone portion dried and weighed; nitric acid portion cooled.	Entire filter digested with sample and combined with digested probe and nozzle rinse.
		Metals-Filter	Dried to 105°C to constant weight.	
		Metals-Impinger 1 & 2		For metals in vapor phase.
		Metals-Impinger 3 & 4		For mercury analysis only.
	SW 0011	Formaldehyde Impinger	Rinsed with water and MeCl2.	
	Radian Method	Anion Train		

Table A-1

(Continued)

Sampling Stream	Collection Method	Fraction Description	Sample Handling	Comments
Solids:				
Coal	Grab Composite		None	
Limestone	Grab Composite			
Fly Ash	Grab Composite (auto sampler)			
Bottom Ash	Grab Composite			

Table A-2

Summary of Preparation Procedures and Analytical Methods Used to Measure Organic Chemical Components in Non-Coal Solids and Flue Gas

Component	Method Reference	Non-Coal Solids	Flue Gas
Volatile Organic Compounds			
Sample Collection			
VOA Vials		X	
VOST	SW 0030		X
Canisters	TO-14		X
Analysis by GC/MS			
Benzene	SW 8240		X
Toluene	SW 8240		X
Formaldehyde			
Sample Collection			
DNPH Impinger[a]	SW 0011		X
Analysis by HPLC			
Formaldehyde	TO 5[b]		X
Polynuclear Aromatic Organic Compounds			
Sample Collection			
Grab		X	
MM5	SW 0010		X
Preparation			
Liquid/Liquid Extraction	SW 3520		
Soxhlet Extraction	SW 3540	X	X
Analysis by GC/MS			
Acenaphthene	SW 8270	X	X
Acenaphthylene	SW 8270	X	X
Anthracene	SW 8270	X	X

Table A-2

(Continued)

Component	Method Reference	Non-Coal Solids	Flue Gas
Benzo(a)anthracene	SW 8270	X	X
Benzo(a)pyrene	SW 8270	X	X
Benzo(b)fluoranthene	SW 8270	X	X
Benzo(g,h,i)perylene	SW 8270	X	X
Benzo(k)fluoranthene	SW 8270	X	X
Chrysene	SW 8270	X	X
Dibenzo(a,h)anthracene	SW 8270	X	X
Fluoranthene	SW 8270	X	X
Fluorene	SW 8270	X	X
Indeno(1,2,3-cd)pyrene	SW 8270	X	X
Naphthalene	SW 8270	X	X
Phenanthrene	SW 8270	X	X
Pyrene	SW 8270	X	X

[a]DNPH is 2,4-dinitrophenylhydrazine.

[b]TO 5 is EPA Compendium of methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA 600/4/84/041.

SW is EPA SW-846 Test Methods for Evaluating Solid Waste.

Table A-3

Preparation Methods and Chemical Analysis Methods Applied to Coal for the FCEM Project

Component	Method Reference	Coal
Ultimate Analysis of Coal		
Ash	Perkin/Elmer Model 240C Instructions	X
Carbon	Perkin/Elmer Model 240C Instructions	X
Hydrogen	Perkin/Elmer Model 240C Instructions	X
Nitrogen	Perkin/Elmer Model 240C Instructions	X
Sulfur	Perkin/Elmer Model 240C Instructions	X
Heating Value	Perkin/Elmer Model 240C Instructions	X
Proximate Analysis of Coal		
Moisture	Perkin/Elmer Model TGA 7 Instructions	X
Ash	Perkin/Elmer Model TGA 7 Instructions	X
Volatiles	Perkin/Elmer Model TGA 7 Instructions	X
Fixed Carbon	Perkin/Elmer Model TGA 7 Instructions	X
FCEM Target Elements by INAA		
Preparation		None
Analysis by INAA		
Arsenic	Karr, Chapters 12 and 46	X
Barium	Karr, Chapters 12 and 46	X
Cadmium	Karr, Chapters 12 and 46	X

Table A-3

(Continued)

Component	Method Reference	Coal
Chromium	Karr, Chapters 12 and 46	X
Chlorine	Karr, Chapters 12 and 46	X
Cobalt	Karr, Chapters 12 and 46	X
Copper	Karr, Chapters 12 and 46	X
Manganese	Karr, Chapters 12 and 46	X
Mercury	Karr, Chapters 12 and 46	X
Molybdenum	Karr, Chapters 12 and 46	X
Nickel	Karr, Chapters 12 and 46	X
Selenium	Karr, Chapters 12 and 46	X
Vanadium	Karr, Chapters 12 and 46	X
Beryllium and Lead Analysis in Coal		
Preparation		
Oxygen Bomb Digestion	Lindahl and Bishop	X
MW Digestion for Solids	Lindahl and Bishop	X
Analysis by ICP-AES		
Beryllium	SW 6010	X
Analysis by GFAA		
Lead	SW 7421	X
Chlorine, Fluorine, and Total Phosphorous Analysis in Coal		
Preparation		
Oxygen Bomb Digestion	ASTM 2361/ASTM 3761	X
Analysis by Ion Chromatography		
Chloride	EPA 300.0	X

Table A-3

(Continued)

Component	Method Reference	Coal
Analysis by Ion Selective Electrode		
Fluoride	ASTM D 3761	X
Spectrophotometric Analysis		
Total P, Spectrophotometric	EPA Method 365.2	X
Mercury Analysis in Coal		
Preparation		
Double Amalgamation	Karr, Chapter 14	X
Analysis by CVAA		
Mercury	Karr, Chapter 14	X
Additional Inorganic Analytes in Coal		
Preparation		None
Analysis by INAA		
Aluminum	Karr, Chapters 12 and 46	X
Calcium	Karr, Chapters 12 and 46	X
Iron	Karr, Chapters 12 and 46	X
Magnesium	Karr, Chapters 12 and 46	X
Potassium	Karr, Chapters 12 and 46	X
Sodium	Karr, Chapters 12 and 46	X
Titanium	Karr, Chapters 12 and 46	X
Zinc	Karr, Chapters 12 and 46	X

Karr, C., Jr. (ed), Analytical Methods for Coal and Coal Products.

SW is EPA SW-846, Test Methods for Evaluating Solid Waste.

EPA is EPA Methods for Chemical Analysis of Waters and Wastes.

Table A-4

Inorganic Chemical Components Measured in Non-Coal Solids and Flue Gas

Component	Method Reference	Non-Coal Solids	Fabric Filter Inlet Solids	Stack Solids	Metals Impingers 1 and 2	Metals Impingers 3 and 4	Anions Impingers (Combined)
FCEM Target Elements by ICP-AES							
Preparation							
Water Digestion for ICP-AES	SW 3005				X		
MW Digestion for Solids	CEM-FA		X				
Perchloric Acid Digestion (Ash)		X					
Acid Digestion (Limestone)	SW 3050	X					
MW Digestion for Filters	CEM-F			X			
Analysis by ICP-AES							
Barium	SW 6010	X	X	X	X		
Beryllium	SW 6010	X	X	X	X		
Cadmium	SW 6010	X	X	X	X		
Chromium	SW 6010	X	X	X	X		
Cobalt	SW 6010	X	X	X	X		
Copper	SW 6010	X	X	X	X		
Manganese	SW 6010	X	X	X	X		
Molybdenum	SW 6010	X	X	X	X		
Nickel	SW 6010	X	X	X	X		
Vanadium	SW 6010	X	X	X	X		
FCEM Target Elements by GFAAS							
Preparation							
MW Digestion for Solids	CEM-FA		X				
Perchloric Acid Digestion (Ash)		X					
Acid Digestion (Limestone)	SW 3050	X					
MW Digestion for Filters	CEM-F			X			

Table A–4

(Continued)

Component	Method Reference	Non-Coal Solids	Fabric Filter Inlet Solids	Stack Solids	Metals Impingers 1 and 2	Metals Impingers 3 and 4	Anions Impingers (Combined)
Analysis by GFAAS							
Arsenic by GFAAS	SW 7061	X	X	X	X		
Lead by GFAAS	SW 7421	X	X	X	X		
Selenium by GFAAS	SW 7741	X	X	X	X		
Mercury by CVAA							
Preparation							
MW Digestion for Solids	CEM-FA	X	X				
Perchloric Acid Digestion (Ash)		X					
Acid Digestion (Limestone)	SW 3050	X					
MW Digestion for Filters	CEM-F			X			
Analysis by CVAA							
Mercury	SW7470	X	X	X		X	
FCEM Acid-Forming Anions							
Aqueous Extraction of Solids	Radian	X					
Chloride by IC	EPA 300.0	X					X
Acid Dissolution[a]	FGD I3	X					
Sodium Hydroxide Fusion	McQuaker and Gurney	X					
Fluoride by SIE	McQuaker and Gurney	X[b]					
Fluoride by SIE	EPA 340.2	X[c]					X
Total P Spectrophotometric	EPA 365.2						X

Table A-4

(Continued)

Component	Method Reference	Non-Coal Solids	Fabric Filter Inlet Solids	Stack Solids	Metals Impingers 1 and 2	Metals Impingers 3 and 4	Anions Impingers (Combined)
Additional Inorganic Analytes by ICP-AES							
Preparation							
Water Digestion for ICP-AES	SW 3005				X		
MW Digestion for Solids	CEM-FA		X				
Lithium Metaborate Fusion (Ash)		X					
Acid Digestion (Limestone)	SW 3050	X					
MW Digestion for Filters	CEM-F			X			
Analysis by ICP-AES							
Aluminum	SW 6010	X	X	X	X		
Calcium	SW 6010	X	X	X	X		
Iron	SW 6010	X	X	X	X		
Magnesium	SW 6010	X	X	X	X		
Potassium	SW 6010	X	X	X	X		
Titanium	SW 6010	X	X	X	X		
Zinc	SW 6010	X	X	X	X		
Total Sulfur Analysis							
Acid Dissolution[a]	FGD I3	X					
Sulfate by IC[a]	EPA 300.0	X					X

Table A-4

(Continued)

[a]Acid dissolutions were applied only to limestone solids.

[b]Solution of limestone brought into solution by NaOH fusion.

[c]Acid dissolutions of limestone and NaOH fusions of fly ash and bottom ash.

FGD Chemistry and Analytical Methods Handbook, Volume 2, Revision 1, EPRI CS 3612, 1988, Method 13, page 13-22.

ASTM American Society for Testing and Materials.

EPA is EPA Methods for Chemical Analysis of Water and Wastes.

SW is EPA SW-846, Test Methods for Evaluating Solid Waste, 3rd ed.

CEM-FA is CEM Corporation, Matthews, NC Procedure for microwave digestion of coal fly ash.

CEM-F is CEM Corporation, Matthews, NC Procedure for microwave digestion of glass or quartz filters.

CLP is EPA Contract Laboratory program SDW 3/90.

McQuaker, N.R., and M. Gurney, "Determination of Total Fluoride in Soil and Vegetation Using an Alkali Fusion-Selective Ion Electrode Technique," Analytical Chemistry, Vol. 49, No. 1, January 1977, pp. 53-56.

Appendix B

Analytical Data Tables

Table B-1

Coal Analyses

Species	Sample C1-10B (ppmw)	C1-10B Duplicate Analysis (ppmw)	Duplicate Sample C1-20B (ppmw)	C1-20B Duplicate Analysis (ppmw)	Average Concentration (ppmw)
FCEM Elements					
Arsenic	1.5208	1.4042	1.328	1.3335	1.397
Arsenic (reanalyzed)	1.5172	1.6388	1.5038	1.6756	1.584
Barium	183.26	181.21	171.86	173.46	177.4
Beryllium	0.60	NA	NA	NA	NC
Cadmium	< 2.3032	< 2.3818	< 2.3938	< 2.3922	< 2.368
Chlorine	57.306	58.09	< 54.49	68.766	59.66
Chromium	7.8422	7.9299	7.2398	7.1299	7.535
Cobalt	1.6921	1.745	1.6927	1.7587	1.722
Copper	< 30	< 27	< 29	< 30	< 29
Fluoride	144.00	NA	NA	NA	NC
Lead	6.10	NA	NA	NA	NC
Manganese	11.23	11.107	11.332	11.41	11.3
Mercury (NAA)	< 0.2	< 0.25	< 0.25	< 0.25	< 0.238
Mercury (gold amal.)	0.08	-	-	-	0.08
Molybdenum	< 1.3872	< 1.5243	< 1.4464	< 1.4291	< 1.447
Nickel	< 10.198	< 10.488	< 9.7938	< 9.9206	< 10.1
Phosphorus	200.00	NA	NA	NA	NC
Vanadium	18.917	16.953	18.232	20.655	18.69
Additional Elements					
Aluminum	26964	25783	28197	28779	27430
Antimony	0.6817	0.6572	0.6673	0.6469	0.663
Boron	NA	NA	NA	NA	NA
Calcium	1919.6	1893.3	1953.2	1834.8	1900
Iron	2259.2	2210.3	2066.8	2136.5	2168
Lithium	NA	NA	NA	NA	NA
Magnesium	1002.4	978.67	1000.3	1109.3	1023
Potassium	< 2025	< 1879.6	< 1815.3	< 2325.6	< 2011
Selenium	1.5327	1.5615	1.3998	1.3973	1.473
Silicon	NA	NA	NA	NA	NA
Silver	0.45	0.47	0.47	0.45 <	0.462
Sodium	806.6	783.08	858.7	866.94	828.8
Strontium	220.3	222.54	217.18	205.45	216.4
Tin	< 15	< 14.5	< 15	< 15	< 14.88
Titanium	933.52	926.94	1015.50	1013.90	972.5
Zinc	8.0683	10.219	11.018	11.922	10.3
Ultimate Analysis (wt %)					
Carbon	62	NA	63	NA	62.5
Hydrogen	4.3	NA	4.4	NA	4.35
Nitrogen	1.5	NA	1.5	NA	1.5
Oxygen	6.8	NA	6.8	NA	6.82
Sulfur	0.53	NA	0.53	NA	0.53
Proximate Analysis (wt %)					
Moisture	7.2	NA	7.4	NA	7.3
Ash	17	NA	17	NA	17
Volatiles	33	NA	33	NA	33
Fixed Carbon	43	NA	43	NA	43
Higher Heating Value (btu/lb)	11000	NA	11000	NA	11000

NA=not analyzed
NC=not calculated
< indicates the concentration was less than the reporting limit.

Table B-2

Limestone Analyses: Elements

Substance		Sample D1-10A (ppmw)	Duplicate Sample D1-10B (ppmw)		Average Concentration (ppmw)
FCEM Elements					
Arsenic		20	18		19
Barium		22.6	22.7		22.7
Beryllium	<	0.17<	0.16	<	0.17
Cadmium	<	0.44<	0.40	<	0.43
Chloride		78	76		77
Chromium	*	2.52*	2.09		2.31
Cobalt	*	0.87*	0.90		0.88
Copper	<	1.7<	1.6	<	1.7
Fluoride		33	66		50
Lead		7.2	6.9		7.1
Manganese		284	278		281
Mercury	<	0.045<	0.045	<	0.045
Molybdenum		4.4	4.0	<	4.2
Nickel	*	2.12*	2.16		2.14
Phosphorus		26	24	<	25
Vanadium	*	4.61*	4.64		4.63
Additional Elements					
Aluminum		623	578		601
Antimony		1000	960		980
Boron		52	69	<	61
Calcium		365000	354000	<	359500
Iron		1320	1350		1335
Lithium	*	5.17*	5.01		5.10
Magnesium		4060	3990		4025
Potassium	<	260<	240		250
Selenium	<	0.45<	0.34	<	0.40
Silicon		716	638	<	677
Silver	<	0.87<	0.81		0.84
Sodium	*	293*	270		282
Strontium		384	375		380
Sulfur	*	1590*	1760		1675
Tin	<	210<	190		200
Titanium	<	4.4<	4.0	<	4.2
Zinc		10.40	11.20	<	10.80

< indicates a concentration less than the reporting limit.
* indicates a concentration less than 5 times reporting limit.

Table B-3

Bottom Ash Analyses: Elements

Substance		Sample E1-10A (ppmw)		Duplicate Sample E1-10B (ppmw)		Average Concentration (ppmw)
FCEM Elements						
Arsenic	<	12		NA		NC
Barium		557.8		572.9		565.4
Beryllium	*	1.15	*	1.16		1.15
Cadmium	<	1.00	<	0.88	<	0.94
Chloride		110		120		115
Chromium		29.55		28.63		29.10
Cobalt	*	9.98		9.60		9.79
Copper		26.91		27.85		27.38
Fluoride		13.00		5.10		9
Lead		41		45		43
Manganese		233.0		239.7		236.4
Mercury	<	0.18	<	0.16	<	0.17
Molybdenum	<	10.00	<	8.80	<	9.40
Nickel	*	17.06		18.46		17.76
Phosphorus		389.7		413.8		401.8
Vanadium		40.66		39.79		40.23
Additional Elements						
Aluminum		105032		106590		105811
Antimony	<	610	<	520	<	565
Boron	<	110	<	120	<	110
Calcium		150144		154379		152262
Iron		10017		10320		10169
Lithium		52.20		59.64		55.92
Magnesium		4879		4983		4931
Potassium		6596		6770		6683
Selenium	<	1.00	<	0.98	<	0.99
Silicon		78300		118000		98150
Silver	*	2.68	*	2.06		2.37
Sodium		3638		3730		3684
Strontium		273.10		282.50		277.80
Sulfur		19860		20314		20087
Tin		120		100	<	110
Titanium		2181		2227		2204
Zinc		38.95		39.11		39.03

< indicates a concentration less than the reporting limit.
* indicates a concentration less than 5 times reporting limit.
NA=not analyzed
NC=not calculated

Table B-4

Fly Ash Analyses: Elements

Substance		Sample F1-10A (ppmw)	Duplicate Sample F1-10B (ppmw)		Average Concentration (ppmw)
FCEM Elements					
Arsenic	<	25	NA		NC
Barium		236	834		535
Beryllium		4.75	4.75		4.75
Cadmium	<	0.96	< 1.00	<	0.98
Chloride		190	200		195
Chromium		39.11	38.94		39.03
Cobalt		17.71	17.37		17.54
Copper		40.06	40.47		40.27
Fluoride		420	320		370
Lead		32	54		43
Manganese		174.6	178.5		176.6
Mercury	<	0.17	< 0.18	<	0.18
Molybdenum	<	9.60	< 10.00	<	9.80
Nickel		24.04	24.61		24.33
Phosphorus		2110	2115		2113
Vanadium		84.91	85.03		84.97
Additional Elements					
Aluminum		109368	111332		110350
Antimony	<	580	< 610	<	595
Boron	<	120	< 120	<	115
Calcium		131158	134085		132622
Iron		9329	9587		9458
Lithium		63.10	67.11		65.11
Magnesium		4066	4119		4093
Potassium		4888	4903		4896
Selenium	*	4.2	* 4.2		4.2
Silicon		74500	69200		71850
Silver		4.49	3.31		3.90
Sodium		2996	3073		3035
Strontium		822.4	873.8		848.1
Sulfur		13727	14078		13903
Tin	<	120	< 120	<	120
Titanium		4341	4456		4399
Zinc		48.67	48.23		48.45

< indicates a concentration less than the reporting limit.
* indicates a concentration less than 5 times reporting limit.
NA=not analyzed
NC=not calculated

Table B-5

Elemental Analyses for Solids Streams

Substance	Coal	Limestone	Bottom Ash	Fly Ash	Emitted Particulate	BH Inlet Particulate
	Average Concentration (ppmw)					
FCEM Elements						
Arsenic	1.40E+00	< 1.90E+01	< 1.20E+01	< 2.50E+01	< 1.27E+02	3.26E+01
Barium	1.77E+02	2.27E+01	5.65E+02	5.35E+02	1.46E+03	2.15E+02
Beryllium	6.00E-01	< 1.65E-01	1.15E+00	4.75E+00	< 1.69E+01	2.18E+00
Cadmium	< 2.37E+00	< 4.25E-01	< 9.40E-01	< 9.80E-01	< 4.17E+01	< 2.77E-01
Chloride	5.97E+01	7.70E+01	1.15E+02	1.95E+02	6.85E+03	3.96E+01
Chromium	7.54E+00	2.31E+00	2.91E+01	3.90E+01	1.73E+02	1.40E+01
Cobalt	1.72E+00	8.84E-01	9.79E+00	1.75E+01	< 8.46E+01	8.87E+00
Copper	< 2.90E+01	< 1.65E+00	2.74E+01	4.03E+01	< 1.69E+02	2.78E+01
Fluoride	1.44E+02	4.95E+01	9.05E+00	3.70E+02	5.96E+02	2.51E+00
Lead	6.10E+00	7.05E+00	4.30E+01	4.30E+01	< 2.54E+01	1.45E+01
Manganese	1.13E+01	2.81E+02	2.36E+02	1.77E+02	1.79E+03	8.75E+01
Mercury	8.00E-02	< 4.50E-02	< 1.70E-01	< 1.75E-01	< 1.69E+01	< 1.08E-01
Molybdenum	< 1.45E+00	< 4.20E+00	< 9.40E+00	< 9.80E+00	1.68E+03	6.19E+00
Nickel	< 1.01E+01	2.14E+00	1.78E+01	2.43E+01	< 1.69E+02	4.98E+01
Phosphorus	2.00E+02	< 2.50E+01	4.02E+02	2.11E+03	< 2.54E+03	1.14E+03
Vanadium	1.87E+01	4.63E+00	4.02E+01	8.50E+01	< 1.69E+02	5.05E+01
Additional Elements						
Aluminum	2.74E+04	6.01E+02	1.06E+05	1.10E+05	5.84E+03	1.14E+04
Antimony	6.63E-01	< 9.80E+02	< 5.65E+02	< 5.95E+02	< 8.46E+02	< 5.54E+00
Boron	NA	< 5.05E+01	< 1.10E+02	< 1.15E+02	< 5.08E+03	NA
Calcium	1.90E+03	3.60E+05	1.52E+05	1.33E+05	1.02E+05	3.37E+04
Iron	2.17E+03	1.34E+03	1.02E+04	9.46E+03	6.63E+04	3.04E+03
Lithium	NA	5.10E+00	5.59E+01	6.51E+01	< 1.69E+02	4.52E+01
Magnesium	1.02E+03	4.03E+03	4.93E+03	4.09E+03	< 8.46E+03	8.52E+02
Potassium	< 2.01E+03	< 2.50E+02	6.68E+03	4.90E+03	< 2.54E+04	2.23E+03
Selenium	1.47E+00	< 4.00E-01	< 9.90E-01	4.20E+00	< 1.69E+03	< 1.09E+01
Silicon	NA	6.77E+02	9.82E+04	7.19E+04	< 8.46E+03	7.65E+04
Silver	< 4.62E-01	8.40E-01	2.37E+00	4.05E+00	< 8.46E+01	7.63E-01
Sodium	8.29E+02	2.82E+02	3.68E+03	3.04E+03	< 8.46E+03	1.98E+03
Strontium	2.16E+02	3.80E+02	2.78E+02	8.48E+02	1.64E+03	4.73E+02
Sulfur		1.68E+03	2.01E+04	1.39E+04	1.03E+05	1.41E+04
Tin	< 1.49E+01	< 2.00E+02	< 1.10E+02	< 1.20E+02	< 5.08E+03	< 3.32E+01
Titanium	9.73E+02	< 4.20E+00	2.20E+03	4.40E+03	5.09E+03	2.12E+03
Zinc	1.03E+01	1.08E+01	3.90E+01	4.85E+01	< 1.69E+02	8.59E+03

NA=Not Analyzed

Table B-6

Gas Analysis Calculations: Fabric Filter Inlet Metals

Species: Metals
Sample Date: 05-01-90
Sample ID: FCEM1-A1-30 FCEM1-A1-31A/B,32,33 FCEM1-A1-34a FCEM1-A1-34b

Run Number: 1
Stream: Baghouse #4 Inlet Flue Gas

Particulate Loading (grains/dscf): 10.63
Moisture (vol %): 6.10
Gas Volume Sampled (dscf): 31.3
Gas %W:
Flowrate (dscfh): 8300000

Species	Cyclone (ug)	Part. PNR (ug)	Impinger 1 (ug)	Impinger 2 (ug)	Concentrations: Particulate (ug/dscf)	Concentrations: Impinger (ug/dscf)
Aluminum	43000	207589	38.3	242	8006.0	6.955
Antimony	< 72	< 50	< 12	< 13	3.9	0.799
Arsenic	169	547	< 0.5	1.65	22.9	0.069
Barium	1650	2877	< 1.2	< 1.3	151.0	0.080
Beryllium	17	30.9	< 0.25	0.984	1.5	0.039
Bismuth	570	< 400	< 100	148	31.0	7.923
Boron			198	839	0.0	
Cadmium	< 3.6	< 2.5	< 0.62	< 0.64	0.2	0.040
Calcium	192000	549720	< 120	428	23697.1	17.508
Chromium	76.8	232	< 1.3	< 1.3	9.9	0.083
Cobalt	88.2	107	< 1.2	4.93	6.2	0.196
Copper	230	382	< 2.5	3.81	19.6	0.202
Gold	9300	6430	< 25	39.2	502.6	2.051
Indium	214	< 100	< 25	131	10.0	4.984
Iron	10800	56349.6	5.48	36.6	2139.0	1.344
Lead	105	212	< 0.38	12.4	10.1	0.408
Lithium	324	671.48	< 2.5	< 2.6	31.8	0.163
Magnesium	3060	15700	< 120	306	599.4	13.610
Manganese	557	1367	5.6	186500	61.5	5958.645
Molybdenum	88.7	46.1	< 6.2	8.84	3.7	0.481
Nickel	658	437.2	< 2.5	22.7	35.0	0.805
Phosphorus	10700	14376	< 38	99.1	801.2	4.380
Platinum	174	< 100	< 25	< 2600	8.8	83.866
Potassium	16000	33000	< 380	124500	1565.5	3989.776
Selenium	< 140	< 100	< 0.62	< 0.64	7.7	0.040
Silicon	1000000	684900	639	188	53830.7	26.422
Silver	11.8	< 5	< 1.2	31.5	0.5	1.045
Sodium	17000	26510	< 120	153	1390.1	8.722
Strontium	2810	7596.5	< 0.38	0.676	332.5	0.034
Sulfur	113000	197000	25600	925000	9904.2	30376.997
Tellurium	240	130	< 25	28.2	11.6	1.700
Thallium	146	87.3	< 12	221	7.5	7.444
Tin	< 430	< 300	< 75	189	23.3	8.435
Titanium	21700	25000	< 6.2	37.8	1492.0	1.406
Tungsten	81.4	50	< 12	29.4	4.2	1.323
Uranium	< 360	250	< 62	< 64	19.5	4.026
Vanadium	445	667	< 2.5	12.3	35.5	0.473
Yttrium	11	43.2	< 1.1	< 1.2	1.7	0.073
Zinc	171	188978.4	25	45.7	6043.1	2.259
Mercury	< 1.4	< 0.98	< 0.24	< 0.25	0.076	0.080
Fluoride			Hg A1-35= (imp. 3+4)	< 2		
Chloride						

Table B-7

Gas Analysis Calculations: Stack Metals

Site:

Species:
Sample Date: 05-01-90
Sample ID: FCEM1-B1-31, 32,33 FCEM1-B1-34
Run Number: 1
Stream: Emitted Flue Gas

Particulate Loading (grains/dscf): 0.00517
Moisture (vol %): 8.20
Gas Volume Sampled (dscf): 35.2
Gas MW:
Flowrate (dscfh): 15500000

Species		Part, PNR (ug)		Impinger 1,2 (ug)	Concentrations: Particulate (ug/dscf)	Concentrations: Impingers (ug/dscf)
Aluminum		69		152	1.960	4.316
Antimony	<	10	<	11	0.284	0.313
Arsenic	B	1.2	<	0.45	0.034	0.013
Barium		13.8		1.32	0.392	0.038
Beryllium	<	0.2	<	0.22	0.006	0.006
Bismuth	<	80	<	90	2.273	2.557
Boron	<	60		265	1.705	7.528
Cadmium	B	0.5	<	0.56	0.014	0.016
Calcium		1200		289	34.091	8.210
Chromium		2.04	B	1.1	0.058	0.031
Cobalt	<	1	<	1.1	0.028	0.031
Copper	<	2	<	2.2	0.057	0.063
Gold		1810	<	22	51.420	0.625
Indium	<	20	<	22	0.568	0.625
Iron		783.6		52.4	22.261	1.489
Lead	B	0.3		0.72	0.008523	0.020
Lithium	<	2	<	2.2	0.057	0.063
Magnesium	<	100	<	110	2.841	3.125
Manganese		17.7		20.4	0.503	0.580
Molybdenum	B	5	<	5.6	0.142	0.159
Nickel	B	2	<	2.2	0.05682	0.063
Phosphorus	B	30	<	34	0.852	0.966
Platinum	<	20	<	22	0.568	0.625
Potassium	<	300	<	340	8.523	9.659
Selenium	<	20	<	0.56	0.568	0.016
Silicon	<	100		1025	2.841	29.119
Silver	<	1	<	1.1	0.028	0.031
Sodium	<	100		300	2.841	8.523
Strontium		19.4		1.55	0.551	0.044
Sulfur		1220		136000	34.659	3863.636
Tellurium	<	20	<	22	0.568	0.625
Thallium		13	<	11	0.369	0.313
Tin	<	60	<	67	1.705	1.903
Titanium		60.1	<	5.6	1.707	0.159
Tungsten	<	10	<	11	0.284	0.313
Uranium	<	50	<	56	1.420	1.591
Vanadium	<	2	<	2.2	0.057	0.063
Yttrium	<	0.9	<	1	0.026	0.028
Zinc	<	2		29	0.05682	0.824
Mercury	<	0.2	<	0.22	0.006	0.017
Fluoride		Hg for B1-35=	<	0.39		
Chloride						

Table B-8

Gas Calculations: Baghouse Inlet Anions

Species: Anions (F, Cl, SO4, PO4)
Sample Date: 05-01-90
Run Number:
Stream: Baghouse Inlet Flue Gas

Particulate Loading (grams/scf):
Moisture (vol %):
Impinger Gas Volume Sampled (dscf): 24.65
Filter Gas Volume Sampled (dscf): 32.88
Gas MW:
Flowrate (DSCFH): 15600000
Flowrate (lb/hr):

	FCEM1-A1-40	FCEM-A1-41	FCEM1-A1-42	FCEM1-A1-43	Concentrations	
Species	Particulate (mg)	PNR (mg)	Impinger 1 (mg)	Impinger 2 (mg)	Particulate (mg/dscf)	Impinger (mg/dscf)
Chloride	0.916		0.5168	0.3	0.028	0.033
Fluoride	0.058	NOT	< 0.0136	< 0.0125	0.0018	0.0011
Total Phosphate	< 0.0919	ANALYZED	< 0.00544	< 0.005	0.0026	0.0004
Sulfate	15.2		353.6	2.5	0.462	14.446

Table B-9

Gas Calculations: Stack Gas Anions

Species:	
Sample Date:	05-01-90
Run Number:	
Stream:	Emitted Flue Gas
Particulate Loading (grams/scf):	
Moisture (vol %):	
Impinger Gas Volume Sampled (dscf):	45.9
Filter Gas Volume Sampled (dscf):	54.74
Gas MW:	
Flowrate (DSCFH):	15500000
Flowrate (lb/hr):	

Concentrations

Species		Particulate (mg)	PNR (mg)		Impinger 1 (mg)		Impinger 2 (mg)	Part./PNR (mg/dscf)	Impinger (mg/dscf)
Chloride		0.124			0.9952		0.4471	0.0023	0.031
Fluoride	<	0.005	NOT	<	0.01556	<	0.01315	0.00009	0.00083
Total Phosphate	<	0.1164	ANALYZED	<	0.00622	<	0.00528	0.00213	0.00025
Sulfate		0.227			590.9		3.682	0.0041	12.954

Table B-10

Gas Analysis Calculations: Semivolatile Organics

Species:				
Sample Date:	05-01-90		05-01-90	
Run Number:				
Stream:	Baghouse Inlet Flue Gas		Emitted Flue Gas	
Particulate Loading (grams/scf):				
Moisture (vol %):				
Gas Volume Sampled (dscf):	31.7		132	
Gas MW:				
Flowrate (DSCFH):	15500000		15500000	
Flowrate (lb/hr):				
	Concentrations		Concentrations	
Species	Total (ug)	Total (ug/dscf)	Total (ug)	Total (ug/dscf)
Acenaphthalene	< 10.1	0.319	< 9.9	0.0750
Acenaphthylene	< 10.1	0.319	< 9.9	0.0750
4-Aminobiphenyl	< 10.1	0.319	< 9.9	0.0750
Anthracene	< 10.1	0.319	< 9.9	0.0750
Benzo(a)anthracene	< 10.1	0.319	< 9.9	0.0750
Benzo(a)pyrene	< 10.1	0.319	< 9.9	0.0750
Benzo(b)fluoranthene	< 10.1	0.319	< 9.9	0.0750
Benzo(g,h,i)perylene	< 10.1	0.319	< 9.9	0.0750
Benzo(k)fluoranthene	< 10.1	0.319	< 9.9	0.0750
p-Benzoquinone	< 100.8	3.180	< 99	0.7500
Butyl benzyl phthalate	< 10.1	0.319	< 9.9	0.0750
Chrysene	< 10.1	0.319	< 9.9	0.0750
Di-n-octyl phthalate	< 10.1	0.319	< 9.9	0.0750
Dibenzo(a,h)anthracene	< 10.1	0.319	< 9.9	0.0750
Dibenz(a,j)acridine	< 10.1	0.319	< 9.9	0.0750
Dibutyl phthalate	163	5.142	10.9	0.0826
1,4-Dichlorobenzene	< 10.1	0.319	< 9.9	0.0750
Diethyl phthalate	< 10.1	0.319	< 9.9	0.0750
p-Dimethylaminoazobenzene	< 10.1	0.319	< 9.9	0.0750
7,12-Dimethylbenz(a)anthracene	< 10.1	0.319	< 9.9	0.0750
2,4-Dimethyl phenol	< 10.1	0.319	< 9.9	0.0750
Dimethyl phthalate	< 10.1	0.319	< 9.9	0.0750
4,6-Dinitro-2-methylphenol	< 48	1.514	< 49.5	0.3750
1,3-Dinitrobenzene	< 10.1	0.319	< 9.9	0.0750
2,4-Dinitrotoluene	< 10.1	0.319	< 9.9	0.0750
2,6-Dinitrotoluene	< 10.1	0.319	< 9.9	0.0750
1,2-Diphenylhydrazine	< 10.1	0.319	< 9.9	0.0750
Bis(2-ethylhexyl)phthalate	62.4	1.968	20.8	0.1576
Fluoranthene	< 10.1	0.319	< 9.9	0.0750
Fluorene	< 10.1	0.319	< 9.9	0.0750
Hexachlorobenzene	< 10.1	0.319	< 9.9	0.0750
Hexachloro-1,3-butadiene	< 10.1	0.319	< 9.9	0.0750
Hexachloroethane	< 10.1	0.319	< 9.9	0.0750
Indeno(1,2,3-cd)pyrene	< 10.1	0.319	< 9.9	0.0750
3-Methylcholanthrene	< 10.1	0.319	< 9.9	0.0750
2-Methylnaphthalene	< 10.1	0.319	< 9.9	0.0750
3-Methylphenol	< 10.1	0.319	< 9.9	0.0750
2-Methylphenol	< 10.1	0.319	< 9.9	0.0750
4-Methylphenol	< 10.1	0.319	< 9.9	0.0750
N-Nitroso-di-n-butylamine	< 10.1	0.319	< 9.9	0.0750
N-Nitrosodiethylamine	< 10.1	0.319	< 9.9	0.0750
N-Nitrosodimethylamine	< 10.1	0.319	< 9.9	0.0750
N-Nitrosodipropylamine	< 10.1	0.319	< 9.9	0.0750
N-Nitrosomorpholine	< 10.1	0.319	< 9.9	0.0750
N-Nitrosopiperidine	< 10.1	0.319	< 9.9	0.0750
NiNitrosopyrrolidine	< 10.1	0.319	< 9.9	0.0750
Naphthalene	< 10.1	0.319	< 9.9	0.0750
1-Naphthylamine	< 10.1	0.319	< 9.9	0.0750
1,4-Naphthaquinone	< 10.1	0.319	< 9.9	0.0750
Nitrobenzene	< 10.1	0.319	< 9.9	0.0750
2-Nitrophenol	< 10.1	0.319	< 9.9	0.0750
4-Nitrophenol	< 48	1.514	< 49.5	0.3750
Pentachlorophenol	< 48	1.514	< 49.5	0.3750
Phenanthrene	< 10.1	0.319	< 9.9	0.0750
Phenol	< 10.1	0.319	< 9.9	0.0750
2-Picoline	< 10.1	0.319	< 9.9	0.0750
Pyrene	< 10.1	0.319	< 9.9	0.0750
Pyridine	< 10.1	0.319	< 9.9	0.0750
Resorcinol	< 48	1.514	< 49.5	0.3750
o-Toluidine	< 10.1	0.319	< 9.9	0.0750
2,4,5-Trichlorophenol	< 48	1.514	< 49.5	0.3750
2,4,6-Trichlorophenol	< 10.1	0.319	< 9.9	0.0750

Table B-11

Gas Analyses Calculations: Aldehydes

Sample Date:			05-01-90		05-01-90	
Run Number:						
Stream:			Baghouse Inlet Flue Gas		Emitted Flue Gas	
Particulate Loading (grams/scf):						
Moisture (vol %):						
Gas Volume Sampled (dscf):			8.23		8.84	
Gas MW:						
Flowrate (DSCFH):			15500000		15500000	
Flowrate (lb/hr):						
Flow Rate Error (+/- 2 std dev)						
			Concentrations		11% Concentrations	
Species			Total (ug)	Total (ug/dscf)	Total (ug)	Total (ug/scf)
Formaldehyde	NOTE: SUSPECT RESULTS, FIELD BLANK	<B	3.6	0.437	<B 3.6	0.407
Acetaldehyde	RESULTS APPROX 5X SAMPLES	<B	4.3	0.522	<B 4.3	0.486
	156, 119 ug RESPECTIVELY					

Table B-12

Gas Analyses Calculations: Nitrosamines

Species:	Nitrosamines		
Sample Date:		05-01-90	05-01-90
Run Number:			
Stream:		Baghouse Inlet Flue Gas	Emitted Flue Gas
Particulate Loading (grams/scf):			3.29
Moisture (vol %):			15500000
Gas Volume Sampled (dscf, 60 F, 29.92" Hg):			11%
Gas MW:			
Flowrate (DSCFH):			
Flowrate (lb/hr):			
Flowrate Error (+/- 2 std dev)			

Species		Concentrations					
		Total (ug)	Total (ug/scf)	Total (mg/Nm3)	Total (lb/hr)	Total (ug)	Total (ug/dscf)
N-nitrosodiethylamine						0.61	0.185
N-nitrosodimethylamine						1.31	0.398
N-nitrosodipropylamine	<					1	0.304
N-nitrosomorpholine	<					2	0.608
N-nitrosopiperidine	<					2	0.608
N-nitrosopyrrolidine	<					2	0.608
		NOT SAMPLED					

Table B-13

December 8, 1990

Canister Sample Results - Stack Gas

Sample ID	Benzene (ppbv)	TNMHC [a] (ppbv)
CU-003	1.7	186
CU-004 [b]	0.2	278
CU-006	0.3	264
CU-007 [b]	0.5	444
CU-015	1.5	1084
CU-016 [b]	0.8	432
CU-018	1.3	568
CU-019 [b]	2.2	588
CU-024	NR(0.2) [c]	226
CU-025 [b]	NR(0.2) [c]	238

[a]Total nonmethane hydrocarbons.

[b]Duplicate sample.

[c]Not reported; reporting limit in parentheses.

Table B-14

December 8, 1990

Canister Sample Results - Fabric Filter Inlet

Sample ID	Time, Hours From Start	Benzene (ppbv)	TNMHC [a] (ppbv)
CU-005	1	1.2	204
CU-010A	3	1.1	280
CU-010B	3	4.3	4120
CU-010C	3	3.0	412
CU-011A [b]	3	1.6	1008
CU-011B	3	1.5	836
CU-020	5	1.1	598

[a]Total non-methane hydrocarbons.

[b]Duplicate of CU-010C.

Appendix C

Summary of Stream Flows

Table C-1

Stream Flow Rate Distribution for the Site 10 CFBC Process

Stream	Stream Flow Rate (Dry Basis)	Concentration[a]	Component Flow Rate (lb/hr)
Inlet Streams			
Coal	108,626 lb/hr	--	--
Ash		17 wt%	18,500
Unreacted Coal		2 wt%	2,200
Sulfur (as SO_3)		0.53 wt%	1,100
Limestone	8,252 lb/hr	--	
Limestone (as CaO)		--	4,600
Intermediate Streams			
Air Heater, Economizer Ash		--	2,200[f]
Baghouse Inlet Gas	15,500,000 dscfh	--	
Ash[b]		10.83 gr/dscf	24,000[f]
Outlet Streams			
Bottom Ash (bed material)	1,760 lb/hr	--	1,760
Collected Ash[c]	26,170 lb/hr	--	26,170
Stack Gas[e]	15,500,000 dscfh	--	
Ash		0.00517 gr/dscf	11.5

[a] wt% = percent by weight on dry basis; gr/dscf = grains per dry standard cubic feet.

[b] Baghouse inlet flow does not include economizer ash or air heater ash.

[c] Collected ash includes baghouse ash, economizer ash, and air heater ash calculated from ash balance and known bottom ash discharge rate.

[d] dscfh = dry standard cubic feet per hour.

[e] Calculated as difference between calculated ash rate and measured baghouse inlet rate.

[f] Measured

Appendix D

Quality Assurance and Quality Control

As part of the FCEM project, Quality Assurance/Quality Control (QA/QC) procedures are conducted to ensure specific data needs of the projects are met. The primary objectives of the QA/QC effort are to control, assess, and document data quality. To achieve these objectives, the QA/QC program is used to assess data quality in terms of precision and accuracy and to control data quality within prescribed limits of acceptability.

To assess and control data quality, the QA/QC approach has three key elements:

- Data quality objectives;
- QA/QC in sample collection, analyses, and data analysis; and
- Corrective action when pre-established specifications are not met.

Based on this general QA/QC approach, a project-specific QA/QC program was developed for the FCEM project. The following sections describe the details of the QA/QC program and present the results for the tests conducted at the Site 10 CFBC unit.

Data Quality Objectives

Specific data quality objectives (DQOs) for each of the measurement properties of interest are provided in Table D-1. These DQOs are specified in terms of precision, accuracy, and completeness of the measurement data. Sampling, analytical, QC, and data analysis procedures capable of meeting these objectives are used for this project. Precision and bias estimates for analysis of samples are based on results of spiked samples, duplicate samples, duplicate analyses, and QC check samples. The difference between duplicate sample results will provide a measure of total sampling and analytical variability; whereas, results for duplicate analyses will provide a measure of analytical variability. Precision values shown in the table represent a measure of variability for replicate measurements of the same parameter, expressed in terms of the relative percent difference. Accuracy includes components of both random error (i.e., variability due to imprecision) and systematic error (i.e., bias), and thus reflects the total error for a single measurement, expressed as percentage of the true value. For this project, accuracy is determined from matrix spike recoveries.

Sampling and Analytical QC

Table D-2 presents the QC procedures associated with the various sampling and analytical efforts which provide the basis for control and assessment of data quality. Also given are the frequency, acceptance criteria, and corrective action for each QC check. The internal QC procedures for this project can be divided into two categories: sampling QC procedures and analytical QC procedures. For this program, sampling QC procedures included the collection of field blanks for each type of sample collection procedure and collection of duplicate samples. Analytical QC procedures consisted of

Table D-1

Data Quality Objectives for the FCEM Project

Measured Parameter	Method	Precision [a] (%)	Accuracy [b] (%)	Data Capture [c]
Volatile Organic Compounds	8240	See Method	See Method	90%
Semivolatile Organic Compounds	8270	See Method	See Method	90%
Formaldehyde	HPLC	NS[d]	NS	90%
Metals	ICAPES	<20	75 - 125	90%
Metals	GFAAS	<20	75 - 125	90%
Metals	HGAAS	<20	75 - 125	90%
Mercury	CVAAS	<20	75 - 125	90%
Chloride	Ion Chromatography	<20	75 - 125	90%
Fluoride	Selective Ion Electrode	<20	75 - 125	90%
Sulfate	Ion Chromatography	<20	75 - 125	90%
Phosphate	Colorimetry	<20	75 - 125	90%

[a]Precision calculated based on duplicate laboratory analyses and expressed as relative percent difference $100(|X_1-X_2|)/\bar{X}$ where $\bar{X}$ = mean and X_1 and X_2 are replicate measurements).

[b]Accuracy based on percent recovery of known additions (i.e., spikes). Recovery is a function of sample matrix.

[c]Valid data percentage of the total tests conducted.

[d]NS = Not specified.

analytical instrument calibrations, instrument checks, system and analytical method blanks, spiked samples, and duplicate analyses.

Field Blank Results

Matched matrix field blanks were collected once for each of the gas stream analyses (e.g., metals train, anions train, etc.). Field blanks do not apply to solid samples. Results for field blanks were used to monitor contamination in the sample handling process. Overall, results for the field blanks were acceptable; however, analyses indicated potential contamination in some field blank samples which may bias gas sample results. Details of the field blank analyses are discussed in the following paragraphs.

Metals Train. The field blank for the metals train was collected at the baghouse inlet location. Concentrations greater than five times the reporting limit (based on the instrument reporting limit and a sample dissolution volume of 100 mL) were reported in the front half blank sample (filter plus probe and nozzle rinse 1 and 2) for the elements listed in Table D-3. Element concentrations in the back half blank sample (impingers 1 and 2) were all less than five times the reporting limit for all elements except manganese. The field blank data suggest that results for this element in the baghouse inlet and outlet samples (front half only) may be biased high. The relatively large amounts of material found in the field blank undoubtedly come from the filter used to collect the suspended particulate matter. The microwave digestion technique used to bring the particulate matter into solution was applied to the filter used to collect the particulate matter as well as the particulate matter itself.

Anions. Chloride was found in the thimble filter from the field blank at levels greater than five times the reporting limit. This indicates that the measured chloride concentrations for the thimble filter and the associated particulate collected at the inlet to the baghouse may be biased high.

Formaldehyde. Formaldehyde was found in the field blank at levels approximately 30 times the reporting limits. This indicates potential contamination of the DNPH impinger solution or contamination of the sampling apparatus during equipment preparation. This substance also was found in the flue gas samples collected at the baghouse inlet and outlet locations; however, concentrations in the samples were five to six times lower than concentrations in the field blank (approximately 23 μg in the samples versus 156 μg in the field blank). Since the results for the field blank are high and only one set of flue gas samples could be collected, the results for both the inlet and outlet gas samples should be considered questionable.

Analytical Quality Control

Analytical quality control procedures included instrument calibrations, instrument QC check samples, system and analytical method blanks, spiked samples, and duplicate analyses.

Table D-2

Summary of Quality Control Objectives for the Analytical Methods

Property/Test	Quality Control Check	Frequency	Quality Objective	Corrective Action	Comments
Volatile Organic Compounds (GC/MS Method 8240)	Mass scale calibration using PFTBA	Daily before sample analyses	Refer to method	Repeat calibration	
	Check of mass spectral ion intensities using BFB	Daily before sample analyses	Refer to method	Re-tune instrument, repeat BFB analysis	
	Surrogate spikes	Every sample	Refer to method	Flag data	
	System performance check compounds	Every 12 hours	RF ≥0.300 (0.250 for bromoform)	1) Evaluate system 2) Repeat calibration	
	Calibration check compounds	Every 12 hours	Relative percent difference <30%	1) Evaluate system 2) Repeat calibration	
	Internal standard	All samples	Based on acceptability tests (refer to method)	Flag results as outside data control limits	
	System Blank	Daily	<5 x DL for any target compound	1) Clean system 2) Rerun Blank	
	Spiked sample analysis (MS/MSD)	5% or at least 1 MS/MSD per batch	Refer to Method	1) Run check standard 2) Correct problem 3) Flag data	
	Duplicate Samples	One set for each matrix type	None	None	Used to determine overall variability
	Duplicate Analyses	Duplicate analyses on duplicate samples	None	None	Used to separate components of variability
Semivolatile Organic Compounds (GC/MS Method 8270)	Mass scale calibration with PFTBA	Daily before sample analyses	Refer to method	Repeat calibration	
	DFTPP relative ion abundance check	Daily before sample analyses	Refer to method	Repeat calibration	
	Internal standard check	Daily before sample analyses	Refer to method	Re-tune instrument, repeat	
	System performance check compounds	Every 12 hours	Refer to method	1) Evaluate system 2) Take corrective action 3) Repeat test 4) See lab manager	
	Surrogate spike	All samples	Based on acceptability tests (refer to method)	Flag results as outside data control limits	

Table D–2

(Continued)

Property/Test	Quality Control Check	Frequency	Quality Objective	Corrective Action	Comments
Semivolatile Organic Compounds (GC/MS Method 8270) (Continued)	Extraction blank	Daily before sample analysis	Refer to method	1) Clean system 2) Repeat blank analysis	
	Spiked sample analysis (MS/MSD)	5% or at least 1 MS/MSD per batch	Refer to method	1) Run check standard 2) Correct problem 3) Flag data	
	Duplicate Samples	One set for each matrix type	None	None	Used to determine overall variability
	Duplicate Analyses	Duplicate analyses on duplicate samples	None	None	Used to separate components of variability
Formaldehyde/ Acetaldehyde HPLC	Method blank	10% or minimum of 1 per sample set	None	None	Used to indicate analytical contaminants
	Matrix spike/matrix spike duplicate on DNPH blank	One MS/MSD per matrix type	None	None	Used to determine accuracy and precision
	Duplicate Samples	One set for each matrix type	None	None	Used to determine overall variability
	Duplicate analyses	Duplicate analyses on duplicate samples	None	None	Used to separate components of variability
Metals ICP-AES (Method SW 6010) (Ag, Ba, Be, Cd, Cr, Co, Cu, Mn, Mo, Ni, Sb, Sn, V, Zn)	Mixed standard calibration plus blank	Daily	Standard within 95-105% of true value	Repeat calibration	
	QC check sample	10% or minimum of 1 per batch	Measured value within 90-110% of true value for element of interest	Repeat calibration	Used to verify calibration accuracy
	Method blank	10% or minimum of 1 per batch	≤5 x method reporting limit	1) Repeat test, average results 2) Evaluate system 3) Recalibrate	Used to report contamination
	Matrix spike analysis	5% or minimum of 1 per batch	Recovery within 75-125%	Flag data	
	Matrix spike duplicate	5% or minimum of 1 per batch	RPD <20%	Flag data	

Table D-2

(Continued)

Property/Test	Quality Control Check	Frequency	Quality Objective	Corrective Action	Comments
Metals ICP-AES (Method SW 6010) (Continued)	Duplicate samples	One set for each matrix type	None	None	Used to determine overall variability
	Duplicate analyses	Duplicate analyses on duplicate samples	None	None	Used to separate components of variability
	ICP interference check	Run at beginning, middle, and end of daily run	80-120% of true value for EPA check sample elements	1) Repeat calibration 2) See Lab Manager	
	ICP linear range check	Quarterly	Measured value within 85-115% of expected value	Tests upper limit of linear range	
	LOD check	Quarterly	≤current LOD	Used to verify current LOD	
Metals by Graphite Furnace and Hydride Generation Arsenic SW 7060/7061 Cadmium SW 7181 Lead SW 7421 Selenium SW 7740/7741	Multipoint calibration	Daily, before analyses	r ≥0.995	Repeat calibration	
	QC check sample	10% or minimum of 1 per batch	Measured value within 85-115% of expected value	1) Repeat test 2) Repeat calibration and test 3) See Lab Manager	
	Method blank	10% or minimum of 1 per batch	≤5 x method reporting limit	Used to indicate analytical contaminants; reanalyze	Used to indicate analytical contaminants
	Matrix spike analysis	5% or minimum of 1 per batch	Recovery within 75-125%	Flag data	
	Matrix spike duplicate analysis	5% or minimum of 1 per batch	RPD <20%	Flag data	
	Duplicate samples	One set for each matrix type	None	None	Used to determine overall variability
	Duplicate analyses	Duplicate analyses on duplicate samples	None	None	Used to separate components of variability
	LOD check	Quarterly	≤ current LOD	Used to verify current LOD	

Table D-2

(Continued)

Property/Test	Quality Control Check	Frequency	Quality Objective	Corrective Action	Comments
Mercury by Cold Vapor - AAS Mercury SW 7470	Multipoint calibration	Daily, before analyses	r ≥0.995	Repeat calibration	
	QC check sample	10% or minimum of 1 per batch	Measured value within 80-120% of expected value	1) Repeat test 2) Repeat calibration and test 3) See Lab Manager	
	Method blank	10% or minimum of 1 per batch	≤10 x method reporting limit	Used to indicate analytical contaminants; reanalyze	Used to indicate analytical contaminants
	Matrix spike analysis	5% or minimum of 1 per batch	Recovery within 75-125%	Flag data	
	Matrix spike duplicate analysis	5% or minimum of 1 per batch	RPD <20%	Flag data	
	Duplicate samples	One set for each matrix type	None	None	Used to determine overall variability
	Duplicate analyses	Duplicate analyses on duplicate samples	None	None	Used to separate components of variability
	LOD check	Quarterly	≤ current LOD	Used to verify current LOD	
Anions by IC Chloride, Sulfate	Calibration - multipoint, at least 3 concentrations	Daily	Correlation coefficient ≥0.995 (0.9995 for sulfate)	Repeat calibration	
	Control sample	10% or a minimum of 1 in each sample set	Recovery between 90% and 110%	Repeat control sample analysis, repeat calibration	
	Duplicate samples	One set for each matrix type	None	None	Used to determine overall variability
	Duplicate analyses	10% or a minimum of 1 per batch. Duplicate analyses for duplicate samples.	Replicate analysis RPD ≤10%	Repeat sample analysis	
	Field blank for impinger samples	1 per trip	None	None	Used to determine ambient background concentration
	Spiked sample analysis	10% or a minimum of 1 per matrix type	Spike recovery between 80% and 120%	Appropriate dilution and repeat spike analysis	

Table D-2

(Continued)

Property/Test	Quality Control Check	Frequency	Quality Objective	Corrective Action	Comments
Fluoride by Ion Selective Electrode (EPA Method 340.2)	Multipoint calibration	Daily, before analyses	r ≥0.995	Repeat calibration	
	QC check sample	10% or minimum of 1 per batch	90-110% of expected value	Repeat calibration	
	Laboratory blank	10% or minimum of 1 per batch	≤5 x method reporting limit	Reanalyze	
	Duplicate samples	One set for each matrix type	None	None	Used to determine overall variability
	Duplicate analyses	10% or minimum of 1 per batch. Duplicate analyses for duplicate samples.	RPD <10%	1) Obtain 3rd value 2) Flag data	
	Matrix spike	10% or minimum of 1 per batch	85-115% of expected value	Dilute sample and repeat analysis; increase amount of TISB	
Phosphate, Total, by Spectrophotometry (EPA Method 365.2)	Multi-point calibration	Daily, before analysis	r≥ 0.995	Repeat calibration	
	QC check sample	Daily and at least 1 per 15 samples	Recovery between 90-110%	Repeat calibration	
	Method blank	1 per day	<1.5 x reporting limit	Find contamination source; repeat analyses	
	Duplicate samples	5%	NA	Will be used to determine sampling/ analytical variability	
	Duplicate analyses	Duplicate analyses for duplicate samples	None	None	Used to separate components of variability
	Spiked sample analyses (MS/MSD)	Daily and 1 per 20 samples	Spike recovery between 80-120%, relative percent difference (RPD) ≤20%	Repeat spike analysis/use method of standard additions	

Table D-3

Elements Present in the Metals Train Filter Plus Probe/Nozzle Rinse Field Blank at Greater than Five Times the Instrument Reporting Limit

Element	Amount (Total μg)	Instrument Reporting Limit (μg)[a]
Aluminum	1010	20
Cadmium	3.04	0.50
Calcium	1780	100
Iron	50.4	4.0
Lead	1.52	0.30
Nickel	99.8	2.0
Silicon	234,000	100
Sodium	4290	100
Strontium	3.50	0.30
Zinc	21.6	2.0

[a]Based on instrument reporting limit concentration and 100 mL dissolution volume of solids.

Instrument Calibrations. Standards of known concentration were used to prepare calibration standards for use in calibrating a particular instrument before conducting the sample analysis. Instrument calibrations were performed according to the specifications listed in Table D-2.

Instrument QC Check Samples. One type of standard analytical QC check performed during this project was to analyze one or more applicable standards obtained from an independent source before analyzing any of the samples. This was done to verify the acceptability of the calibration curve data. If the concentration of the independent calibration QC sample, as determined from the analysis, matched the reported concentration within the value listed in Table D-2, analysis of the samples proceeded and the calibration curve data were used to determine the concentration of the samples. But, if the independent calibration standards was outside the acceptable limit of $\pm$ 10%, a new set of calibration standards was prepared and the above process was repeated until an acceptable calibration curve was generated.

Method Blanks. Method blanks were analyzed for each type of sample matrix to monitor contamination in the analytical system and the reagents used to prepare samples. Results for method blanks were acceptable with the following exceptions:

- Sodium was reported in the method blank for bottom ash and fly ash major metals analysis performed by the lithium borate digestion procedure. A sodium concentration of 14,770 μg/g was reported which is significantly greater than the reporting limit of 1,000 μg/g.

Spiked Samples. Another standard analytical QC check performed during this program was spiking a sample or spiking a blank reagent with the species of interest before analysis. Spiked samples are referred to as matrix spikes and spiked blank reagents are termed method spikes. Results of the analysis of the spiked and unspiked samples are used to determine the percentage of the spike recovered from the sample, thus providing an indication of the accuracy of a particular analytical method. Problems in recovering the mass of the species spiked into a particular sample usually indicates an error on the part of the analyst or the presence of matrix effects when using that analytical method. Method spikes provide an indication of contamination in the reagents used to prepare the samples or problems in recovering a particular species from the blank reagent.

Samples to be spiked were randomly selected (10% of all samples). The acceptance criteria for spike recoveries, listed previously in Table D-2, varied depending on the type of analysis. The acceptance criteria are applicable for larger sets of spike recoveries and not any individual recovery value. However, poor individual recoveries are used as an indication of possible bias. (The reverse is not true; good spike recovery for an individual spike does not ensure the absence of bias.) Spike recoveries greater than the upper control limit indicate a potential high bias in the sample results, while recoveries less than the lower limit indicate a possible low bias. Spike recoveries which were outside control limits are listed in Table D-4 and discussed below.

Table D-4

Summary of Spike Recoveries Which Were Outside Control Limits (Matrix Spikes and Method Spikes)

Sample Type/Substance	Analytical Method[a]	Acceptable Recovery (%)	Spike (%)	Spike Duplicate (%)
Metals Train (front half)[b]				
Selenium	GFAAS	75-125	66	50
Cadmium	Perchloric, ICP-AES	75-125	62	68
Potassium	Perchloric, ICP-AES	75-125	150	159
Limestone Metals[c]				
Boron	Perchloric, ICP-AES	75-125	63	70
Cadmium	Perchloric, ICP-AES	75-125	72	76
Nickel	Perchloric, ICP-AES	75-125	74	79
Zinc	Perchloric, ICP-AES	75-125	66	70
Arsenic	GFAAS	75-125	141	93[d]
Lead	GFAAS	75-125	90[d]	71
Selenium	GFAAS	75-125	29	29
Bottom Ash Metals[c]				
Silver	Perchloric, ICP-AES	75-125	95[d]	62
Fly Ash Metals[c]				
Antimony	Perchloric, ICP-AES	75-125	75	72
Boron	Sodium Carbonate, ICP-AES	75-125	96[d]	78

[a] GFAAS = Graphite furnace atomic absorption spectroscopy.
Perchloric acid = Perchloric acid digestion procedure followed by ICP-AES analysis.
Sodium carbonate = Sodium carbonate fusion followed by ICP-AES analysis.
IC = Ion chromatography.
8270 = GC/GC MS analysis according to Method 8270.

[b] Results of method spike and method spike duplicate.

[c] Results of matrix spike and matrix spike duplicate.

[d] Result within acceptable limits, shown for comparison.

Elements. Method spike and method spike duplicate recoveries were low for selenium (analyzed by GFAAS) and cadmium in the method blank associated with analysis of the front half metals train samples. This indicates that concentrations reported for these elements in the front half samples collected at the inlet and outlet gas locations may be biased low. Method spike results for potassium were high indicating a possible high bias for potassium analyses in the front half metals train samples. Matrix spike recoveries that were outside control limits for metals analyses in limestone samples are summarized in Table D-4. A high recovery was reported for arsenic (by GFAAS) in one of the two analyses. Recoveries were low for cadmium, lead (by GFAAS), nickel, and selenium (by GFAAS).

Surrogate Spiked Samples. All MM5 samples for semivolatiles were spiked with surrogate compounds. MM5 samples were spiked in the lab before analysis. The following compounds were used as surrogate spikes (control limits are shown in parentheses):

- MM5 Semivolatiles--2-fluorobiphenyl (30 to 115%), 2-fluorophenol (25 to 121%), nitrobenzene-d5 (23 to 120%), phenol-d5 (24 to 113%), terphenyl-d14 (18 to 137%), and 2,4,6-tribromophenol (19 to 122%).

MM5 surrogate recoveries were within acceptable limits for all compounds.

Duplicate Analyses. Duplicate analyses are performed to measure the precision of the analytical method. Random duplicate analyses (10% of samples collected) were usually in the form of matrix spike duplicate analyses (MSD). Duplicate analyses of a coal sample were performed since MS/MSD analyses are not appropriate for NAA analyses. Results from duplicate analysis are used to track the ongoing precision performance of the laboratory.

$$RPD = \frac{|(X_1 - X_2)| \times 100}{(X_1 + X_2) / 2}$$

where: X_1 = the result of the first analysis; and

X_2 = the result of the second analysis.

Acceptance criteria for duplicate analyses, listed previously in Table D-2, varied depending on the type of analysis. Analyses which did not meet acceptance criteria are summarized in Table D-5 and discussed below. RPD for all other duplicate analyses were within acceptable limits.

Elements. The results of the method spike and method spike duplicate were used to assess the precision of the analyses for the front and back half metals train samples.

Table D-5

Summary of Results for Duplicate Analyses Which Did Not Meet Data Quality Acceptance Criteria

Sample Type/Substance	Analytical Method [a]	Acceptable RPD [b] (%)	First Result	Second Result	Relative Percent Difference (%)
Metals Train (front half)					
Selenium [c]	GFAAS	≤20	66.4%	50.4%	27
Coal Metals					
Zinc [d]	NAA	≤20	8.06 μg/g	10.2 μg/g	23
Limestone Metals					
Arsenic [c]	GFAAS	≤20	141%	93%	41
Lead [c]	GFAAS	≤20	90%	71%	24

[a]GFAAS = Graphite furnace atomic absorption spectroscopy.
NAA = Neutron activation analysis.
Lithium borate = Lithium borate digestion procedure.
Perchloric = Perchloric acid digestion procedure.
SIE = Selective ion electrode. 8270 = GC/GCMS analysis by method 8270.

[b]RPD = Relative percent difference.

[c]Results for matrix spike and matrix spike duplicate expressed as percent recovery.

[d]Results for duplicate analyses expressed as a measured concentration.

The RPD for selenium analyses (by GFAAS) in the front half method spikes was slightly outside the acceptable limit of ≤ 20% (RPD=27%).

Coal samples were analyzed in duplicate by neutron activation. Precision was within acceptable limits for all elements with the exception of zinc (RPD = 24%).

RPDs for arsenic (by GFAAS, RPD=41%) and lead (by GFAAS, RPD=24%) analyses in limestone samples were outside the acceptable limit of ≤ 20% based on the results of the matrix spike and matrix spike duplicate.

RPDs calculated from MS/MSD metals analyses for bottom ash and fly ash were ≤ 20 percent. Duplicate analyses were acceptable for both the perchloric acid and lithium borate digestion procedures.

Anions. No duplicate or matrix spike/matrix spike duplicate analyses were performed for anions (fluoride, chloride, sulfate, and phosphate) in the inlet or outlet gas samples.

Duplicate analyses of limestone, bottom ash, and fly ash samples indicate low precision for fluoride (RPDs >25%). RPDs calculated based on matrix spike/matrix spike duplicate analyses (MS/MSD) were within acceptable limits for all anions in solid samples.

Duplicate Samples. Duplicate samples of coal, limestone, bottom ash, and fly ash were collected and analyzed to determine overall sampling and analytical variability. Although there are no prescribed acceptance criteria for duplicate samples, results were generally in close agreement (RPDs ≤ 20%).

Additional Analytical QC Checks. In addition to the analytical QC procedures discussed above, QC checks were performed for the lithium borate and perchloric acid metals digestion procedure and the NAA coal analyses. Each of these is briefly discussed below.

Lithium Borate and Perchloric Acid Digestion. Lithium borate and perchloric acid (PAD) digestion followed by ICP-AES analysis was performed on the bottom ash and fly ash samples to determine the concentration of major elements (i.e., aluminum, calcium, iron, magnesium, potassium, silicon, and titanium). Lithium borate digestion is considered the best technique for determining major element concentrations in this type of sample matrix. A reliable indicator of the data quality for both digestion procedures is the closure of the metal oxide balance for the sample. Tables D-6 and D-7 present the metal oxide content (determined by lithium borate digestion) of the bottom ash and fly ash samples, respectively. The oxide content is calculated based on the assumption that these elements exist as metal oxides in the ash samples.

Closures for the two bottom ash analyses (68 and 80%) and the two fly ash analyses (61%) are lower than expected, which suggests the major element data for these

Table D-6

Calculated Element Oxide Content of Bottom Ash Samples Prepared by Lithium Borate Digestion Procedure

	Elemental Concentration (mg/kg)			Element Oxide Concentration (wt %)	
Element	Bottom Ash	Bottom Ash Duplicate	Element Oxide	Bottom Ash	Bottom Ash Duplicate
Silicon	72,300	118,000	SiO_2	15.50	25.20
Aluminum	97,253	96,400	Al_2O_3	18.40	18.20
Iron	9,180	9,160	Fe_2O_3	1.30	1.31
Calcium	142,000	147,000	CaO	19.90	20.60
Magnesium	4,230	4,450	MgO	0.70	0.74
Potassium	5,540	5,660	K_2O	0.67	0.68
Sodium	0	0	Na_2O	0.00	0.00
Sulfur	47,500	51,667	SO_3	11.90	12.90
Titanium	2,020	2,090	TiO_2	0.34	0.35
		Total		68.60	80.00
		Undetermined		31.40	20.00

Table D-7

Calculated Element Oxide Content of Fly Ash Samples Prepared by Lithium Borate Digestion Procedure

	Elemental Concentration (mg/kg)			Element Oxide Concentration (wt %)	
Element	Fly Ash	Fly Ash Duplicate	Element Oxide	Fly Ash	Fly Ash Duplicate
Silicon	74,500	69,200	SiO_2	15.90	14.80
Aluminum	98,468	96,939	Al_2O_3	18.60	18.30
Iron	8,200	8,010	Fe_2O_3	1.17	1.15
Calcium	118,000	115,000	CaO	16.50	16.10
Magnesium	3,430	3,360	MgO	0.57	0.56
Potassium	3,950	3,670	K_2O	0.47	0.44
Sodium	0	0	Na_2O	0.00	0.00
Sulfur	30,000	35,000	SO_3	7.50	8.75
Titanium	3,950	3,830	TiO_2	0.66	0.64
		Total		61.40	60.70
		Undetermined		38.60	39.20

samples is biased low. Incomplete digestion of the solids is probably the reason for the low metal oxide closures.

Element oxide data and concentrations for major elements determined by the perchloric acid digestion procedure are presented in Tables D-8 and D-9. The concentration of major elements in the bottom ash and fly ash are higher for the samples prepared by PAD compared to the samples prepared by lithium borate digestion. This indicates that the PAD procedure provided a more complete digestion; therefore, analytical results from the PAD procedure were used in the material balance calculations (except for silicon).

Results from the lithium borate digestion procedure were used for silicon since the perchloric digestion procedure is not designed to measure silicon quantitatively. The low silicon concentration also explains the low closure of the metal oxide balance for the PAD results.

NBS Coal Standards. One National Bureau of Standards (NBS) coal standard was analyzed in conjunction with the coal samples as a QC check for the NAA procedure. All element concentrations determined by NAA analysis of the NBS standard were within the limits specified for the standard as shown in Table D-10.

Table D-8

Calculated Element Oxide Content of Bottom Ash Samples Prepared by Perchloric Acid Digestion

	Elemental Concentration (mg/kg)			Element Oxide Concentration (wt %)	
Element	Bottom Ash	Bottom Ash Duplicate	Element Oxide	Bottom Ash	Bottom Ash Duplicate
Silicon	515	2,868	SiO_2	0.11	0.61
Aluminum	105,032	106,590	Al_2O_3	19.80	20.10
Iron	10,017	10,320	Fe_2O_3	1.40	1.50
Calcium	150,144	154,379	CaO	21.00	21.60
Magnesium	4,879	4,983	MgO	0.81	0.83
Potassium	6,596	6,770	K_2O	0.79	0.82
Sodium	3,638	3,730	Na_2O	0.49	0.50
Sulfur	19,860	20,314	SO_3	5.00	5.10
Titanium	2,181	2,227	TiO_2	0.36	0.37
		Total		49.80	51.40
		Undetermined		50.10	48.60

Table D-9

Calculated Element Oxide Content of Fly Ash Samples Prepared by Perchloric Acid Digestion

	Elemental Concentration (mg/kg)			Element Oxide Concentration (wt %)	
Element	Fly Ash	Fly Ash Duplicate	Element Oxide	Fly Ash	Fly Ash Duplicate
Silicon	332	2,963	SiO_2	0.07	0.63
Aluminum	109,368	111,332	Al_2O_3	20.70	21.00
Iron	9,329	96	Fe_2O_3	1.30	0.01
Calcium	131,518	134,085	CaO	18.40	18.80
Magnesium	4,066	4,119	MgO	0.67	0.68
Potassium	4,888	4,903	K_2O	0.59	0.59
Sodium	2,996	3,073	Na_2O	0.40	0.41
Sulfur	13,727	14,078	SO_3	3.40	3.52
Titanium	4,341	4,456	TiO_2	0.72	0.74
		Total		46.30	46.40
		Undetermined		53.70	53.60

Table D-10

Analyses of NBS Coal Standard by NAA

Species	NBS SRM 1632-A (ppmw)	Certified Values (ppmw)	Certified Error Limit (ppmw)
FCEM Elements			
Arsenic	9.6212	9.3+/-	1.00
Barium	122.11	120+/-	15.00
Beryllium	NA	NA	
Cadmium	< 4.2625	0.17+/-	0.02
Chlorine	765.18	756+/-	30.00
Chromium	34.903	34.3+/-	1.50
Cobalt	6.8177	6.7+/-	0.40
Copper	< 25	16.5+/-	10.00
Fluoride	NA	NA	
Lead	NA	NA	
Manganese	28.08	28+/-	2.00
Mercury	< 0.25	0.13+/-	0.03
Molybdenum	< 2.3237	NS	
Nickel	< 33.963	19.4+/-	1.00
Phosphorous	NA	NA	
Vanadium	44.098	44+/-	3.00
Additional Elements			
Aluminum	29679	29500+/-	1000.00
Antimony	0.6207	0.6+/-	0.05
Boron	NA	NA	
Calcium	2452.3	2410+/-	170.00
Iron	11295	11100+/-	200.00
Lithium	NA	NA	
Magnesium	1157.8	1150+/-	225.00
Potassium	NA	NA	
Selenium	2.6457	2.6+/-	0.70
Silicon	NA	NA	
Silver	< 1.52	0.30+/-	NS
Sodium	856.6	828+/-	77.00
Strontium	NA	NA	
Tin	NA	NA	
Titanium	1641.10	1630.00+/-	130.00
Zinc	24.892	28+/-	2.00

NA=not analyzed
NS=Not Specified

Appendix E

Blank Correction Data

For most of the metallic elements of interest to this program, small traces are present in both the reagents and filter media used in sampling and analyses. Consequently, we routinely use a blank correction in the calculation of gas stream concentrations for metals and anions. Semivolatile gas analyses have not indicated the presence of semivolatile organic compounds in the blanks. Aldehyde samples occasionally require blank correction. In the following tables, the mass or concentrations are presented for those substances reported in the blank. The ratio of the blank value to the measured value is then calculated. Measured values which are equal to or greater than 50% of the blank values are denoted with a "B". As shown in Appendix D, for the large majority of substances, the blank levels reported are within five times of the reporting limit indicating that the substance levels in the reagent and filter media are low.

Table E-1 presents (1) the probe and nozzle rinse and filter blank, and (2) anion corrections for Site 10. Nine substances were reported in the blanks. Of the 17 values which were blank corrected, corrections of 50% or more were made to the levels of arsenic, cadmium, fluoride, lead, molybdenum, nickel, and phosphorus measured in the stack. Cadmium was the only substance with a blank correction of greater than 50% in the baghouse inlet gas.

Table E-2 presents the metal impinger blank corrections for Site 10. Three metals (chromium, lead, and manganese) were reported in the blank impinger solution. The blank correction was less than 50% for lead and manganese in both the baghouse inlet and stack gas streams. Blank corrections for chromium were greater than 50% for both gas streams.

Table E-3 presents the aldehyde blank corrections for Site 10. Levels of acetaldehyde and formaldehyde in the blank were five to six times the levels found in the flue gas samples; therefore, blank corrections were greater than 50% for all four measurements.

Table E-1

Site 10 Probe and Nozzle Rinse and Filter Blank Corrections

Sample	Substance	Run, 1 µg		Blank/ Run 1	Blank, µg	RL, µg
Baghouse Inlet Gas, Solid Phase	Arsenic	548		0.3%	1.42	
Stack Gas, Solid Phase	Arsenic	1.50	B	95%	1.42	1.2
Baghouse Inlet Gas, Solid Phase	Barium	2,880		0.1%	3.46	
Stack Gas, Solid Phase	Barium	17.3		20.0%	3.46	
Baghouse Inlet Gas, Solid Phase	Cadmium	<2.50	B	122%	3.04	
Stack Gas, Solid Phase	Cadmium	0.90	B	337%	3.04	0.50
Stack Gas, Solid Phase	Fluoride	8.9	B	135%	12	5
Baghouse Inlet, Solid Phase	Lead	214		1.0%	1.52	
Stack Gas, Solid Phase	Lead	1.15	B	132%	1.52	0.30
Baghouse Inlet Gas, Solid Phase	Manganese	1,370		0.2%	3.36	
Stack Gas, Solid Phase	Manganese	21.1		16%	3.36	
Baghouse Inlet, Solid Phase	Molybdenum	67.5		32%	21.4	
Stack Gas, Solid Phase	Molybdenum	19.9	B	108%	21.4	5.0
Baghouse Inlet, Solid Phase	Nickel	537		19%	99.8	
Stack Gas, Solid Phase	Nickel	96.0	B	104%	99.8	2.0
Baghouse Inlet, Solid Phase	Phosphorus	14,500		1.0%	124	
Stack Gas, Solid Phase	Phosphorus	150	B	83%	124	30

B = Blank correction of 50% or more.

Table E-2

Site 10 Metal Impinger Blank Corrections

Sample	Substance	Run, 1 µg		Blank/ Run 1	Blank, µg	RL, µg
Baghouse Inlet Gas, Gas Phase	Chromium	2.13	B	85%	1.82	1.30
Stack Gas, Gas Phase	Chromium	1.55	B	117%	1.82	1.10
Baghouse Inlet Gas, Gas Phase	Lead	12.80		3%	0.40	0.38
Stack Gas, Gas Phase	Lead	1.12		36%	0.40	0.34
Baghouse Inlet Gas, Gas Phase	Manganese	186,506		0%	9.32	130
Stack Gas, Gas Phase	Manganese	29.7		31%	9.32	1.10

B = Blank correction of 50% or more.

Table E-3

Site 10 Aldehyde Blank Corrections

Sample	Substance	Run, 1 µg		Blank/ Run 1	Blank, µg	RL, µg
Baghouse Inlet Gas, Gas Phase	Acetaldehyde	23.1	B	675%	156	4.3
Stack Gas, Gas Phase	Acetaldehyde	23.6	B	661%	156	4.3
Baghouse Inlet Gas, Gas Phase	Formaldehyde	25.0	B	476%	119	3.6
Stack Gas, Gas Phase	Formaldehyde	24.0	B	496%	119	3.6

B = Blank correction of 50% or more.