PISCES Water Characterization Field Study Report

Volume 1: Site C Report

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Prepared by
CH2M HILL, Inc.
625 Herndon Parkway
Herndon, VA 20170

Principal Investigators
P. Benson, P.E.
D. Fink, P.E.
K. Sanders
T. Higgins, P.E.
S. Lehmann
J. Newman
B. Steglitz

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

EPRI Project Manager
P. Chu

Generation Group

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REPORT SUMMARY

Background

In 1988, EPRI initiated the Power Plant Integrated Systems-Chemical Emissions Study (PISCES) project to characterize the distribution of trace substances in air, liquid, and solid waste streams from fossil-fuel-fired electric utility power plants. With the com-completion of EPRI's Trace Substances Synthesis Report (TR-104614), which summarized EPRI's air toxics research, EPRI is expanding its focus to complete the characterization of water and solids streams. The purpose of the PISCES program is to expand the level of knowledge of toxics concentrations in internal and effluent streams in fossil-fuel power plants and to identify the factors controlling those concentrations. This report provides a comprehensive characterization of wastewater at a coal-fired power plant. The Site C station has observed periodic toxic events in its operational sampling within the ash pond during the springtime. Although regulated discharge samples have been nontoxic, these in-pond toxic events have led to work on wastewater characterization and toxicity identification and reduction.

Objectives

The objectives of the report are to identify the cause of toxicity in the host site's ash pond water, to expand an existing water quality database of toxic discharges from utilities, to evaluate sampling and analytical methods for wastewater characterization, to identify sources of toxics, to characterize existing treatment processes, and to develop guidance for evaluating toxicity management options.

Approach

Whole effluent toxicity tests, Toxicity Identification Evaluation (TIE) tests, and chemical analysis of the ash pond water were performed to evaluate toxicity and its causes. Sources of pollutants, including ash sluice waste, plant wastes, coal pile runoff, and plant intake water, were also evaluated. Samples were taken over a one-year period.

Results

Samples taken from within the ash pond were toxic, defined by the state where Site C is located as an LC_{50} below 77% ash pond water, in September, December, and November. Dissolved copper and nickel were determined to be the most likely cause of the ash pond water toxicity. Dissolved zinc may contribute to the toxicity. Metals were determined to be in a complexed form, likely as organically complexed. Fly ash sluice water

was the largest source of these metals to the ash pond. Toxicity was found to occur at 6 to 13 µg/L copper and 7 to 13 µg/L nickel. These concentrations are near the low end of what has been found in past research in individual metal toxicity studies. This suggests that a number of metals combine to cause toxicity. The concentration of copper, and other cationic metals, is based on solubility that was, in turn, observed to be related to the pH in the ash pond and ash sluice water. Low pH conditions, especially below 7.5 pH units, dissolve more copper and result in higher, more toxic ash pond water concentrations. Preliminary toxicity management alternatives identified for the site include options for maintaining a pH of about 7.5 in the ash pond. Options include controlling the type of coal being burnt; reducing or eliminating the use of sulfur trioxide fly ash conditioning; and optimizing caustic addition to control pH when coals that produce acidic sluice wastes are fired.

EPRI Perspective

This report summarizes the results from a one-year sampling effort to characterize wastewater at a coal-fired power plant. The results from this study provide information about the cause and source of toxicity in the ash pond water. State-of-the-art sampling and analytical methods were employed, and thus the results from this site should provide utilities with the best data currently available. The results from this study provide utilities with information on the relationship between trace metal contamination and toxicity. The user is cautioned that some of these test methods have not been approved for regulatory use by EPA or fully validated. In addition, ash pond chemistry, wastewater discharges, and toxicity are expected to be site-specific, and thus the results must be considered in this light when extrapolating to different fuels, power plant systems, and wastewater systems. The method detection limits (MDL) and critical levels (L_c) used in the report are as determined by the laboratories performing analyses and are not endorsed by EPRI. The user is cautioned that quantitation levels will be greater than MDL and L_c values.

In parallel with Site C, EPRI completed another similar wastewater study at Sites A and B (TR-108890). An additional study is ongoing at Site D (TR-108892, planned completion in summer 1998), with additional sites planned in 1998 and beyond. This report does not attempt to review the results from the other sites and literature. An interim report summarizing all the PISCES results and the literature is planned for December 1998. This summary report will provide interim results from EPRI's ongoing data evaluation, will identify potential approaches for estimating trace substances in water discharges, and will present preliminary options for wastewater management.

TR-108891

Interest Categories
Waste & Water Management, Environmental Compliance Planning

Key Words
PISCES, Water Quality Water Toxics, Trace Metals, Water Management, Effluent Toxicity

ABSTRACT

This report identifies the cause and source of toxicity in the ash pond water of a bituminous coal-fired power plant. Laboratory toxicity identification evaluations and ash pond water quality tracking indicated that dissolved copper and nickel were the most likely causes of toxicity. The concentrations of copper and nickel were observed to be related to the pH of fly ash sluice water and ash pond water, increasing at low pH conditions. Fly ash handling wastes were the largest source of pollutants to the ash pond and were evaluated using both field sampling and laboratory sluice simulations. The fly ash sluice water was observed to vary based on the type of coal being fired and the operation of the sulfur trioxide fly ash conditioning system. Preliminary toxicity management options were developed to meet current and potential future discharge requirements.

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EPRI would like to thank the host utility for participating in this PISCES water characterization study. In addition, we would like to thank all the EPRI utilities, including ESKOM, that have supported the PISCES research area. We would also like to thank the Utility Water Act Group (UWAG), the Project Advisory Committee (PAC), and Jim Rice and Wayne Micheletti who have assisted EPRI in providing direction and guidance to the PISCES project.

GLOSSARY

EPA Method Detection Limit (MDL)

The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero [1].

EPA Minimum Level (ML)

The concentration at which the entire analytical system must give a recognizable signal and acceptable calibration point. ML is the concentration in a sample that is equivalent to the concentration of the lowest calibration standard analyzed by a specific analytical procedure, assuming that all the method-specified sample weights, volumes, and processing steps have been followed [2].

MLs are analyte and method specific and are established during the development and validation of the method. Currently there are very few published (promulgated) MLs.

EPA Interim ML

To be used in the absence of promulgated MLs. The interim ML should be developed by multiplying the established MDL for the analyte from a specific analytical method by 3.18, and rounding the calculated value to the nearest multiple of 1, 2, 5, 10, 50, 100, 200, 500, etc. [2].

Currie's Critical Level L_C

The point at which one may decide whether or not the result of an analysis indicates detection. Statistically, the critical level is the concentration at which the response signal is significantly different from zero [3].

Alternative Minimum Level (AML)

It is defined as ten times the interlaboratory standard deviation (s_{CI}) at the lowest concentration that is differentiable from zero (L_{CI}). In the AML computational process, the raw “10s” value is corrected for errors in estimating the standard deviation and true concentration [4].

Reporting Limits

Term used to include both conventional method detection limit and clean method critical level. Quantitation levels will be higher than the reporting limits.

Relative Percent Difference (RPD)

Measure of precision between duplicates. Equal to 200 times the absolute value of the difference between the native result and duplicate result divided by the sum of the two results.

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PISCES Overview

The Electric Power Research Institute (EPRI) is conducting the Power Plant Integrated Systems-Chemical Emissions Study (PISCES), a multimedia chemical assessment study. The purpose of the PISCES program is to expand the level of knowledge of toxics concentrations in internal and effluent streams in fossil-fuel power plants and to identify the factors controlling those concentrations.

Regulatory Background

There are several developments that may lead to more stringent regulation of the steam electric utility industry. Historically, the steam electric utility industry has been regulated based on the categorical effluent limitations shown in Table ES-1. The U.S. Environmental Protection Agency (EPA) currently is evaluating whether to revise these limitations. Also, in response to the 1987 Clean Water Act (CWA) Amendments, states have developed in-stream water quality criteria (WQC) for the protection of human health and aquatic life. These criteria are in-stream standards and are not discharge limits. Actual discharge limits may be imposed at stations discharging to waterways with insufficient dilution to ensure the protection of in-stream standards. For stations discharging to large waterways, actual discharge limits will likely be significantly higher than WQC. Table ES-2 presents the most commonly used water quality criteria. Finally, the Great Lakes Water Quality Initiative (GLI) and potential CWA amendments may change existing wastewater permitting procedures.

Site Description

Site C was selected to evaluate sources of, and management options for, toxicity caused by power plant operations. Table ES-3 describes the major process variables at Site C.

Table ES-1
Utility Industry Categorical Technology-Based Effluent Limits

Parameter	Monthly-Average Discharge Limit (mg/L)	Daily-Maximum Discharge Limit (mg/L)	Comments
pH	6 to 9	6 to 9	
TSS	30	100	
Oil and Grease	15	20	
Chlorine	0.2	0.5	Limits are for free residual chlorine at existing plants. For new plants, the limit is for total residual chlorine.
PCBs	Not detected	Not detected	
Iron		1	Categorical limit encompasses boiler chemical cleaning wastes only.
Copper		1	Categorical limit encompasses boiler chemical cleaning wastes only.
Chromium	0.2	0.2	Regulated in cooling tower blowdown when cooling water treatment chemicals containing chromium are used.
Zinc	1	1	Regulated in cooling tower blowdown when cooling treatment chemicals containing zinc are used.
Priority Pollutants	Not detected	Not detected	Regulated in cooling tower blowdown at zero discharge.

Table ES-2
Federal Water Quality Criteria

Parameter	Freshwater Criteria[1] (μg/L)	Note
Aluminum	--	Regulated at 87 μg/L by some states.
Antimony	14	Lowest Federal WQC.
Arsenic	50	Regulation in some states is as low as 0.018 μg/L.
Beryllium	0.07	Not a Federal criteria but used in some states.
Cadmium	1.0	Lowest Federal WQC.
Chromium	180	Lowest Federal WQC (for Chromium III).[2]
Copper	11	The lowest saltwater criteria is 2.4 μg/L.
Lead	2.5	Lowest Federal WQC.
Mercury	0.012	Lowest Federal WQC.
Nickel	160	The lowest saltwater criteria is 8.3 μg/L.[2]
Selenium	5	Lowest Federal WQC.
Silver	3.4	The lowest saltwater criteria is 1.9 μg/L.[2]
Thallium	1.7	Lowest Federal WQC.
Zinc	100	The lowest saltwater criteria is 81 μg/L.[2]

[1] Criteria listed in 40CFR131.36. [1]
[2] Criteria is based on hardness; a default hardness of 100 mg/L was used.

Table ES-3
Site C Description

Parameter	Site C
Fuel	Bituminous coal; southwestern Virginia and eastern Kentucky
Rated Net Generating Capacity	2 units: 400 MW combined (baseload status)
Process Water Source	River water pumped to lake
Cooling System	Once-through cooling using lake water; stainless steel condensers
Ash-Handling System	Wet bottom ash and fly ash handling
Wastewater Treatment Technologies	Settling in ash pond; pH adjustment using caustic at influent to the ash pond as necessary
Water Treatment Technologies	Once-through cooling water: debris removal using screening, chlorination Boiler water makeup and ash hopper seal water: sandbed filters, softeners, evaporation (approximately 140 gpm [530 liters per minute])
Coal Characteristics During Study	10.9 to 16.3% ash 0.9 to 1.2% sulfur 3.7 to 8.2% moisture 11,600 to 12,900 BTU/lb (27,000 to 30,000 kJ/Kg) heating value

Ash Pond Water Quality and Toxicity

Samples taken from the ash pond were toxic, defined by the state in which Site C is located as an LC_{50} below 77% ash pond water, in September, December, and November of 1996. LC_{50} is defined as the concentration at which 50% test organism mortality occurs. Lower levels of toxicity were observed at several times throughout the study. The ash pond water sampling location was separated from the regulated outfall by a discharge channel that produces significant aeration of the wastewater streams, and a secondary settling basin; therefore, samples did not characterize actual discharge toxicity. Table ES-4 summarizes ash pond water quality data from Site C.

Table ES-4
Summary of Ash Pond Water Quality
All metals in µg/L

Parameter	Maximum	Average
Aluminum	1,900	650
Antimony	25	17
Arsenic	130	30
Beryllium	1.2	0.40
Cadmium	1.4	0.50
Chromium	14	4.0
Copper	32	9.2
Lead	1.8	0.34
Mercury	0.00012	0.00009
Nickel	24	12
Selenium	110	70
Silver	0.82	<0.023*
Thallium	4.9	1.5
Zinc	57	18

*Average is less than clean method critical level, which was determined using an alternative minimum level study of reagent water standards. The quantitation limit is higher than the critical level.

On the basis of the data collected during the field study, the parameters listed below were identified as of potential interest, either to the host utility or to the industry as a whole. The likely cause of the ash pond toxicity was identified as dissolved, organically complexed metals.

<u>Likely Causes of Ash Pond Water Toxicity</u>

- Copper
- Nickel
- Zinc (believed to be a secondary toxic agent)

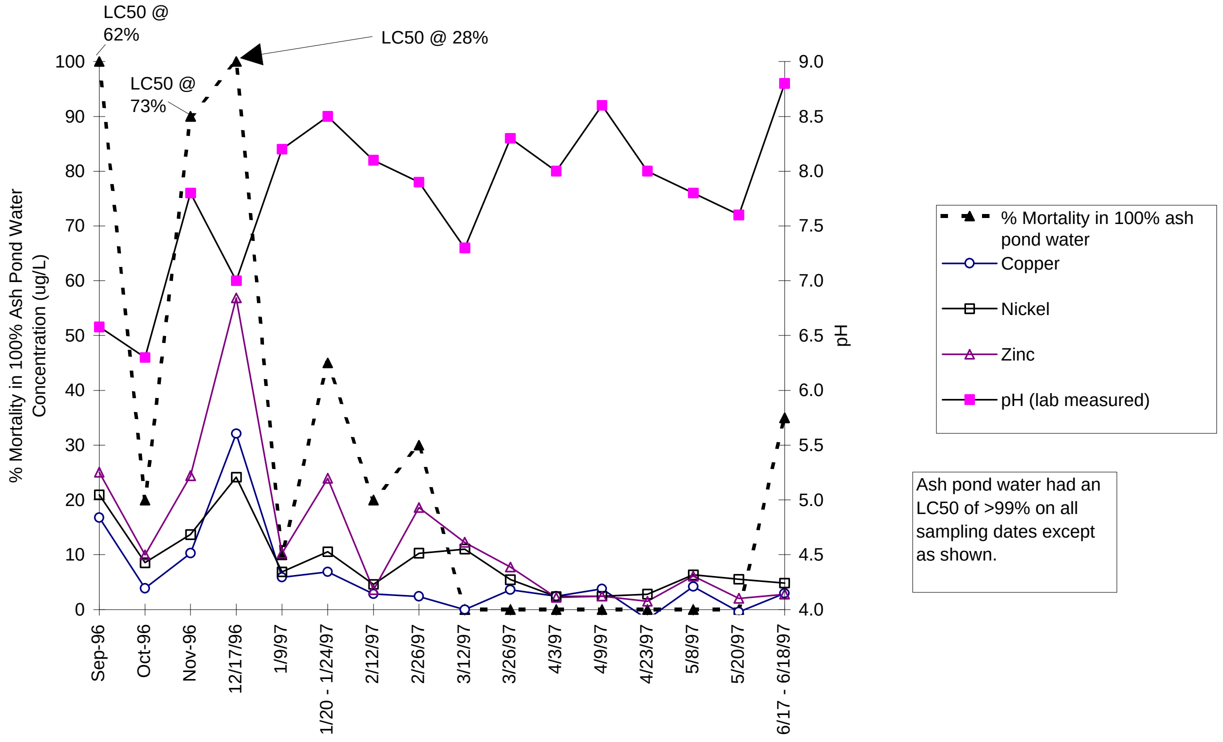
<u>Parameters Exceeding Water Quality Criteria</u>

- Antimony
- Arsenic
- Cadmium
- Copper
- Nickel (saltwater criteria only)
- Selenium
- Thallium

No organic pollutants were detected in the ash pond water. Conventional pollutants, such as ammonia, residual chlorine, and oil and grease, did not approach regulatory standards.

Toxicity Identification Activities

Toxicity identification activities included analyses of ash pond water to correlate water quality changes with toxicity, treatment simulations to remove specific potential toxicants, analyses of treated ash pond water to confirm treatment effectiveness, and spiking studies to confirm toxic concentrations of suspected toxicants. On the basis of these activities, dissolved copper and nickel were identified as being the most likely primary toxicants. Zinc was identified as a potential contributor to ash pond toxicity. Copper, nickel, and zinc concentrations correlated strongly with ash pond water toxicity, as shown in Figure ES-1. The decrease in toxicity beginning in early 1997 corresponds to operational changes, including the type of coal fired that raised pH of pond and decreased metals concentration. Treatment studies confirmed that a dissolved metal in organically complexed form was the most likely toxicant. Table ES-5 summarizes the results of the treatment study. Spiking studies confirmed the toxic effects of copper and nickel at concentrations found in the ash pond water, as shown in Table ES-6.



Ash pond water had an LC50 of >99% on all sampling dates except as shown.

Figure ES-1
Relationship Between Ash Pond Water Toxicity Versus Trace Metals Likely To Be Cause of Toxicity

Table ES-5
Summary of Toxicity Identification Evaluation (TIE) Testing

TIE Treatment	Acute Toxicity LC_{50} @ % Sample	Conclusion
September 1996—TIE Round 1		
Untreated (pre-TIE)	35%	
Baseline	24%	
Cation Exchange	>99%	Indicates dissolved metals were a cause of toxicity.
GAC	>99%	Metals were effectively removed; therefore, supports dissolved metals as cause of toxicity. Is also consistent with an organically complexed metal being the primary toxicant.
Silica Gel	93%	Designed to remove polar organics, but likely removed metals as well.
Hardness Elevation	48%	Toxicity reduction is consistent with metals toxicity.
EDTA Addition	65%	EDTA caused some toxicity; the effect on metals is inconclusive.
September 1996—TIE Round 2		
Baseline	23%	
0.1 µm Filtration	22%	No effect on toxicity shows dissolved parameter is the cause of toxicity.
November 1996		
Baseline	71%	
Cation Exchange	>99%	Indicates dissolved metals were a cause of toxicity.
December 1996		
Baseline	49%	
Cation Exchange	>99%	Indicates dissolved metals were a cause of toxicity.
GAC	>99%	Water testing showed that metals were effectively removed; therefore, supports dissolved metals as cause of toxicity. Is also consistent with an organically complexed metal being the primary toxicant.
XAD-4 Resin	>99%	Water testing showed that metals were effectively removed; therefore, supports dissolved metals as cause of toxicity. Is also consistent with an organically complexed metal being the primary toxicant.

Table ES-6
Metal Spiking Tests in Ash Pond Water

Sample Collected	Metal	Estimated LC_{50} Concentration	Initial pH
2/26/97	Copper	5.5 µg/L	7.9
3/26/97	Copper	13 µg/L	8.3
6/17/97	Nickel	~11 µg/L*	8.9

*Results are estimates because of poor dose response during test.

Ash pond water toxicity was determined to be strongly related to pH, which increased copper, nickel, and zinc solubility and resulting ash pond water concentrations. It appeared that the pH of the fly ash sluice water may be as important as the pH of the pond itself. The TIE results in which the GAC and XAD-4 treatments reduced toxicity also suggest that non-polar organic complexes of copper and nickel are present. Tests of XAD-4 treatment of ionic forms of copper and nickel showed that these metals were present in organically complexed forms.

Pollutant Sources

Fly ash handling at Site C was the dominant source of copper and nickel to the ash pond. The use of the sulfur trioxide (SO_3) flue gas conditioning system is believed to increase metals solubility and resulting toxicity for some of the coals used at Site C. In order to evaluate the effects of the different coals used at Site C and the effects of SO_3 addition, five ashes produced throughout the year were collected from before the SO_3 addition point and mixed with water in a laboratory simulation of sluicing to produce fly ash sluice water. Each of the ash sluice waters produced were further manipulated by adding sulfuric acid to replicate the effect of SO_3 addition. Table ES-7 summarizes the results of the fly ash sluice experiment.

Several ashes produced a neutral to acidic fly ash sluice water stream. The acidic sluice water had high concentrations of dissolved cationic metals such as copper, nickel, and zinc. The neutral sluice waters were significantly affected by the addition of acid (simulating the effects of SO_3 addition). Neutral ash waters subject to acidification had a 1 to 4 unit drop in pH with associated higher dissolved cationic metals concentrations. Alkaline ash water had very low dissolved cationic metals concentrations and appeared to be much less affected by the SO_3 process. Selenium was present at higher concentrations in the sluice water from ashes that produced alkaline sluice water. Acidification of neutral ashes, which generated sluice water of 7 to 8 pH units, resulted in water with pH of 4 and lowered the concentration of selenium in the sluice water produced. There appeared to be an increase of selenium at pHs below 4, evidenced by the increase in selenium concentration when acid was added to acidic ash (from 9/27/96). Arsenic concentrations in the sluice water did not appear to be related to the pH, but are likely more related to the amount of available arsenic in the fly ash.

Data Quality

Less than 5 percent of the data developed during the field study were rejected as unusable. The most significant data quality problems were observed in the collection and analyses of solids samples. A significant percent of the solids data were rejected as unusable because of a low bias observed in the initial analytical methods (EPA SW846 3050A digestion) used. Bottom ash was most affected by this problem. The method was changed in later site visits to 3050A after ASTM D3682 preparation, which produced data of higher quality.

Table ES-7
Comparison of Response to Sulfuric Acid Dosing in Simulated Sluice Water

	Liquid After Sluicing - Dissolved Metal Concentrations (μg/L)									
Unit and Date of Collection	**U2 on 9/27/96**		**U1 on 10/31/96**		**U1 on 11/21/96**		**U1 on 5/20/97**		**U1 on 6/19/97**	
		Acid Added		**Acid Added**		**Acid Added**		**Acid Added**		**Acid Added**
pH - After sluicing[1]	**4.5**	**3.2**	**11.6**	**11.1**	**7.8**	**4.1**	**8.1**	**4.1**	**12.1**	**12.2**
pH - After settling[1]	**5.3**	**4.1**	**11.2**	**10.7**	**6.4**	**5.5**	**8.8**	**5.0**	**12.1**	**12.0**
Aluminum	2,500	12,000	7,000	5,900	790	2,700	1,300	5,000	3,800	3,600
Arsenic	4.2	76	100	200	110	44	69	17	5.0	7.8
Copper	780	1,900	3.0	4.6	<1.7[2]	730	3.4	1,000	5.1	4.2
Iron	630	2,900	51	26	21	680	21	1,000	24	25
Nickel	1,500	1,500	<1.3[2]	<1.3[2]	15	370	10	250	<1.3[2]	<1.3[2]
Selenium	<1.5[2]	7.8	120	120	30	5.9	40	5.0	160	160
Zinc	400	470	5.3	6.7	3.8	420	4.4	700	24	20
Calcium	47,000	54,000	100,000	130,000	50,000	66,000	50,000	59,000	220,000	230,000
Dry fly ash calcium content	4,000 mg/kg		13,000 mg/kg		6,100 mg/kg		3,300 mg/kg		18,000 mg/kg	

[1] pH was taken of unfiltered samples and used for both total and filtered samples.

[2] Result is less than method detection limit (MDL) for conventional method achieved by the conventional laboratory as defined in 40CFR136 [1]. Quantitation limit is higher than MDL.

Each ash was collected from ductwork prior to SO_3 addition.

Method for sluice is simulation included in Appendix D.

A large number of data values are considered to be estimated because they were close to the detection limit and therefore below the quantitation level. The method detetection limits (MDL) and critical levels (L_c) used in the report are as determined by the laboratories performing analyses. The user is cautioned that quantitation levels will be greater than MDL and L_c values. In addition, a large number of data values are considered questionable due to blank contamination. Characterization of ash sluice streams also was affected by poor precision of field duplicate samples.

Levels at which quantitation can be made with confidence are determined by metal concentrations detected in blanks and by instrument variability near the detection limit. Clean sampling techniques produced higher quality data than did conventional techniques for ash pond water. The clean techniques permitted quantitation of copper, nickel, and zinc at the concentrations believed to cause toxicity. However, as is shown in Table 6-15, the conventional method resulted in blank contamination at concentrations that led to many of the results being considered questionable. An example is copper, which is considered questionable below 4.5 µg/L by the clean method, and below 60 µg/L by the conventional method due to higher concentrations of copper in blanks analyzed by the conventional method. In addition, the freshwater Water Quality Criteria for copper is 11 µg/L, below the level at which the conventional method produces results considered questionable. In addition, copper was biased high by conventional methods, and zinc contamination was observed in the majority of conventional field samples.

Wastewater Management Alternatives

The following preliminary wastewater management alternatives were identified to address toxicity in ash pond water:

- Implement a tracking program so that the type of coal burned each day is known.
- Where possible, use coals that produce an alkaline ash instead of an acidic ash. This can be accomplished by specifying the content of several minerals in the coal such as calcium as CaO, iron as Fe_2O_3, and magnesium as MgO.
- Evaluate options to replace the SO_3 system.
- Evaluate optimizing the SO_3 feed rate for higher-sulfur coals.
- Continue to use the caustic feed system, in order to maintain an ash pond pH from 7.5 to 9.
- Evaluate adding caustic directly to the ash sluice lines.

1

INTRODUCTION

PISCES Overview

The Electric Power Research Institute (EPRI) is conducting the Power Plant Integrated Systems-Chemical Emissions Study (PISCES), a multimedia chemical assessment study. In 1988, EPRI initiated the PISCES project to characterize the distribution of trace substances in air, liquid, and solid waste streams from fossil-fuel-fired electric utility power plants. With the passage of the 1990 Clean Air Act Amendments, EPRI focused the PISCES field studies on flue gas stack emissions, with only limited water and solid sampling. With the completion of EPRI's Trace Substances Synthesis Report (TR-104614), which summarized EPRI's air toxics research, EPRI is expanding its focus to complete the characterization of water and solids streams.

The PISCES project is conducting similar studies at three additional utility field sites, and EPRI envisions additional sites in 1998 and beyond. The results from all sites will be used to better characterize utility wastewater streams. The field results will help develop options to recycle/reuse wastewater as well as guidelines to improve wastewater management. The improved water quality database also will support development of the PISCES Plant Chemical Assessment Model (AP-107036).

Currently, there are substantial gaps in the water quality database, thus limiting the model's estimates of wastewater streams. New wastewater modules will be developed based on the PISCES field results. EPRI envisions that, with the new modules, the PISCES model will allow utilities to evaluate options toward multimedia toxics management.

The purpose of the PISCES program is to expand the level of knowledge of toxics concentrations in internal and effluent streams in fossil-fuel power plants and to identify the factors controlling those concentrations. Specific program objectives are to:

- Expand an existing water quality database to assist utilities in evaluating potential toxics issues at their facilities, in negotiating discharge permits, and in assessing the effect of wastewater management options

- Develop information on toxics loadings, control technology performance, and control technology costs that the industry can use in regulatory negotiations

- Develop sampling and analytical protocols for assisting member utilities in developing their own characterization programs for aqueous streams
- Identify and quantify potential toxics sources within power plants to assist in the development of predictive relationships for estimating internal stream composition
- Quantify or measure the performance of treatment processes for incorporation into the PISCES computer model
- Develop guidance that electric utilities can use to evaluate options for water management, reuse, and pollution prevention

The PISCES model is a multimedia contaminant model that predicts plant emissions based on the raw materials used by the plant and on in-plant processes. Plant emissions may be to the air, to water, or within solid waste. The model is intended to assist utilities in managing multimedia toxic discharges from fossil-fuel-fired power plants.

Regulatory Background

Site C currently is regulated for ash pond effluent toxicity, total suspended solids (TSS), and oil and grease (O&G). Copper, iron, arsenic, and selenium, nitrogen, and phosphorus must be monitored but have no permitted limit. Table 1-1 presents the current National Pollutant Discharge Elimination System (NPDES) discharge limitations for Site C.

Table 1-1
NPDES Ash Pond Effluent Limits at Site C

	Units	Monthly Average	Daily Maximum
Acute Toxicity	LC_{50}*	>77% effluent, monitored quarterly	
TSS	mg/L	30	100
Oil and Grease	mg/L	15	20

*Concentration at which 50% test organism mortality occurs.

Before receiving its current, toxicity-based discharge permit, the site had several events of toxicity in operational sampling within the ash pond. Each of the events occurred in the spring.

There are several regulatory developments that may result in increasingly stringent discharge limitations for the steam electric utility industry. The U.S. Environmental Protection Agency (EPA) currently is evaluating whether to revise the existing categorical effluent limitations for the steam electric utility industry. Also, in response to the 1987 Clean Water Act (CWA) Amendments, states have developed in-stream water quality criteria for the protection of human health and aquatic life. Table 1-2 presents the concentrations recommended by EPA for state adoption as water quality criteria (WQC). These criteria are in-stream standards and are not discharge limits. Actual discharge limits may be imposed at stations discharging to waterways with insufficient dilution to ensure the protection of in-stream standards for stations discharging to large waterways, actual discharge limits will likely be significantly higher than WQC. For utilities in the Great Lakes watershed, the 1996 Great Lakes Water Quality Initiative (GLI) may significantly change wastewater permitting procedures. Specifically, the GLI identifies as a class of pollutants called "bioaccumulating chemicals of concern," which may be subject to discharge prohibitions. Finally, the United States Congress currently is considering additional CWA amendments. The potential impacts of any new CWA amendments are uncertain at this time.

Table 1-2
Federal WQC for Trace Metals

Parameter	Freshwater Criteria[1] (µg/L)	Note
Aluminum	--	Regulated at 87 µg/L by some states.
Antimony	14	Lowest Federal WQC.
Arsenic	50	Regulated in some states as low as 0.018 µg/L.
Beryllium	0.07	Not a Federal criteria but used in some states.
Cadmium	1.0	Lowest Federal WQC.
Chromium	180	Lowest Federal WQC (for Chromium III).
Copper	11	The lowest saltwater criteria is 2.4 µg/L.[2]
Lead	2.5	Lowest Federal WQC.
Mercury	0.012	Lowest Federal WQC.
Nickel	160	The lowest saltwater criteria is 8.3 µg/L.[2]
Selenium	5	Lowest Federal WQC.
Silver	3.4	The lowest saltwater criteria is 1.9 µg/L.[2]
Thallium	1.7	Lowest Federal WQC.
Zinc	100	The lowest saltwater criteria is 81 µg/L.[2]

[1] Criteria is listed in 40CFR131.36. [1]

[2] Criteria is based on hardness; a default hardness of 100 mg/L was used.

Field Study Purpose

The purpose of the field study is to support EPRI's research into trace substance emissions in aqueous and solid waste streams and to meet the following host utility objectives:

- Identify the pollutant(s) that cause ash pond water toxicity
- Understand in-plant sources of the pollutants that cause ash pond water toxicity
- Investigate changes in source water chemistry that may contribute to episodes of ash pond water toxicity
- Monitor the impacts that Site C has on the receiving river for ash pond discharge and on the lake that serves as the source and receiving body for cooling water

Field Study Approach

The Site C field study consisted of a preliminary site visit, three 3- to 5-day in-plant sampling and flow monitoring visits, and frequent sampling and toxicity screening of the ash pond water and plant source water. The ash pond water sampling location was separated from the regulated outfall by a discharge flume that produces significant aeration of the wastewater stream and a secondary settling basin; therefore, samples did not characterize actual discharge toxicity. Samples found to be toxic were used in toxicity identification evaluation (TIE) work. In a TIE, a sample is treated and then tested for toxicity. Survival of organisms in the treated sample was compared to survival in the untreated sample to determine the effect of each treatment on toxicity.

Dry fly ash was collected from two locations during the study. Typically, the ash was collected using a cyclone from the ductwork between the economizer and the electrostatic precipitator (ESP). This location was prior to the sulfur trioxide (SO_3) injection point. There was no sample point after the SO_3 injection accessible when a unit was being operated. Therefore, ash was collected from out of the ESP during outages to obtain SO_3-treated ash.

Sluice simulation studies were performed to analyze the fly ash sluice waste stream under controlled conditions so that sluice water from various ashes could be compared. The study consisted of mixing fly ash with plant intake water using a recirculating pump for 15 minutes to simulate the turbulence of ash sluicing. The solids were then separated from the liquid and each were analyzed. In early tests, centrifuging was used for separation. This method was changed to settling for 24 hours to better simulate ash pond operating conditions. Additions of caustic and acid were used to simulate the station's caustic treatment and the effects of the SO_3 injection system. The standard operating procedure for the simulation studies is included in Appendix D.

During the in-plant sampling visits, numerous process and wastewater streams were sampled for metals, major cations and anions, and conventional pollutants. In addition, the wastewater streams were screened for organic pollutants. Sampling and analysis of plant intake water, ash pond water, and cooling water for metals were conducted using EPA Method 1669 "clean" sampling protocols and 1600-series analytical methods [5-9]. These methods, which are about to undergo interlaboratory validation and may thereafter by codified into law, are intended to provide more accurate results of trace metal concentrations. Other streams and parameters were sampled and analyzed using conventional techniques.

Detection and quantitation limits are used throughout the report in discussing results. There has not been a scientific consensus reached concerning detection and quantification levels appropriate for compliance monitoring. In its March 1994 draft guidance, the U.S. EPA recommended that the Minimum Level (ML) be used as the quantitation level for the setting of, and determining compliance with, permit limits with water quality-based effluent limitations in the National Pollutant Discharge Elimination System (NPDES). MLs are analyte- and method-specific and are supposed to be established during the development and validation of the measurement method. However, at this time, there are very few promulgated MLs. In the absence of promulgated MLs, EPA requires the use of interim MLs, and indicated that the interim MLs should be developed by multiplying the established method detection limits (MDL) [1] for the analyte from a specific analytical method by 3.18, and rounding the calculated value to the nearest multiple of 1, 2, 5, 10, 50, 100, 200, 500, etc. Setting the compliance quantitation level at the interim ML is not justified for a number of technical reasons [4, 10, 11]. To address the shortcomings of EPA's MDL and interim ML in the context of permit compliance monitoring, EPRI participated in an inter-industry coalition that developed a technical consensus on principles and properties associated with detection and quantitation levels for compliance monitoring. As a result of this effort, a statistically defensible estimate of a quantitation level, called the Alternative Minimum Level (AML) was developed [4, 11]. The AML uses Currie's Critical Level (L_C) as the starting point [3]. Statistically, the critical level is the concentration at which the analytical instrument response signal is significantly different from zero. EPRI is playing a key role in the Inter-Industry Analytical Group's (IIAG) negotiations with U.S. EPA's Office of Water, regarding the use of the AML as the quantitation level for compliance monitoring. Recently, EPA has indicated their willingness to drop their interim ML approach for quantitation. Discussions for its replacement continue.

The laboratory reporting limits used in this report correspond to the Method Detection Limits (MDLs) for conventional analytical techniques, and the Critical Levels (L_C) for "clean" analytical techniques. The MDLs were determined in deionized water by the analytical laboratories using the protocols described in 40 CFR part 136 [1]. The L_C was determined by the PISCES project team for deionized water based on a series of spiked samples submitted blindly to the analytical laboratory. Both the MDL and the L_C represent a minimum concentration that is detectable. However, at these concentrations, quantification is not possible, and the data results should be considered estimated.

In order to evaluate the performance of the “clean” sampling and analytical methods, several additional studies were performed. Duplicate samples were collected for each ash pond water sample. One duplicate sample was collected and analyzed using “clean” methods, while the other duplicate sample was collected and analyzed using conventional methods. Also, AML evaluations were conducted for the Site A ash pond water and the Site B plant intake streams.

To evaluate the performance of the “clean” sampling and analytical methods, several additional studies were performed. Duplicate samples were collected of ash pond water. One duplicate sample was collected and analyzed using “clean” methods, while the other duplicate sample was collected and analyzed using conventional methods.

Report Structure

The report is structured to summarize ash pond water toxicity and water quality issues, identify streams that contribute to these issues, discuss data quality in relation to these parameters, and identify wastewater management options. The report consists of nine sections. Section 2 presents a general description of the station, its wastewater management systems, and its operating practices. Section 3 presents the overall sampling, analytical, flow monitoring, and data quality methods used. Section 4 presents ash pond water toxicity and water quality results. Section 5 characterizes sources of pollutants and reasons for the variability of the ash pond water toxicity. Section 6 presents an evaluation of data quality control. Section 7 presents toxicity management options for the two stations. Section 8 present modifications to the program implemented during work at Site C. References are presented in Section 9. The appendices include analytical data, plant process data, waste-stream-specific sampling methods, and quality control data.

2

SITE DESCRIPTION

The PISCES program assigns a site code to each plant sampled. The station in this effort is designated Site C. The station is a coal-fired electric generating station. Table 2-1 summarizes the major variables that affect a plant's wastewater. A complete listing of station data to be used in the PISCES database is included in Appendix C.

Facility Description

Site C consists of two steam-generating units, both constructed in the late 1960s and early 1970s. Unit 1 is a balanced draft boiler and Unit 2 is a pressurized furnace. Both are base-loaded units. Both units burn pulverized coal and are front-fired. Figure 2-1 shows a process flow diagram of the major water uses and wastewater sources at Site C.

Coals Fired

The station uses coals from eight different mines supplied on the spot market. The coals are predominately from southwestern Virginia, with some use of coal from eastern Kentucky.

Ash Handling System

Particulate emissions are controlled by electrostatic precipitators (ESPs) at each unit. Both units have cold-side, wire-and-plate type ESPs. The ESPs were installed in the early 1970s. The Unit 2 precipitator is considered by the station to be undersized for its current opacity limit, and replacement options are being evaluated. Both units have SO_3 injection for fly ash conditioning.

There are two ash sluice lines to the ash pond, one pipe for each unit. Mill rejects are returned to the coal pile.

Table 2-1
Site C Description

Parameter	Site C
Fuel	Bituminous coal; southwestern Virginia and eastern Kentucky
Rated Net Generating Capacity	2 units: 400 MW combined (baseload status)
Process Water Source	River water pumped to lake
Cooling System	Once-through cooling using lake water; stainless steel condensers
Ash-Handling System	Wet bottom ash and fly ash handling
Wastewater Treatment Technologies	Settling in ash pond; pH adjustment using caustic at influent to the ash pond as necessary
Water Treatment Technologies	Once-through cooling water: debris removal using screening, chlorination Boiler water makeup and ash hopper seal water: sandbed filters, softeners, evaporation (approximately 140 gpm [530 liters per minute])
Coal Characteristics During Study	10.9 to 16.3% ash 0.9 to 1.2% sulfur 3.7 to 8.2% moisture 11,600 to 12,900 BTU/lb (27,000 to 30,000 kJ/kg) heating value

Cooling System

The average circulating cooling water is 150 million gallons per day (mgd) (570 million liters per day [mld]) per unit. The condensers were replaced in 1994 and are stainless steel. Sodium hypochlorite is added to the cooling water during periods of warm water to control biological growth. Chlorination occurs four times per day in 20-minute doses.

Wastewater Treatment Facilities

All process wastewater at the station, except once-through condenser cooling water, is discharged to the ash pond for treatment. The surface area of the ash pond is roughly 25 acres (100,000 square meters) and is approximately 7 feet (2 meters) deep. The

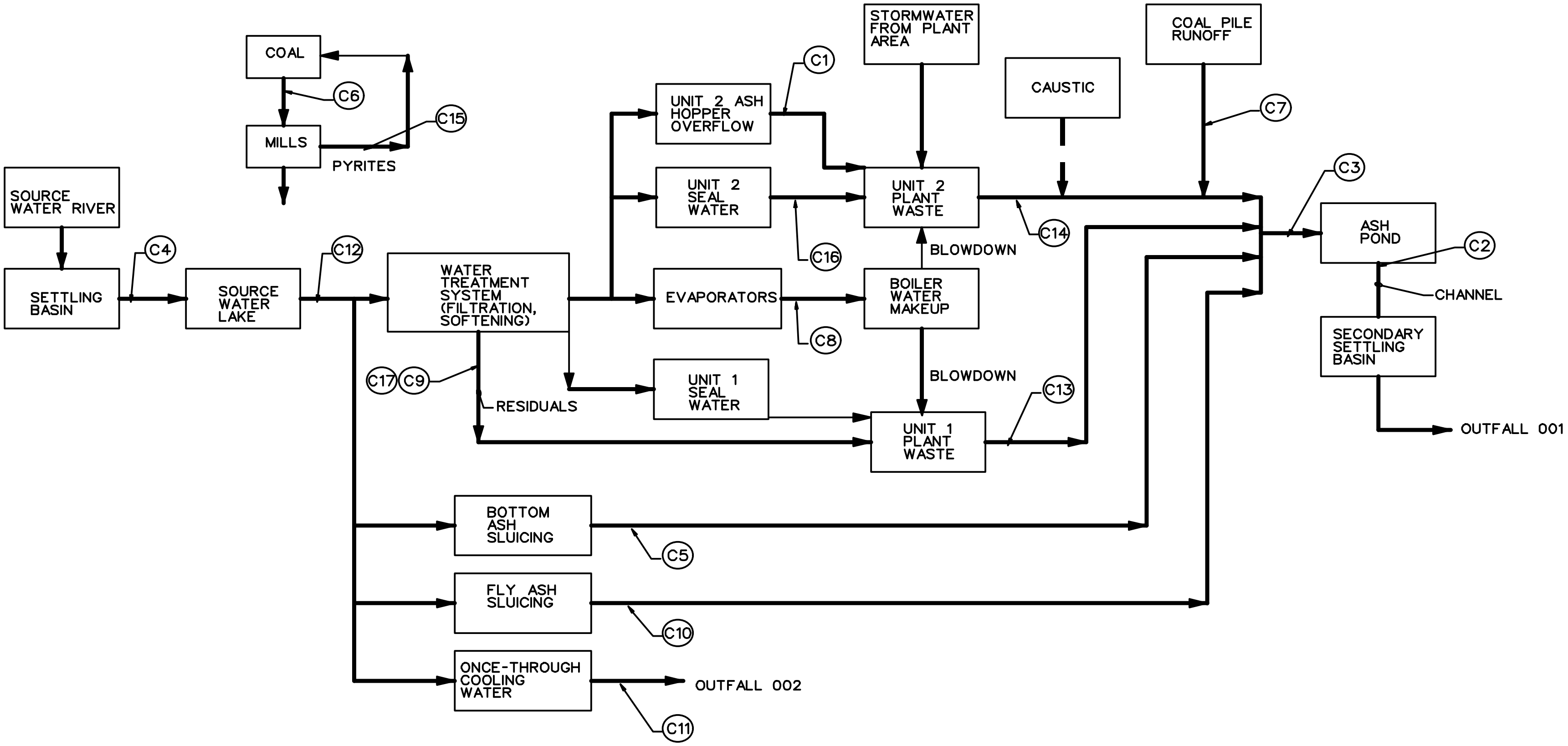


Figure 2-1
Simplified Flow Diagram for Wastewater Streams at Site C

retention time of the pond was estimated by station personnel as 30 days. Ash sluice waste and plant wastes flow into the pond in a bank of pipes. The streams combine and flow over a delta of previously deposited ash in a channel that splits and reforms as it moves towards the open water of the pond. Roughly half the pond has filled in with ash. Currently, the distance from where the channel enters the open water of the pond to the pond effluent point is roughly 200 yards (180 meters). The water flows from the ash pond through an open channel to a secondary settling pond. From there it is discharged to the receiving river.

Waste Streams Sampled at Site C

Sampling locations for Site C are shown in Figure 2-1. Description of sampling locations are listed in Table 2-2.

Table 2-2
Sampling Locations at Site C

Locations	
C1	Ash hopper overflow, Unit 2
C2	Ash pond water
C3	Ash pond influent
C4	Background lake water
C5	Bottom ash sluice water and ash
C6	Coal
C7	Coal pile runoff
C8	Evaporator brine
C9	Filter backwash waste
C10	Fly ash sluice water and ash
C11	Once-through cooling water
C12	Plant intake water
C13	Plant waste, Unit 1
C14	Plant waste, Unit 2
C15	Pyrites
C16	Seal water, Unit 2
C17	Softener regeneration waste

3

METHODS USED

Overview of Sampling Strategy

The sampling strategy was developed to understand the source of ash pond water toxicity and toxics discharges from coal-fired power stations, and to characterize toxics sources and treatment technology performance. Project activities are shown in Table 3-1. Week-long sampling was conducted three times from September 1996 to June 1997. Each event included sample collection, flow monitoring, and process data collection. Waste streams at power stations include continuous and intermittent or episodic flow components. The approach for sampling varied, depending on the importance of characterizing a particular stream and the nature of the flow. Sampling was scheduled so that samples were collected when operations were normal. The project goal was to characterize the normal variation in station activities not to characterize highly unusual station operating conditions such as rarely fired coals.

Table 3-1
Sampling at Site C

Comprehensive Sampling Events	One-Day Sampling
September 23-27, 1996	May 23, 1996 (preliminary visit)
January 20-24, 1997	October 28, 1996
June 17-19, 1997	November 22, 1996
	December 17, 1996
	January 9, 1997
	February 12, 1997
	February 26, 1997
	March 12, 997
	March 26, 1997
	April 9, 1997
	April 23, 1997
	May 8, 1997
	May 20, 1997

Sampling frequencies were selected based on waste stream significance, variability, and frequency of generation. Sampling frequencies ranged from three to four samples per week for the ash pond water, to two samples for the entire study of filter backwash waste. The number of samples taken from each location is shown in Appendix A.

Locations were selected to:

- determine cause and source of ash pond water toxicity
- determine ash pond treatment performance
- characterize waste streams going to the ash pond
- characterize cooling water

Twelve additional visits were made to the site to analyze ash pond water toxicity and chemical quality. Plant source water quality and coal characteristics also were tracked.

The EPA Method 1669 "clean" sampling protocols and 1600-series analytical techniques were used at locations where concentrations of metals were expected to be near or below detection limits of conventional methods. Some of these test methods have not been approved for regulatory use by EPA or fully validated. These locations included the plant intake, cooling water, source lake water, and ash pond water.

To get a representative sample of heterogeneous streams such as ash sluice wastes, composite samples were taken. During the first visit, ash sluice waste samples were taken by pumping water from the pool at the discharge point of the sluice water pipe. It was determined that this did not collect a representative sample of the solids in the stream. Therefore, on subsequent visits, grab samples were taken from the end of the pipe and composited. The composite was then allowed to settle for an hour. The liquid decanted was considered representative of the flow entering the ash pond after larger solids settle out in the ash delta. Compositing the entire sluice cycle and analyzing the portion of the stream not easily settled focused on the impact of the sluice activities on the ash pond.

For processes that may add or remove toxic constituents, paired influent and effluent samples were taken. The goal of collecting paired samples is to identify the effect of the process on water quality.

Automatic compositors were used to characterize streams that were known to change during a day, such as ash pond influent, plant wastes, and coal pile runoff.

Overview of Laboratory Fly Ash Sluice Simulation

Fly ash sluice waste was the greatest contributor of pollutants to the ash pond; however, the initial field data were highly variable. Therefore, laboratory ash sluice simulations were added to the sampling program. The studies were performed to analyze the fly ash sluice waste stream under controlled conditions so that sluice water from various ashes could be compared. The simulation procedure was designed to evaluate that part of the waste from fly ash sluicing that is difficult to treat in an ash pond. It has been shown through in-pond sampling at EPRI PISCES Sites A and B that over 90% of the solids entering an ash pond settle out near the head of the pond [12]. It is the smaller, more difficult to settle solids and the dissolved material that are of interest from a wastewater management standpoint. Therefore, a separation method of a 24-hour settling time is used to simulate the removal of those particles that would be quickly removed in ash ponds.

Dry fly ash was collected from two locations during the study. Typically, the ash was collected using a cyclone from the ductwork between the economizer and the ESP. This location point was prior to the SO_3 injection point. There was no sample point after the SO_3 injection accessible when a unit was being operated. Therefore, ash was collected from out of the ESP during outages to obtain SO_3-treated ash. The laboratory procedure consisted of mixing fly ash with plant intake water using a recirculating pump for 15 minutes to simulate the turbulence of ash sluicing. The solids were then separated from the liquid and each were analyzed. In early tests, centrifuging was used for separation. This method was changed to settling for 24 hours to better simulate ash pond operating conditions. Additions of caustic and acid were used to simulate the station's caustic treatment and the effects of the SO_3 injection system. The standard laboratory operating procedure for the simulation is included in Appendix D.

Overview of Flow Monitoring

Flow monitoring was done to allow the mass loading of pollutants to be calculated. The flow of most of the waste streams was measured by the station using pump run-time meters. Discharge from the ash pond was measured by a depth gauge at the discharge structure. Additional flow monitoring was done using open-channel velocity meters and visual observation.

Sampling and Flow Monitoring Methods

Brief descriptions of the sampling and flow monitoring methods used at each sampling location are provided in Appendix D.

Toxicity Evaluation Methods

Ash pond water was analyzed for 48-hour acute toxicity to *Ceriodaphnia Dubia* during each visit. The tests used four 30-milliliter (mL) test chambers with five organisms each. Moderately hard reconstituted laboratory water was used for dilution and as a control. The organisms were not fed during the tests.

Total alkalinity, hardness, total residual chlorine, and total ammonia were measured initially on the sample. Total alkalinity and hardness also were measured in the laboratory control water. Dissolved oxygen (DO), pH, and conductivity were measured in all concentrations at the initiation of each test. DO and pH were measured in one test chamber after 48 hours in all test concentrations. Bioassay incubator temperature was electronically monitored hourly by a thermocouple and data logger, and a 24-hour summary of mean values was recorded. When appropriate, an LC_{50} (concentration at which 50% test organism mortality occurs) was calculated from the toxicity data.

Samples found to be toxic were used in toxicity identification evaluation (TIE) work. In a TIE, a sample is treated and then tested for toxicity. Survival of organisms in the treated sample was compared to survival in untreated sample to determine the effect of each treatment on toxicity [13]. Treatments involving pumping sample through a column using 100 mL of resin or activated carbon in a 30-centimeter-long column. Laboratory water was treated first to ensure that the treatment itself was not introducing toxicity. The sample was then pumped through the column. Treatments included:

- **GAC Treatment.** An ash pond water aliquot was pumped (50 milliliter per minute [mL/min]) through a column of granular activated carbon to remove primarily nonpolar organics.
- **Silica Gel Treatment.** An ash pond water aliquot was pumped (50 mL/min) through a column of silica gel to remove primarily polar organics.
- **Cation Exchange Treatment.** An ash pond water aliquot was pumped (50 mL/min) through a column of cation exchange resin to remove primarily heavy metals.
- **EDTA Treatment.** After the multiple concentrations were prepared using the ash pond water and dilution water, a stock solution of EDTA was used to spike each concentration to a level of 6 mg/L EDTA. This treatment was used to chelate metals, rendering them less toxic/bioavailable.
- **Hardness Elevation.** The hardness of an ash pond water aliquot was elevated to twice its initial level using the EPA procedure for preparing synthetic reconstituted laboratory water. The reagents used were $NaHCO_3$, $CaSO_4 \bullet 2H_2O$, $MgSO_4$, and KCl to reduce the toxicity of those metals whose toxicity is based on hardness.
- **Filtration Treatment.** An ash pond water aliquot was filtered through a 0.1 micrometer (µm) pore membrane to remove primarily solids and colloidal material.
- **XAD-4 Treatment.** An ash pond water aliquot was pumped (50 mL/min) through a column of XAD-4 hydrophobic polyaromatic resin to remove primarily organically bound metals. Additional testing of lab water spiked with ionic copper and nickel verified that XAD-4 poorly removes ionic metals.

Spiking tests also were conducted to determine the concentration of a metal that will cause toxicity.

Analytical Methods

Table 3-2 presents the analytical methods that were used. State-of-the-art analytical methods were used. Some of the test methods have not been approved for regulatory use by EPA or fully validated. Brief descriptions of the methods employed for the quantitation of metallic analytes and any deviations from, exceptions to, or observations on these methods during the study are detailed below.

EPA Method 1638 [8]: This is an analytical method for determining elemental constituents in a sample at subpart-per-billion and part-per-trillion levels using clean sampling and highly sensitive analytical techniques. Deviations from the analytical method as published included: (1) Hydrochloric acid was not used in the digestion process. Nitric acid alone was employed. Increasing chloride concentration can present additional molecular ion interferences. (2) During the first two weeks of sampling, the clean laboratory used a single internal standard (Indium) to process the data rather than the method that required three internal standards. Side-by-side comparisons of data processed with the single and three internal standards resulted in significantly better recoveries of blank spikes, matrix spikes, and low level standard reference materials (SRMs) using one internal standard. (3) High total dissolved solids concentration in the ash pond water inhibited analysis of four metals (beryllium, zinc, arsenic, and selenium) by approximately 30% compared to deionized water during the week 3 clean sampling. Therefore, a matrix spike addition curve was developed for the matrix which improved the accuracy of results.

SW-846 Method 6010 [15]: The SW-846 method for Inductively Coupled Plasma Emission Spectroscopy (ICPES) applied to conventional sampling and analysis procedures. A "trace" ICP was used for these data, providing detection limits in the part-per-billion to subpart-per-billion ranges, roughly one order of magnitude better than traditional ICP limits. It is noted that quantitation levels are greater than the detection limits. A few observations of significance pertaining to the analysis of field samples using this method were made. (1) An internal standard produces significantly better data, accounting for any physical effects in sample introduction. (2) Extremely high concentrations of interfering analytes requiring dilution result in elevated detection limits for all target elements. (3) Background and interelement correction factor accuracy and stability are important as matrix effects can be significant in quantified results at or near the method detection limit, yielding false positives and false negatives.

SW-846 Method 7471 [15]: The SW-846 method for the determination of mercury by cold-vapor atomic absorption (CVAA) applied to conventional sampling methods. The only observation pertaining to this method involves sensitivity issues. Detection limits associated with this method are highly dependent upon the spectrometer used for measurement. Method detection limits could range from 0.05 to 0.5 micrograms per liter (μg/L). It is noted that quantitation levels are greater than the detection limits.

Table 3-2
Analytical Methods Used in the PISCES Study

Parameter	Liquid and Solid, Conventional [14-16]	Liquid, Clean [6-9]
Metals	EPA SW846-6010[1] (ICPES) ASTM D 3682-3684 (solids)[3]	EPA 1638[2] (ICPMS)
Mercury	EPA SW846-7471 (CVAA)	EPA 1631 (CVAF) and EPA 1631M
Arsenic	EPA SW846-7060 (GFAA)	
Chromium VI		EPA 1636 (Ion Chromatography)
Arsenic and selenium speciation		Battelle EA4641-1 and Battelle EA4641-2 EPA 1632M (hydride generation)
Toxicity	EPA's Acute Toxicity Methods [13,17]	
Hardness	EPA 130.2	
Total Dissolved Solids	EPA 160.1	
Total Solids	EPA 160.3	
Acidity	EPA 305.1	
Alkalinity	EPA 310.1	
Carbonate	EPA 310.1	
Chlorides	EPA 325.1	
Total Residual Chlorine	EPA 330.4	
Fluoride	EPA 340.2	
Ammonia-N	EPA 350.2	
NO_3, NO_2	EPA 353.2	

Table 3-2
Analytical Methods Used in the PISCES Study

Parameter	Liquid and Solid, Conventional [14-16]	Liquid, Clean [6-9]
Dissolved Oxygen	EPA 360.1	
Phosphorus	EPA 365.1	
Sulfate	EPA 375.4	
Biological Oxygen Demand	EPA 405.1	
Chemical Oxygen Demand	EPA 410.4	
Oil and Grease	EPA 413.1	
DOC, TOC	EPA 415.2	
Chlorophyll-A	Standard Method 1002G	
Redox potential	EPA 3-52	
pH	EPA 150.1 & Field	
Conductivity	EPA 120.1 & Field	
Organics (VOAs, SVOAs)	EPA SW8260	
	EPA SW8270	
Pesticides	EPA SW8080	

[1] Metals = Aluminum, Antimony, Barium, Beryllium, Boron, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Nickel, Potassium, Selenium, Silicon, Silver, Sodium, Thallium, Vanadium, Zinc.

[2] Clean metals = Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Copper, Lead, Nickel, Selenium, Silver, Thallium, Titanium, Vanadium, Zinc.

[3] ASTM D 3682 preparation of solids used for Barium, Cadmium, Chromium, Vanadium, Nickel, Lead, Manganese, and Zinc. ASTM D 3683 method used for Beryllium, Boron, and Silver. ASTM D 3684 used for Arsenic, Selenium, Antimony, and Thallium [16].

ICPES = Inductively Coupled Plasma Emission Spectroscopy
ICPMS = Inductively Coupled Plasma Mass Spectroscopy
CVAA = Cold-Vapor Atomic Absorption
GFAA = Graphite Furnace Atomic Absorption
CVAF = Cold-Vapor Atomic Fluorescence

EPA Method 1631 and 1631M [5]: This is designed as an analytical method for determining mercury (and speciated mercury as 1631M) in a sample at subpart-per-trillion and part-per-trillion levels using clean sampling and analytical techniques. Modification from the analytical method as published included extra steps pertaining to the speciation of mercury only. It should also be noted that as long as certain detailed requirements are met, samples may be preserved upon receipt in the laboratory rather than in the field.

SW 846 Method 7060 [15]: The SW-846 method for the determination of total arsenic by graphite furnace atomic absorption (GFAA) applied to conventional sampling methods. Detection limits associated with this method are highly dependent upon dilutions required because of the matrix coupled with the type of background correction used.

EPA Method 1636 [7]: This is designed as an analytical method for the determination of hexavalent chromium in a sample at subpart-per-billion and part-per-billion levels using clean sampling and analytical techniques.

Battelle Method EA4641-1/2 and 1632M [6]: These methods are designed as analytical methods for the determination of total arsenic (and speciated arsenic as 1632M) in a sample at subpart-per-billion and part-per-billion levels using clean sampling and analytical techniques.

Quality Assurance Procedures

Quality control (QC) procedures were used to assess the sampling and analytical processes on the usability of the data. The two major areas of analytical QC are precision and accuracy of data. Table 3-3 shows the types of QC samples taken during the program.

Table 3-3
Types of Quality Control Samples

QC Activity	Characteristic Measured	Frequency
Precision		
Field duplicate samples	Sampling plus analytical method variability of detectable concentrations in a sample matrix. Homogeneity or heterogeneity indicator in a matrix.	Metals: 1/10 samples, General Chemistry: 1/20 samples
Laboratory duplicate samples	Analytical method variability associated with detectable concentrations in a sample matrix. Homogeneity or heterogeneity indicator in a matrix.	1/20 samples
Laboratory matrix spike duplicates (MSD)	Sampling plus analytical method variability at known concentrations in a matrix.	1/visit
Laboratory control sample (LCS) duplicates	Analytical method variability at known concentrations without matrix effects.	1/visit
Surrogate spiked sample sets	Analytical method variability at known concentrations in a matrix.	1/visit with organic analyses
Replicate stream samples collected over time under the same conditions	Total variability, including process, temporal, sampling, and analytical.	
Standard reference materials (SRM) submitted over time	Analytical method variability at known concentrations in a selected matrix.	1/visit
Reference toxicant (sodium chloride) test	Reproducibility of toxicity tests	1/month
Accuracy		
Matrix spiked (MS) samples	Target analyte recovery in a sample matrix. Reflects matrix interferences.	1/20 samples
Surrogate spiked (SS) samples	Recovery of a homologous target in a sample matrix. Indicates matrix effects and extraction efficiency for similar classes of compounds.	1/visit when organics sampled
Laboratory control sample (LCS)	Target analyte recovery in an ideal matrix. Indicative of method performance without matrix effects.	1/visit
Standard reference materials (SRM)	Target analyte recovery of certified concentrations in a similar matrix to samples being collected. Generally submitted “double blind” (laboratory does not know that material was known standard) to measure unbiased laboratory performance.	1/visit

Table 3-3
Types of Quality Control Samples

QC Activity	Characteristic Measured	Frequency
Blank Effects		
Field blanks	Effects of equipment rinsate blank source water and analytical method, including contamination and contributions from instrument noise at or near the reporting limit.	1/visit/ source of decontamination water
Equipment rinsate blank (ERB)	Total sampling and analytical method effects, including contamination and contributions from instrument noise at or near the reporting limit.	1/visit/sampling technique
Trip blanks	Contamination associated with sample transport and storage, and analytical method effects, including contamination and contributions from instrument noise at or near the reporting limit. Normally associated with volatile organic compounds methods.	1/visit
Laboratory method blanks	Analytical method effects, including contamination and contributions from instrument noise at or near the reporting limit.	Conventional: 1/20 samples Clean: 1/10 samples
Laboratory control water toxicity tests	Effects of laboratory environmental conditions on test organisms.	1/toxicity test

4

ASH POND TOXICITY AND WATER QUALITY DATA

The following conclusions can be made from analysis of ash pond water quality and toxicity data:

1. Ash pond toxicity occurred more frequently than was initially thought to occur. Toxic events, defined by the state where Site C is located as an LC_{50} below 77% ash pond water, occurred in September, December, and November. LC_{50} is the concentration of sample that produces 50% test organism mortality. Lower levels of toxicity were observed at several times throughout the year.
2. Dissolved copper and nickel are the most likely cause of the ash pond water toxicity. Dissolved zinc appears to be a secondary cause of toxicity. These metals are likely present in organically complexed forms.
3. Toxicity occurs at low part-per-billion metal concentrations near the low end of what has been found in past research in individual metal toxicity studies. This suggests that a number of metals combine to cause toxicity. Organically complexed metal compounds may be present in the ash pond increasing the toxicity.
4. The concentration of copper and other cationic metals, is based on solubility that is affected by the pH in the ash pond. Low pH conditions dissolve more copper and nickel and result in higher, more toxic ash pond water concentrations. Organic complexing is also likely to affect the concentration of dissolved metals.

Toxicity of Ash Pond Water

The toxicity of the ash pond water samples taken as part of the PISCES program is shown in Table 4-1. Historically, samples from within the ash pond at Site C have experienced toxicity events in the springtime. However, there were three ash pond samples (taken in September, November, and December 1996) that tested positive for toxicity. The pond water was nontoxic during the October 1996 sampling. This is evidence of the variable nature of the toxicity.

Station operations are a factor in the toxicity variation. The amount of metals entering the pond is determined, in part, by the pH of the water at the head of the ash pond. The solubility and concentration of metals in the water entering the pond, and ultimately exiting the ash pond, affects toxicity because dissolved metals are poorly removed in the ash pond. The pH has been affected by the station’s periodic addition of caustic in batches of 2,000 gallons as is shown in Table 4-1. In January 1997, the station began managing their coal use to raise the pH in the ash pond. This resulted in a more consistently high pH and enabled the station to stop adding caustic. After the coal management was started, no toxic events were observed.

Table 4-1
Ash Pond Water Toxicity During PISCES Program

Date Sampled	Percent of Ash Pond Water at Which LC_{50} Occurred [1,2]	Notes
9/25/96	62%	
9/26/96	35%	
10/28/96	>99%	4,000 gallons (15,000 liters) of caustic added in October to ash pond influent
11/22/96	73%	
12/17/96	28%	
1/9/97	>99%	2,000 gallons (7,600 liters) of caustic added in late December to ash pond influent. Began coal management to control ash pond pH.
1/20/97	>99%	
2/12/97	>99%	
2/26/97	>99%	
3/12/97	>99%	
3/26/97	>99%	
4/3/97	>99%	
4/9/97	>99%	
4/23/97	>99%	
5/8/97	>99%	
5/20/97	>99%	
6/17/97	>99%	

[1] Percent of ash pond water that caused 50% mortality in 48-hour acute toxicity test.
[2] Values reported as >99% had less than 50% mortality in undiluted ash pond water; therefore, there is no LC_{50}.

Causes of Toxicity

Treatment Results

Dissolved, organically complexed metals were identified as the most likely cause of toxicity using Toxicity Identification Evaluations (TIE) during the three toxic events. Results of the treatments used in the TIEs are shown in Table 4-2. Results used to determine the cause of toxicity include:

- Filtering did not reduce the toxicity of the ash pond water. This shows that the toxic agents are in the dissolved state or in soluble complexes with organic matter.

Table 4-2
Summary of Toxicity Identification Evaluation Testing

TIE Treatment	Acute Toxicity LC_{50} at % Sample*	Fractionation Designed to Remove	Effect on Toxicity
September 1996—TIE Round 1			
Untreated (before TIE began)	35%		
Baseline (during TIE)	24%		
Cation Exchange Treated	>99%	Metals, plus other suspended solids	Indicates that metals were a cause of toxicity.
GAC Treated	>99%	Non-polar organics, plus other suspended solids and removes some metals cation exchange	Removed toxicity which would typically indicate organics-caused toxicity. However, water quality data from the December test show that metals were effectively removed by GAC. Is also consistent with an organically complexed metal being the primary toxicant.
Silica Gel Treated	93%	Polar organics	Removed most of the toxicity. No water quality data, so it is uncertain if metals were effectively removed.
Hardness Elevation	48%	Competes with divalent cationic metals reducing their toxicity	Toxicity was reduced by 50%, which is consistent with metals as the cause of toxicity.
EDTA Treated	65%	Makes metals less bioavailable	Mortalities at lowest dilutions indicate EDTA caused toxicity.
September 1996—TIE Round 2			
Baseline (during TIE)	23%		
0.1 µm Filtration Treated	22%	Suspended solids and particulate form of metals	Lack of effect on toxicity shows that dissolved parameter causes toxicity. Also confirms that ion exchange and GAC were removing toxicity by removing dissolved metals, not just acting as a filter.
November 1996			
Baseline (during TIE)	71%		
Cation Exchange Treated	>99%	Metals, plus other suspended solids	Indicates that metals were a cause of toxicity.
December 1996			
Baseline (during TIE)	49%		

Table 4-2
Summary of Toxicity Identification Evaluation Testing

TIE Treatment	Acute Toxicity LC_{50} at % Sample*	Fractionation Designed to Remove	Effect on Toxicity
Cation Exchange Treated	>99%	Metals, plus other suspended solids	Indicates that metals were a cause of toxicity.
GAC Treated	>99%	Non-polar organics, plus other suspended solids	Removed toxicity that would typically indicate organics-caused toxicity. However, water quality data show that metals were effectively removed by GAC. Is also consistent with an organically complexed metal being the primary toxicant.
XAD-4 Treated	>99%	Organically bound metals	Removed toxicity, indicates organically bound metals caused toxicity. Water quality data show that metals were effectively removed which is consistent with an organically complexed metal being the primary toxicant.
September 1997			
XAD-4 Resin			Failed to remove metals spiked into lab water in ionic form. Removal of metals from ash pond water in December test indicates metals present in organically complexed form.

*Values reported as >99% had less than 50% mortality in undiluted ash pond water; therefore, there is no LC_{50}.

- Ion exchange eliminated toxicity. Because the simple filtration did not remove toxicity, it can be concluded that the metals removal capabilities of the ion exchange resin is what removed toxicity. Because metals are bound to exchange resin more tightly than to organic ligands, it is not clear from this test if metals present in water are in organo-metal complexes.
- EDTA treatment reduced, but did not eliminate, toxicity. However, because the 6.25% ash pond water dilution was toxic in only this test, it appears that the EDTA itself was causing toxicity. Therefore, results from this test are inconclusive. In addition, organically complexed metals may have reacted differently with EDTA than is predicted for ionic forms of metals.
- Increasing hardness reduced but did not eliminate the ash pond water toxicity. Increasing hardness does not remove metals from a sample, but along with

alkalinity, reduces the toxicity of some cationic metals [19, 20]. In this treatment, the sample hardness was doubled from 195 mg/L as $CaCO_3$ to 390 mg/L. The expected response of metal-related toxicity to a doubling of hardness is a reduction of the percent of sample at the LC_{50}. The treated sample LC_{50} was 48%, twice the 24% of the untreated baseline sample. The relationship between metals toxicity and hardness is not linear; however, the response to the hardness elevation does suggest metals as the cause of toxicity.

- Granular activated carbon (GAC) reduced toxicity. This normally indicates toxicity caused by non-polar organic compounds. However, an analysis of the water from each treatment, summarized in Table 4-3, shows that the GAC treatment removes metals as well as, and for some metals better than, the ion exchange treatment. Therefore, it is likely that the toxicity reduction that resulted from GAC treatment was caused by a reduction in metals concentrations. This removal may be due to metals present as organo-metallic compounds.

- The XAD-4 resin is designed to remove organically bound metals. This treatment also reduced toxicity, although as is shown in Table 4-3, there was only a 70% survival in undiluted treated samples rather than 100% as in the other treatments. This supports the conclusion from the GAC test that metals may be present as organo-metallic compounds. The treatment was as efficient at removing copper as the GAC and cation exchange resin, but not as efficient for nickel and zinc.

- Although copper was well removed from ash pond water by XAD-4, a subsequent test showed that ionic copper is poorly removed by XAD-4. Results are included in Table 4-3. This indicates that the copper in the ash pond water was present in forms other than ionic, most likely as organic complexes.

- It should be noted that selenium was poorly removed by the treatments that reduced the toxicity. This indicates that selenium is not the cause of toxicity.

Ash Pond Water Quality Tracking

A correlation was found between the concentrations of some trace metals and ash pond toxicity, which suggests that specific metals cause toxicity. The ash pond water quality and toxicity analyzed during this project are shown in Table 4-4. Trends in toxicity, metals concentration, and general water quality are shown in Figures 4-1 to 4-3.

Copper, nickel, and zinc all were present at higher levels during the three toxic events than during the nontoxic events as is shown in Figure 4-1. Arsenic and selenium concentrations are inversely proportional to toxicity, having the highest concentrations when the water is nontoxic. This finding is strong evidence that neither arsenic nor selenium are the cause of toxicity in the Site C ash pond water. This also suggests that these metals are reacting differently than other trace metals to the changes in water quality that cause toxicity. Other metals that do not relate to toxicity include iron, cadmium, chromium, and lead.

Literature research indicates that hardness, alkalinity, and organic content affect the toxicity of several metals, including copper [19]. The relationship between these parameters and toxicity at Site C by themselves was not clear. However, the higher organic content of the ash pond water in the January 1997 samples may have helped reduce copper toxicity despite the low hardness. Some forms of organic matter such as ligands can complex metals and increase the amount of metals solubilized in the ash pond water. Organic matter measured as total organic carbon (TOC) measures both dissolved and particulate organic material. Dissolved organic carbon (DOC) ranged only from the conventional laboratory's method detection limit of 1 mg/L to 2.3 mg/L, it is the dissolved organic material that can solubilize metals. However, TOC and DOC are crude measures of organic content and do not differentiate between ligands and other non-solubilizing forms of organic matter. Concentrations of ligands below 1 mg/L could solubilize metals and affect the toxicity of ash pond water.

Table 4-3
Comparison of Water Quality and Toxicity of Treated Samples from Toxicity Identification Evaluation and XAD-4 Study

		December 1996				**September 1997**
		Ash Pond Water				**Spiked Lab Water[2]**
	Units	**Untreated**	**GAC Treated**	**Cation Exchange Treated**	**XAD-4 Resin Treated**	**XAD-Resin Treated**
Toxicity[1]	LC_{50}	**49%**	**>99%**	**>99%**	**>99%**	
Survival in 100% Sample		**0%**	**100%**	**100%**	**70%**	
Aluminum	μg/L	210	77	150	98	
Arsenic	μg/L	2.2	<D.L. (< 1.6)	<D.L. (< 1.6)	<D.L. (< 1.6)	
Beryllium	μg/L	0.6	0.16	0.19	0.25	
Cadmium	μg/L	1.3	0.6	0.44	0.42	
Copper	μg/L	15	2.7	5.8	3.4	25
Iron	μg/L	31	9.7	16	28	
Nickel	μg/L	21	9.4	5	7.3	21
Selenium	μg/L	29	20	30	16	
Zinc	μg/L	53	25	7.9	19	
Hardness of treated sample	mg/L	100	Not reported	120	80	
pH of treated sample		7.8	7.9	8.6	8.7	

<D.L. = Result is below method detection limit (MDL) for conventional method achieved by the conventional laboratory as defined in 40CFR136 [1]. Quantitation level is higher than MDL.

[1] Values reported as >99% had less than 50% mortality in undiluted ash pond water; therefore, there is no LC_{50}.

[2] Lab water prepared by raising hardness to 168 mg/L and spiked with copper to 33 μg/L and nickel to 23 μg/L.

Table 4-4
Comparison of Ash Pond Water

Parameter	**Unit**	**12/17/96**	**9/96**	**11/22/96**	**1/20 - 1/24/97**	**2/26/97**	**10/28/96**	**2/12/97**	**1/9/97**
Toxicity	**LC_{50}[1]**	**28%**	**62%**	**73%**	**>99%**	**>99%**	**>99%**	**>99%**	**>99%**
Survival in 100% ash pond water		**0%**	**0%**	**10%**	**55%**	**70%**	**80%**	**80%**	**90%**
Survival in 50% ash pond water		**10%**	**80%**	**100%**	**100%**	**95%**	**100%**	**100%**	**100%**
Method		**Conventional**	**Clean**	**Conventional**	**Clean**	**Conventional**	**Conventional**	**Conventional**	**Conventional**
Aluminum	µg/L	1500	350	560	500	150	160	900	440
Arsenic	µg/L	7.1	10	4.2	8.9	7.1	8.7	55	28
Beryllium	µg/L	<D.L. (<0.29)	0.97	<D.L. (<0.29)	0.24	0.26	0.32	<D.L. (<0.18)	0.11
Copper	**µg/L**	**32**	**17**	**10**	**6.9**	**2.4**	**3.9**	**2.9**	**5.9**
Iron	µg/L	270	130	180	210	55	88	210	110
Nickel	**µg/L**	**24**	**21**	**14**	**11**	**10**	**8.6**	**4.6**	**6.9**
Selenium	µg/L	32	64	49	59	65	48	86	56
Zinc	**µg/L**	**57**	**25**	**24**	**24**	**19**	**10.0**	**3.6**	**10**
Calcium	µg/L	39,000	56,000	48,000	39,000	42,000	46,000	44,000	41,000
Total Dissolved Solids	mg/L	260	310		270	260		280	260
Total Organic Carbon	mg/L	<D.L. (<1.0)	2.98	<D.L. (<1.0)	23	<D.L. (<1.0)	2	<D.L. (<1.0)	8.9
Dissolved Organic Carbon	mg/L	<D.L. (<1.0)		<D.L. (<1.0)		<D.L. (<1.0)	<D.L. (<1.0)	<D.L. (<1.0)	<D.L. (<1.0)
Total Suspended Solids	mg/L	12	5.8		6.8	4		7	7
Alkalinity[2]	mg/L	26	30	10	28	30	10	22	22
Hardness as $CaCO_3$[2]	mg/L	170	220	230	110	160	140	140	140
pH (lab measured)[2]		7.0	6.6	7.8	8.5	7.9	6.3	8.1	8.2
pH (field measured)		5.8	6.0	6.6	7.4	7.1	6.4	8.1	7.1
Dissolved Oxygen [2]	mg/L	10		8.8	12		14	10	9

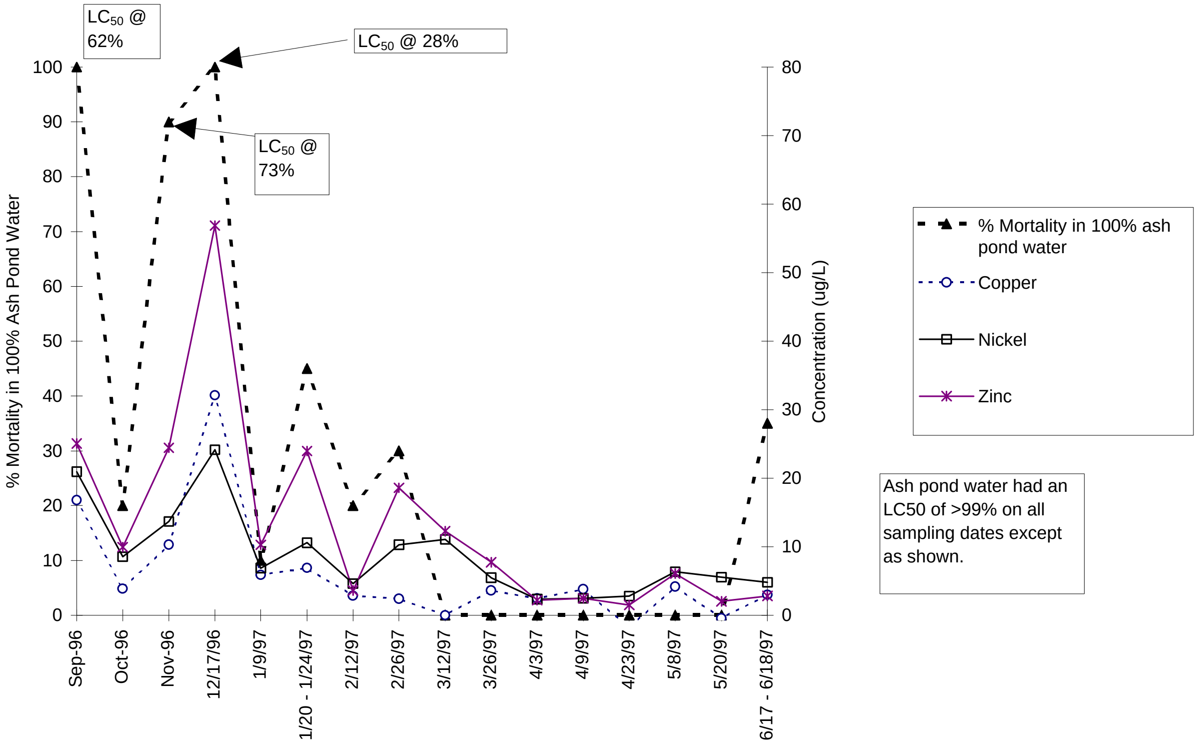
Table 4-4
Comparison of Ash Pond Water

Parameter	**Unit**	**3/12/97**	**3/26/97**	**04/03/97**	**4/9/97**	**4/23/97**	**5/8/97**	**5/20/97**	**6/17 - 6/18/97**
Toxicity	LC$_{50}$[1]	**>99%**	**>99%**	**>99%**	**>99%**	**>99%**	**>99%**	**>99%**	**>99%**
Survival in 100% ash pond water		**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**65%**
Survival in 50% ash pond water		**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**
Method		**Conventional**	**Conventional**	**Conventional**	**Conventional**	**Conventional**	**Conventional**	**Conventional**	**Clean**
Aluminum	μg/L	250	590	1020	1100	1900	950	910	1600
Arsenic	μg/L	9.2	35	86	94	130	88	79	101
Beryllium	μg/L	0.21	<D.L. (<0.18)	<D.L. (<0.18)	<D.L. (<0.18)	<D.L. (<0.9)	<D.L. (<0.18)	<D.L. (<0.18)	0.19
Copper	**μg/L**	**<D.L. (1.7)**	**3.6**	**2.4**	**3.8**	**<D.L. (<8.3)**	**4.2**	**<D.L. (<1.7)**	**3.0**
Iron	μg/L	53	92	74	110	180	150	160	130
Nickel	**μg/L**	**11**	**5.5**	**2.4**	**2.5**	**<D.L. (<6.4)**	**6.3**	**5.5**	**4.8**
Selenium	μg/L	52	63	85	85	100	100	100	100
Zinc	**μg/L**	**12**	**7.7**	**2.2**	**2.5**	**<D.L. (<7.9)**	**6.1**	**2.0**	**2.8**
Calcium	μg/L	44,000	46,000	52,000	52,000	58,000	56,000	58,000	65,000
Total Dissolved Solids	mg/L	260	260	280	260			290	280
Total Organic Carbon	mg/L	<D.L. (<1.0)	11		1.3	2.3	<D.L. (<1.0)	1.2	1.0
Dissolved Organic Carbon	mg/L	<D.L. (<1.0)	2.3		<D.L. (<1.0)	<D.L. (<1.0)	<D.L. (<1.0)	1.1	
Total Suspended Solids	mg/L	4.0	4.0	4.0	4.0			13	4.0
Alkalinity[2]	mg/L	30	30	32	34	50	32	60	90
Hardness as CaCO$_3$[2]	mg/L	160	150	170	210	160	170	170	230
pH (lab measured)[2]		8.0	8.3	8.0	8.6	8.0	7.8	7.6	8.8
pH (field measured)		8.2	8.4		8.7	9.2	7.9	8.5	8.8
Dissolved Oxygen [2]	mg/L	9	10		10	9	8	8	8

[1] Values reported as >99% had less than 50% mortality in undiluted ash pond water; therefore, there is no LC$_{50}$.

[2] Measured by bioassay lab, except hardness on 6/17/97. This value used corresponds to conventional laboratory ash pond water sample.

<D.L. = Value is less than the method detection limit (MDL) for conventional methods achieved by conventional laboratory as defined in 40CFR136 [1]. Quantitation limit is higher than MDL.



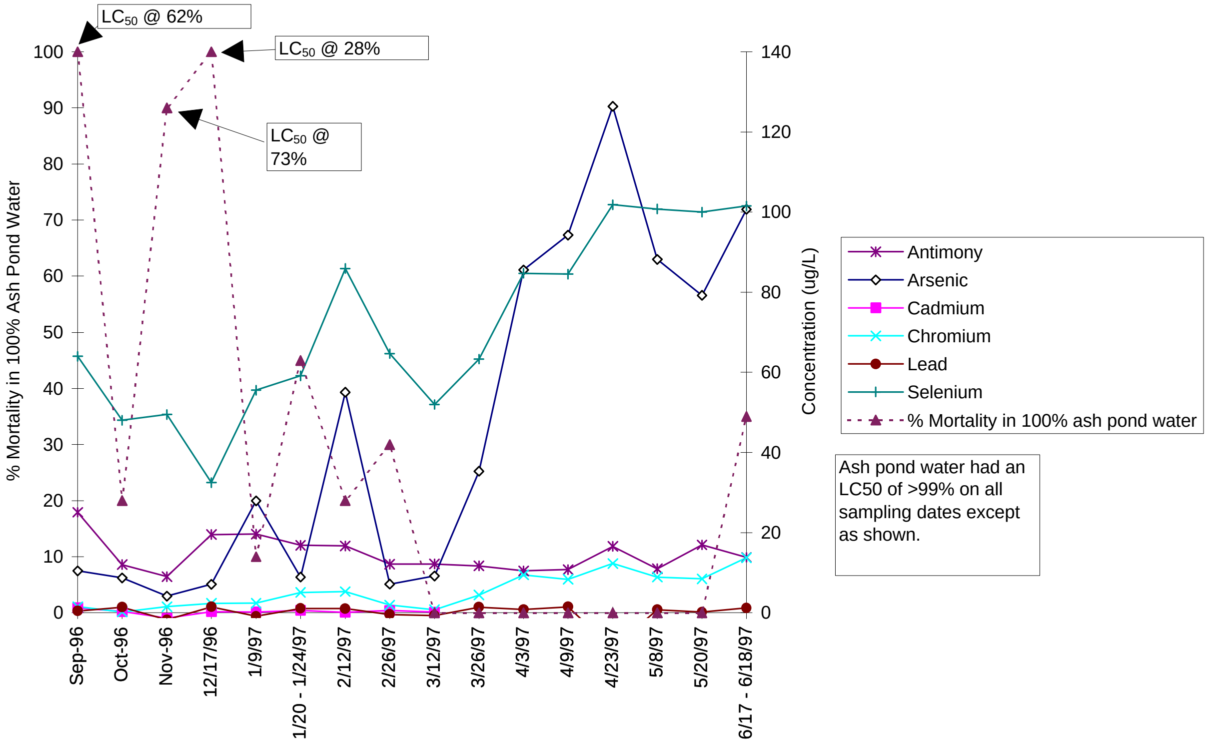
LC_{50} @ 62%

LC_{50} @ 28%

LC_{50} @ 73%

Ash pond water had an LC50 of >99% on all sampling dates except as shown.

Figure 4-1
Relationship Between Ash Pond Water Toxicity and Metals Likely To Be Cause of Toxicity



LC_{50} @ 62%

LC_{50} @ 28%

LC_{50} @ 73%

Ash pond water had an LC50 of >99% on all sampling dates except as shown.

Figure 4-2
Ash Pond Water Toxicity and Metals That Appear Not To Be Cause of Toxicity

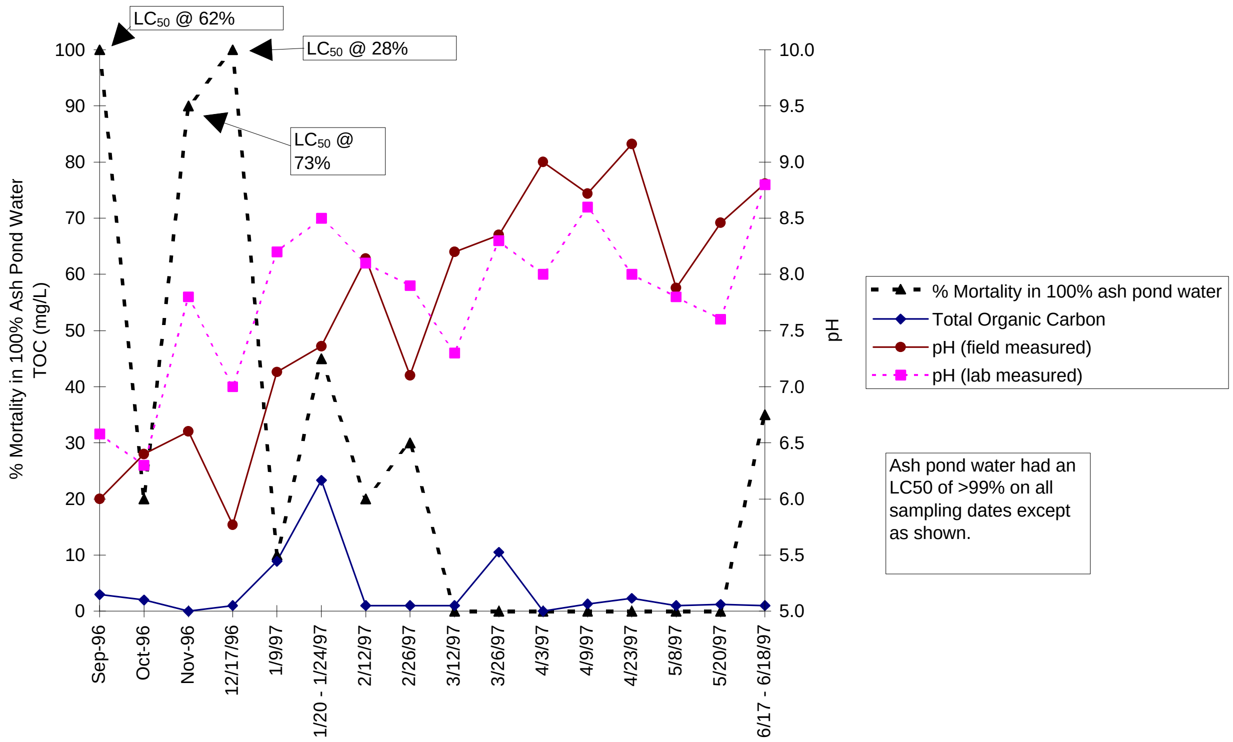


Figure 4-3
Ash Pond Water Toxicity Versus pH and TOC

The pH of the ash pond water tracks well with toxicity. This is most likely due to the solubilization of metals such as copper and nickel at lower pH values. Some anomalies to this trend do appear, such as the nontoxic sample in October 28, 1996, despite a pH of less than 7. This is an example of the importance that the pH at the head of the ash pond has in determining the solubility and concentration of metals. A pH decrease later in the pond has less impact on toxicity because the metals-rich particulate matter has already settled out and is no longer available to be solubilized.

Metal Concentrations at Which Toxicity Occurs

Toxicity occurred at part-per-billion levels of trace metals in the toxic ash pond water samples as shown in Table 4-5. Research from literature has determined that the *Ceriodaphnia dubia* LC_{50} concentrations of copper range from 7 to 40 µg/L at pH up to 7.5, nickel ranges from 13 to over 200 µg/L, and zinc ranges from 65 to over 500 µg/L [20-25]. Toxicity occurred at concentrations towards the low end of the ranges for copper and nickel. Therefore, it appears that both copper and nickel are potential causes of toxicity. Zinc appears not to be the sole cause of toxicity; however, past toxicity studies have shown that copper and zinc together in water are more toxic than the same concentration of copper alone [26].

Table 4-5
Metal Concentrations That Cause Toxicity in Ash Pond Water Samples

Sample Date	Metal	Concentration (µg/L)	% Ash Pond Water at LC_{50}	Concentration at LC_{50}* (µg/L)
9/96	Copper	17	62%	11
11/96	Copper	10	73%	7
12/96	Copper	32	28%	9
9/96	Nickel	21	62%	13
11/96	Nickel	14	73%	10
12/96	Nickel	24	28%	7
9/96	Zinc	25	62%	15
11/96	Zinc	24	73%	18
12/96	Zinc	57	28%	16

* Copper concentration at LC_{50} is computed using the dilution of ash pond water at LC_{50}. For example, in September: 17 µg/L in 100% ash pond water* (62% ash pond water at LC_{50}) = 17 µg/L * 0.62 = 11 µg/L

Copper was found to have a comparable toxicity in the ash pond water as reconstituted laboratory water with an equal hardness. Both had copper concentrations at the LC_{50} of 10 µg/L. The test served to evaluate potential benefits and synergistic effects of ash pond water quality. Potential benefits include organic matter binding with metals to make them less toxic. Synergistic effects include other metals increasing the toxicity of copper. Because metals are added in dissolved form, this test will not measure if ligands are complexing metals into solution and increasing their toxicity.

The concentration of copper that is toxic was supported by two spiking tests. Results of these tests, which consisted of adding copper to nontoxic ash pond water samples, are shown in Table 4-6. Work done by the host utility found similarly low levels of copper to be toxic at low pH. This past work also found that LC_{50} copper concentrations increased at pH 8.0 and above, to the range of 20 to 50 µg/L of copper. This was possibly due to measuring total rather than dissolved (bioavailable and therefore toxic) copper. Spiking tests also were conducted for nickel and zinc as is shown in Table 4-6. However, results were less conclusive due to poor relationship of toxicity to metal concentrations at various spiking amounts.

Table 4-6
Copper Concentrations That Caused Toxicity in Metal Spiking Tests in Ash Pond Water

Sample	Metal	Estimated LC_{50} Concentration	Initial pH
2/26/97	Copper	5.5 µg/L	7.9
3/26/97	Copper	13 µg/L	8.3
6/17/97	Nickel	~11 µg/L*	8.9
6/17/97	Zinc	~44 µg/L*	8.9

*Results are estimates due to poor dose response during test.

Relationship of Metals to Ash Pond Water pH

Concentrations of copper, nickel, and zinc increase at low pH in the ash pond because the solubility of cationic metals is higher in acidic conditions. Solubilization of metals into organo-metallic compounds also may increase concentrations of metals in the ash pond water. This solubilization may be one factor of ash pond water chemistry that results in a pH and metal relationship that differs from theoretical. Metal concentration in an ash pond receiving fly ash also will be affected by the characteristics of the ash itself. The amount of iron hydroxide present in the water will influence the removal of trace metals by precipitation. The availability of the trace metals in the suspended ash will influence the reaction with the ferric oxy-hydroxides. However, at Site C metal concentrations and the pH of the ash pond water were directly related over the course of the PISCES sampling as is shown in Figures 4-4 to 4-6. The relationship between copper, nickel, zinc, and pH also was seen at Sites A and B of the EPRI PISCES program, at several locations sampled across the pond [12]. Factors potentially modifying the relationships from theoretical [27, 28] include the presence of particulate metal, organo-metallic solubilization, and the influence of other cations and anions.

Dissolved metal concentrations fluctuated between the three sampling weeks as shown in Table 4-7. TIE work and past research [29] indicates that dissolved copper is more bioavailable, and therefore, more toxic than particulate copper. At higher pH values, the copper becomes insoluble, and much less bioavailable, and therefore, less toxic. Conversely, arsenic and selenium are more soluble at higher pH values. The higher total concentrations are due to the increase in the dissolved species of these metals as is shown in Table 4-7.

Theories of Toxicity Causes Evaluated and Rejected During Study

Several possible causes of toxicity were examined during the study. A summary of two of these theories follows:

1. **Periodic basin carryover is not the cause of toxic events.** A review of suspended solids concentration shows no evidence of a relationship between toxicity and solids

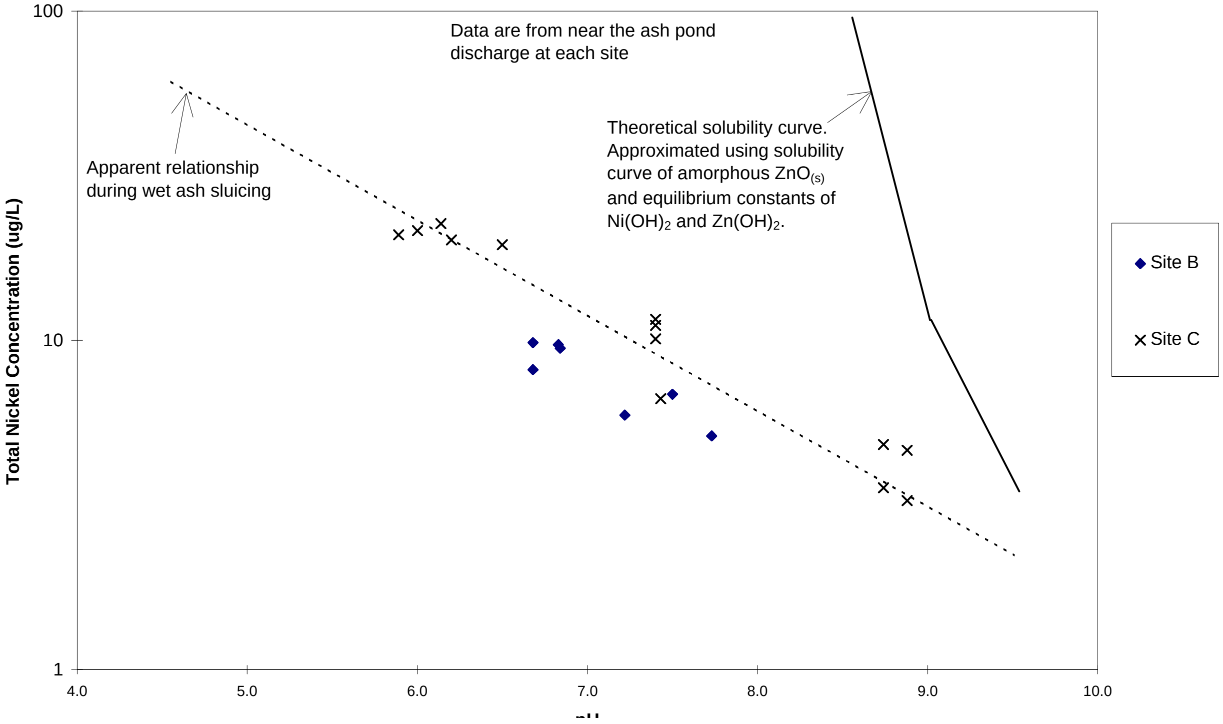
content of the ash pond water. Further, the TIE work showed that the toxicant is not removed by filtration.

2. **Short duration changes in plant operation, such as weekend operation, do not affect ash pond water.** A conductivity meter was placed at the ash pond water sample location for three weeks in January 1997. Conductivity was used as a surrogate measure of changes in water quality. No changes from day to day were noted in the three weeks.

Other Ash Pond Water Quality Issues

Comparison of Ash Pond Water with Water Quality Criteria

One objective of the PISCES study is to evaluate the impact of potential discharge limits on utilities around the country based on data collected at the study sites. Federal water quality criteria (WQC), which are based on aquatic toxicity and human health limits, represent the most stringent potential discharge limits [19]. These criteria were exceeded for several metals in the ash pond water. Actual discharge limits may be imposed at stations discharging to waterways with limited mixing zones. Stations discharging to larger water bodies would likely receive less stringent discharge limits, unless background levels of pollutants were high.



Data are from near the ash pond discharge at each site

Apparent relationship during wet ash sluicing

Theoretical solubility curve. Approximated using solubility curve of amorphous $ZnO_{(s)}$ and equilibrium constants of $Ni(OH)_2$ and $Zn(OH)_2$.

Figure 4-4
Copper and pH in Ash Ponds

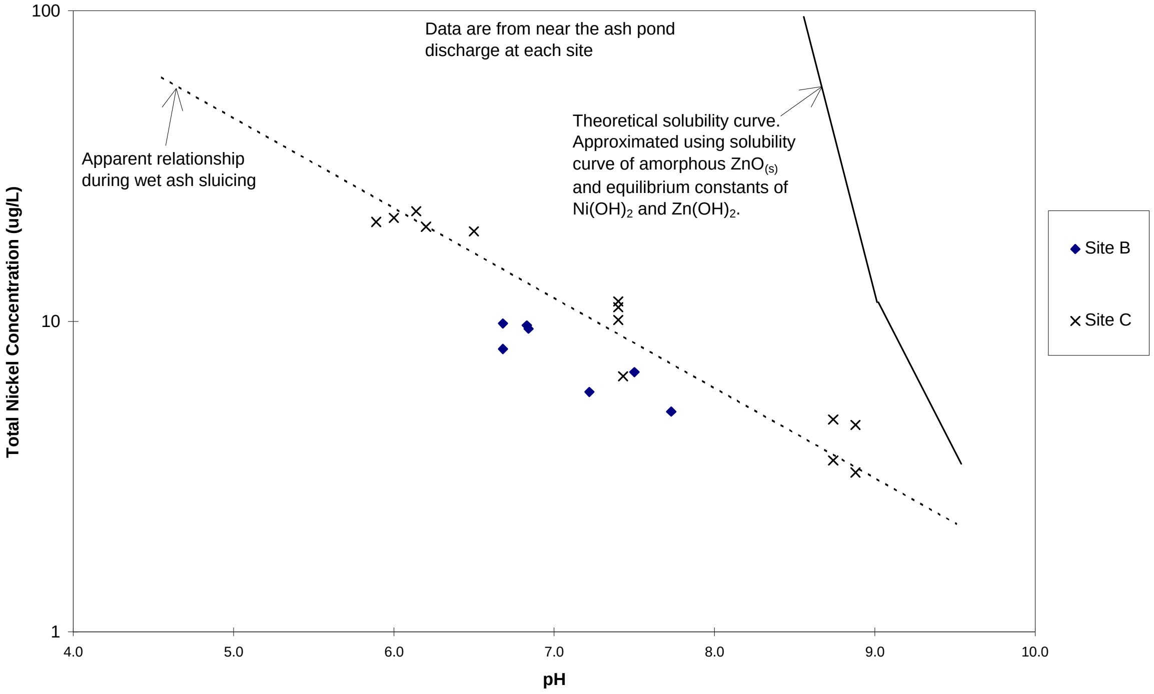


Figure 4-5
Nickel and pH in Ash Ponds

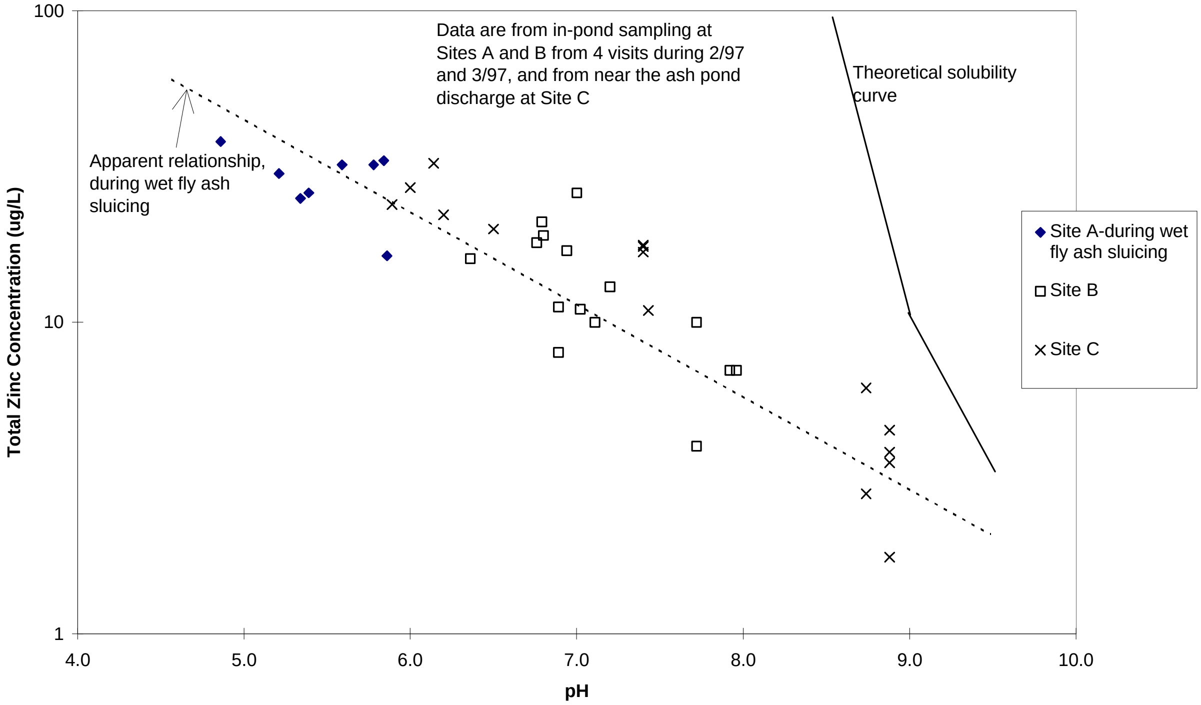


Figure 4-6
Zinc and pH in Ash Ponds

Table 4-7
Effect of Dissolved Metal Concentrations on Ash Pond Water Toxicity

Parameter	Week 1	Week 2	Week 3
	Average Dissolved Metal Concentration (µg/L)		
Aluminum*	130	67	1200
Arsenic	5.2	4.4	98
Copper	**16**	**5.1**	**0.71**
Iron*	21	41	<D.L. (<13)
Nickel	**20**	**8.7**	**3.2**
Selenium	60	57	110
Zinc	**25**	**17**	**3.3**
pH	5.6 to 7.4	7.1 to 7.5	8.7 to 8.9
LC_{50} (% ash pond water)	9/25: 62% 9/26: 35%	>99%	>99%

*These parameters were sampled and analyzed using conventional methods. All other parameters were measured and analyzed using clean methods.

<D.L. = Average is less than method detection limit (MDL) for conventional method achieved by the conventional laboratory as defined in 40CFR136 [1]. Quantitation limit is higher than MDL.

The ash pond water quality changed as a result of coal management begun in January 1997. This is reflected in Table 4-8. During 1996, the metals at or above federal WQC at Site C on average included antimony, beryllium, copper, selenium, thallium, and nickel (saltwater criteria only). The maximum measured concentrations of cadmium also exceeded WQC. Once coal management was implemented in 1997, the pH of the pond increased and the concentration of divalent metals decreased. Several metals decreased to below WQC, including copper (below freshwater WQC but still above saltwater criteria), cadmium (both average and maximum), and thallium (average). However, the concentration of arsenic increased, at maximum concentrations above the WQC. This increase was due to changes in coal characteristics and, potentially, to higher pH water.

Other water quality parameters were present at concentrations that did not approach typical discharge limits. These included volatile and semivolatile organic compounds, nutrients, and oil and grease.

Ash Pond Treatment Performance

The average ash pond influent concentration at Site C was 10,000 mg/L total suspended solids (TSS). This was reduced to an average concentration at the end of the ash pond of 6 mg/L. Water at the end of the pond contained TSS concentrations in compliance with discharge limits typically placed on utilities; the highest measured concentration was 13 mg/L TSS. As at Sites A and B, over 99% of the suspended solids entering the ash pond were removed.

Table 4-8
Comparison of Ash Pond Water to Water Quality Criteria Before and After Coal Management

	Samples from September to December 1996		**Samples from January to June 1997**			
	Average	**Maximum**	**Average**	**Maximum**	**Most Stringent federal Water Quality Criteria**	
	(µg/L)	**(µg/L)**	**(µg/L)**	**(µg/L)**	**(µg/L)**	**Notes**
Aluminum	**500**	**1,490**	**730**	**1,920**		Regulated at 87 mg/L by some states.
Antimony	**19**	**25**	**15**	**20**	14	Lowest federal WQC.
Arsenic	7.9	11	40	**130**	50	Regulation in some states is as low as 0.018 µg/L.
Beryllium	**0.72**	**1.2**	**0.16**	**0.41**	0.07	Not a federal criteria but used in some states.
Cadmium	0.86	**1.4**	0.24	0.78	1.0	Lowest federal WQC.[2]
Chromium	1.2	2.4	6.0	14	180	Lowest federal WQC for Chromium III. Lowest freshwater criteria for Chromium VI is 11 mg/L, based on chronic toxicity.[2]
Copper	**18**	**32**	3.9	8.0	11	Lowest saltwater criteria is 2.4 µg/L.[2]
Lead	0.58	1.8	0.20	1.7	2.5	Lowest federal WQC.[2]
Mercury[1]					0.012	Lowest federal WQC.[2]
Nickel	19	24	7.1	12	160	Lowest saltwater criteria is 8.3 µg/L.[2]
Selenium	**64**	**110**	**72**	**100**	5	Lowest federal WQC.
Silver	0.085	0.82	<0.023[3]	0.33	3.4	Lowest saltwater criteria is 1.9 µg/L.[2]
Thallium	**2.6**	**4.9**	0.85	**3.8**	1.7	Lowest federal WQC.
Zinc	29	57	10	31	100	Lowest saltwater criteria is 81 µg/L.[2]

Includes clean method data from three main sampling events and conventional method data for additional events.

[1] Conventional analytical data indicated a significant high bias for mercury. Therefore, values shown are for clean method results only.

[2] Criteria are based on hardness; a default hardness of 100 mg/L was used.

BOLD values are in excess of strictest freshwater WQC.

[3] The average value was below the clean method critical level, which was determined using an alternative minimum level study of reagent water standards. Quantitation limit is higher than critical level.

Iron in the Site C ash pond water near the effluent of the pond was over 80% particulate. However, the form of aluminum varied between sampling weeks as is seen in Table 4-9. This variation appears to be caused by changes in pH. The total concentration also is affected by pH, increasing as pH increased from 6 to 9 pH units. This agrees with solubility theory. The minimum solubility pH for aluminum hydroxide ($Al(OH)_3$) is 7 pH units in a system free of other cations and anions [18]. At above or below this, pH the solubility increases. Iron and aluminum were found to be predominately particulate in the ash pond water of Sites A and B.

Table 4-9
Form of Iron and Aluminum in Ash Pond Water

Parameter	Week 1 September 1996	Week 2 January 1997	Week 3 June 1997
Iron, total (µg/L)	130	210	130
Iron, % dissolved	16%	19%	6%
Aluminum, total (µg/L)	350	500	1,600
Aluminum, % dissolved	38%	13%	74%
TSS (mg/L)	5	6	<D.L. (<4)
pH	5.6 to 7.4	7.1 to 7.5	8.7 to 8.9

<D.L. = Average is less than the method detection limit (MDL) for conventional method, achieved by the conventional laboratory as defined in 40CFR136 [1]. Quantitation limit is higher than MDL.

Site C ash pond water contained predominately dissolved selenium. However, the form of arsenic varied due to low concentrations of dissolved arsenic during the low-pH condition of the first week of sampling. In the last week of sampling when the pH was elevated, the dissolved concentrations of arsenic and selenium increased. The observation made at Sites A and B that ash ponds are able to remove particulate arsenic and selenium to below 10 µg/L, but that dissolved arsenic and selenium concentrations are related to pH, were supported by Site C data. This relationship is due to solubility of the metals which increases at higher pH values and the improved effectiveness of iron coprecipitation at removing arsenic and selenium at low pH conditions [30 to 33].

Arsenate (V) and selenite (IV) were the predominate forms in the Site C ash pond water as at Sites A and B. Concentrations of arsenic and selenium species in the ash pond are shown in Table 4-10. In the September sample, the selenium (VI) was present at 34 µg/L; the other weeks, it was below method detection limits. The September sample was toxic while the other two weeks were not. Note that selenium (VI) is the more toxic form of selenium. However, toxicity identification evaluation work described above has shown that total selenium does not show a relationship to toxicity.

Table 4-10
Comparison of Speciated Metals Data for Site C

	Concentration (μg/L)			Percentage		
Parameter	**Week 1**	**Week 2**	**Week 3**	**Week 1**	**Week 2**	**Week 3**
Arsenic III	0.63	0.09	0.85	8%	1%	1%
Arsenic V	6.8	8.7	101	90%	99%	99%
Total As	7.5	8.8	102			
Selenium IV	55	60	120	61%	90%	100%
Selenium VI	34	6.7	<0.5[1]	39%	10%	0%
Total Se	89	66	100[2]			
Chromium VI	0.31	1.0	NA	20%	52%	NA
Chromium	1.5	2.0	13			
pH	5.6 to 7.4	7.1 to 7.5	8.7 to 8.9			

NA = Not analyzed

[1] Average value is less than detection limit achieved by laboratory for speciated selenium analysis by clean methods.

[2] Value estimated due to poor agreement between EPA methods 1638 and 1632 for these samples.

Mercury was removed to near or below the strictest water quality criteria. The ash pond removed over 90% of the mercury entering the pond. Methyl and dimethyl mercury species were less than 1% of the total mercury. Therefore, these species were not considered of interest.

At Site C, chromium and hexavalent chromium were removed to below their WQC. The percent of chromium that was present as hexavalent chromium varied between September and January sampling events, increasing at higher pH values. Chromium VI also was found to represent a larger portion of total chromium at higher pH conditions at Sites A and B [12]. Total chromium concentration also increased at higher pH values at the other sites.

5

TOXICITY SOURCES AND REASONS FOR VARIABILITY

The cause of toxicity was found to be dissolved cationic metals, particularly copper, nickel, and zinc in organically complexed form. The solubility and ash pond water concentration of these metals is related primarily to the pH of the ash pond. The largest source of these metals, and largest influence on pH, is fly ash handling, as shown in Table 5-1.

The sources of these cationic metals, and the factors in toxicity variation, include the range of fly ash handling wastes produced by various coals used at the site, the operation of a SO_3 fly ash conditioning system, and the pH of water in the ash pond. Section 5 addresses these sources and variation factors.

Sources of Pollutants to the Ash Ponds

Fly ash sluice water is the largest source of metals to the ash pond. More than 90% of copper, nickel, arsenic, and selenium entering the pond are in fly ash sluice water. The fly ash sluice water also has the lowest pH of the plant waste streams, other than the intermittent coal pile runoff stream. Therefore, it is the most important factor affecting the toxicity of ash pond water. The other streams had minor contributions of the metals identified as causes of toxicity, the highest of which was the plant waste from Unit 2 which contributed over 10% of the zinc discharged to the ash pond.

Effect of Various Coals on Ash Handling Wastes

Ash sluice water from simulated sluices in the laboratory were observed to vary in pH from 4 to 12, and metal content by 3 orders of magnitude. Site C uses coal from eight mines which differ in their makeup and in the ash they produce. The site was not able to identify which coal or coals were being fired on a particular day.

Chemical analyses of ashes collected at different times during the year are shown in Table 5-2. Each ash was collected from the ductwork leading to the ESPs. The trace metal content of the ashes is relatively consistent. For example, copper ranges between 49 and 110 milligrams per kilogram (mg/kg). However, other parameters varied more such as calcium, which ranged from 3,300 mg/kg to 18,000 mg/kg. Differences in

Table 5-1
Sources of Pollutants to the Ash Pond

	Flow	Flow	Aluminum	Arsenic	Copper	Iron	Nickel	Selenium	Zinc	TSS	pH
	(MGD)	**(10^6 L/day)**	**Loadings (kgs/day)**								
Fly ash sluice water	0.98	3.7	190	1.4	3.0	23	0.9	0.5	2.0	1,220	3.5 to 9.2
Percent of total load			**90%**	**90%**	**96%**	**60%**	**93%**	**96%**	**80%**	**58%**	
Bottom ash sluice water	1.3	5.0	7.8	0.1	0.05	4.6	0.04	0.01	0.2	320	4.9 to 8.8
Percent of total load			**4%**	**7%**	**2%**	**12%**	**4%**	**3%**	**7%**	**15%**	
Plant Waste Unit 2[1]	0.50	1.9	7.0	0.04	0.04	6.1	0.02	0.002	0.3	480	6.1 to 7.6
Percent of total load			**3%**	**3%**	**1%**	**16%**	**2%**	**1%**	**10%**	**23%**	
Plant Waste Unit 1[1]	0.043	0.16	0.03	0.0005	0.01	0.04	0.0006	0.0003	0.03	2.2	6.4
Percent of total load			**0%**	**0%**	**0%**	**0%**	**0%**	**0%**	**1%**	**0%**	
Coal Pile Runoff [1,2]	0.02	0.08	2.4	0.002	0.02	4.5	0.02	0.0009	0.04	120	1.5
Percent of total load			**1%**	**0%**	**1%**	**12%**	**2%**	**0%**	**1.6%**	**6%**	
Total	**2.9**	**11**	**210**	**1.5**	**3.1**	**38**	**1.0**	**0.47**	**2.5**	**2,100**	

[1] Samples of plant waste and coal pile runoff were shaken to resuspend solids, rather than allowed to settle like ash sluice wastes.

[2] Coal pile runoff flow is annualized over a year from 5 years of rainfall data.

Table 5-2
Range of Fly Ashes Produced At Site C

	Dry fly ash, unmixed (mg/kg)				
Unit	**Unit 2**	**Unit 1**	**Unit 1**	**Unit 1**	**Unit 1**
Collection Date	**9/27/96**	**10/31/96**	**11/21/96**	**5/20/97**	**6/19/97**
Aluminum	130,000	120,000	120,000	140,000	130,000
Antimony	4	4	4	4	4
Arsenic	79	110	81	50	83
Beryllium	21	16	17	15	14
Boron	26	20	20	32	20
Cadmium	4	10	5	4	5
Chromium	96	70	62	43	63
Copper	74	82	83	32	98
Iron	45,000	120,000	46,000	48,000	54,000
Lead	100	84	43	26	27
Mercury	0.03	0.04	0.04	0.04	0.04
Nickel	90	41	100	53	69
Selenium	24	11	7	7	13
Silver	2	2	2	2	2
Thallium	4	5	5	4	4
Vanadium	86	64	98	62	82
Zinc	56	34	41	39	66
Calcium	4,000	13,000	6,100	3,300	18,000
Magnesium	6,800	6,200	5,100	8,400	7,700
Manganese	170	1,600	160	210	230
Potassium	30,053	27,812	21,668	34,702	27,480
Silicon	230,000	220,000	220,000	270,000	230,000
Sodium	2,800	2,500	1,700	2,800	2,800
Mineral Analysis (% weight, ignited basis)					
CaO	0.63	1.9	0.94	1.9	2.8
Fe_2O_3	7.2	18	7.2	8.2	8.5
MgO	1.3	1.1	0.93	1.6	1.4
Na_2O	0.43	0.36	0.25	0.46	0.42
K_2O	4.1	3.6	2.9	4.1	3.6
SiO_2	56	50	53	54	54
Al_2O_3	28	24	25	29	28
Ratio of Base/Acid	**0.16**	**0.33**	**0.16**	**0.20**	**0.20**

	Simulated Sluice Water pH				
	4.5	11.6	7.8	8.1	12.1

	Ash Pond Water Samples Associated with Collection of Dry Fly Ash				
Date	**9/27/96**	**10/28/96**	**11/22/96**	**5/20/97**	**6/18/97**
Ash Pond Water pH (field measured)	6.1	6.4	6.6	8.5	8.8

All data shown for ash characterization are from ASTM method analyses [11].

mineral content can affect the alkalinity of the sluice water produced and also the reaction between the ash and the SO_3 added as an ash conditioner. Sluice simulations supported this relationship; the pH of the sluice water created varied with calcium content. Field observations of ash pond water quality show that the pH of the fly ash sluice water affects the pH of the ash pond. Frequent variations in the types of coal used and mixing within the ash pond cloud can this relationship, but the site has seen that consistent use of some types of coals results in alkaline conditions in the pond. Minerals that produce an alkaline ash include calcium oxide (CaO), iron oxide (Fe_2O_3), magnesium oxide (MgO), sodium oxide (Na_2O), and potassium oxide (K_2O). Minerals that produce an acidic ash include silica (SiO_2) and alumina (Al_2O_3).

The metal concentration and ash content of coal used at the site varies due to the different suppliers used. The metal content of the coal samples taken during the PISCES program is included in Appendix A. The coal characteristics such as percent ash and heating value are included in Appendix B.

Simulations of fly ash sluice water were run using ashes collected at different times during the year. The standard operating procedure used in the simulations is included in Appendix D. The sluice waters produced had a wide variation in both pH and metal concentration. Results are shown in Table 5-3. Observations include:

- The ash collected on September 27, 1996, produced a sluice water with much lower pH, 4.5 compared to 7.8 to 12.1 for the other four sluice waters.
- This ash also produced the highest total and dissolved concentrations of cationic metals in the sluice water. Total and dissolved copper concentrations were 800 µg/L, compared to between 1 and 7 µg/L in the other four sluice waters.
- For each sluice water, settling for 24 hours after sluicing removed nearly all particulate copper, nickel, and zinc. The concentration of dissolved copper, nickel, and zinc were a function of pH, increasing at low pH. This is shown in Figure 5-1.
- Selenium behaved differently from other metals. This is shown in Figure 5-2. It had a much lower concentration in the acidic sluice water from the September 27, 1996, ash. Selenium is known to be more soluble at low pH’s, so this is consistent with solubility theory [28].
- Arsenic did not show a pH relationship; its concentration may be dependent on its concentration in the coal or other factors such as particle size and surface arsenic concentrations.
- Aluminum exhibited a minimum solubility at neutral pH, increasing in concentration in both acidic and alkaline ashes. This is consistent with theoretical aluminum solubility [18].

Table 5-3
Effect of Fly Ash on Simulated Sluice Water

	Metals Concentration in Simulated Sluice Water (μg/L)									
	Total	**Dissolved**	**Total**	**Dissolved**	**Total**	**Dissolved**	**Total**	**Dissolved**	**Total**	**Dissolved**
Unit and Date of Collection	**U2 on 9/27/96**		**U1 on 10/31/96**		**U1 on 11/21/96**		**U1 on 5/20/97**		**U1 on 6/19/97**	
Aluminum	2,800	2,500	7,500	7,000	1,100	790	1,900	1,300	4,300	3,800
Arsenic	4.7	4.2	120	120	110	110	68	69	5.9	5.0
Beryllium	5.0	4.8	0.26	<D.L. (<0.18)	0.23	<D.L. (<0.18)	0.27	0.18	0.19	<D.L. (<0.18)
Copper	810	780	4.9	3.0	3.4	<D.L. (<1.7)	4.8	3.4	6.8	5.1
Iron	740	630	240	51	140	21	170	21	120	24
Nickel	1,500	1,500	<D.L. (<1.3)	<D.L. (<1.3)	17	15	12	10	<D.L. (<1.3)	<D.L. (<1.3)
Selenium	<D.L. (<1.5)	<D.L. (<1.5)	120	120	29	30	40	40	160	160
Zinc	410	400	5.5	5.3	3.6	3.8	5.3	4.4	25	24
Calcium	48,000	47,000	110,000	100,000	51,000	50,000	52,000	50,000	220,000	220,000
Manganese	1,200	1,200	4.7	0.88	33	31	22	20	1.3	0.48
pH - After sluicing	**4.5**		**11.6**		**7.8**		**8.1**		**12.1**	
pH - After settling	**5.3**		**11.2**		**6.4**		**8.8**		**12.1**	
Chloride (mg/L)	17		14		11		17		24	
Sulfate (mg/L)	230		200		180		180		240	
Alkalinity as $CaCO_3$ (mg/L)	3.0		190		40		38		450	
Hardness as $CaCO_3$ (mg/L)	260		300		150		220		600	
Total Dissolved Solids (mg/L)	370		420		270		300		650	
Total Suspended Solids (mg/L)	6		4		10		14		23	

<D.L. = Result is less than method detection limit (MDL) for conventional method achieved by the conventional laboratory as defined in 40CFR136 [1]. Quantitation limit is higher than MDL.

Each ash was collected from the ductwork prior to SO_3 addition.

Method for sluice simulation is included in Appendix D.

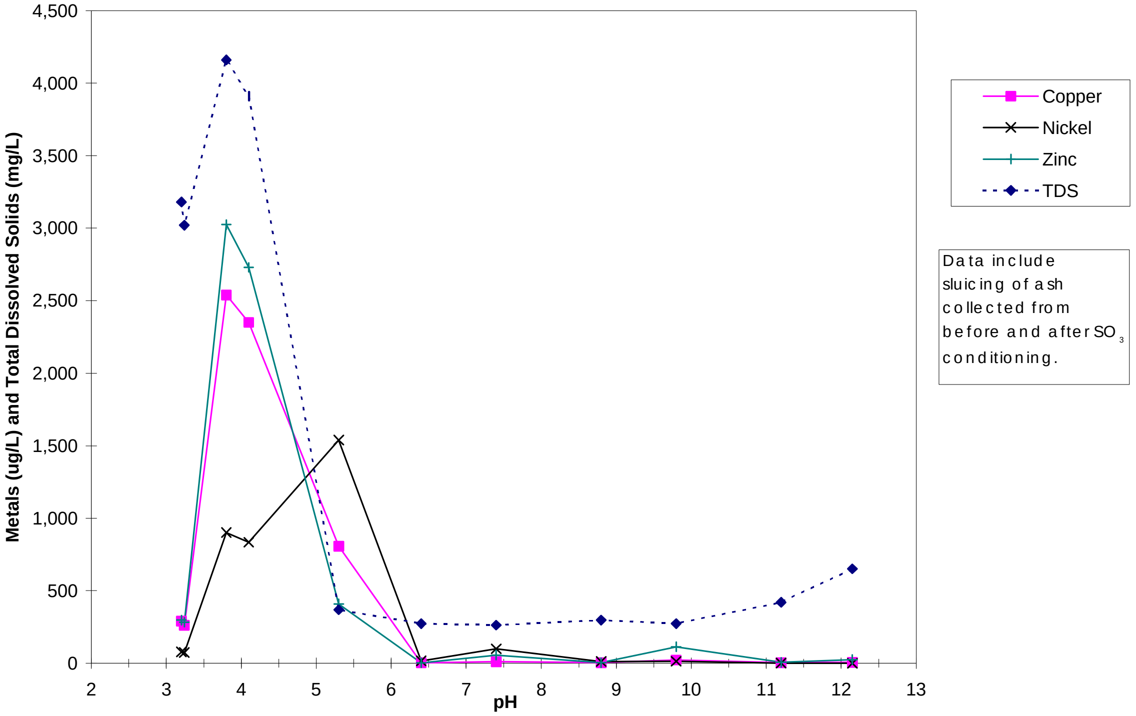


Figure 5-1
Total Metal in Sluiced Liquid from Ash Sluice Simulations

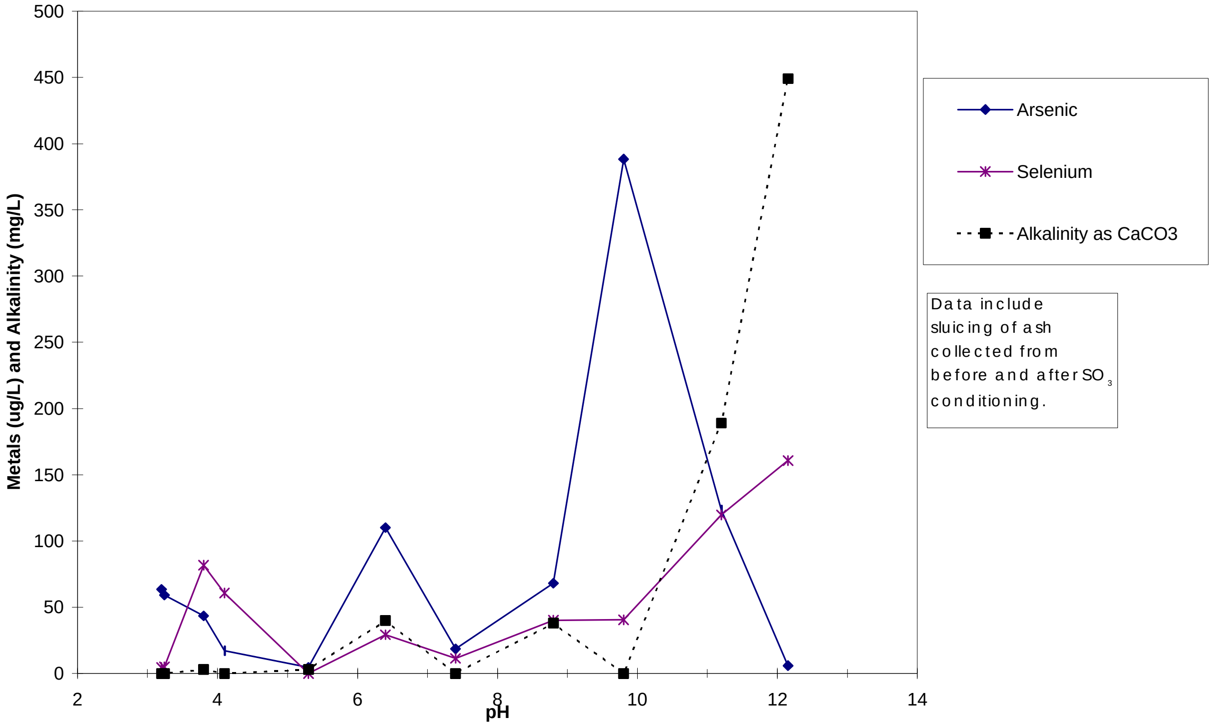


Figure 5-2
Total Metal in Sluiced Liquid from Ash Sluice Simulations

During the year, changes in both fly ash handling waste and ash pond water quality have been observed. This was seen in the simulations and in end-of-pipe pH readings of fly ash sluice water, which ranged from 3.5 to 9. The bottom ash sluice water pH ranged from 4.9 to 8.8. This waste stream is affected by the bottom ash fines created during the sluicing process, which in turn are related to the coal composition. The pH of ash pond water also changed during the study, ranging from 5.8 to 9.2, as is shown in Table 4-4.

Effects of SO_3 Injection System on Fly Ash Handling Waste

Sluicing ash treated with the molten-sulfur (SO_3) fly ash conditioning system creates a waste stream with lower pH and higher concentration of dissolved metals for some coals. A comparison of treated and untreated ash is shown in Table 5-4. It is not possible to sample ash from after the SO_3 injection port at Site C under normal conditions. However, during outages, ash that has been treated with SO_3 was sampled from the ESP. The sluice water from SO_3-treated ash had a lower pH and higher concentrations of total and dissolved copper, nickel, zinc, and iron. The effects of the SO_3 conditioning are likely due to two factors. The efficiency of the ESPs are improved; therefore, more fine particles are collected and eventually sluiced to the pond. These fine particles appear to have more metal content available to water possibly because of a greater surface area to volume ratio than larger particles. The second effect is the acidification of ash caused by SO_3 condensing and forming sulfuric acid on the ash. This acidifies the sluice water; lower pH conditions increase the solubilization of cationic metals as is discussed in Section 4. Metals that do not solubilize at low pH, such as arsenic and selenium, did not show similar increases in the sluice water.

The effect of the SO_3 conditioning system on fly ash is based on the operating conditions of the boiler. Some acidification can be expected for most ashes as SO_3 is added up to its optimal dose. The exit temperature of the air carrying the fly ash will determine whether SO_3 above the optimal dose continues to condense on the ash particles or passes through the ESP as a gas. The dew point of sulfuric acid is the primary determinant of this critical temperature; however, it also is affected by the coal. The vendor of the SO_3 conditioning system reports that for coals such as those burned at Site C this critical temperature is between 280 and 380 degrees Celsius. The Site C exit temperature is typically near 270 degrees Celsius; therefore, if SO_3 is overfed, the sluice water will be further acidified.

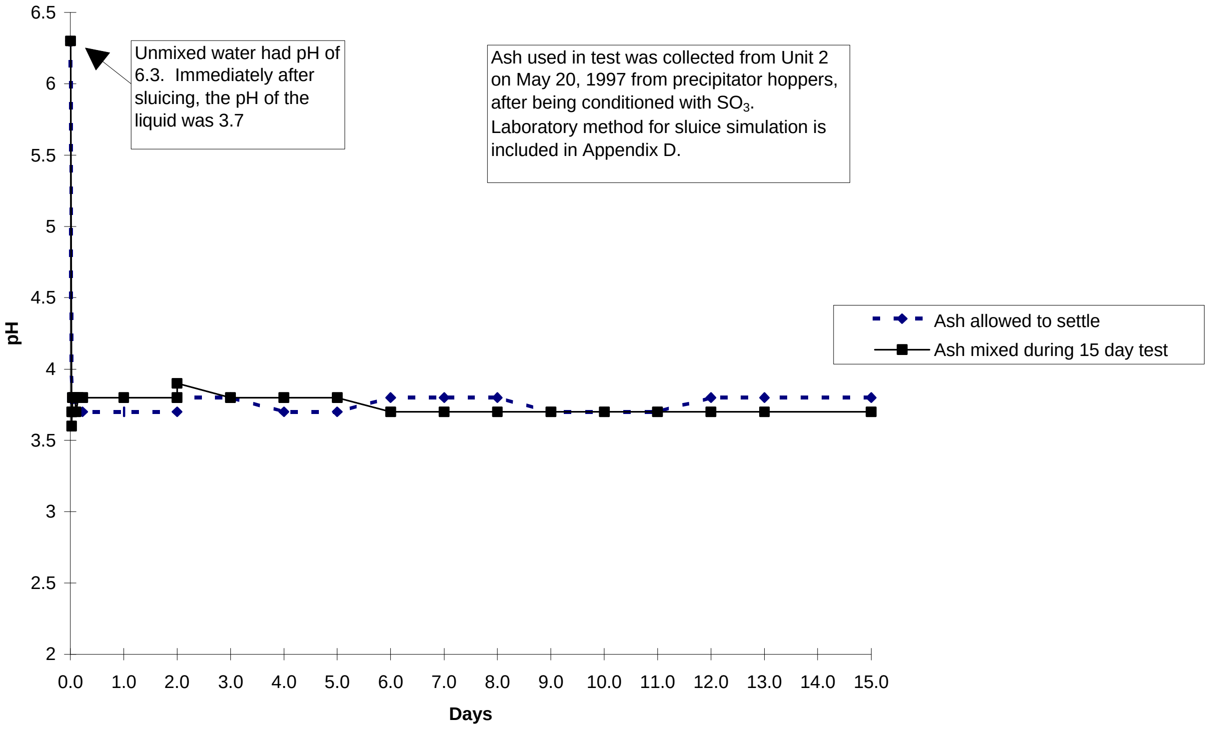
The depression of pH by sluicing ash conditioned with SO_3 was determined to be a long-term phenomenon. In a laboratory simulation, ash collected from the ESP on May 20, 1997, was mixed with water. The pH of the “sluice” water created was depressed after the 15-minute rapid mixing to 3.7 pH units. Both settled and mixed samples of sluice water maintained this low pH over the 15-day study as is shown in Figure 5-3. The results indicate that the pH depression of sluice water caused by acidified fly ash is not short-term.

Table 5-4
Comparison of Simulated Sluice Waste from SO_3-Conditioned and Nonconditioned Ash

	Dry Ash	Dissolved Metals in Liquid Stream	Dry Ash	Dissolved Metals in Liquid Stream
	(mg/kg)	(µg/L)	(mg/kg)	(µg/L)
	SO_3 Conditioned Ash from U2 on 5/20/97		Nonconditioned Ash from U1 on 5/20/97	
Aluminum	140,000	240,000	140,000	290
Arsenic	340	22	50	23
Copper	120	2,300	32	9
Iron	52,000	12,000	48,000	23
Nickel	56	810	53	97
Selenium	110	53	7	14
Zinc	150	2,700	39	60
Calcium	13,000	340,000	3,300	37,000
Magnesium	8,600		8,400	
pH–After settling*		**4.1**		**7.4**
Sulfate in unfiltered liquid (mg/L)		2,900		140

*pH was taken of unfiltered samples and used for both total and filtered samples, unless otherwise noted.

Method for sluice simulation included in Appendix D.



Unmixed water had pH of 6.3. Immediately after sluicing, the pH of the liquid was 3.7

Ash used in test was collected from Unit 2 on May 20, 1997 from precipitator hoppers, after being conditioned with SO_3. Laboratory method for sluice simulation is included in Appendix D.

Figure 5-3
pH Over Time After Simulated Sluicing of SO_3-Conditioned Ash

Variation of Effects of SO_3 on Fly Ash Handling Waste

SO_3 conditioning has differing effects on the ashes produced from the various coals. The SO_3 conditioning system adds an acid to airborne ash. However, this addition affects coals differently due to the chemical composition of the ash. High calcium oxide content ashes can neutralize the acid. Other minerals that can cause a high pH sluice water are MgO, Fe_2O_3, Na_2O, and K_2O. Mineral analyses of the ashes are shown in Table 5-5. Calcium, calcium oxide, and iron oxide concentration appears to be a good first indicator of the pH an ash will produce.

The variable effect of SO_3 on the different ashes was demonstrated by adding a fixed amount of sulfuric acid to five ashes at the beginning of the 15-minute "sluicing" to simulate the addition of SO_3. Effects ranged from no change to lowering the sluice water pH by up to 4 units and increasing concentrations of cationic metals such as copper, nickel, and zinc up to 3 orders of magnitude. It appears that the high calcium content of two of the ashes helped buffer the sluice water. These two buffered sluice waters had low concentrations of cationic metals both with and without acid addition. The other three ashes were affected by the addition of the sulfuric acid, with significant changes in pH, which in turn raised the total and dissolved cationic metals content of the sluice water as is shown in Table 5-5. Selenium was present at higher concentrations in the sluice water from ashes that produced alkaline sluice water of 11 to 12 pH units. Acidification of neutral ashes, which generated sluice water of 7 to 8 pH units, resulted in water with pH of 4 and lowered the concentration of selenium in the sluice water produced. There appeared to be an increase of selenium at pHs below 4, which was evidenced by the increase in selenium concentration when acid was added to the most acidic ash (from September 27, 1996). Arsenic concentrations in the sluice water did not appear to be related to the pH. It is likely more related to the amount of arsenic in the fly ash and the amount of arsenic that is available to partition out of the ash into sluice water. This partitioning is determined by the size and structure of the ash particle.

The fixed amount of acid to be used in the test was determined by the amount needed to acidify the liquid after sluicing nonconditioned ash taken on May 20, 1997, from pH 7.4 to pH 4.1. The pH 4.1 end point simulated the pH of the conditioned ash that was also taken on May 20. This addition of a set amount of acid simulates the station's SO_3 system operation because the chemical addition rate is not tied to the type of coal or the pH of the ash produced.

Other Studies on Flue Gas Conditioning

Site B of the EPRI PISCES program has one unit operated with SO_3 ash conditioning when necessary to meet air pollution requirements [12]. Other units at the site do not have SO_3. During one sampling event of the PISCES study, the end-of-pipe fly ash

Table 5-5
Comparison of Response to Sulfuric Acid Dosing in Simulated Sluice Water

Unit and Date of Collection	**U2 on 9/27/96**		**U1 on 10/31/96**		**U1 on 11/21/96**		**U1 on 5/20/97**		**U1 on 6/19/97**	
		Acid Added		**Acid Added**		**Acid Added**		**Acid Added**		**Acid Added**
pH - After sluicing*	**4.5**	**3.2**	**11.6**	**11.1**	**7.8**	**4.1**	**8.1**	**4.1**	**12.1**	**12.2**
pH - After settling*	**5.3**	**4.1**	**11.2**	**10.7**	**6.4**	**5.5**	**8.8**	**5.0**	**12.1**	**12.0**
Aluminum	2,500	12,000	7,000	5,900	790	2,700	1,300	5,000	3,800	3,600
020,Antimony										
Arsenic	4.2	76	120	200	110	44	69	17	5.0	7.8
Copper	780	1,900	3.0	4.6	<D.L. (<1.7)	730	3.4	960	5.1	4.2
Iron	630	2,900	51	26	21	680	21	1,000	24	25
Nickel	1,500	1,500	<D.L. (<1.3)	<D.L. (<1.3)	15	370	10	250	<D.L. (<1.3)	<D.L. (<1.3)
Selenium	<D.L. (<1.5)	7.8	120	120	30	5.9	40	5.0	160	160
Zinc	400	470	5.3	6.7	3.8	420	4.4	700	24	20
Calcium	47,000	54,000	100,000	130,000	50,000	66,000	50,000	59,000	220,000	230,000
Dry fly ash calcium content	4,000 mg/kg		13,000 mg/kg		6,100 mg/kg		3,300 mg/kg		18,000 mg/kg	
Dry Fly Ash Mineral Analysis (% weight, ignited basis)										
CaO	0.63		1.9		0.94		1.9		2.8	
Fe_2O_3	7.2		18		7.2		8.2		8.5	
MgO	1.3		1.1		0.93		1.6		1.4	
Na_2O	0.43		0.36		0.25		0.46		0.42	
K_2O	4.1		3.6		2.9		4.1		3.6	
Minerals that make an ash acidic										
SiO_2	56		50		53		54		54	
Al_2O_3	28		24		25		29		28	

*pH was taken of unfiltered samples and used for both total and filtered samples.

<D.L. = Result is less than method detection limit (MDL) for conventional method, achieved by the conventional laboratory as defined in 40CFR136 [1]. Quantitation limit is higher than MDL.

Each ash was collected from ductwork prior to SO_3 addition. Method for sluice simulation included in Appendix D.

sluice water from all units as collected. The water displayed differences supportive of the theory that SO_3 affects sluice water, including lower pH and higher cationic metal concentrations in the water with the treated ash. However, it should be noted that the units are not identical, so SO_3 treatment is not the only variable between the two sets of sluice water.

Ammonia treatment of ash at Site A of the EPRI PISCES program did not affect the ash sluice water's pH or metal content, except selenium which was lower in the ammonia-treated wastewater. Ammonia theoretically increases copper solubility. Although this was not seen at Site A, an evaluation of copper solubilization is an important factor in evaluating the use of ammonization of ash at Site C.

Impact of Ash Pond Water Quality on Ash Handling Waste

Because the solubility of metals is dependent on pH, the water in the ash pond can affect the amount of metals solubilized from the fly ash handling waste once it enters the pond. Factors that affect the water quality at the head of the ash pond include caustic addition, coal pile runoff, and equipment washes.

Caustic Addition

Raising the pH of fly ash sluice water reduced its dissolved metals concentration and therefore its toxicity. In two experiments with SO_3-conditioned ash, the dissolved copper and zinc concentrations were reduced by 95% when caustic was added after the "sluicing." Results of these two tests are shown in Table 5-6. However, the dissolved nickel was poorly removed, indicating a lower limit for nickel concentration at the pH in these studies. Nickel is known to be difficult to precipitate once it has been dissolved. Selenium concentrations increased with caustic addition. This is expected as selenium is more soluble at higher pH values. However, arsenic, which also is known to be more soluble at higher pH values, decreased in concentration upon the addition of caustic. One possible reason for this decrease is the enhancement of iron coprecipitation by the pH elevation. As is shown in Table 5-6, the concentration of dissolved iron decreased by over 2 orders of magnitude when caustic was added. The precipitation of iron hydroxides has been shown to coprecipitate arsenic in past research [31]. Iron coprecipitation also may contribute to the decrease in cationic metal concentration. Previous work has shown that cationic metals are removed by iron coprecipitation [30 to 33].

Adding caustic after the 15-minute "sluicing" simulates the way the caustic carried by the Unit 2 plant waste line is mixed with the ash sluice water after it has entered the ash pond. Adding caustic at different times in the sluice simulation was found to affect the metals concentration of the sluice water generated. Liquid produced from mixing the caustic before the sluicing had a pH of one unit higher, and lower dissolved concentrations of copper, nickel, and zinc than adding it after sluicing. The effect of the earlier caustic addition was seen most in dissolved concentrations of zinc and nickel, both of which had lower dissolved concentrations by an order of magnitude. This supports the observation that nickel has a lower limit that is pH-dependent. The results of adding caustic before the sluicing are compared to adding caustic after the sluicing in Table 5-6.

Table 5-6
Effect of Caustic Addition After Sluicing of SO_3-Conditioned Ash

	Dissolved Metal Concentrations (µg/L)				
	No Caustic	**Caustic Added After Sluice**	**No Caustic**	**Caustic Added After Sluice**	**Caustic Added During Sluice**
Unit and Date of Collection	**U2 on 2/25/97**		**U2 on 5/20/97**		
Solids Separation Method	**Centrifuging**		**Settling**		
Aluminum	22,000	1,300	260,000	220	600
Arsenic	52	2.6	33	<D.L. (<2.4)	3.1
Beryllium	15	<D.L. (<1.8)	96	0.30	<D.L. (<0.18)
Copper	280	<D.L. (<18)	2,440	8.3	4.9
Iron	1,100	<D.L. (<130)	12,000	20	17
Lead	<D.L. (<30)	<D.L. (<30)	20	3.1	<D.L. (<3)
Nickel	77	120	880	230	11
Selenium	<D.L. (<15)	37	75	120	180
Zinc	287	19	2,900	43	3.7
Calcium	18,000	170,000	370,000	330,000	210,000
Magnesium	3,800	35,000			
Manganese	130	410	2,300	1,300	140
pH - After sluicing*	**3.2**		**3.8**	**3.9**	**8.3**
pH - After Chemical Addition				**7.4**	
pH - After solids separation*	**3.2***	**7.5***	**3.8***	**5.4***	**6.5***
	Non-metals are from Unfiltered Samples				
Chloride (mg/L)	23	22	41	33	30
Sulfate (mg/L)	2,400	2,600	3,300	3,400	2,800
Alkalinity as $CaCO_3$ (mg/L)			3.0	30	56
Hardness as $CaCO_3$ (mg/L)			2,600	990	1,000
Total Dissolved Solids (mg/L)	3,200	3,800	4,200	4,300	3,700
Total Suspended Solids (mg/L)	69	89	13	8.0	4.0

*pH was taken of unfiltered samples and used for both total and filtered samples.

<D.L. = Result is less than method detection limit (MDL) for conventional method, achieved by the conventional laboratory as defined by 40CFR136 [1]. Quantitation limit is higher than MDL.

Ash was collected from precipitator after SO_3 addition.

Method for sluice simulation included in Appendix D.

Caustic is sodium hydroxide (NaOH).

Coal Pile Runoff

Coal pile runoff may be a contributor to the ash pond water toxicity. The stream is acidic, which can cause the metals in ash sluice water to be solubilized and pass through the pond causing toxicity. Strong anecdotal evidence of this relationship was observed in a toxic event recorded by the plant, following 20 inches (50 centimeters) of snow and then a quick thaw. The pH of one coal pile runoff sample collected at Site C was 1.5. The pH of the coal pile runoff in the PISCES database from bituminous coal piles ranges from 1.5 to 3.1. If the metals entering the ash pond in ash handling waste mix with an acidic waste stream, more metals will solubilize and pass through the ash pond. The increase in solubility will be larger with neutral or acidic ashes that cannot buffer the lower pH waste. Coal pile runoff mixing with the sluice water at the head of the pond is similar to the addition of sulfuric acid in ash sluice simulations and will increase the dissolved metal concentration.

During periods of heavy rainfall or snow melt, coal pile runoff can represent a high percentage of the ash pond influent flow. For example, coal pile runoff from a 2-inch (5-centimeter) rainfall in one day would produce approximately 13% of flow and represent 25% of nickel and zinc loading to the pond.

Equipment Washes

Air preheater washes are performed periodically. The ESPs are vacuumed out rather than washed down. Two air preheater washes were done during the year of the study. No correlation between the washes and toxicity were noted; however, the sampling was not designed to specifically track the effects of the washes on effluent water toxicity. The wash water is sent to the ash pond via the ash sluice lines. Testing of air preheater washes at EPRI PISCES program Site D showed that equipment wash water typically is very high in fly ash solids, and therefore, is high in metals content. In addition, the wash streams are very acidic. The initial phase of the wash sampled at Site D had a copper concentration 6 times the average ash pond influent concentration. The wash sampled at Site D had pHs as low as 3 pH units. Because washes are done when one or both units at Site C are off-line, they result in a large amount of high-pollutant concentration, low-pH water entering the pond. This may have a large effect on ash pond toxicity because of increased dissolved metal concentrations.

Other PISCES Stream Characterizations

Other streams characterized during the study included plant wastes, source water, and condenser cooling water.

Plant Wastes

Plant wastes include ash hopper overflow water and seal water from Unit 2, estimated by the plant at 250 gallons (950 liters) per minute. Wastes also include stormwater from the plant area, coal dust and ash hose down, boiler water blowdown, and water treatment residuals. During the study, eight 24-hour composite samples of Unit 2 plant wastes were taken with pH ranging from 6.1 to 7.6. It was noted that the amount of solids varied significantly (TSS varied from 7 to 560 mg/L). The changes were based largely on plant activities, such as wash downs within the plant. Because plant waste from Unit 2 is a constant stream of 200 to 300 gallons (800 to 1,100 liters) per minute, it represents approximately 20% of the flow to the ash pond and therefore can affect its water quality. Plant waste from Unit 1 had very low flow and metals concentrations.

Intake Water

Little variation was noted in trace metal concentration of the intake water. Concentrations of metals in the clean samples taken during the three main weeks of sampling were below 2 μg/L of copper, nickel, and zinc with the exception of one sample at 4 μg/L of copper. Samples taken during other visits to the site had periodic higher concentrations, such as 15 μg/L of copper on December 17, 1996. These samples were taken using conventional methods. Therefore, these results are considered estimates due to blank contamination issues and cannot be conclusively associated with source water quality. Estimated data are discussed in Section 6. Water quality parameters of the source water may affect the ash pond water quality and toxicity. Some forms of organic matter have been shown in research to bind metals and thereby reduce their toxicity [29] while other organics act as ligands, increasing the amount of metal solubilized. The total organic content, measured as TOC, did vary as is shown in Table 5-7. Some correlation was seen with ash pond toxicity, possibly reducing toxicity in January 1997 as discussed in Section 4.

The intake water hardness decreased during the spring of 1997. Hardness reduces the toxicity of cationic metals such as copper [19, 20]. If the drop in hardness is characteristic of springtime source water conditions, it could help account for previous toxicity events appearing in the spring. Effluent toxicity would increase during those springs in which an acidic ash was being produced that was resulting in a low-pH, high copper sluice water. No rise in toxicity occurred during 1997 because of concurrent low copper concentration present in the ash pond water.

The contribution of plant activities is shown in Table 5-8. The source water is a significant net contributor of the copper discharged from the station, but is not for nickel.

Table 5-7
Plant Intake Water

Date of Collection	Method	Aluminum	Arsenic	Copper	Iron	Nickel	Selenium	Zinc	Calcium	Alkalinity as CaCO3	Hardness as CaCO3	pH	TOC	Dissolved Organic Carbon
		(μg/L)	(μg/L)	(μg/L)	(μg/L)	(μg/L)	(μg/L)	(μg/L)	(mg/L)	(mg/L)	(mg/L)		(mg/L)	(mg/L)
9/23/96	Clean	47		3.5	59	0.36		0.68				7.0		
9/24/96	Clean	50		1.4	77	0.44		0.59	6.5	28	133	7.0	2.5	
9/25/96	Conventional	34	0.93	4.2	74	< 1.6[2]	< 4.4[2]	14	6.3	28	116	7.8	4.0	
9/25/96	Clean			1.5		0.44		0.58						
9/26/96	Clean	33		1.4	50	0.38		0.74	6.3	36	102	7.9	8.8	
9/27/96	Clean	21		1.5	49	0.45		0.80				6.6		
10/28/96	Conventional	8.6	8.2	3.4	54	< 1.6[2]	< 4.4[2]	2.5	6.1		31	6.8	3.6	2.7
11/22/96	Conventional	< 63[2]	< 1.6[2]	< 2.1[2]	< 77[2]	< 3.2[2]	< 4.4[2]	5.4	6.5		97	7.9	19	2.2
12/17/96	Conventional	112	< 1.6[2]	15	89	4.4	< 4.4[2]	4.3	6.7	26	79	7.7	2.4	2.3
1/9/97	Conventional	52	< 1.6[2]	3.7	53	1.7	2.2	5.1	6.4			7.0	2.3	1.9
1/21/97	Clean	54	0.35	1.8	65	1.9	< 0.39[1]	1.3	6.5	69	65	7.3		
1/22/97	Clean	< 18[2]	0.33	1.9	89	0.34	< 0.39[1]	1.3	6.2	75	51	7.8	4.0	
1/23/97	Clean	23	0.31	1.6	150	0.32	1.4	1.1	6.5	44	50	7.8	16	
1/24/97	Clean	44	0.31	1.7	121	0.33	1.3	1.1	6.6	50	42	7.7	2.2	
2/12/97	Conventional	76	< 1.9[2]	2.9	75	< 1.3[2]	< 1.5[2]	4.3	6.5			7.0	3.4	2.6
2/26/97	Conventional	46	< 2.4[2]	2.7	76	< 1.3[2]	3.9	26	6.4			7.8	2.3	2.2
3/12/97	Conventional	23	< 1.9[2]	< 1.7[2]	50	< 1.3[2]	2.3	4	6.2			7.6	2.8	2.6
3/26/97	Conventional	113	< 2.4[2]	3.9	91	< 1.3[2]	< 1.5[2]	3.7	6.4			8.7	21	3.1
4/9/97	Conventional	79	< 1.9[2]	7.2	68	< 1.3[2]	< 1.5[2]	22	6.4			8.0	2.6	2.6
4/23/97	Conventional	685	< 2.4[2]	< 8.3[2]	65	< 6.4[2]	< 7.5[2]	< 7.9[2]	6.1	64	44	8.2	2.2	1.0
5/8/97	Conventional	40	< 1.9[2]	< 1.7[2]	68	< 1.3[2]	2.5	5.1	5.7	26	38	7.3	2.2	2.2
5/20/97	Conventional	58	< 2.4[2]	< 1.7[2]	105	< 1.3[2]	< 1.5[2]	2.1	5.1			8.0	11	2.5
6/17/97	Clean											6.4		
6/19/97	Clean		0.67	1.9		0.27	1.6	0.89						

[1] Result is less than clean method critical level, which was determined using an alternative minimum level study of reagent water standards.

[2] Result is less than method detection limit (MDL) for conventional method, achieved by the conventional laboratory as defined in 40CFR136 [1]. Quantitation limit is higher than MDL.

Table 5-8
Contribution of Plant Activities to Ash Pond

	Arsenic	Copper	Iron	Nickel	Selenium	Zinc
Averages from 1996 Data						
Plant Intake (µg/L)	1.2	3.0	62	0.52	<0.393*	3.3
Ash Pond Water (µg/L)	7.9	18	150	19	64	29
Contribution	16%	16%	41%	3%	None	11%
Averages from 1997 Data, After Coal-Management Implemented						
Plant Intake (µg/L)	0.24	2.2	78	0.62	0.81	5.9
Ash Pond Water (µg/L)	40	3.9	150	7.1	72	10
Contribution	1%	56%	52%	9%	1%	59%

*Result is less than method detection limit (MDL) for clean method achieved by clean lab for selenium. Quantitation limit is higher than MDL.

Cooling Water

The condenser cooling water is discharged back into the source water lake. Contribution of metals from the cooling water system were minor as is shown in Table 5-9. The condenser material is stainless steel. Two samples were taken during chlorine addition. These showed an average concentration of 0.6 µg/L total residual chlorine, above Site C’s 0.2 µg/L discharge limit. The samples were operational samples taken upstream of where the cooling water from the two units combine and flow to the permitted outfall point. Because chlorine is added to only one unit at a time, the concentration at the outfall will be less by a factor of 2 when both units are operating. Samples collected when the chlorine system was not operating had chlorine concentration below the method detection limit of 0.1 mg/L, and therefore below the quantitation level.

Table 5-9
Contribution of Cooling Water System

Average Values	Copper	Iron	Nickel	Zinc	Chlorine, Total Residual*
	(μg/L)	(μg/L)	(μg/L)	(μg/L)	(mg/L)
Plant Intake	1.7	61	0.77	0.97	0.45
Once-Through Cooling Water	1.9	58	0.43	1.1	0.60
Average Contribution	0.24	No addition	No addition	0.17	0.15

*Chlorine addition system was operating only during the June 1997 visit. Two paired samples were taken this week. Therefore, data shown in this table are only from this one week. Sample location collected cooling water from only one unit. Therefore, was an operational sample, upstream of discharge point. Because chlorine is added to only one unit at a time, the concentration at the outfall will be less by a factor of 2 when both units are operating. During other weeks, there was no contribution of chlorine from the system.

6

DATA EVALUATION

Data collected during the study were evaluated for usability. Results of the data evaluation include:

- Station operations during each sample visit represented normal operations.
- Conventional sampling and analytical methods produced less precise results and were more prone to contamination than clean methods for ash pond water samples.
- Sampling methods for ash sluice wastes produced field duplicate precision results outside data quality objectives for some parameters because of heterogeneous nature of the streams.
- Flow monitoring methods of liquid streams produced closure of a flow balance around the ash pond within data quality objectives.
- Sampling, flow, and analytical methods were evaluated using a mass balance around the station. The balance closed within the project data quality objectives for roughly half the metals of interest. The balance was predominately influenced by solid streams rather than liquid streams, so conclusions drawn about liquid streams were not affected by this data quality. Parameters meeting the objective of 70% to 130% input to output ratio included aluminum, nickel, iron, mercury, beryllium, and calcium. Parameters that did not meet the closure objective included copper, lead, selenium, and zinc.
- The original analysis method for solids provided values lower than historically seen and produced by an alternative method. This led to data rejection for many parameters associated with these matrices, especially bottom ash and pyrites. The analytical method was modified for later field visits.
- Field and laboratory QA/QC samples showed that laboratory precision for ash pond water and cooling water streams were within data quality objectives.
- Matrix spike and surrogate recoveries for most matrices demonstrated good method accuracy and a lack of substantial matrix interferences with the quantitation process. However, accuracy of coal was outside of data quality objectives for some samples. Three data points had to be rejected because of poor spike recovery.

- Data from conventional sampling for some parameters in cleaner streams were considered questionable due to results near the maximum concentration present in the blanks. Results from conventional sampling of the ash pond water would have been difficult to draw conclusions with regarding metals toxicity because conventional data were questionable at concentrations measured in the pond. Examples include copper, nickel, and zinc. Conventional data are treated as questionable below 60, 55, and 91 µg/L, respectively, all of which were found to be potentially toxic concentrations.

- Data for some parameters in cleaner streams were considered to be estimates due to results near the methods' critical level or detection limit, and therefore below the quantitation level. These did not include metals of interest in the ash pond water.

- One data outlier was encountered in performing statistical analysis for the report and was rejected.

- Less than 5% of the data was rejected, accomplishing completeness goals. The remaining data are usable for database population.

Station Operations

Station operation was recorded during each sampling event. Operational variables are shown in Appendix B. One of EPRI's goals for the PISCES project is to characterize the station under different operating conditions. Therefore, visits were scheduled to get a variety of operating conditions, but also were selected to avoid unusual operating conditions. Examples of operational variety included changes in load, changes in number of units on-line, and type of coal being fired.

Sample Collection

Comparison of Clean and Conventional Sampling Results

The ash pond water location was sampled using both clean and conventional methods during the first two sampling events to compare the precision, accuracy, and contamination of the two methods. Some of the clean analytical methods have not been approved for regulatory use by EPA or been fully validated. The comparison of data shows the following results for the Site C ash pond matrix:

- Copper was consistently biased high by approximately 20% using the conventional method.

- Zinc was subject to contamination by the conventional method. Four of the six samples over the two weeks were approximately 50% higher by the conventional method.

- Other metals are biased high by the conventional method because they are present at concentrations below the conventional detection and quantitation limits. These include lead, mercury, and silver. The accuracy of analytical results below the quantitation levels are questionable. Therefore, if these metals are of interest to a utility, inability of the conventional method to quantify these parameters at regulatory levels will be a factor in choosing a sampling method.

- The nickel results were consistently higher using the clean method and were well above the conventional method detection and quantitation limits.

- Beryllium and cadmium were biased low by the conventional method in several paired samples. Concentrations of these metals were below the conventional method quantitation levels, and therefore, are less accurate than the results from the clean method.

- Antimony was biased low by the conventional method in several paired samples. The conventional method produced poor accuracy for antimony in the ash pond water and other waste streams sampled. The accuracy of the conventional method results are considered questionable.

- Vanadium and selenium concentrations were more than 20 times higher than the reporting limits for both methods. Therefore, the conventional method should provide as accurate results as the clean method. The clean method results appeared to have accuracy problems with the ash pond matrix evidenced by wider data scatter across sampling days.

The difference between clean and conventional results was more pronounced at PISCES program Sites A and B because of lower concentrations of metals at these two sites.

Table 6-1 shows the WQC compared to the clean critical level and conventional method detection limits achieved by the laboratories. The WQC are in-stream standards and are not discharge limits, nor do they apply to Site C. The WQC are at or near the conventional method detection limits for several metals, including selenium, beryllium, copper, mercury, and thallium. The accuracy of using the conventional sampling methods is a factor when sampling at discharge points where any of the metals that are biased high or near the detection limits are regulated at concentrations near the conventional method quantitation levels.

Table 6-1
Comparison of Ash Pond Water Data Using Clean and Conventional Methods at Site C

All units are µg/L

Date/Time of Collection	Method	Antimony	Arsenic	Beryllium	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Thallium	Vanadium	Zinc
1/20/97 2:26:00 PM	Clean	12	9.2	0.1	0.5	1.5	3.3	0.7	0.0008	6.7	40.3	0.03	0.7	25	11
1/20/97 2:26:00 PM	Conventional	17	10.4	0.25	0.56	1.9	5.7	<1.3[1]	<0.082[1]	8.7	61	<1.5[1]	<1.7[1]	35	17
1/21/97 1:40:00 PM	Clean	17	7.3				4.9	0.5	0.0008		63.0		1.1	32	
1/21/97 1:40:00 PM	Conventional	17	7.5				6.6	<3[1]			62		3.8	31	
1/22/97 9:16:00 AM	Clean	16	7.9	0.4	0.8	2.4	5.7	0.5	0.0006	12	69	<0.011[2]	1.0	38	18
1/22/97 10:56:00 AM	Conventional	18	7.8	0.23	0.66	8.3	7.2	1.7	<0.082[1]	12	58	<1.5[1]	3.2	29	31
1/23/97 9:00:00 AM	Clean	17	9.8				6.2	0.7	0.0008		58		1.2	32	
1/23/97 9:39:00 AM	Conventional	16	9.9				8.0	1.7			56		<1.7[1]	31	
9/24/96 9:30:00 AM	Clean	25		0.9	1.1	1.8	14	0.5	0.0010	20		<0.023[2]	2.5	76	22
9/24/96 9:55:00 AM	Conventional	14	11.3	0.73	1.2	1.2	21	1.6	<0.2[1]	18	61	0.34	<5.3[1]	68	35
9/25/96 9:45:00 AM	Clean	25	9.2	0.9	1.2	1.4	17	0.5	0.0012	21	62	<0.023[2]	2.6	69	24
9/25/96 10:42:00 AM	Conventional	15	9.3	0.80	1.0	0.86	20	1.8	<0.12[1]	16	57	<0.31[1]	<5.3[1]	59	35
9/26/96 9:53:00 AM	Clean	25	9.8	1.1	1.3	1.3	19	0.4	0.0012	22	102	0.05	2.7	70	27
9/26/96 10:50:00 AM	Conventional	13	8.9	0.88	0.91	<0.45[1]	19	<1.3[1]	<0.2[1]	16	60	<0.31[1]	<5.3[1]	60	28
9/27/96 8:30:00 AM	Clean	25	9.2	1.2	1.4	1.4	22	0.5	0.0012	23	63	0.01	2.9	68	32
9/27/96 9:35:00 AM	Conventional	17	7.9	1.2	1.3	0.20	27	<1.3[1]	0.086	19	61	0.50	<5.3[1]	60	34
Average Results - Clean[4]		20	8.9	0.77	1.1	1.6	12	0.5	0.00094	17	65	<0.019[2]	1.83	51	22
Average Results - Conventional[4]		16	9.1	0.68	0.92	2.5	14	<1.3[1]	<0.082[1]	15	60	<0.031[1]	<1.3[1]	47	30
Conventional Sample Contamination[5]		1	0	0	0	1	5	4	NA	0	1	NA	NA	1	4
Critical Level - Clean		0.012	0.076	0.0020	0.011	0.029	0.066	0.092	0.00044	0.055	0.39	0.023	0.0020	0.09	0.61
Detection Limit - Conventional[3]		1.5	0.88	0.088	0.16	0.45	0.84	1.3	0.082	1.2	1.4	0.31	1.3	0.39	0.62
Strictest Water Quality Criteria		14	0.018	0.070	1.0	180	2.4	2.5	0.012	8.3	5.0	1.9	1.7		81

[1] Result or average is below method detection limit (MDL) for conventional method achieved by the conventional laboratory as defined in 40CFR136 [1]. Quantitation limit is higher than MDL.

[2] Result or average is below clean method critical level, which was achieved by the first clean laboratory in AML study of reagent water standards. Quantitation limit is higher than critical level.

[3] Lowest reported detection limits from ash pond water analysis using the conventional method.

[4] Averages are computed assuming <D.L. values are zero.

[5] Considered contamination if conventional result is 1.3 times clean result, or more. Comparison is not applicable for silver, mercury, and thallium because of high conventional detection limit.

Comparison of Clean Analysis Methods

Clean samples were split and sampled and analyzed by two clean method approaches during the third week of sampling. Some of the clean analytical methods in both approaches have not been approved for regulatory use by EPA or been fully validated. The first approach, which is the approach used in the first two weeks of sampling, includes preservation of samples in the field with ultraclean preservatives prior to shipping the samples on ice to the laboratory for analysis. The second approach includes shipping the samples on ice to the laboratory where they are preserved. The approaches were used by two different laboratories. The second approach reduces the level of effort required in the field and the steps required while in "clean" sampling gear. The results for paired samples showed the two approaches produced very similar results. The blanks showed that the second approach maintained clean conditions as well as the first approach. In addition, it produced results from the analysis of the SRM that were within project data quality objectives for the SRM of 80 to 120% of the certified values for all parameters except beryllium, lead, and cadmium. These parameters also presented data quality problems for the first approach. The concentration of beryllium and cadmium were below the quantitation levels of each method. Results of paired samples of ash pond water, cooling water, plant intake water, blanks, and certified standard reference materials are shown in Table 6-2.

Stream Characterization

Sampling methods were designed to collect samples representative of each waste stream, source water, and coal. Those duplicate pairs that did not meet 20% relative percent difference (RPD) for liquids or 35% RPD for solids are shown in Table 6-3. The RPD for all field duplicates taken at Site C is shown in Appendix E, Table E-1.

A wide difference in the precision of field duplicates can be due to a sampling method that fails to get representative samples of a nonhomogenous stream or a parameter concentration near the method quantitation level producing questionable accuracy. Particular issues are discussed by matrix below.

Field duplicates that were collected using clean sampling methods (ash pond water and plant intake water) reflected good reproducibility (< 20% RPD) for most metals. Exceptions did occur in a minority of the duplicate sets for some parameters such as arsenic in ash pond water and nickel, thallium, and iron in the plant intake water. Conventional sampling and analysis of metals in the ash pond water also had good precision between duplicates, except for some metals present near their detection limits, and therefore below the quantitation levels, such as lead. The general chemistry parameter field duplicates experienced better precision than the metals. Exceptions included ash pond water alkalinity, which had RPDs of more than 20% for two of the three duplicate sets for which it was analyzed.

Table 6-2
Comparison of Paired Samples from Two Clean Sampling and Analysis Methods
All units are µg/L

Stream Sample	Date/Time of Collection	Antimony	Arsenic	Beryllium	Cadmium	Chromium	Copper	Lead
Ash pond water, total, Method #1	6/17/97 2:05:00 PM	12	81.3	0.07	0.26	10.5	1.6	0.36
Ash pond water, total, Method #2	6/17/97 2:05:00 PM	14	93.8	0.08	0.13	13.2	2.1	0.57
Ash pond water, total, Method #1	6/18/97 2:01:00 PM	14	108	0.10	0.28	12.8	1.97	0.51
Field duplicate - Ash pond water, total, Method #1	6/18/97 2:01:00 PM	14	109	0.09	0.29	12.7	2.05	0.55
Ash pond water, Method #2	6/18/97 2:01:00 PM	14	101	0.22	0.23	13.7	2.93	1.23
Field Duplicate - Ash pond water, total, Method #2	6/18/97 2:01:00 PM	14	101	0.19	0.20	13.7	2.98	1.19
Once-through cooling water U2, Method #1	6/19/97 10:09:00 AM	0.21	0.37	0.01	<0.011[1]	<0.029[1]	1.87	<.092[1]
Once-through cooling water, Method #2	6/19/97 10:09:00 AM	0.14	0.70	<.019[2]	0.03	0.50	1.96	0.05
Plant intake water, Method #1	6/19/97 8:52:00 AM	0.15	0.35	0.00	<0.011[1]	0.08	1.83	<.092[1]
Plant intake water, Method #2	6/19/97 8:52:00 AM	0.15	0.68	<.019[2]	<.012[2]	0.50	1.87	0.04
Standard reference material, Method #1	6/17/97 4:10:00 PM	0.27	0.78	0.01	<0.011[2]	0.27	1.43	<.092[1]
Standard reference material, Method #2	6/17/97	0.14	0.68	<.019[2]	<.012[2]	0.33	1.43	0.06
Certified Values of SRM		0.12	0.72	0.01	0.01	0.30	1.35	0.09
Equipment blank, Method #1	6/19/97 1:47:00 PM	0.01	<0.076[1]	0.01	0.01	<0.029[1]	<0.066[1]	<.092[1]
Equipment blank, Method #2	6/19/97 1:56:00 PM	<.019[2]	<.11[2]	<.019[2]	.0206	.03954	<.029[2]	<.009[2]
Field Blank, Method #1	6/18/93 1:57:00 PM	<0.012[1]	<0.076[1]	0.01	<0.011[1]	<0.029[1]	<0.066[1]	<.092[1]
Field Blank, Method #2	6/19/97 1:37:00 PM	<.009[2]	<.11[2]	<.019[2]	<.012[2]	0.05	<.029[2]	<.009[2]

Table 6-2
Comparison of Paired Samples from Two Clean Sampling and Analysis Methods
All units are µg/L

Stream Sample	Date/Time of Collection	Nickel	Selenium	Silver	Thallium	Vanadium	Zinc
Ash pond water, total, Method #1	6/17/97 2:05:00 PM	3.3	88.4	<0 .023[1]	0.54	65.8	3.5
Ash pond water, total, Method #2	6/17/97 2:05:00 PM	4.6	102	< .008[2]	0.84	79	1.8
Ash pond water, total, Method #1	6/18/97 2:01:00 PM	3.57	110	0.05	0.61	83	6.15
Field duplicate - Ash pond water, total, Method #1	6/18/97 2:01:00 PM	3.54	111	0.03	0.61	83	4.69
Ash pond water, Method #2	6/18/97 2:01:00 PM	4.83	101	0.73	0.88	82	2.78
Field Duplicate - Ash pond water, total, Method #2	6/18/97 2:01:00 PM	4.83	102	0.33	0.86	82	2.81
Once-through cooling water U2, Method #1	6/19/97 10:09:00 AM	0.23	<.393[2]	0.02	0.01	0.17	1.21
Once-through cooling water, Method #2	6/19/97 10:09:00 AM	0.28	1.77	< .008[2]	0.10	0.30	0.99
Plant intake water, Method #1	6/19/97 8:52:00 AM	0.23	<.393[2]	0.03	0.011	0.15	1.31
Plant intake water, Method #2	6/19/97 8:52:00 AM	0.27	1.62	< .008[2]	0.10	0.27	0.90
Standard reference material, Method #1	6/17/97 4:10:00 PM	0.88	<.393[2]	0.14	0.009	0.30	1.29
Standard reference material, Method #2	6/17/97	0.98	<.22[2]	< .008[2]	0.011	0.31	1.01
Certified Values of SRM		0.83				0.30	1.04
Equipment blank, Method #1	6/19/97 1:47:00 PM	0.23	<.393[2]	0.11	<.002[1]	<0.09[2]	<0.61[1]
Equipment blank, Method #2	6/19/97 1:56:00 PM	.02518	<.22[2]	< .008[2]	<.003[2]	<.017[2]	<.047[2]
Field Blank, Method #1	6/18/93 1:57:00 PM	<0.055[1]	<.393[2]	0.09	<.002[1]	<0.09[2]	<0.61[1]
Field Blank, Method #2	6/19/97 1:37:00 PM	0.02	<.22[2]	< .008[2]	<.003[2]	0.03	<.047[2]

[1] Result is less than clean method critical level, which was determined using an alternative minimum level study of reagent water standards at first lab used for clean sample analysis. Quantitation limit is higher than critical level.

[2] Result is less than method detection limit (MDL) determined by lab used for clean sample analysis. Quantitation limit is higher than MDL.

Table 6-3
Field Duplicate Precision Outside Criteria

Stream Sample	Analytical Method	Parameter ID	Units	RPD
Ash Solids and Pyrites				
Fly ash solids, U2	SW7000’s	Selenium	mg/kg	60
Fly ash solids, U2	SW7000's	Arsenic	mg/kg	43
Fly ash solids, U2	SW6010	Cadmium	mg/kg	40
Fly ash solids, U1	E365.1	T. Orthophosphate	mg/kg	50
Fly ash solids, U1	SW6010	Silicon	mg/kg	42
Process Waters				
Ash pond water, dissolved, clean	1638	Silver	µg/L	47
Ash pond water, dissolved, clean	1638	Beryllium	µg/L	31
Ash pond water, dissolved, clean	SW6010	Iron	µg/L	23
Ash pond water, total, clean	E310.1	Alkalinity as CaCO3	mg/L	144
Ash pond water, total, clean	1632	Arsenic V	µg/L	102
Ash pond water, total, clean	1632	Arsenic	µg/L	90
Ash pond water, total, clean	1632	Arsenic	µg/L	86
Ash pond water, total, clean	1632	Selenium IV	µg/L	60
Ash pond water, total, clean	1632	Arsenic III	µg/L	57
Ash pond water, total, clean	1638	Selenium	µg/L	53
Ash pond water, total, clean	1632	Selenium VI	µg/L	47
Ash pond water, total, clean	EA-4641-1	Selenium VI	µg/L	43
Ash pond water, total, clean	1632	Selenium	µg/L	41
Ash pond water, total, clean	1638	Arsenic	µg/L	22
Ash pond water, total, clean, Clean Lab #1	EA-4641-2	Arsenic III	µg/L	114
Ash pond water, total, clean, Clean Lab #1	E310.1	Alkalinity as CaCO3	mg/L	47
Ash pond water, total, clean, Clean Lab #1	E310.1	Carbonate	µg/L	33
Ash pond water, total, clean, Clean Lab #1	E375.4	Sulfate	µg/L	33
Ash pond water, total, clean, Clean Lab #1	1638	Zinc	µg/L	27
Ash pond water, total, clean	1638	Silver	µg/L	76
Ash pond water, total, conventional	E310.1	Alkalinity as CaCO3	mg/L	94
Ash pond water, total, conventional	SW6010	Iron	µg/L	72
Ash pond water, total, conventional	E305.1	Acidity as CaCO3	µg/L	40
Ash pond water, total, conventional	SW6010	Copper	µg/L	38
Ash pond water, total, conventional	SW6010	Zinc	µg/L	35
Ash pond water, total, conventional	SW6010	Aluminum	µg/L	34
Ash pond water, total, conventional	E350.2	Ammonia-N	mg/L	30
Ash pond influent	SW6010	Sodium	µg/L	96
Ash pond influent	E130.2	Hardness as CaCO3	mg/L	33
Ash pond influent	SW6010	Lead	µg/L	27
Bottom ash sluice water, composite	SW6010	Zinc	µg/L	151
Bottom ash sluice water, composite	SW6010	Copper	µg/L	76
Bottom ash sluice water, composite	SW6010	Nickel	µg/L	63
Bottom ash sluice water, composite	SW6010	Lead	µg/L	59
Bottom ash sluice water, composite	E310.1	Alkalinity as CaCO3	mg/L	51
Bottom ash sluice water, composite	SW6010	Iron	µg/L	45
Bottom ash sluice water, composite	SW6010	Aluminum	µg/L	43
Bottom ash sluice water, composite	E130.2	Hardness as CaCO3	mg/L	38
Bottom ash sluice water, composite	E410.4	Chemical Oxygen Demand	mg/L	36
Bottom ash sluice water, composite	SW6010	Silicon	µg/L	32
Bottom ash sluice water, composite	SW6010	Chromium	µg/L	31

Table 6-3
Field Duplicate Precision Outside Criteria

Stream Sample	Analytical Method	Parameter ID	Units	RPD
Bottom ash sluice water, composite	SW6010	Beryllium	µg/L	29
Bottom ash sluice water, composite	SW6010	Manganese	µg/L	24
Bottom ash sluice water, composite	SW6010	Potassium	µg/L	22
Bottom ash sluice water, U2	E160.2	Total Suspended Solids	mg/L	108
Bottom ash sluice water, U2	E415.2	Total Organic Carbon	mg/L	106
Bottom ash sluice water, U2	SW6010	Iron	µg/L	104
Bottom ash sluice water, U2	E365.1	Orthophosphate-P, Total	mg/L	86
Bottom ash sluice water, U2	SW6010	Zinc	mg/L	71
Bottom ash sluice water, U2	SW6010	Aluminum	mg/L	69
Bottom ash sluice water, U2	SW6010	Copper	mg/L	66
Bottom ash sluice water, U2	SW6010	Nickel	mg/L	66
Bottom ash sluice water, U2	E130.2	Hardness as CaCO3	mg/L	56
Bottom ash sluice water, U2	E375.4	Sulfate	mg/L	22
Fly ash sluice water, U1	E160.2	Total Suspended Solids	mg/L	110
Fly ash sluice water, U1	SW6010	Thallium	mg/L	47
Fly ash sluice water, U1	SW7060	Arsenic	mg/L	25
Fly ash sluice water, U1	SW6010	Lead	mg/L	23
Fly ash sluice water, U1	E365.1	Orthophosphate-P, Total	mg/L	22
Fly ash sluice water, U2	SW6010	Zinc	mg/L	53
Fly ash sluice water, U2	E310.1	Alkalinity as CaCO3	mg/L	42
Fly ash sluice water, U2	SW6010	Copper	mg/L	33
Fly ash sluice water, U2	SW6010	Nickel	mg/L	20
Plant waste, U2	E160.2	Total Suspended Solids	mg/L	134
Plant waste, U2	E130.2	Hardness as CaCO3	mg/L	68
Plant waste, U2	E365.1	Orthophosphate-P, Total	mg/L	67
Plant waste, U2	SW6010	Iron	mg/L	59
Plant waste, U2	E415.2	Total Organic Carbon	mg/L	58
Plant waste, U2	SW6010	Copper	mg/L	54
Plant waste, U2	E365.1	Phosphorous-P, Total	mg/L	43
Plant waste, U2	SW6010	Potassium	mg/L	30
Plant waste, U2	SW6010	Vanadium	mg/L	28
Uncontaminated Water				
Plant intake water	1638	Nickel	mg/L	156
Plant intake water	E415.2	Total Organic Carbon	mg/L	85
Plant intake water	1638	Thallium	mg/L	30
Plant intake water	1638	Antimony	mg/L	30
Plant intake water	E130.2	Hardness as CaCO3	mg/L	26
Plant intake water	SW6010	Iron	mg/L	22
Plant intake water	E310.1	Alkalinity as CaCO3	mg/L	20

Two sets of field duplicates were collected of fly ash. The matrix did not prove to be a significant factor in collecting representative samples. All of the metals analyzed except arsenic had an RPD below 35%.

Ash sluice water (two sets each for bottom ash and fly ash) and ash pond influent (one set) were both sampled as composites. Duplicates were created by pouring the large composite container out into two sets of bottles. The ash pond influent was shaken before sampling and the sluice water was decanted out of the large container after solids settling. The ash pond influent met data quality objectives for most parameters. With the exception of lead, which was near its detection limit and therefore below its quantitation level, all metals were within data quality objectives. The sluice water duplicates did not meet data quality objectives for most parameters, including metals and nonmetals. This was most likely due to poor collection of water by decanting that could have allowed more metals-bearing solids to be collected in one container of a duplicate set. This is reflected in the difference in the TSS results. This suggests that it is possible to take representative samples; however, field sampling can affect the quality of the duplicates. Field duplicate sets that have numerous parameters outside criteria are the primary evidence of matrix heterogeneity.

One duplicate set was taken of the Unit 2 plant waste. This was sampled as composite and duplicates were created by shaking the container and pouring into two sets of containers. This stream had mixed precision between duplicates. Roughly half the parameters had precision outside data quality objectives. This was apparently due to higher solids content in one of the samples.

Flow Balance Around Ash Ponds

Table 6-4 shows a flow balance around the ash pond at Site C. The balance was prepared from flow measurements taken in the field using a flow velocity meter in the channel between the ash pond and the secondary settling basin. The flow balance at Site C had a closure of 119% (inflow divided by outflow).

Rainfall runoff from the ash pond drainage area was estimated using rainfall data corresponding to sampling and flow monitoring site visits. No mass balances were computed around the ash pond because the solids that settle out within the pond were not analyzed.

Mass Balance Around Station

Table 6-5 shows a mass balance around the station at Site C. The goal for the closure was 70 to 130%. Parameters meeting this goal included aluminum, nickel, iron, mercury, beryllium, and calcium. Parameters that did not meet the closure goal included copper, lead, selenium, and zinc. Problems encountered in closing the mass balance included:

Table 6-4
Flow Balance Around Ash Pond

Stream	**Flow**	
IN	**(MGD)**	**(10^6 L/day)**
Fly ash sluice water	0.98	3.7
Bottom ash sluice water	1.3	5.0
Plant Waste, Unit 1	0.043	0.16
Plant Waste, Unit 2	0.50	1.9
Stormwater runoff (avg. during sampling)	0.039	0.15
Total	**2.9**	**10.9**
OUT	**Flow Meter**	**Depth Gauge**
Ash pond effluent	2.43 MGD 9.2 * 10^6 L/day	1.87 MGD 7.1 * 10^6 L/day
IN/OUT	**119%**	**154%**

Does not account for evaporation or groundwater flows in or out of ash pond.

- Most of the metals in the coal went to the solid ash. Liquids were not an important part of the mass balance, representing less than 10% of the outflow of most parameters. Therefore, the poor closure of some metals makes the solid data, but not the liquid data, suspect for those parameters. Those parameters that exhibit poor closure had sampling and analytical problems associated with the solids data.

- Bottom ash and pyrite analyses resulted in underreported concentrations of metals in most samples taken during the study. This was evidenced in an inter-laboratory comparison of samples taken during the last visit. The revised analytical methods were used on one visit. Therefore, for those parameters that were underreported by the original method, only one week of field data was available.

  The flow of fly ash and bottom ash is estimated using the station's estimate of the split between each of the two ashes produced. The coal's percent ash is used along with this split to estimate production of both streams. These are the largest streams exiting at the station, and therefore, have the largest impact on closing the mass balance. Metals with the highest concentration in the fly ash will be most sensitive to accuracy of the estimated quantity of ash. Fly ash represents more than 75% of the station loading for aluminum, iron, lead, nickel, vanadium, and zinc.

- Metals that have large differences in concentrations between fly ash and bottom ash will be most affected by the accuracy of the ash split. Metals with more than 50% difference in concentration are arsenic, copper, lead, selenium, and zinc.

- Variations in coal quality may affect the mass balance.

Table 6-5
Mass Balance Around the Station

Stream Sample	**Average Flow**		**Flow June 17-19, 1997**			**Aluminum**	**Arsenic**	**Beryllium**	**Chromium**	**Copper**	**Iron**
In	**(short tons)**	**(metric tons)**	**(short tons)**	**(metric tons)**		**Loadings (kg/day)**					
Coal	2,581 TPD	2,344 TPD	2,007 TPD	1,822 TPD	+/- 1%	37,428	22	3.2	14	39	13,228
Plant intake water	3.1 MGD		3.1 MGD		+/- 10%	0.9	0.007	0.00	0.003	0.027	0.9
Out											
Liquid load	3.1 MGD	12 MLD	3.1 MGD	12 MLD	+/- 10%	257	3.9	0.08	1.4	5.4	69
Fly ash solids[1]	253 TPD	230 TPD	215 TPD	195 TPD	+/- 15%	30,098	28	3.9	16	19	13,839
Bottom ash solids[1]	63 TPD	57 TPD	54 TPD	49 TPD	+/- 15%	6,117	0.37	0.030	7	1.7	2,500
Pyrites	0.6 TPD	0.6 TPD	0.6 TPD	0.6 TPD	+/- 15%	4.6	0.1	0.00	0.00	0.01	6.0
Air emissions[2]											
Total In						37,428	22	3.2	14	39	13,229
Total Out						36,477	33	4.0	25	26	16,414
In/Out						103%	68%	80%	59%	152%	81%

NA = Parameter not analyzed in this waste stream.
MLD = Million of liters/day
MGD = Million of gallons/day

[1] Solids were sampled after sluicing so had contributed contamination to liquid load.

[2] Estimate of volatile metals emissions are 70% of mercury and 80% of selenium present in fuel becomes air emissions. Estimate from previous EPRI work.

Table 6-5
Mass Balance Around the Station

Stream Sample	**Average Flow**		**Flow June 17-19, 1997**			**Lead**	**Mercury**	**Nickel**	**Selenium**	**Zinc**	**Calcium**
In	**(short tons)**	**(metric tons)**	**(short tons)**	**(metric tons)**		**Loadings (kg/day)**					
Coal	2,581 TPD	2,344 TPD	2,007 TPD	1,822 TPD	+/- 1%	14	0.14	21	6.1	33	2,267
Plant intake water	3.1 MGD		3.1 MGD		+/- 10%	0.003	0.0003	0.007	0.006	0.1	71.1
Out											
Liquid load	3.1 MGD	12 MLD	3.1 MGD	12 MLD	+/- 10%	0.10	0.00017	0.7	0.5	2.3	485
Fly ash solids[1]	253 TPD	230 TPD	215 TPD	195 TPD	+/- 15%	28	0.03	17	6.6	15	2,174
Bottom ash solids[1]	63 TPD	57 TPD	54 TPD	49 TPD	+/- 15%	0.4	0.0029	1.6	0.07	0.6	450
Pyrites	0.6 TPD	0.6 TPD	0.6 TPD	0.6 TPD	+/- 15%	0.00	NA	0.01	0.01	0.01	2.5
Air emissions[2]							0.10		4.9		
Total In						14	0.14	21	6.1	33	2,338
Total Out						29	0.13	19	12	18	3,112
In/Out						49%	110%	112%	51%	190%	75%

Solids Analysis

The solid streams were analyzed for metals during the first two visits by the conventional laboratory using method SW-846 digestion method 3050A, which is traditionally used in the environmental field for the analysis of solids. It was noted that the initial solids data were not consistent with historical data reported in the PISCES database. In addition, mass balances around the station computed using the data from the original method had poor closure for those metals that were expected to be found in the pyrites and bottom ash, such as iron.

Therefore, a revised method was used for analyzing samples from the third visit. Samples were prepared for analysis using a preparation method from ASTM D 3682. The method includes ashing the solid sample in a muffle oven and grinding the sample to pass a number 200 sieve [16]. This preparation is then followed by the 3050A digestion for most metals. Digestion and preparation vary by parameter. Volatile metals, such as arsenic and selenium, were analyzed by ASTM 3685 [16]. Beryllium and boron were analyzed using ASTM D 3683 [16]. The data shown in Table 6-6 are rejected from the original method.

Toxicity Test QC Results

QA/QC testing at the bioassay laboratory included running concurrent toxicity tests in laboratory media to ensure that mortality is not due to a weakness in the organisms. All controls were within the project data quality objective of greater than 90% survival. Results of these concurrent tests are shown in Table 6-7.

A reference toxicant test using reagent-grade sodium chloride performed monthly measures the reproducibility of toxicity tests. All tests were within data quality objectives of an LC_{50} within two standard deviations of the 12-month average value. Results for the period of the PISCES study are shown in Appendix E.

Analytical QC Results

Quality Control Approach

The data quality evaluation process (DQEP) assesses the effect of the overall analytical process on the usability of the data. Evaluation of laboratory performance is a check for compliance with the method requirements; either the laboratory did, or did not, analyze the samples within the limits of the analytical method. Evaluation of matrix interferences is more subtle and involves the analysis of several areas of results, including the results of surrogate spike recoveries, matrix spike recoveries, contamination, and duplicate samples. Precision and accuracy measurements are based primarily on the actual sample matrices. Sampling precision and accuracy are unique to each sample matrix.

Table 6-6
Data Rejected Due to Low Bias of Solids Analysis

Matrix	Parameters	Data Points*
Coal	Aluminum	16
	Antimony	16
	Magnesium	16
	Potassium	16
	Silicon	11
	Sodium	16
Fly ash solids Dry and wet-sluiced solids	Aluminum	24
	Beryllium	24
	Iron	24
	Lead	24
	Manganese	22
	Silicon	4
	Sodium	12
	Potassium	7
Bottom ash solids	Aluminum	10
	Cadmium	10
	Chromium	10
	Copper	10
	Iron	10
	Nickel	10
	Vanadium	7
	Zinc	10
	Calcium	7
	Magnesium	7
	Manganese	7
	Potassium	7
	Silicon	4
	Sodium	7
Total Data Points Rejected		**348**

* Criteria for rejection: Original SW846 3050A digestion method data were less than the fifth percentile from PISCES data. If samples were split as with dry fly ash samples, they were less than data from the ASTM method data by at least a factor of 2.

All data for a particular matrix and parameter are rejected. The data point count varies because not all parameters were analyzed for in each sample.

Table 6-7
Survival of *Ceriodaphnia* in Laboratory Control Media

Test Start Date	Survival	Test Start Date	Survival
9/26/96	100%	2/13/97	100%
10/2/96	95	3/1/97	100
10/9/96	100	3/7/97	90
10/15/96	100	3/13/97	100
10/29/96	100	3/27/97	100
11/23/96	100	4/4/97	100
11/26/96	100	4/9/97	100
12/18/96	100	4/10/97	100
12/20/96	100	4/24/97	100
1/6/97	100	5/10/97	100
1/10/97	100	5/21/97	100
1/21/97	90	6/19/97	100

Measures of quality control include the PARCCs:

- **Precision**—Is defined as the agreement between duplicate results, and was estimated by comparing the results of duplicate matrix spike recoveries, native duplicates, and field duplicate samples.

- **Accuracy**—Is a measure of the agreement between an experimental determination and the true value of the parameter being measured. For the organic analyses, each of the samples was spiked with a surrogate compound; and for the inorganic analyses, each sample was spiked with a known reference material before digestion. Each of these approaches provides a measure of the matrix effects on the analytical accuracy.

- **Representativeness**—This criterion is a qualitative measure of the degree to which sample data accurately and precisely represent a characteristic environmental condition. Representativeness is a subjective parameter and is used to evaluate the efficacy of the sampling plan design. Representativeness was demonstrated by providing full descriptions in the project scoping documents of the sampling techniques and the rationale used for selecting sampling locations.

- **Completeness**—Is defined as the percentage of measurements that are judged to be valid compared to the total number of measurements made.

- **Comparability**—Is another qualitative measure designed to express the confidence with which one data set may be compared to another. Factors that affect comparability are sample collection and handling techniques, sample matrix type, and analytical method. Comparability is limited by the other PARCC parameters because data sets can be compared with confidence only when precision and accuracy are known.

Quality Control Results

Precision and accuracy measurements are based primarily on the actual sample matrices. Sampling precision and accuracy are unique to each site and each sample matrix. A complete list of the results of the laboratory precision QC is shown in Appendix E, Table E-2. A summary of the results of the laboratory accuracy QC are shown in Table E-3.

Precision

Table E-2 lists all calculated RPDs regardless of the native concentration levels. Many of the measurements at or near the reporting limits will reflect biased RPDs due to the deviation in measurements inherent at these levels. All precision measurements were evaluated using goals of 20% RPD for water and 35% RPD for solid matrices. Duplicates with poor RPDs were screened to evaluate if the poor precision was caused by the results being at or near the reporting limits and therefore below quantitation levels. Table 6-8 indicates screened values outside precision goals by matrix.

Overall, precision values fell well within established limits. Laboratory duplicate precision results outside control limits were minimal. However, the majority of results outside criteria were associated with two stream sample types, coal and conventionally sampled ash pond water. These data indicate that the matrix can have minor impacts on laboratory precision.

The “clean” laboratory matrix spike duplicate precision results were also well within criteria for almost all elements. Precision results from ash pond water from clean and conventional methods show the clean method to be more accurate, producing far fewer results outside of data quality objectives. Those that were outside criteria were due to inappropriate spiking levels in relation to the native sample concentration. The 1600-series matrix spike duplicate precision data were within the method target acceptance ranges, indicating that the specific sample matrix did not significantly influence the overall analytical process or the final numerical sample result.

Table 6-8
Laboratory Duplicate Precision Outside Criteria

Stream Sample	Sample ID	Analytical Method	Parameter ID	Native Result	Units	RPD
Coal						
Coal	CAB050	SW6010	Cadmium	0.11	mg/kg	122
Coal	CAB050	SW6010	Iron	13,474	mg/kg	51
Coal	CAB050	SW6010	Manganese	237	mg/kg	88
Coal	CAB050	SW6010	Potassium	533	mg/kg	44
Coal	CAB050	SW6010	Selenium	1.2	mg/kg	59
Coal	CAB050	SW6010	Silver	0.28	mg/kg	88
Coal	CBB001	SW6010	Cadmium	0.25	mg/kg	200
Coal	CBB001	SW6010	Silicon	175	mg/kg	38
Coal	CBB001	SW6010	Sodium	42	mg/kg	42
Coal	CBD003	SW7060	Arsenic	9.0	mg/kg	52
Coal	CBD003	SW6010	Chromium	5.5	mg/kg	97
Coal	CBD003	SW6010	Manganese	30	mg/kg	83
Coal	CBD003	SW6010	Nickel	8.5	mg/kg	42
Coal	CBD003	SW6010	Zinc	10	mg/kg	37
Coal	CBE003	SW6010	Sodium	112	mg/kg	63
Coal	CBF003	SW6010	Silicon	350	mg/kg	42
Coal	CBJ003	E365.1	T. Phosphorous	29	mg/kg	92
Ash Solids and Pyrites						
Bottom ash solids, composite	CAB038	SW6010	Lead	61	mg/kg	179
Bottom ash solids, composite	CAB038	SW6010	Chromium	22	mg/kg	87
Bottom ash solids, composite	CAB038	SW6010	Magnesium	406	mg/kg	45
Process Waters						
Ash pond water, dissolved, clean	CBB501	1638	Cadmium	0.62	µg/L	200
Ash pond water, dissolved, clean	CBB501	1638	Thallium	0.95	µg/L	200
Ash pond water, dissolved, clean	CBB501	1638	Copper	2.8	µg/L	23
Ash pond water, dissolved, clean	CBB501	1638	Beryllium	0.18	µg/L	23
Ash pond water, dissolved, conventional	CAC001F	SW6010	Nickel	8.6	µg/L	50
Ash pond water, dissolved, conventional	CAC001F	SW6010	Antimony	14	µg/L	21
Ash pond water, dissolved, conventional	CAC001F	SW6010	Iron	122	µg/L	21
Ash pond water, total, clean	CBB500	EA-4641-1	Selenium VI	4.6	µg/L	81
Ash pond water, total, clean	CBB500	1638	Selenium	40	µg/L	69
Ash pond water, total, conventional	CBA001	SW6010	Copper	5.9	µg/L	200
Ash pond water, total, conventional	CBF001	SW6010	Zinc	7.7	µg/L	200
Ash pond water, total, conventional	CAE001	SW6010	Arsenic	7.1	µg/L	164
Ash pond water, total, conventional	CBI001	SW6010	Zinc	6.1	µg/L	75
Ash pond water, total, conventional	CBA001	SW6010	Zinc	10	µg/L	75
Ash pond water, total, conventional	CAC001	SW6010	Nickel	8.6	µg/L	50
Ash pond water, total, conventional	CBF001	SW6010	Iron	92	µg/L	38
Ash pond water, total, conventional	CAB511	SW6010	Zinc	35	µg/L	30
Ash pond water, total, conventional	CAB540	SW6010	Antimony	17	µg/L	29
Ash pond water, total, conventional	CBB504	SW6010	Boron	535	µg/L	23
Ash pond water, total, conventional	CAC001	SW6010	Antimony	12	µg/L	21
Ash pond water, total, conventional	CAC001	SW6010	Iron	88	µg/L	21
Ash pond water, total, conventional	CBG001	SW6010	Chromium	8.4	µg/L	20
Coal pile runoff	CAB100	SW6010	Potassium	3,109	µg/L	34
Fly ash sluice water, U1	CBB018	SW6010	Thallium	9.8	µg/L	50
Fly ash study-liquid	CBB804	SW6010	Beryllium	0.64	µg/L	29
Fly ash study-liquid	CBB804	SW6010	Iron	2,102	µg/L	26

Table 6-8
Laboratory Duplicate Precision Outside Criteria

Stream Sample	Sample ID	Analytical Method	Parameter ID	Native Result	Units	RPD
Uncontaminated Water						
Fly ash study - Plant intake water	CBJ800	SW6010	Iron	55	µg/L	40
Fly ash study - Plant intake water	CBJ800	SW6010	Copper	12	µg/L	37
Fly ash study-plant intake water, unmixed	CBB800DIS	SW6010	Iron	53	µg/L	30
Plant intake water	CBJ001	E160.1	TDS	57	mg/L	176
Plant intake water	CBJ001	SW6010	Iron	105	µg/L	58
Plant intake water	CBB526	1638	Chromium	0.22	µg/L	31
Plant intake water	CBB526	1638	Selenium	1.4	µg/L	25
Plant intake water	CBJ001	SW6010	Aluminum	58	µg/L	22
TRE sample - lab water	CAERW96.168	SW6010	Aluminum	64	µg/L	54

Accuracy

Table E-3 lists all calculated matrix spike recoveries regardless of the native concentration levels. All spike accuracy measurements were evaluated using control limits of 75 to 125% recovery. Many of the native sample concentrations were much greater than the spike added to the sample during digestion. Recoveries outside criteria where the native sample concentration was greater than four times the spike added were not considered because the native concentration would mask the spike added and not provide meaningful accuracy data. Table 6-9 indicates screened values outside accuracy goals by matrix.

Overall, prespike recoveries fell well within the established limits. The majority of data found to be outside matrix spike control limits were associated with difficult matrices analyzed by conventional methods, such as coal and ash pond water samples. Clean method spike recoveries ranged mainly between 82 and 130%. Conventional spike recoveries were generally found to lie between 60 and 130%. The majority of the recoveries outside criteria were attributed to coal and ash pond waters. The results indicate that the specific sample matrix can influence the overall analytical process.

General chemistry matrix spike recoveries were all within criteria. These QC samples indicate that the matrices sampled did not influence the overall analytical process or the final numerical sample result for these nonmetal compounds.

There were no matrix spike/matrix spike duplicate (MS/MSD) QC samples requested for the organic analytical fractions. Organic matrix effects were evaluated using the surrogate results. The surrogate spike recoveries for the samples submitted for organic analysis were within the method target acceptance limits.

Data reported at less than the reporting limit with recoveries below 30% (associated by digestion batch) were rejected as unusable data. The data shown in Table 6-10 were rejected because of poor spike recovery.

Table 6-9
Matrix Spike Recoveries Outside Criteria

Stream Sample	Sample ID	Analytical Method	Parameter ID	Percent Recovery
Coal				
Coal	CBB001	SW7060	Arsenic	194
Coal	CBB001	SW6010	Silicon	188
Coal	CBF003	SW7060	Arsenic	182
Coal	CBC003	SW7060	Arsenic	160
Coal	CBF003	SW6010	Thallium	74
Coal	CBI003	SW6010	Thallium	74
Coal	CBC003	SW6010	Antimony	72
Coal	CBE003	SW6010	Thallium	72
Coal	CBD003	SW6010	Silicon	71
Coal	CBF003	SW6010	Silicon	71
Coal	CBD003	SW6010	Thallium	70
Coal	CBD003	SW6010	Antimony	70
Coal	CBB001	SW6010	Thallium	69
Coal	CBE003	SW6010	Silver	68
Coal	CBE003	SW6010	Antimony	66
Coal	CAB050	SW6010	Thallium	63
Coal	CBI003	SW6010	Antimony	62
Coal	CBJ003	SW6010	Thallium	61
Coal	CBC003	SW6010	Thallium	60
Coal	CBJ003	SW6010	Silicon	59
Coal	CBJ003	SW6010	Antimony	55
Coal	CBF003	SW6010	Antimony	51
Coal	CBI003	SW7060	Arsenic	42
Coal	CBD003	SW7060	Arsenic	36
Coal	CBJ003	SW6010	Silver	5.3
Coal	CBJ003	SW7060	Arsenic	-10
Coal	CAB050	SW6010	Manganese	-68
Coal	CBE003	SW7060	Arsenic	-185
Ash Solids and Pyrites				
Bottom ash solids, composite	CAB038	SW6010	Thallium	62
Bottom ash solids, composite	CAB038	SW6010	Lead	49
Bottom ash solids, composite	CAB038	SW6010	Selenium	-0.1
Process Waters				
Ash pond water, clean	CBK518	EPA 1638	Vanadium	158
Ash pond water, clean	CBK518	EPA 1638	Vanadium	145
Ash pond water, clean	CBK518	EPA 1638	Thallium	132
Ash pond water, clean	CBK518	EPA 1638	Thallium	131
Ash pond water, clean	CBK518	EPA 1638	Zinc	73
Ash pond water, clean	CBK518	EPA 1638	Zinc	73
Ash pond water, clean	CBK518	EPA 1638	Beryllium	72
Ash pond water, clean	CBK518	EPA 1638	Zinc	71
Ash pond water, clean	CBK518	EPA 1638	Beryllium	71
Ash pond water, clean	CBK518	EPA 1638	Beryllium	70
Ash pond water, total	CAE001	SW6010	Iron	145
Ash pond water, total, conventional	CBH001	SW6010	Silicon	139
Ash pond water, total, conventional	CAE001	SW6010	Silicon	136
Ash pond water, total, conventional	CBH001	SW6010	Aluminum	129
Ash pond water, total, conventional	CAB540	SW7060	Arsenic	38

Table 6-10
Data Rejected Due to Poor Spike Recovery

Sample ID	Stream Sample	Parameter ID	Result	Reporting Units	Method Detection Limit	Analytical Method
Matrix spike recoveries below 30%						
CBJ003S	*MS-Coal*	*Silver*	*5.3*	*Percent recovery*		*SW6010*
CBJ001S	*MS-Plant intake water*	*Silver*	*4.4*	*Percent recovery*		*SW6010*
Data associated with the MS recoveries that were therefore rejected						
CBJ003	Coal	Silver	0.03	mg/kg	0.16	SW6010
CBJ001	Plant intake water	Silver	0.23	µg/L	1.5	SW6010
CBJ002	Ash pond water total, conventional	Silver	-0.47	µg/L	1.5	SW6010

Data that meet the following criteria are rejected:
1) The batch matrix spike has a recovery of less than 30% for that parameter. *Shown in italics.*
2) Matrix spike recoveries <30% are screened; those that were not spiked with at least 25% the native concentration are not considered poor data quality because the native concentration can mask the spike.
3) Only samples with similar matrix to matrix used in spike test were considered. Those samples associated with the poor recoveries are screened; only those samples with results less than the method detection limits (MDL) are rejected for the parameter of concern. Quantitation limits are higher than MDL.

Analytical results of SRM analyses are presented in Table 6-11. With the exception of cadmium, beryllium, and lead, recoveries were within normal limits. The laboratory-specific reporting limit for beryllium, lead, and cadmium is 0.002 µg/L, 0.092 µg/L, and 0.011 µg/L, respectively; thus the true value is near the reporting limit and below the quantitation level. One of the three measurements for lead, zinc, and chromium exhibited low level contamination.

Table 6-11
Blind Standard Reference Material Recovery

Sample ID	Element	Analytical Method	True Value (µg/L)	Result (µg/L)	Reporting Limit[1]	% Recovery
CAB535	Antimony	EPA 1638	0.12	0.15	0.012	129
	Arsenic	EPA 1638	0.72	0.76	0.076	105
	Beryllium	EPA 1638	0.005	0.0013	0.002	27
	Cadmium	EPA 1638	0.013	0.022	0.011	171
	Chromium	EPA 1638	0.3	0.53	0.029	176
	Copper	EPA 1638	1.35	1.5	0.066	112
	Lead	EPA 1638	0.086	0.13	0.092	149
	Nickel	EPA 1638	0.83	1.1	0.055	129
	Vanadium	EPA 1638	0.3	0.35	0.09	115
	Zinc	EPA 1638	1.04	1.8	0.061	174
CBB531	Antimony	EPA 1638	0.12	0.14	0.012	118
	Arsenic	EPA 1638	0.72	0.61	0.076	85
	Beryllium	EPA 1638	0.005	0.00	0.002	0
	Cadmium	EPA 1638	0.013	0.015	0.011	112
	Chromium	EPA 1638	0.3	0.36	0.029	119
	Copper	EPA 1638	1.35	1.1	0.066	81

Table 6-11
Blind Standard Reference Material Recovery

Sample ID	Element	Analytical Method	True Value (µg/L)	Result (µg/L)	Reporting Limit[1]	% Recovery
	Lead	EPA 1638	0.086	0.041	0.092	47
	Nickel	EPA 1638	0.83	0.81	0.055	97
	Vanadium	EPA 1638	0.3	0.27	0.09	91
	Zinc	EPA 1638	1.04	1.1	0.061	106
CBK505[2]	Antimony	EPA 1638	0.12	0.14	0.012	120
	Arsenic	EPA 1638	0.72	0.68	0.076	95
	Beryllium	EPA 1638	0.005	0.0017	0.002	34
	Cadmium	EPA 1638	0.013	-0.0027	0.011	-21
	Chromium	EPA 1638	0.3	0.33	0.029	110
	Copper	EPA 1638	1.35	1.4	0.066	106
	Lead	EPA 1638	0.086	0.062	0.092	72
	Nickel	EPA 1638	0.83	0.98	0.055	119
	Vanadium	EPA 1638	0.3	0.31	0.09	102
	Zinc	EPA 1638	1.0	1.0	0.061	97

[1] Reporting limits for CAB and CBB are critical level determined in alternative minimum level study of reagent water standard at first laboratory. Reporting limits for CBK sample are method detection limits (MDL) achieved by second clean laboratory. Quantitation limits are higher than critical levels and MDLs.

[2] Results are from clean method number 2, used only in week 3 of sampling.

Blank Effects

Fifteen equipment rinsate blanks and 15 field blanks were submitted to the laboratories for inorganic analysis with the samples. Table A-1 shows all field and equipment rinsate blank results. Laboratory method blanks were run with each laboratory batch of samples. Results above the reporting limits from the blanks are summarized in Table 6-12. Reporting limits are method detection limits as defined in 40CFR136 for conventional samples [1], and critical levels achieved in AML study for clean samples. The table presents all laboratory method blanks analyzed to date under the PISCES study. Thus, the table includes results corresponding to sample batches for Sites A, B, and C. This is reflective of overall laboratory performance.

It is significant to note the differences in clean method critical levels and conventional method detection limits. Moreover, these data reflect the importance of choosing the proper sampling techniques and the proper analytical method for the data quality objectives required. In many instances, several elements, such as mercury, silver, thallium, and zinc, were reported in the blanks just over the method detection limit (MDL) or critical level. These values are indicative of instrument noise or low level blank contamination and are considered below quantitation levels. These data support the lack of accuracy and precision at the MDL.

Table 6-12
Field, Equipment, and Method Blank Frequency of Detection

Parameter	Blank Type	Analytical Method	Blanks Taken	Number of Detects	Detects/ Blanks	Minimum Detect	Maximum Detect	Average of Detects	Units
LIQUIDS - CLEAN METHOD									
Antimony	Equipment	1638	8	4	50%	0.009	0.031	0.017	µg/L
Arsenic	Equipment	1632	1	0	0%				µg/L
Arsenic	Equipment	1638	7	0	0%				µg/L
Arsenic V	Equipment	1632	1	1	100%	0.034	0.034	0.034	µg/L
Beryllium	Equipment	1638	4	3	75%	0.004	0.029	0.015	µg/L
Cadmium	Equipment	1638	7	2	29%	0.012	0.021	0.016	µg/L
Chromium	Equipment	1638	7	5	71%	0.04	0.34	0.15	µg/L
Chromium VI	Equipment	1636	2	0	0%				µg/L
Copper	Equipment	1638	4	1	25%	0.13	0.13	0.13	µg/L
Lead	Equipment	1638	6	1	17%	0.17	0.17	0.17	µg/L
Mercury	Equipment	1631	3	2	67%	1.0E-04	1.5E-04	1.3E-04	µg/L
Nickel	Equipment	1638	7	3	43%	0.025	0.23	0.11	µg/L
Selenium	Equipment	1632	1	0	0%				µg/L
Selenium	Equipment	1638	4	1	25%	0.44	0.44	0.44	µg/L
Selenium VI	Equipment	1632	1	0	0%				µg/L
Silver	Equipment	1638	7	4	57%	0.10	0.23	0.13	µg/L
Thallium	Equipment	1638	8	1	13%	4.5E-03	4.5E-03	4.5E-03	µg/L
Vanadium	Equipment	1638	7	0	0%				µg/L
Zinc	Equipment	1638	6	3	50%	0.28	0.36	0.33	µg/L
Antimony	Field	1638	9	2	22%	0.013	0.018	0.015	µg/L
Arsenic	Field	1632	2	0	0%				µg/L
Arsenic	Field	1638	9	0	0%				µg/L
Arsenic	Field	EA-4641-2	1	1	100%	0.051	0.051	0.051	µg/L
Arsenic V	Field	1632	2	2	100%	0.036	0.049	0.043	µg/L
Arsenic V	Field	EA-4641-2	1	1	100%	0.051	0.051	0.051	µg/L
Beryllium	Field	1638	4	2	50%	0.006	0.025	0.016	µg/L
Cadmium	Field	1638	6	0	0%				µg/L
Chromium	Field	1638	9	6	67%	0.05	0.34	0.13	µg/L
Chromium VI	Field	1636	2	1	50%	0.25	0.25	0.25	µg/L

Table 6-12
Field, Equipment, and Method Blank Frequency of Detection

Parameter	Blank Type	Analytical Method	Blanks Taken	Number of Detects	Detects/ Blanks	Minimum Detect	Maximum Detect	Average of Detects	Units
Copper	Field	1638	4	1	25%	0.89	0.89	0.89	µg/L
Lead	Field	1638	6	0	0%				µg/L
Mercury	Field	1631	6	5	83%	7.1E-05	1.7E-04	1.2E-04	µg/L
Methylmercury	Field	Bloom	1	0	0%				µg/L
Nickel	Field	1638	8	1	13%	0.018	0.018	0.018	µg/L
Selenium	Field	1638	5	0	0%				µg/L
Silver	Field	1638	9	7	78%	0.04	0.14	0.067	µg/L
Thallium	Field	1638	7	2	29%	4.3E-03	4.3E-03	4.3E-03	µg/L
Vanadium	Field	1638	8	1	13%	0.034	0.034	0.034	µg/L
Zinc	Field	1638	6	3	50%	0.18	0.70	0.43	µg/L
Antimony	Method	1638	11	3	27%	0.007	0.037	0.024	µg/L
Arsenic	Method	1638	12	0	0%				µg/L
Arsenic V	Method	EA-4641-2	1	1	100%	0.046	0.046	0.046	µg/L
Arsenic, total	Method	EA-4641-2	2	0	0%				µg/L
Beryllium	Method	1638	6	0	0%				µg/L
Cadmium	Method	1638	8	1	13%	0.010	0.010	0.010	µg/L
Chromium	Method	1638	10	4	40%	0.04	0.40	0.15	µg/L
Copper	Method	1638	9	2	22%	0.10	0.13	0.12	µg/L
Lead	Method	1638	10	0	0%				µg/L
Mercury	Method	1631	4	0	0%				µg/L
Methylmercury	Method	Bloom	4	0	0%				µg/L
Nickel	Method	1638	10	0	0%				µg/L
Selenium	Method	1638	7	1	14%	0.47	0.47	0.47	µg/L
Silver	Method	1638	12	1	8%	0.033	0.033	0.033	µg/L
Thallium	Method	1638	10	3	30%	2.3E-03	3.8E-03	3.1E-03	µg/L
Titanium	Method	1638	1	1	100%	0.089	0.089	0.089	µg/L
Vanadium	Method	1638	11	0	0%				µg/L
Zinc	Method	1638	10	3	30%	0.41	0.87	0.59	µg/L
LIQUIDS - CONVENTIONAL METHOD									
Acidity as $CaCO_3$	Equipment	E305.1	6	3	50%	9.0	16.0	13.00	mg/L
Alkalinity as $CaCO_3$	Equipment	E310.1	6	4	67%	4	44	15.00	mg/L

Table 6-12
Field, Equipment, and Method Blank Frequency of Detection

Parameter	Blank Type	Analytical Method	Blanks Taken	Number of Detects	Detects/ Blanks	Minimum Detect	Maximum Detect	Average of Detects	Units
Aluminum	Equipment	SW6010	8	8	100%	14	66	36.47	µg/L
Ammonia-N	Equipment	E350.2	4	3	75%	0.3	2.3	1.03	mg/L
Antimony	Equipment	SW6010	7	4	57%	2.1	7.5	4.62	µg/L
Arsenic	Equipment	SW7060	7	0	0%				µg/L
Barium	Equipment	SW6010	1	1	100%	1.5	1.5	1.46	µg/L
Beryllium	Equipment	SW6010	5	0	0%				µg/L
BOD, 5 Day	Equipment	E405.1	2	0	0%				mg/L
Boron	Equipment	SW6010	5	0	0%				µg/L
Cadmium	Equipment	SW6010	6	0	0%				µg/L
Calcium	Equipment	SW6010	7	6	86%	59	267	108.29	µg/L
Carbonate	Equipment	E310.1	6	0	0%				mg/L
Chemical Oxygen Demand	Equipment	E410.4	2	1	50%	72	72	72.00	mg/L
Chloride	Equipment	E325.1	6	0	0%				mg/L
Chlorine, Total Residual	Equipment	E330.4	1	0	0%				mg/L
Chromium	Equipment	SW6010	6	2	33%	0.6	5.0	2.77	µg/L
Copper	Equipment	SW6010	6	3	50%	1.9	8.1	5.45	µg/L
Fluoride	Equipment	E340.2	4	0	0%				mg/L
Hardness as $CaCO_3$	Equipment	E130.2	6	1	17%	6.0	6.0	6.00	mg/L
Hydrazine	Equipment	CHA-113	2	0	0%				mg/L
Iron	Equipment	SW6010	8	7	88%	3	45	19.91	µg/L
Lead	Equipment	SW6010	6	0	0%				µg/L
Magnesium	Equipment	SW6010	7	6	86%	3.7	21	9.83	µg/L
Manganese	Equipment	SW6010	7	6	86%	0.2	4.8	1.28	µg/L
Mercury	Equipment	SW7471	6	1	17%	0.16	0.16	0.16	µg/L
Nickel	Equipment	SW6010	6	1	17%	2.3	2.3	2.27	µg/L
Nitrate-N	Equipment	E353.2	6	4	67%	0.06	0.14	0.10	mg/L
Nitrite-N	Equipment	E353.2	6	0	0%				mg/L
Oil and Grease	Equipment	E413.1	2	0	0%				mg/L
Orthophosphate-P, Total	Equipment	E365.1	6	0	0%				mg/L
Phosphorous-P, Total	Equipment	E365.1	3	2	67%	0.040	0.15	0.10	mg/L
Potassium	Equipment	SW6010	7	2	29%	204	1493	848.78	µg/L

Table 6-12
Field, Equipment, and Method Blank Frequency of Detection

Parameter	Blank Type	Analytical Method	Blanks Taken	Number of Detects	Detects/ Blanks	Minimum Detect	Maximum Detect	Average of Detects	Units
Selenium	Equipment	SW6010	6	0	0%				µg/L
Silicon	Equipment	SW6010	4	2	50%	156	248	202.15	µg/L
Silver	Equipment	SW6010	6	1	17%	0.91	0.91	0.91	µg/L
Sodium	Equipment	SW6010	7	7	100%	176	495	291.36	µg/L
Sulfate	Equipment	E375.4	6	0	0%				mg/L
Thallium	Equipment	SW6010	6	0	0%				µg/L
Total Dissolved Solids	Equipment	E160.1	6	2	33%	18	25	21.50	mg/L
Total Organic Carbon	Equipment	E415.2	5	2	40%	3.4	7.7	5.55	mg/L
Total Suspended Solids	Equipment	E160.2	6	1	17%	9.0	9.0	9.00	mg/L
Vanadium	Equipment	SW6010	6	2	33%	0.40	0.56	0.48	µg/L
Zinc	Equipment	SW6010	6	6	100%	3.5	6.7	5.27	µg/L
Acidity as $CaCO_3$	Field	E305.1	3	1	33%	18	18	18.00	mg/L
Alkalinity as $CaCO_3$	Field	E310.1	3	2	67%	4.0	4.0	4.00	mg/L
Aluminum	Field	SW6010	5	1	20%	43	43	42.57	µg/L
Ammonia-N	Field	E350.2	3	0	0%				mg/L
Antimony	Field	SW6010	5	2	40%	3.1	3.5	3.31	µg/L
Arsenic	Field	SW7060	5	0	0%				µg/L
Beryllium	Field	SW6010	4	0	0%				µg/L
BOD, 5 Day	Field	E405.1	2	0	0%				mg/L
Boron	Field	SW6010	4	0	0%				µg/L
Cadmium	Field	SW6010	5	0	0%				µg/L
Calcium	Field	SW6010	5	2	40%	50	174	111.88	µg/L
Carbonate	Field	E310.1	3	0	0%				mg/L
Chemical Oxygen Demand	Field	E410.4	2	2	100%	35	51	43.00	mg/L
Chloride	Field	E325.1	3	0	0%				mg/L
Chlorine, Total Residual	Field	E330.4	1	0	0%				mg/L
Chromium	Field	SW6010	5	3	60%	3.1	12.1	7.47	µg/L
Copper	Field	SW6010	5	1	20%	3.7	3.7	3.67	µg/L
Fluoride	Field	E340.2	3	1	33%	0.19	0.19	0.19	mg/L
Hardness as $CaCO_3$	Field	E130.2	3	1	33%	28	28	28.00	mg/L
Hydrazine	Field	CHA-113	1	0	0%				mg/L

Table 6-12
Field, Equipment, and Method Blank Frequency of Detection

Parameter	Blank Type	Analytical Method	Blanks Taken	Number of Detects	Detects/ Blanks	Minimum Detect	Maximum Detect	Average of Detects	Units
Iron	Field	SW6010	5	4	80%	15	53	28.69	µg/L
Lead	Field	SW6010	5	0	0%				µg/L
Magnesium	Field	SW6010	5	4	80%	4.1	16.7	8.72	µg/L
Manganese	Field	SW6010	5	5	100%	0.4	3.5	1.19	µg/L
Mercury	Field	SW7471	5	0	0%				µg/L
Nickel	Field	SW6010	5	3	60%	1.6	11.0	6.32	µg/L
Nitrate-N	Field	E353.2	3	3	100%	0.060	0.090	0.070	mg/L
Nitrite-N	Field	E353.2	3	0	0%				mg/L
Oil and Grease	Field	E413.1	1	1	100%	1.1	1.1	1.10	mg/L
Orthophosphate-P, Total	Field	E365.1	3	0	0%				mg/L
Phosphorous-P, Total	Field	E365.1	2	2	100%	0.05	0.13	0.090	mg/L
Potassium	Field	SW6010	5	1	20%	131	131	131.29	µg/L
Selenium	Field	SW6010	5	2	40%	1.6	1.9	1.77	µg/L
Silicon	Field	SW6010	3	1	33%	718	718	717.83	µg/L
Silver	Field	SW6010	5	0	0%				µg/L
Sodium	Field	SW6010	5	5	100%	94	405	240.84	µg/L
Sulfate	Field	E375.4	3	0	0%				mg/L
Thallium	Field	SW6010	5	3	60%	1.9	4.7	3.48	µg/L
Total Dissolved Solids	Field	E160.1	3	0	0%				mg/L
Total Organic Carbon	Field	E415.2	3	3	100%	2.2	11.7	7.13	mg/L
Total Suspended Solids	Field	E160.2	3	0	0%				mg/L
Vanadium	Field	SW6010	5	0	0%				µg/L
Zinc	Field	SW6010	5	5	100%	2.3	6.9	4.03	µg/L
Alkalinity as $CaCO_3$	Method	E310.1	1	0	0%				mg/L
Aluminum	Method	SW6010	55	31	56%	9	146	48.29	µg/L
Ammonia-N	Method	E350.2	38	0	0%				mg/L
Antimony	Method	SW6010	48	9	19%	1.6	6.2	3.47	µg/L
Arsenic	Method	SW6010	4	0	0%				µg/L
Arsenic	Method	SW7060	48	10	21%	1.0	2.5	1.95	µg/L
Barium	Method	SW6010	16	6	38%	0.6	1.2	0.99	µg/L
Beryllium	Method	SW6010	49	3	6%	0.11	0.14	0.12	µg/L

Table 6-12
Field, Equipment, and Method Blank Frequency of Detection

Parameter	Blank Type	Analytical Method	Blanks Taken	Number of Detects	Detects/ Blanks	Minimum Detect	Maximum Detect	Average of Detects	Units
BOD, 5 Day	Method	E405.1	23	0	0%				mg/L
Boron	Method	SW6010	49	10	20%	20	294	110.44	µg/L
Cadmium	Method	SW6010	45	9	20%	0.2	2.2	0.77	µg/L
Calcium	Method	SW6010	52	21	40%	46	311	123.54	µg/L
Chemical Oxygen Demand	Method	E410.4	16	0	0%				mg/L
Chloride	Method	E325.1	29	0	0%				mg/L
Chlorine, Total Residual	Method	E330.4	26	0	0%				mg/L
Chlorophyll-A	Method	SM1002G	3	0	0%				mg/m3
Chromium	Method	SW6010	46	4	9%	0.6	2.9	1.37	µg/L
Cobalt	Method	SW6010	1	0	0%				µg/L
Conductivity	Method	E120.1	5	0	0%				UMHOS/CM
Copper	Method	SW6010	54	18	33%	0.9	11.9	5.64	µg/L
Dissolved Organic Carbon	Method	E415.2	13	0	0%				mg/L
Fluoride	Method	E340.2	17	0	0%				mg/L
Hardness as $CaCO_3$	Method	E130.2	26	0	0%				mg/L
Hydrazine	Method	CHA-113	6	0	0%				mg/L
Iron	Method	SW6010	55	28	51%	3	74	21.92	µg/L
Lead	Method	SW6010	50	7	14%	1.5	3.4	2.27	µg/L
Lead	Method	SW7421	1	0	0%				µg/L
Magnesium	Method	SW6010	48	34	71%	3	128	26.39	µg/L
Manganese	Method	SW6010	51	30	59%	0.2	1.1	0.52	µg/L
Mercury	Method	SW7470	48	2	4%	0.13	0.26	0.19	µg/L
Nickel	Method	SW6010	52	12	23%	1.3	8.3	2.57	µg/L
Nitrate-N	Method	E353.2	35	0	0%				mg/L
Nitrite-N	Method	E353.2	42	0	0%				mg/L
Oil and Grease	Method	E413.1	18	0	0%				mg/L
Orthophosphate-P, Total	Method	E365.1	38	0	0%				mg/L
Phosphorous-P, Total	Method	E365.1	23	0	0%				mg/L
Potassium	Method	SW6010	46	12	26%	180	3238	1178.09	µg/L
Selenium	Method	SW6010	2	0	0%				µg/L
Selenium	Method	SW6010	52	4	8%	2.0	3.0	2.34	µg/L

Table 6-12
Field, Equipment, and Method Blank Frequency of Detection

Parameter	Blank Type	Analytical Method	Blanks Taken	Number of Detects	Detects/ Blanks	Minimum Detect	Maximum Detect	Average of Detects	Units
Silicon	Method	SW6010	41	13	32%	69	10311	1854.45	µg/L
Silver	Method	SW6010	46	6	13%	0.41	0.60	0.48	µg/L
Sodium	Method	SW6010	48	11	23%	100	1125	278.34	µg/L
Soluble Boron	Method	SW6010	1	0	0%				mg/L
Sulfate	Method	E375.4	31	0	0%				mg/L
Thallium	Method	SW6010	46	4	9%	2.0	2.4	2.12	µg/L
Thallium	Method	SW7841	1	0	0%				µg/L
Titanium	Method	SW6010	11	0	0%				µg/L
Total Dissolved Solids	Method	E160.1	51	0	0%				mg/L
Total Organic Carbon	Method	E415.2	39	0	0%				mg/L
Total Solids	Method	E160.3	2	0	0%				mg/L
Total Suspended Solids	Method	E160.2	54	0	0%				mg/L
Vanadium	Method	SW6010	51	5	10%	0.4	1.5	0.94	µg/L
Zinc	Method	SW6010	54	45	83%	1.7	18	5.53	µg/L
SOLIDS									
Aluminum	Method	SW6010	26	18	69%	0.88	580	37.2	mg/kg
Ammonia-N	Method	E350.2	1	0	0%				mg/kg
Antimony	Method	SW6010	23	6	26%	0.21	3.0	1.20	mg/kg
Arsenic	Method	SW7060	23	1	4%	0.49	0.49	0.49	mg/kg
Arsenic	Method	SW6010	3	2	67%	1.1	1.2	1.13	mg/kg
Barium	Method	SW6010	8	3	38%	0.030	0.33	0.21	mg/kg
Beryllium	Method	SW6010	25	5	20%	0.0040	0.14	0.046	mg/kg
Boron	Method	SW6010	22	5	23%	2.1	57	16.0	mg/kg
Cadmium	Method	SW6010	22	5	23%	0.028	0.18	0.10	mg/kg
Calcium	Method	SW6010	27	12	44%	1.8	59	22.4	mg/kg
Chloride	Method	E325.1	12	0	0%				mg/kg
Chlorine, Total Residual	Method	E330.4	1	0	0%				mg/kg
Chromium	Method	SW6010	21	5	24%	0.11	2.0	0.55	mg/kg
Copper	Method	SW6010	27	7	26%	0.26	0.86	0.47	mg/kg
Fluoride	Method	E340.2	6	0	0%				mg/kg
Hardness as $CaCO_3$	Method	E130.2	1	0	0%				mg/kg

Table 6-12
Field, Equipment, and Method Blank Frequency of Detection

Parameter	Blank Type	Analytical Method	Blanks Taken	Number of Detects	Detects/ Blanks	Minimum Detect	Maximum Detect	Average of Detects	Units
Iron	Method	SW6010	26	11	42%	0.96	22	5.5	mg/kg
Lead	Method	SW6010	26	4	15%	0.10	0.43	0.33	mg/kg
Magnesium	Method	SW6010	25	18	72%	0.49	24	4.3	mg/kg
Manganese	Method	SW6010	27	19	70%	0.010	0.59	0.12	mg/kg
Mercury	Method	SW7470	24	0	0%				mg/kg
Nickel	Method	SW6010	25	1	4%	0.57	0.57	0.57	mg/kg
Nitrate-N	Method	E353.2	15	0	0%				mg/kg
Nitrite-N	Method	E353.2	16	0	0%				mg/kg
Orthophosphate-P, Total	Method	E365.1	18	0	0%				mg/kg
Phosphorous-P, Total	Method	E365.1	8	0	0%				mg/kg
Potassium	Method	SW6010	23	5	22%	12	281	97.7	mg/kg
Selenium	Method	SW6010	26	7	27%	0.16	2.5	0.69	mg/kg
Silicon	Method	SW6010	11	4	36%	27	31	29.2	mg/kg
Silver	Method	SW6010	19	3	16%	0.10	0.97	0.46	mg/kg
Sodium	Method	SW6010	24	21	88%	22	803	113.7	mg/kg
Sulfate	Method	E375.4	15	0	0%				mg/kg
Thallium	Method	SW6010	22	2	9%	0.34	0.53	0.43	mg/kg
Titanium	Method	SW6010	1	0	0%				mg/kg
Vanadium	Method	SW6010	25	3	12%	0.050	0.28	0.15	mg/kg
Zinc	Method	SW6010	27	22	81%	0.15	2.7	0.70	mg/kg
Total Solids	Method	E160.3	11	0	0%				mg/kg

*Reporting limits are method detection limits as defined in 40CFR136 for conventional samples [1] and the critical level achieved in AML study for clean samples. Quantitation limits are higher than critical levels.

There were no organic compounds detected in any of the corresponding laboratory method blanks. A few of the general chemistry parameters were detected at low levels in the field blanks and not in the laboratory method blanks.

According to the EPA Functional Guidelines, concentrations of contaminants detected in samples at less than five times the maximum concentration in the blanks can be attributed to field sampling and laboratory contamination rather than environmental contamination from site activities.

Aluminum, copper, and iron were reported in the method blanks at detectable levels for the conventional methods. Many of these metals are ubiquitous at low levels.

Aluminum, copper, and iron are common elements used in the construction of sinks, faucets, laboratory ventilation hoods, and many other tools or equipment used daily Moreover, all of these elements can be found at trace levels in acids used for digestion in the laboratory. Acidity and alkalinity detections are directly related to pH and exposure to atmospheric carbon dioxide. These data are indicative of low level field contamination and atmospheric exposure.

Data Outliers

The data analyses performed in Sections 4 and 5 omitted data outliers that skewed the results shown by the data trends. Table 6-13 shows the data outliers and the causes for omitting them from analyses.

Table 6-13
Data Outliers Rejected from Data Analyses

Table	Date ID	Parameter and Result	Reason for Omission	Action Taken
4-4	Ash pond water 6/17/97	Bioassay laboratory hardness 350 µg/L	150% above conventional laboratory results for that week's samples and any previous results for ash pond water	Used conventional laboratory's results

Detection and Quantitation

The reporting limits used for this report correspond to the MDL for conventional analytical techniques and the critical level (L_c) for clean analytical techniques. The MDLs were determined on deionized water by the analytical laboratories using the protocols described in 40CFR136 for the determination of MDLs [1]. The L_c was determined by the PISCES project team for deionized water based on a series of spiked samples submitted blindly to the clean analytical laboratory. Both the MDL and the L_c represent a minimum concentration that is detectable. However, at these concentrations, quantification is not possible, the probability of reporting the result as less than the L_c is 50%, and the data results should be considered as estimated.

There has not been a scientific consensus reached concerning the concentrations at which a parameter is quantifiable. Recently, EPA recommended an interim minimum level (ML), which they defined as 3.18 times the MDL. EPRI has been involved in the development and use of a procedure to determine quantifiable levels appropriate for use in compliance monitoring [3, 4, 11]. The Inter-Industry Analytical Group in which UWAG is a member has been involved with negotiations with the EPA Office of Water regarding the use of alternative minimum levels (AML), or some definition that contains the fundamental features of AML, for compliance monitoring. Recently, the EPA has indicated its willingness to drop their ML approach. Negotiations for its replacement continue. As part of the PISCES activities, we calculated AMLs for deionized (DI) water, Site B intake water, and Site A ash pond water using clean analytical methods. The ash pond AML data were determined to be not accurate because they were biased by a high baseline concentration of many of the parameters in the matrix. Table 6-14 compares the MLs included in the methods with the AMLs calculated for DI and intake waters. It is noted that the AML for plant intake water is actually lower than that for the DI water for several parameters, including silver, selenium, arsenic, and nickel. As mentioned, quantitation is a developing field and it is not clear what effects of the plant intake water matrix resulted in AML values below those from DI water.

Heterogeneous Sample Matrices

Some sample streams exhibit heterogeneity in field sampling data. Accurate characterization of these streams at this point is questionable because of the large variability in the stream. Poor field duplicate precision also was considered an indication of stream heterogeneity. These streams vary with time and across the cross-section of the flow depth such as ash sluice wastes that have cycles of higher solids content which are more concentrated at the bottom of the flow.

Very little questionable data affected the conclusions drawn in the data analyses of this report. Most questionable data were related to:

- Matrices with variability between samples, including ash solids.
- Metals present near their detection limits and therefore below quantitation limits had high variability, such as mercury and cadmium.

- Metals in some clean streams where results were near reporting limits and therefore below quantitation limits, such as the plant intake water, had high variability.
- Clean sampling of ash pond water produced less data variability for most parameters than conventional sampling.

Table 6-14
Comparison of Interim Minimum Levels (MLs) and Alternative Minimum Levels (AMLs)
All units in µg/L

Parameter	ML	Deionized Water AML	Site B Intake Water AML [12]
Antimony	0.013	0.084	0.306
Arsenic	0.092	0.346	0.268
Beryllium	0.032	0.009	0.178
Cadmium	0.016	0.045	0.078
Chromium	0.099	0.136	2.275
Copper	0.417	0.282	0.411
Mercury	0.000636	0.001795	N.A.
Nickel	0.169	0.266	0.213
Lead	0.032	0.375	0.696
Selenium	0.957	1.756	0.190
Silver	0.006	0.096	0.009
Thallium	0.010	0.009	0.612
Zinc	0.916	2.566	4.095

N.A. = Not Analyzed.

Results Considered Questionable Due to Blank Contamination

Sample results less than five times the maximum concentration found in the laboratory method or field blanks can be attributed to field sampling or laboratory contamination rather than being indicative of environmental contamination. Table 6-15 shows the limit below which data are considered questionable. This limit is obtained by multiplying the maximum blank concentration above the method’s reporting limit by five. However, it is important to note that results from conventional sampling of the ash pond water would have been difficult to use to draw conclusions meaningful to the site because conventional data were questionable at concentrations measured in the pond. Examples include copper, nickel, and zinc. As is shown in Table 6-15, conventional data are treated as questionable below 60, 55, and 91 µg/L, respectively, all are potentially toxic at these concentrations. In addition the Water Quality Criteria for copper is 11 µg/L, below the level at which conventional results are considered

Table 6-15
Limits Below Which Data Are Considered Questionable Due to Blank Contamination

		5 * Maximum Blank Detection		
Parameter	**Liquids Units***	**Liquids, Clean**	**Liquids, Conventional**	**Solids**
Aluminum			728	2,898
Antimony	µg/L	0.19	37	15
Arsenic	µg/L	0.25	12	6.0
Arsenic V	µg/L	0.25		
Arsenic, total	µg/L	No Detection		
Beryllium	µg/L	0.14	1	0.7
Boron	µg/L		1,468	283
Cadmium	µg/L	0.10	11	0.9
Chromium	µg/L	2.0	60	9.9
Chromium VI	µg/L	1.2		
Copper	µg/L	4.5	60	4.3
Dimethylmercury	µg/L	0.00		
Ionic mercury	µg/L	0.00		
Iron	µg/L		370	110
Lead	µg/L	0.87	17	2.1
Mercury	µg/L	0.65	1	No Detection
Mercury 0	µg/L	0.00		
Methylmercury	µg/L	0.00		
Nickel	µg/L	1.15	55	2.8
Selenium	µg/L	2.4	15	12
Selenium VI	µg/L			
Silver	µg/L	1.2	5	4.9
Thallium	µg/L	0.02	24	2.6
Vanadium	µg/L	0.17	8	1.4
Zinc	µg/L	4.4	91	13
Acidity as CaCO3	mg/L		80	
Alkalinity as CaCO3	mg/L		220	
Ammonia-N	mg/L		11	
BOD, 5 Day	mg/L		No Detection	
Calcium	mg/L		1,556	294
Carbonate	mg/L		No Detection	No Detection
Chemical Oxygen Demand	mg/L		360	
Chloride	mg/L		5	No Detection
Chlorine, Total Residual	mg/L		No Detection	
Conductivity	mg/L		No Detection	
Dissolved Organic Carbon	mg/L		No Detection	
Fluoride	mg/L		1	
Hardness as CaCO3	mg/L		140	
Hydrazine	mg/L		No Detection	
Magnesium	mg/L		639	122
Manganese	mg/L		24	2.9
Nitrate-N	mg/L		1	
Nitrite-N	mg/L		No Detection	
Oil and Grease	mg/L		6	
Orthophosphate-P, Total	mg/L		No Detection	
Phosphorous-P, Total	mg/L		1	No Detection
Potassium	mg/L		16,192	1,405
Silicon	mg/L		51,554	156
Sodium	mg/L		5,623	4,014
Sulfate	mg/L		10	No Detection
Total Dissolved Solids	mg/L		125	
Total Organic Carbon	mg/L		58	
Total Solids	mg/L			
Total Suspended Solids	mg/L		45	

A detection is defined as a concentration above the reporting limit. Blackened cells were not sampled by the method
*Solids data is mg/kg.

Table 6-16
Reporting Limits for Ash Pond Water Samples
All values µg/L

Clean Method				Conventional Method			
Parameter ID	**Analytical Method**	**Minimum Critical Level***	**Maximum Critical Level***	**Parameter ID**	**Analytical Method**	**Minimum MDL Limit***	**Maximum MDL Limit***
				Aluminum	SW6010	6.6	91
Antimony	1638	0.003	0.012	Antimony	SW6010	1.5	20.9
Arsenic	1632	0.05	0.05	Arsenic	SW7060	0.88	12
Arsenic	1638	0.069	0.11				
Arsenic III	1632	0.02	0.02				
Arsenic V	1632	0.02	0.02				
Beryllium	1638	0.002	0.019	Beryllium	SW6010	0.088	0.9
				Boron	SW6010	16.3	392
Cadmium	1638	0.007	0.012	Cadmium	SW6010	0.16	2.8
Chromium	1638	0.027	0.029	Chromium	SW6010	0.45	8.4
Chromium VI	1636	0.23	0.23				
Copper	1638	0.029	0.066	Copper	SW6010	0.84	8.3
				Iron	SW6010	1.7	77.4
Lead	1638	0.009	0.092	Lead	SW6010	1.3	14.8
Mercury	1631	0.000057	0.000437	Mercury	SW7470	0.2	0.2
Mercury	1631M	0.00006	0.00014	Mercury	SW7471	0.082	0.2
Nickel	1638	0.013	0.055	Nickel	SW6010	1.2	6.4
Selenium	1632	0.5	0.5	Selenium	SW6010	1.4	7.5
Selenium	1638	0.22	0.393				
Selenium IV	1632	0.5	0.5				
Selenium VI	1632	0.5	0.5				
Silver	1638	0.007	0.023	Silver	SW6010	0.31	7.5
Thallium	1638	0.002	0.003	Thallium	SW6010	1.3	8.4
Titanium	1638	1.6	1.6	Titanium	SW6010	0.76	8.6
Vanadium	1638	0.015	0.09	Vanadium	SW6010	0.39	6.1
Zinc	1638	0.047	0.339	Zinc	SW6010	0.62	7.9

*Reporting limits are method detection limits (MDL) as defined in 40CFR136 for conventional samples [1] and the critical level achieved in AML study for clean samples. Clean method limits vary because two clean laboratories were used. Quantitation limits are higher than MDL and critical levels.

questionable. Average concentrations of each metal were below these levels in the ash ponds. Many parameters, therefore, would not have been able to be characterized in the ash pond water or other low-concentration streams.

Very little questionable data affected the conclusions drawn in the data analyses of this report. Parameters near blank contamination levels included most conventionally sampled trace metals in the ash pond water; cadmium and silver along with several general chemistry parameters for most matrices; and most clean sampled trace metals in source water and cooling water streams. Clean sampling and analytical methods produced lower blank contamination and, therefore, more data from which to draw conclusions.

Results Considered to be Estimates

Quantitation of results at or near the MDL (or critical level) is suspect because of background shifts and instrument noise. Accuracy and precision at these levels is highly questionable. To account for inaccuracies of results near critical levels or MDLs, results less than 5 times the MDL or critical level can be considered estimates.
Table 6-16 shows the critical levels and MDLs for ash pond water. Conventional method detection limits varied due to changes in method during the project and due to variability of sample dilution. Clean method limits differed due to two laboratories being used.

Several parameters of interest to the data analysis in the ash pond water were near the conventional method MDL, including copper and nickel. Clean sampling and analysis method critical levels were well below average concentrations of all metals of interest in the ash pond water.

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PRELIMINARY TOXICITY MANAGEMENT OPTIONS

The main wastewater management issue at the site currently is the management of toxicity of the ash pond water. The goal of preventing ash pond water toxicity can be accomplished by preventing solubilization of metals. This is best achieved by avoiding low pH conditions in fly ash sluice water and in the pond. Management options include coal management, SO_3 system management, and modifying the ash pond treatment system.

The site also had ash pond water metal concentrations above the strictest freshwater WQC for several metals, including antimony, arsenic, copper, nickel, selenium, and thallium. These parameters could be future management issues at utilities that receive WQC-based discharge limits, but are not likely to be of current interest to the host utility. The primary focus of the wastewater management options evaluated is in response to ash pond water toxicity. The following management options could be made to reduce toxicity.

Coal Management

- Specify content of minerals in coal which affect the pH of the ash sluice wastes produced. These minerals include CaO, Fe_2O_3, and MgO, which cause an ash to be alkaline; and SiO_2 and Al_2O_3, which cause an ash to be acidic. The current coal supplies range in calcium oxide content from 1 to 10%. Require suppliers to submit analysis data sheets characterizing each major source of coal. Data sheets on each coal could then be kept onsite. Controlling coal characteristics can maintain a high pH in the pond and thereby reduce the solubility of copper and nickel in the pond. Coal management is essential to ash pond water pH and toxicity control regardless of fly ash conditioning. This was shown by the events of toxic ash pond water at Site C in the early 1990s prior to when the SO_3 conditioning system was installed. As was shown by the sluice simulation studies, some coals produce ash that even before SO_3 conditioning creates an acidic, high-metals content sluice water.

- Implement a tracking program so that the type of coal being burned on a given day is known and that plant operations can be adjusted. This will be necessary for the success of the other options discussed.

SO_3 System Operation

- Evaluate options to replace the SO_3 system. The site currently is evaluating a retrofit to the ESPs that would reduce or eliminate the need for adding SO_3.
- Reevaluate the SO_3 system operation if it is necessary to meet the air quality requirements at the plant. Evaluate the minimum dosing required to meet air quality requirements for each of the coals fired. The SO_3 system may not be needed with some high-sulfur content coals. Because high-sulfur coals produce acidic ash, which causes increased metal solubility in sluice water, reducing SO_3 use with these coals would have the largest effect on wastewater quality.

Treatment Options

- Continue the use of caustic addition when low-calcium oxide content coal is being fired, to prevent low-pH conditions in the ash pond. Optimize the operation of the caustic addition system so that the dosage rate can be set to maintain an ash pond pH above 7.5. The 7.5 pH value is selected based on the copper/pH relationship shown in Figure 4-5. As the pH decreases below 7.5, the ash pond water copper concentration increases to above the 10 μg/L level at which toxicity was observed. Determine the dosing rate required for each type of coal being fired so that the system can be adjusted with fuel changes.
- Evaluate the addition of caustic in the ash sluice line rather than via the plant waste. Earlier addition of caustic was found to be more efficient at reducing solubilization of toxic metals in simulation studies. Scaling of the sluice lines would be a potential issue.
- Add organic material to the pond during periods of low pH conditions to help reduce the toxicity of solubilized metals. Past research has shown that organic matter complexes dissolved metals, such as copper, making them less toxic [30]. Pretreating and rerouting plant domestic sewage to the pond is one potential means of adding organic material to the pond.
- Evaluate iron coprecipitation as a method for reducing concentrations of trace metals, such as copper and nickel, in the ash pond water. Perform bench-scale or pilot-scale testing with Site C ash pond water to evaluate trace metal removal and effect on toxicity. Research and field trials sponsored by EPRI have shown that major reductions in the concentration of many trace metals can be achieved by their adsorption on iron oxyhydroxide. The latter can be formed by the addition of ferric chloride, with any necessary alkali, such as caustic, to the wastewater followed by sedimentation [29 to 32].

Modifying Station Operations

- Removing solids from the Site C ash pond, which is already roughly 70% filled in, could improve its ability to allow acidic waste streams to be mixed with more alkaline streams and allow for more iron coprecipitation of trace metals.

- Convert to dry fly ash handling to eliminate the largest and most acidic waste stream to the ash pond. Dry fly ash handling is an expensive, capital-intensive option.

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RECOMMENDED FIELD STUDY MODIFICATIONS

Site C was the third site of the PISCES program; its schedule overlapped that of Sites A and B. In addition to the modifications outlined in the Sites A and B report [12], a modification to the PISCES program was made as a result of a comparison done at Site C between two approaches to the clean sampling and analytical methods. Some of the test methods used in both approaches have not been approved for regulatory use by EPA or been fully validated.

Until the third week of sampling at Site C, samples were preserved in the field using clean preservative. During the third week, a comparison was made of the original approach and sending samples unpreserved to the laboratory. Both approaches met the project data quality objectives, which is discussed in Section 6. The second approach saves field samplers a time-consuming step in the sampling procedure, reduces the amount of time clean conditions must be maintained, and also reduces the potential for sample contamination.

The comparison of the two approaches provided an inter-laboratory comparison. Both of the laboratories and the approaches were able to meet data quality objectives of the project. Therefore, future PISCES sampling will be able to use either approach.

The EPA 1638 method is used by both laboratories. Because this method is “performance-based,” modifications can be made as long as method-defined data quality is maintained. The second clean laboratory used the following modifications:

- Six internal standards were used across the mass range of PISCES target parameters. Lithium was added to the method-recommended set of internal standard solutions, which were scandium, yttrium, indium, terbium, and bismuth. The method recommends that five internal standards covering the analytical mass range be used during analysis and defines three as a minimum.

- Hydrochloric acid was not used in the digestion process. Nitric acid alone was used. Increasing chloride concentration can present additional molecular ion interferences.

- A set of five procedural blanks was used for correcting the sample result. In the first laboratory’s approach to the method, blanks used for correction were not carried through the entire procedure. This difference will be resolved in future field study work.

Speciated metals analysis for arsenic, selenium, and chromium have not yet been evaluated with the second clean laboratory. An evaluation and an onsite laboratory audit will be done as part of future PISCES field study work.

9

REFERENCES

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1. U. S. Environmental Protection Agency, *Code of Federal Register, Part 40, Subchapter D*, Parts 100-149. Includes: "Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11," *Federal Register, 49,* (209), 43430, Friday, October 26, 1984.
2. U.S. Environmental Protection Agency, *National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.
3. Currie, L.A., "Limits for Qualitative Detection and Quantitative Determination: Application to Radio Chemistry." *Analytical Chemistry*, Vol. 40, No. 3, p. 586 (1968).
4. *Alternative Minimum Levels for Utility Aqueous Discharges: Chemical Analytical Measurement Guide for National Pollutant Discharge Elimination System (NPDES) Permits*. Electric Power Research Institute, Palo Alto, CA: November 1996. Report TR-106220.
5. U.S. Environmental Protection Agency. *Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*. EPA 821-R-95-027. Washington, D.C.: Engineering and Analysis Division (Mail Code 4303).
6. U.S. Environmental Protection Agency. *Method 1632: Determination of Inorganic Arsenic in Water by Hydride Generation Flame Atomic Absorption*. EPA 821-R-95-028. Washington, D.C.: Office of Water, Analytical Methods Staff (Mail Code 4303).
7. U.S. Environmental Protection Agency. *Method 1636: Determination of Hexavalent Chromium by Ion Chromatography*. EPA 821-R-95-029. Washington, D.C.: Office of Water, Analytical Methods Staff (Mail Code 4303).
8. U.S. Environmental Protection Agency. *Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry.* EPA 821-R-95-031. Washington, D.C.: Office of Water, Analytical Methods Staff (Mail Code 4303).
9. U.S. Environmental Protection Agency. *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. EPA 821-R-95-034. Washington, D.C.: Engineering and Analysis Division (Mail Code 4303).

10. Nott, B.R., et al., "Perspective on Detection and Quantification Levels for Compliance Monitoring," *The Environmental Professional*, Vol. 19, Special Issue No. 1, p. 144 (1997).
11. Gibbons, R.D., D.E. Coleman, R.F. Maddalone, "An Alternative Minimum Level Definition for Analytical Quantification." *Environmental Science and Technology*, Vol. 31, p. 2071 (1997).
12. *PISCES Water Characterization Field Study Report: Site A and B Draft Report.* Electric Power Research Institute, Palo Alto, CA: August 1997. Report TR-108890.
13. U.S. Environmental Protection Agency. *Methods for Aquatic Toxicity Identification Evaluations: Phase I, Toxicity Characterization Procedures*. EPA 600/3-88/034. Duluth, MN.
14. U.S. Environmental Protection Agency. *Methods for Chemical Analysis of Water and Wastes.* EPA 600/4-79-020. Washington, D.C., 1991.
15. U.S. Environmental Protection Agency. *Test Methods for Evaluating Solids Waste: Physical/Chemical Methods, SW-846 (3rd edition) as amended by Updates I, II, and IIA*. Washington, D.C.
16. American Society for Testing and Materials. *Annual Book of ASTM Standards, Section 5 Petroleum Products, Lubricants, and Fossil Fuels, Vol. 5.05.* Philadelphia, PA, 1994, pp. 340-351.
17. U.S. Environmental Protection Agency. *Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms (Fourth Edition),* EPA 600/4-90/027F. Cincinnati, OH: Environmental Monitoring Systems Laboratory.
18. Snoeyink, V.L. and D. Jenkins. *Water Chemistry*. John Wiley & Sons, New York, NY, 1980.
19. U.S. Environmental Protection Agency. *Quality Criteria for Water: 1986*. EPA 440/5-86-001. Washington, D.C.: Office of Water, Regulations and Standards.
20. U.S. Environmental Protection Agency. *Evaluation of Site-Specific Criteria for Copper and Zinc: An Integration of Metal Addition Toxicity, Effluent and Receiving Water Toxicity*. EPA 600/3-86-026. Duluth, MN. 1986.
21. Schubauer-Berigan, M.K., et al. "pH-Dependent Toxicity of Cd, Cu, Ni, Pb and Zn to Ceriodaphnia dubia, Pimephales promelas, Hyalella azteca and Lumbriculus variegatus," *Environmental Toxicology Chemistry*. Vol. 12, p. 1261.

22. Belanger, S.E. and D.S. Cherry. "Interacting Effects of pH Acclimation, pH and Heavy Metals on Acute and Chronic Toxicity to Ceriodaphnia dubia," *Journal of Crustacean Biology*, Vol. 10, No. 2, p. 225.

23. Mount, D. and T. Norber. "A Seven-Day Life-Cycle Cladoceran Toxicity Test," *Environmental Toxicology and Chemistry*. Vol. 3, p. 425 (1984).

24. Elnabarawy, M.T., A.N. Welter, and R.R. Robideau, "Relative Sensitivity of Three Daphnid Species to Selected Organic and Inorganic Chemicals," *Environmental Toxicology and Chemistry*. Vol. 5, p. 393 (1986).

25. Oris, J.T., R.W. Winner, and M.V. Moore, "A Four-Day Survival and Reproduction Toxicity Test for Ceriodaphnia dubia," *Environmental Toxicology and Chemistry.* Vol. 10, p. 1261 (1991).

26. Rand, Gary. *Fundamentals of Aquatic Toxicology: Methods and Application*, 1985.

27. Higgins, Thomas E. *The Fate of Copper in a Eutrophic Lake Following Treatment by Copper Sulfate*. Notre Dame University, South Bend, IN, 1972.

28. Stumm, Werner and J.J. Morgan. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*. John Wiley & Sons, New York, NY, 1981.

29. Hall, J. C., W. T. Hall, and C. T. Simmons, "Water Quality Criteria for Copper," *Water Environment & Technology*. Vol. 9, No. 6, p. 45 (1997).

30. Benjamin, K.F. Hayes, J.O. Leckie, "Removal of Toxic Metals From Power-Generation Waste Streams by Adsorption and Coprecipitation," *Journal Water Pollution Control Federation (WPCF),* Vol. 54, No. 11, p. 11 (1982).

31. *Field Evaluation of Arsenic and Selenium Removal by Iron Coprecipitation*. Electric Power Research Institute, Palo Alto, CA: May 1987. Report CS-5187.

32. Patterson, James W. *Industrial Wastewater Treatment Technology*. Butterworth-Heinemann, Boston, MA, 1985.

33. *Trace Element Removal by Coprecipitation with Amorphous Iron Oxyhydroxide: Engineering Evaluation*. Electric Power Research Institute, Palo Alto, CA: July 1985. Report CS-4087.