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Testimony of Keir Soderberg
References

Ameren Letter from J. Pozzo to B. Buscher, IL Environmental Protection Agency, Re Ash Pond Closures at AmerenUE's Venice Plant (2010, 03-25)

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March 25, 2010

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RECEIVED
MAR 26 2010
DIVISION OF PUBLIC WATER SUPPLIES
ENVIRONMENTAL PROTECTION AGENCY
STATE OF ILLINOIS

Dear Mr. Buscher:

Subject: Ash Pond Closures at AmerenUE's Venice Plant

Union Electric Company d/b/a AmerenUE ("AmerenUE"), pursuant to 35 Ill. Adm. Code 620.250(a)(2), proposes to close the inactive ash pond system[1] at AmerenUE's Venice Power Plant, until recently subject to Illinois Environmental Protection Agency ("IEPA" or "Agency") Permit No. 2005-EO-3215. The approximately 300 acre plant site is located adjacent to the Mississippi River and straddles the county lines of St. Clair and Madison County. AmerenUE requests that the IEPA confirm that the proposed corrective action is being undertaken in a timely and appropriate manner, and establish a Groundwater Management Zone as a three-dimensional region containing groundwater being managed to mitigate impairment caused by the release of contaminants from this site. This letter and the referenced attachments are provided in support of AmerenUE's proposal. We note that our intent to pursue closure in this manner was discussed with IEPA staff in meeting late last year and described conceptually in my prior letter of January 19, 2010.

I. PROPOSED CLOSURE

Details regarding the proposed final capping and closure of the ash pond system at the Venice Power Plant ("Venice" or the "Site") and

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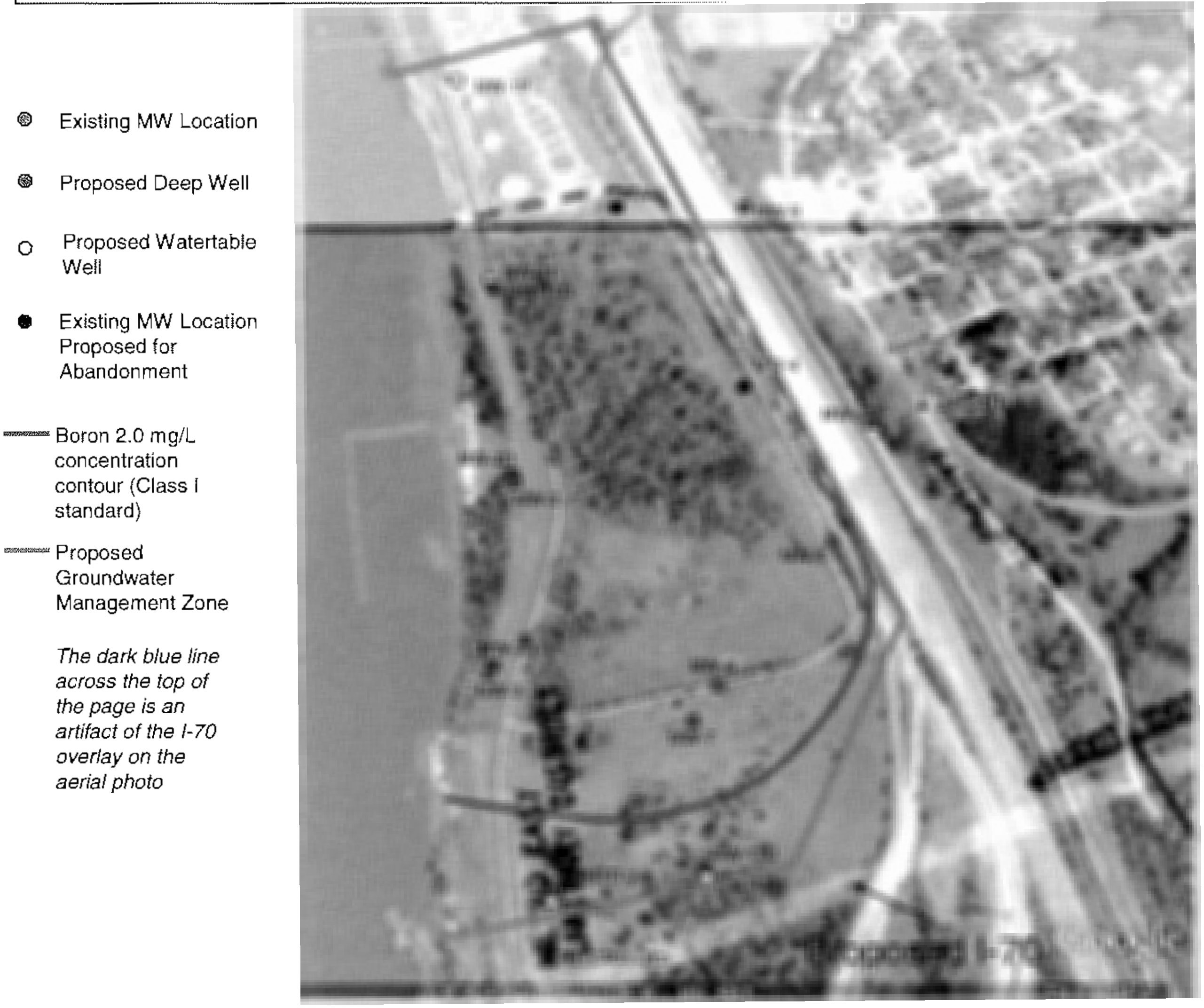
[1] The ash pond system is located at the very southern end of the Venice Power Plant site and is comprised of two ash pond cells[1] (Nos. 2 and 3) (collectively, and unless specifically indicated otherwise, "the ash pond system").

requirements for the ongoing management of impacted groundwater in and around that impoundment system are provided in this document.

The former operation of ash ponds was regulated pursuant to the Board's Water Pollution Control rules. However, upon closure the ash ponds do not explicitly fit any of the types of facilities covered by the Illinois Pollution Control Board's regulations, including the Waste Disposal rules of Subtitle G. They are not landfills as defined in the Board's solid waste regulations. Recently, the Agency has determined that approval of an adequate corrective action and establishment of a Groundwater Management Zone (GMZ), in accordance with Title 35, Subtitle F, Chapter I, Part 620, Appendix D is an appropriate mechanism for closure of these ash impoundments. As described in detail below and shown in Figure 1, we have delineated the boundaries of a proposed GMZ associated with the inactive ash pond system at Venice. The proposed GMZ is conservative in that it covers a larger area than the mapped extent of Class I exceedances.

Figure 1
Proposed Monitoring Network and Groundwater Management Zone



The dark blue line across the top of the page is an artifact of the I-70 overlay on the aerial photo

Pending before the Board is a proposed site-specific rule with respect to the closure of Ash Pond D at the Hutsonville Power Station (*Ameren Ashpond Closure Rules (Hutsonville Power Station) Proposed: 35 Ill. Adm. Code 840.101 through 840.144*, R09-21). That proposal also set out to create a new Subchapter to Subtitle G specific to Surface Impoundments and create a new Part 840, Site-Specific Closure of Surface Impoundments, under Subchapter j.[2] Based on Agency input, AmerenUE is not proposing to close the Venice impoundments via a site-specific rulemaking, however this proposal incorporates many of the agreed upon concepts and approaches embodied in the Hutsonville rulemaking (PCB R09-21) while recognizing the unique geographic characteristics and surrounding land uses of the Venice site. The Site is located in an industrialized region, groundwater on-site and off-site has been impacted from sources other than the ash pond system, and the use of groundwater for potable purposes is restricted by groundwater ordinances enacted by the surrounding municipalities of Brooklyn, Venice, and Granite City. In addition, a commercial/industrial use restriction for a portion of the Venice site has been recorded with the St. Clair County Recorder of Deeds ("Land Use Restrictions – Lot 101 Restricted to Industrial/Commercial", Book 3552, Pages 1105 to 1108, A01622412). Further, there are numerous physical constraints at the site including river levees, active rail lines and transmission towers which impact the closure of the ash impoundment system. The groundwater at and down gradient of the Site is not used for human consumption, irrigation, or any known industrial purpose. In fact, groundwater impacted by the ash pond system is for all practical purposes, inaccessible.

II. TECHNICAL SUPPORT DOCUMENTS

AmerenUE has performed two hydrogeologic investigations of the ash pond system including the installation and expansion of a groundwater monitoring well network and numerous soil borings. We have monitored groundwater quality associated with the ash pond system since 1996. Recently we performed direct-push groundwater sampling to determine, in part, the impact of the 2005 dewatering of the ponds on off-site impairments. In preparation for final closure of the ash pond system, AmerenUE evaluated capping and groundwater management alternatives and modeled their likely outcomes. Supporting documentation is contained in a number of Reports and Technical Memorandums which are referenced throughout this letter and included as Appendices.

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[2] Ameren recognizes that the Board must obtain the number of the new Part from the Secretary of State who may determine that 840 is not the appropriate number for the new Part.

III. THE SITE AND THE AREA AFFECTED BY THE CONTAMINANT PLUME

The Venice Power Plant site is located along the banks of the Mississippi River and across the river from the City of St. Louis, Missouri in a heavily industrialized stretch of the river[3]. Industrial facilities have populated this area since the early 1900s. Due to the lack of industrial waste treatment during much of the twentieth century, former lakes and stream channels in the vicinity of industrial waste sources, past or present, are possible repositories of industrial wastes. In recognition of these historical practices and that certain chemical constituents in the groundwater beneath much of Madison and St. Clair Counties may exceed Class 1 water quality standards for potable resource ground water, the City of Venice and the Village of Brooklyn have enacted ordinances prohibiting the use of groundwater as a potable water supply.[4]

AmerenUE's property holdings in this area are bordered by the Mississippi River to the west and an active rail line corridor and rail yards to the south and east. See the enclosed "Venice Property Control Map" Rev 3 dated 03/2010. It is, therefore, physically segregated from the residential municipalities located east of the rail corridor. The ash pond system was constructed in the early 1950s in conjunction with the flood levee system that was upgraded and relocated to the banks of the Mississippi River. The western berm (approximately 1100 feet) of the ash ponds forms the dike that is part of the United States Army Corps of Engineers ("Corps") flood levee system.[5] As such, it cannot be structurally compromised; any modifications are subject to the Corps jurisdiction. The southern berm of Ash Pond No. 3 is just inside the southern property boundary. The Venice Site is west of the City of Venice and the Village of Brooklyn, Illinois. Drinking water for these municipalities is supplied by the Illinois American Water Company through a surface water intake located at the Mississippi River, upstream of the Site. Adjacent property owners and easement holders include the Terminal Rail Road Association, Kansas City Southern, Missouri Central Railroad, and the Norfolk Southern Railroad. Natural gas and oil pipeline easements are located on the river bank just west of the

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[3] Historical records such as Sanborn maps from 1907, 1950 and 1962 reflect that surrounding land use included creosote plants, corn products refining, rail yards, rail tie storage yards and plaster mills. All of these facilities are up gradient of the site. Virtually all of these operations are now defunct. The 2000 Hydrogeologic Assessment provides an interpretation of the features depicted on these Sandborn maps.

[4] In recognition of the industrial nature of the area and historical waste practices, the cities of East Saint Louis, Wood River, Granite City and the Villages of Brooklyn and Sauget – located in St. Clair and Madison counties – have all enacted groundwater use restriction ordinances.

[5] While located on Ameren property, the river levee was constructed for flood control purposes in the 1950s and is maintained by the Metroeast Sanitary Levee District (per agreements dated May 9, 1952 and March 1, 1956). It is certified by the Corps who must approve all activities that could potentially impact the stability or integrity of the levee.

levee and ash ponds. Various AmerenUE high voltage transmission lines cross the area and at least one transmission tower is located within the ash pond basin. The industrial character of the area is unlikely to change.

The Illinois and Missouri Departments of Transportation intend to construct a new Mississippi River Bridge that will be located approximately 1000 feet south of the Venice site. The Illinois Department of Transportation ("IDOT") requested an easement from AmerenUE to build an access road for the bridge project. The road will be located on top of ash pond berms to the east. Construction contractors for the project will be utilizing railroad property immediately south of Ash Pond No. 3 for a lay-down area and continuation of the bridge access road.

Ameren has been in communication with the local municipalities regarding the closure of the ash pond system and there are no zoning restrictions or municipal requirements which preclude implementation of this proposed rule. Since the river levee forms the western berm of the ash pond system and once engineering designs have been completed, the Corps will need to approve aspects of the closure plans so as to ensure the structural integrity of the levee. The Venice Power Plant is the only source affected by this proposal.

Historical Operation of Ash Pond System

From approximately 1942 until the mid-1970's, the Company operated Venice as a coal-fired electric generating facility. The primary water source for the facility is the Mississippi River via two intake structures. In the 1970's, the Company converted the plant generators to burn either natural gas or oil.[6] Prior to the fuel conversion, the Company managed coal-combustion wastes, along with waste waters from the boilers, water treatment plant, and various other process waters plus storm water runoff, in a series of ponds referred to as Ash Pond Nos. 2 and 3 (collectively, "the ash pond system"). The ash pond system was constructed in the 1950s and is unlined, consistent with the engineering and design practices of that time. The ash pond berms were constructed from indigenous earthen materials. Ash has not been disposed of in the system since 1977.

During active operations, Ash Pond No. 2 and Ash Pond No.3 (collectively the ash pond system) were permitted to handle 116 and 194 million gallons, respectively, of boiler process waters and storm waters. Coal ash, a by-product of the combustion process, was removed from the boilers and wet sluiced to the impoundment system via pipelines. During the operation of the ash pond system, coal ash and other coal combustion byproducts

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[6] In 2003, as a result of a catastrophic fire at the site, the Company abandoned the power plant building and associated generating equipment. Beginning in 2004, AmerenUE installed three additional simple-cycle combustion turbine generators (Units 3, 4 and 5) which are located north of the ash pond system. The Venice Plant operates only intermittently as a peaking facility.

(CCBs) settled within Pond Nos. 2 and 3 and supernatant was discharged to the Mississippi River. After the fuel conversion (to natural gas or oil), the Plant continued to discharge process wastewater and storm water runoff into the ash ponds, however the outfall to the River was eliminated. As a result, water ponded within the basins and eventually dissipated.[7] Authorization for operation of the ash ponds continued until expiration of the facility's Water Pollution Control Permit (No. 2005-EO-3215) on January 31, 2010. The two ponds are connected via an overflow pipe. There are approximately 1,425,500 cubic yards of CCBs located within the ash pond system. The depth of CCBs within the ponds is approximately 27 feet. As described below, borings advanced by Hanson Engineers, indicate the base of ash is at an elevation of approximately 400 feet MSL. Based on a review of groundwater monitoring well data conducted by Natural Resource Technology (also described below) ash is in contact with the groundwater during high water river stages that typically occur approximately 15% of the time.

Current Storm and Wastewater Treatment System

Beginning in 2004, AmerenUE installed three additional combustion turbine generating units (CTGs) at the Venice plant site. To both accommodate the CTGs and to isolate and dewater the ash pond system, AmerenUE constructed a storm water and waste water treatment system which is located north of Ash pond No. 2. In 2005, the Agency issued a revised NPDES permit for this new outfall to accommodate and regulate discharges to the Mississippi River from this wastewater system (NPDES Permit No. IL0000175). At the same time, the Agency re-issued a State Operating Permit allowing the ongoing use of the ash pond system for a full five-year term which terminated on January 31, 2010.[8] The wastewater treatment facility is a concrete structure consisting of several settling cells including a pre-sedimentation, an oil/water separator, and a sand filtration basin. The capital costs associated with constructing the treatment facility were approximately $750,000. With the installation of this treatment system, Ameren eliminated all discharges into the ash pond system. Thus, the ash pond system has been completely isolated since 2005. The water table beneath the ponds (and amount of saturated ash) has dropped considerably since that time. As it has remained out of service for many years, portions of the ash pond system are heavily vegetated.

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[7] All of the plant's process wastewater and storm water runoff (e.g. building roofs, paved plant yards) continued to be transferred to the ash pond system until a new water treatment facility and outfall was constructed in 2005.

[8] In early 2005, the Company requested an interim six month extension to operate the ash pond system while the new treatment facility was being constructed and duly permitted. This followed an earlier commitment from the Company to the Agency to close the ash pond system and not seek renewal of the State Operating permit.

Hydrogeologic Assessments of Ash Pond System

Site Hydrogeology

The site is underlain by about 80 feet of alluvial deposits associated with the Mississippi River. The upper 20 to 30 feet of these deposits contain alternating layers of silt, sand, and clay; while the lower 60 to 50 feet primarily consist of sand and gravel. Groundwater is typically encountered at a depth of 20 to 30 feet.

Groundwater flow in the region is controlled by the Mississippi River. During normal river stage and the majority of the year, groundwater flow is towards and discharges into the river. During high river stage, ground water flow is reversed, with the river recharging the aquifer. Water levels within the monitoring wells rise and fall with the river stages.

1996 Assessment and Groundwater Monitoring System

In 1996 the Company retained Hanson Engineering to perform a hydrogeologic investigation to evaluate groundwater impacts associated with the ash pond system, as a condition of Venice's State Operating Permit (No. 1995-EO-3037). Their report "Hydrogeologic Investigation Former Ash Disposal Pond System, AmerenUE Venice Power Plant" describes the monitoring well system, data collected and site geology. A copy of this report was provided to the Agency in 2000 and is included as Appendix A. The three well groundwater monitoring network installed in 1996 was ultimately expanded to seventeen monitoring wells at varying depths and locations in and around the ash pond system. Monitoring wells 7 and 7P were installed to monitor off-site impacts to the south. Monitoring wells 2, 2P and 3 are located near the river bank to the east, and monitoring wells 8 and 9 are located off-site on railroad property to the west. Additional wells were installed along the perimeter of the ash ponds (MW 1, 4, 5, 5P, 6), and within the basins (MW AP-1, AP-1A, and AP-2). AmerenUE performs groundwater sampling on a quarterly basis and has submitted monitoring results to the Agency since 1996.[9]

2009 Assessment

In early 2009, the Agency issued requests to all of Ameren's Illinois power plants to establish groundwater monitoring systems and to perform hydrogeologic evaluations in connection with active ash pond systems. The Agency letter regarding Venice Plant was dated April 10, 2009 and it requested a hydrogeologic assessment and potable well survey for the Site. In response to that request and in anticipation of the expiration of the State Operating Permit and the need to initiate additional closure activities,

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[9] Since 1996, the Company has monitored for arsenic, barium, boron, cadmium, chromium, copper, lead, manganese, nickel, zinc, pH and TDS.

Ameren retained NRT to update Hanson's 2000 assessment. The Company has been unable to draw groundwater samples from several shallow perched-zone monitoring wells on a consistent basis because the perched-zone has dissipated due to the dewatering of the ash pond system. NRT complied "Technical Memorandum No. 1, Potable Well Survey Hydrogeologic Assessment, and Modifications to the Groundwater Monitoring Program, Venice Ash Impoundment" dated September 17, 2009 to document this work and their findings. Ameren submitted this memorandum previously (with a letter to Mr. Alan Keller, dated September 18, 2009); a copy is included as Appendix B.

Subsequently, additional soil borings and groundwater grab samples were taken south of the Site and beyond the limits of the existing monitoring well network to delineate the extent of the off-site plume associated with the ash pond system. Ameren also asked NRT to identify or re-establish well locations to address the drop in the water table and identify sources of contamination and their contribution to concentrations detected in monitoring wells located down gradient of the ash pond system. NRT complied "Technical Memorandum No. 2, Supplemental Hydrogeological Assessment, Venice Ash Ponds" dated March 3, 2010 to document this work and their findings; it is included as Appendix C. NRT's memorandum delineates the extent of the off-site groundwater contamination and identifies potential up gradient sources of groundwater contamination and their contribution to the groundwater conditions near and adjacent to the ash impoundment system. It also includes an evaluation of the current monitoring well network and recommendations for establishing a monitoring well network appropriate to monitor the effectiveness of the proposed closure approach. This document summarizes the monitoring program AmerenUE intends to submit as part of the site closure plan.

Groundwater Impairments

Groundwater monitoring data show impairments above Class I Groundwater Quality Standards for the following parameters: iron, arsenic, boron, TDS and manganese.[10] Boron will be used as the representative constituent for ongoing groundwater assessments. Boron is typically used as an indicator of coal combustion byproduct plume migration since it is readily available from coal ash and relatively mobile. Direct-push groundwater samples obtained in October 2009 indicate that the extent of any southern groundwater impairments extend approximately 500 feet south of the southern property boundary. These off-site impairments only nominally exceed the Class I standard for boron of 2 mg/l.

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[10] Manganese appears to be ubiquitous and therefore is not a reliable indicator of coal ash leachate.

Arsenic is present inside and outside of the boron plume at levels above the Class I standard. These data suggests that the ash pond system does not contribute a significant source of arsenic to groundwater. Instead, NRT concludes there is likely an alternative source of arsenic. Iron is also present inside and outside the plume in excess of the Class I standard, indicating that the ash ponds are not the source of iron. Manganese is also present inside and outside the boron plume in excess of the Class I standard. Because manganese is present in up gradient wells above Class I standards, but below detection limits in leachate, NRT concludes that there is another source of manganese as well, but the source may be natural rather than anthropogenic. Levels of TDS in the groundwater reflect dissolved concentrations of major ions in groundwater and, therefore, elevated concentrations are not necessarily associated with the ash ponds. Therefore, the data suggests that the ash pond system does not present a significant source of arsenic, iron, manganese, or TDS at these monitoring points.

Offsite, Ameren has confirmed that there is no possible use of the impacted groundwater. In addition, Ameren has been in communication with the adjacent property owner to the south, Terminal Rail Road Association (TRRA), regarding the proposed GMZ, future access to monitoring wells, and the prohibition of future installation of wells on TRRA's property for use of groundwater. On a portion of Ameren's site, a groundwater use restriction limits the future use of groundwater to industrial purposes only. Furthermore, Ameren believes that <u>none</u> of the groundwater impairments associated with the ash pond system significantly impact water quality within the Mississippi River. The estimated low flow of the Mississippi River at the Site is 46,500 cubic feet per second (cfs) and is four million times greater than the estimated groundwater flow into that receiving body. NRT calculated boron loading from the ash pond system to the river and compiled a report entitled "Technical Memorandum No. 3, Boron Loading to the Mississippi River from Venice Ponds 2 and 3" dated March 3, 2010; it is included as Appendix D. As stated previously, boron was chosen because it is readily available and is a very mobile indicator constituent of coal ash leachate. NRT used conservative assumptions as to hydraulic conductivity, water flow conditions and the highest observed concentration value (of 41 mg/l boron at MW4)[11] to calculate an estimate of the resulting incremental increase in boron in the Mississippi River due to discharge from the Venice ash ponds. The result was 0.0019 mg/L boron and this concentration is approximately an order of magnitude lower than the detection limit for boron as listed by USEPA. Accordingly, the loading calculations indicate that boron released from the ash pond system and by extension all other coal ash constituents are negligible and have no perceptible impact on water quality within the Mississippi River.

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[11] The 41 mg/L boron concentration from MW4 is considered suspect because this monitoring well was drilled through coal ash. Monitoring wells that were not drilled through coal ash returned a maximum concentration of 14 mg/L. The use of a potentially anomalously high value is a conservative assumption in the loading calculation.

Based on the groundwater monitoring data and hydrogeologic assessment concluding that several of the groundwater exceedances are not likely attributable to the ash pond system, Ameren is proposing a closure scenario incorporates a protective cap, a GMZ, institutional controls, and groundwater monitoring. The intent of the selected closure scenario is to mitigate the source of groundwater contamination and reduce impacts from the ash pond system to the extent practical.[12]

Ameren anticipates that the approved GMZ will require monitoring of groundwater quality associated with the ash ponds to ensure that the selected closure scenario is working effectively. As discussed below we will submit a Closure Plan for Agency approval, which will include an obligation to perform ongoing trend analyses to identify statistically significant increasing trends in the impacted groundwater. Our plan will also commit Ameren to conduct additional investigation to determine the cause and possibly trigger corrective action if it is determined that a statistically significant increasing trend is attributable to the ash pond system.

IV. AVAILABLE TREATMENT OR CONTROL OPTIONS

As discussed above, in 2005 Ameren initiated its first phase of closure by eliminating discharges into the ash pond system and constructing and operating a storm water and waste water treatment facility. The re-routing of such storm and wastewaters has reduced the physical mechanism by which additional pollutant loading into the groundwater from the ash pond system can occur. Exceedences of Class I groundwater quality standards remain on and offsite. And until the ash pond system is capped, the release of additional leachate from precipitation onto and percolation through the impounded ash into the groundwater will continue.

Ameren has investigated a variety of control options to close the ash pond system in a way that protects human health and the environment. As discussed above, the ash ponds were constructed in the 1950s prior to the adoption of modern environmental regulations and requirements. As the Board acknowledged in <u>Petition of Ameren Energy Generating Company for Adjusted Standards from 35 Ill. Adm. Code Parts 811, 812, and 814</u>, AS 09-1 (Mar. 5, 2009), compliance with current landfill engineering and design standards is not feasible for ash ponds.

Ameren tasked NRT with analyzing alternatives that would bring the Site into compliance and included consideration as to the feasibility of various groundwater hydraulic controls. The alternatives are described in NRT's

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[12] The use of a GMZ to address groundwater impacts from ash ponds has been used in connection with the closure of impoundments at generating facilities formerly owned by Illinois Power Company.

report entitled "Technical Memorandum No. 4, Evaluation of Closure Alternatives, Venice Ash Ponds" dated March 12, 2010 (included as Appendix E) and are discussed below. The viable closure options included three capping alternatives (compacted clay, geomembrane, earthen) and a variety of groundwater management options including institutional controls and installation of groundwater extraction wells. Ash removal and disposal was also considered.

The alternatives were evaluated by AmerenUE based upon a variety of considerations including (a) feasibility of construction and implementation; (b) effectiveness for (i) reducing surface water infiltration and resulting leachate generation and/or (ii) hydraulic capture; (c) economic considerations including capital cost and ongoing maintenance expenses when compared to the potential environmental benefit; and (d) appropriate and reasonableness of the alternative given external factors such as lack of human exposure to groundwater, the availability of restrictive ordinances and covenants, the potential for groundwater contamination from external sources and expected future land uses.

As mentioned previously, the physical configuration of the Venice site impacts the feasibility of implementing the available closure alternatives. The western berm comprises part of the river levee system. It cannot be compromised. In fact, the toe of the levee extends approximately 30 to 60 feet under the ash ponds. Accordingly, all subsurface construction activities that could impact the structural integrity of the levee are prohibited. In practice, the installation of slurry walls, collection trenches or extraction wells within 500 feet of the levee would require approval by the Corps and could be prohibited without extensive engineering analysis.

In addition, the IDOT access road and AmerenUE transmission towers are permanent physical features that must be accommodated under all closure scenarios. The final cap design and installation along the levee must be approved by the Corps as the membrane cap and slope would need to tie into the river levee. Ameren recognizes the Corps' jurisdiction at this site and will accommodate modification of the closure or post-closure care plans in the event the two agencies conflict regarding closure requirements.

Groundwater Management Alternatives Considered

Groundwater impacts from the ash pond system are not adversely impacting the Mississippi River and are predicted to decrease over time after the closure plan is implemented. Monitoring data reflects minor exceedances of Class 1 standards to the south of the property boundary. Furthermore, heavy industrial sources in the region may have contributed to historical groundwater contamination which eventually flows eastward towards the Mississippi River and beneath the site. Ameren's consultant, NRT, prepared a comparison of the available groundwater management alternatives. Based on this comparison and for the reasons set forth below, Ameren determined that a cap in conjunction with a GMZ for managing on-site and off-site groundwater impacts and environmental land use restrictions will be protective of human health and the environment while also being economically reasonable and technically feasible. Each of the groundwater management alternatives is discussed in more detail below.

1. Groundwater Extraction

AmerenUE evaluated the feasibility of installing five extraction wells along the southern property boundary to hydraulically capture groundwater. Because the groundwater in the area is presumed to be contaminated from a variety of industrial sources unrelated to AmerenUE, the extracted water would need to be fully characterized in quantity and quality before it could be discharged to a sanitary sewer system. In 2003, a consultant investigated the possibility of discharging to the Metro East Sewer District ("MESD") Venice Pump Station and transfer to the Granite City Regional Wastewater Treatment Plant. Establishing this discharge would require inclusion of Venice Plant in the sewer district and physically connecting to the sanitary sewer located approximately one mile from the proposed wells. Due to the unknowns regarding the quantity and quality of groundwater the sewer district is able to receive, this alternative has tremendous technical uncertainty.

As an additional consideration, the variable groundwater flow due to the proximity to and influences from the Mississippi River bring the effectiveness of groundwater extraction wells into question. The direction of groundwater flow is dependent on Mississippi River flow/stage conditions which changes seasonally and in response to storm events. Over the long term, groundwater extraction wells would not be consistently mitigating impacts to groundwater caused by the ash pond system.
It is the extremely high operating and maintenance costs, however, that make this alternative economically unreasonable for Ameren. The sanitary district calculates discharge fees based on property tax rates and the quantity of wastewater flows. NRT estimates Operation and Maintenance fees at $600,000 per year based on these sanitary sewer discharge fees. Such costs are economically unreasonable and not justified from any perspective. There are no groundwater receptors or potential human health impacts since there are no users of groundwater down gradient of the Site. The ash pond system is not negatively impacting water quality within the receiving body, the Mississippi River. Further, even if AmerenUE were able to implement some sort of groundwater extraction system, Class I Groundwater Quality Standards for various chemical constituents would still be exceeded due to historical industrial practices in the region, as evidenced by the local groundwater usage ordinances.

2. Ash Removal and Disposal

As part of its preliminary screening of viable alternatives, AmerenUE evaluated the feasibility of removing the source material and disposing of the ash in an off-site solid waste landfill. This alternative is neither technically feasible nor economically reasonable.

As estimated by NRT, costs associated with ash removal and off-site disposal is prohibitive and the technical feasibility of implementing this option is questionable. The costs associated with the excavation, removal, and transport, of nearly 3 million tons of ash for disposal at a solid waste landfill are exorbitant. The cost of excavation and off-site disposal is estimated at approximately $200 million. The Cahokia-Roxford transmission line run north-south across the ash ponds and two transmission towers are located within the basins. In order to excavate ash, these towers would need to be relocated and there is simply no suitable substitute location. Furthermore, the removal of any significant amount of ash creates a surface depression behind the levee that will create a "sink" for ground and surface water to pool. Such ponding increases seepage and could adversely impact the structural integrity of the river levee. To minimize such risk, suitable fill material would need to be trucked to the site to fill in the depression. Therefore, this alternative was not considered viable because of the technical uncertainties and the very high cost compared to other alternatives.

3. GMZ and On and Off-Site Land Use Restrictions

Ameren is requesting establishment of a GMZ extending over the footprint of the ash pond system to manage the on-site contamination and reliance on institutional controls and groundwater monitoring to manage offsite impacts to groundwater. A GMZ recognizes specified areas and contaminants on a site that are not in compliance with applicable groundwater quality standards and contemplates appropriate corrective actions for long periods of time.

Institutional controls are already in place for the municipalities of Brooklyn, Granite City, and Venice. And, as stated previously, Ameren is in discussion with TRRA regarding the need to avoid the use of impaired groundwater at their site. Offsite institutional controls already prohibit the use of groundwater for potable or irrigation purposes. Because they are currently in place, such groundwater ordinances and deed restrictions offer immediate and permanent control of access to the impacted groundwater.

The proposed on and off-site groundwater management approach recognizes the historical industrial land use of the area and the inherent difficulty in establishing background baseline concentrations at the Site. The selected groundwater management scenario is also appropriate given the potential for off-site contamination from sources unrelated to

AmerenUE. Groundwater in the area is not used for human consumption and the local municipalities are connected to a public water supply system operated by American Water Company of Illinois and which draws from the Mississippi River as its water source, not the groundwater aquifer. Finally, groundwater use restrictions already exist on and off-site.

Selected Closure Scenario

After consideration of the available groundwater management and cap alternatives considered, and based on the technical, economic, and environmental considerations discussed in more detail below, Ameren proposes to allow the existing ash to remain in place. Installation of an engineered cap will reduce the production of leachate and provide further groundwater protection which will improve the current environmental condition. Ameren selected a geosynthetic membrane cap and final cover system as this closure option is both technically feasible and economically reasonable. Ameren's Closure Plan will propose a final slope to meeting the stability criteria of 35 Ill. Adm. Code 811.304 and the cap and final cover system will be designed in accordance with the performance criteria for geosynthetic membrane caps set forth in 35 Ill. Adm. Code 811.314. This solution is protective of the environment by requiring capping techniques that comport with performance and stability criteria from the landfill regulations. Our proposal is conditioned upon the establishment of a GMZ and commits to ongoing trend analyses which are intended to recognize the existing, on-going impacts to the groundwater as well as monitor groundwater to ensure that the final closure scenario is protective. Ameren's proposed closure scenario includes the features summarized below:

- A geosynthetic membrane with soil cover.
- Stormwater management during and post-construction.
- A GMZ established both on and offsite (assuming TRRA endorses this proposal).
- Nine additional monitoring wells to be installed to the west, north, and south.
- Monitoring for all 35 Ill. Adm. Code 620.410(a) and (d) constituents except radium 226 and 228 and cadmium, copper, lead, nickel and zinc, as noted in Appendix C, Technical Memorandum No. 2.
- Boron selected as the indicator contaminant for assessment monitoring of concern due to its high mobility and association with ash pond leachate.

Final Cover System Design

As stated above Ameren has determined that the geosynthetic membrane cap is an economically viable and environmentally justified option because it will mitigate the infiltration of surface water.

Before reaching this decision, Ameren evaluated a number of materials including the synthetic geomembrane product, compacted clay, and layered earth. NRT used the Hydrologic Evaluation of Landfill Performance (HELP) model to estimate and compare the rate and volume of percolation from the ash pond system using various cap materials (see NRT's "Technical Memorandum No. 5, Predicted Change in Percolation, Venice Ash Impoundment" dated March 12, 2010 which is included as Appendix F). While the underlying variables and estimated contingencies varied among the particular options, preliminary estimates of construction capital costs to cap the pond system ranged from \$7.5 to \$13.7 million dollars. Ameren selected the geomembrane product, at an estimated capital cost of \$11.2 million, as it is a known and certain technology that is readily available, meets the performance criteria set forth in the landfill regulations (35 Ill. Adm. Code 811.314(b)), and outperforms the other options. NRT's modeling of surface water infiltration estimates that the current percolation volume of 1,120,000 cubic feet per year (ft^3/yr) will be reduced to approximately 116 ft^3/yr after installation of the proposed synthetic cap.

We note that at present, the current grade of the impoundments is below the surface height of both the western (levee) berm and railroad embankment to the east. The stability of both berms must be maintained and therefore considerable material movement within the ponds may need to occur in order to establish appropriate slope and grading for surface water management and installation of the cap.

V. ENVIRONMENTAL IMPACT OF PROPOSED RULE

Ameren has assessed the environmental impact of the selected closure scenario, and found it to be protective of human health and the environment.

As discussed in Hanson's 2000 assessment and confirmed in NRT's 2010 update, groundwater flows towards the Mississippi River. Ameren determined potential impacts of groundwater discharge to the river and concluded that the ash pond system does not adversely impact the Mississippi River as the site-specific loading calculations show the impact of the Venice ash pond system on River water quality to be negligible.

The proposed rule will also be protective of human health and the environment because there is no use of the groundwater in or around the site and no future use is possible given the presence of the railroad on adjacent property, environmental land use controls, and municipal ordinances including: the City of Venice (Ordinance No. 00-6), the Village of Brooklyn (Ordinance 09-006), and the City of Granite City (Ordinance No. 7529) which preclude the potable use of groundwater. Further impacts to groundwater will be mitigated by the installation of a cap and cover system which will prevent future infiltration and allow for natural attenuation. Moreover, due to the adjacent railroad, future property uses of that site are expected to remain the same without any anticipated use of the groundwater. Despite all of these circumstances, AmerenUE has established appropriate groundwater use restrictions for the site to ensure that the groundwater is not used for potable purposes in the future.

Accordingly, the rare circumstances of extraordinarily high costs to remediate groundwater coupled with the lack of potable uses of groundwater now or in the future at the Venice site merit the use of the proposed final closure scenario. Moreover, the technical justification in support of this proposal demonstrates that this combination of compliance alternatives will be protective of human health and the environment.

In order to predict the change in contaminant concentrations following implementation of the proposed final cover system, NRT was tasked with modeling the fate and transport of the existing boron plume. Their report, entitled "Technical Memorandum No. 6, Groundwater Modeling of Venice Former Ash Ponds" dated March 12, 2010 is included as Appendix G. As described in this technical memorandum, NRT was tasked with developing a fate and transport model to simulate changes in groundwater quality resulting from capping the Venice Plant ash ponds. The "Base Case" was assumed to be the geosynthetic final cap as proposed in this request, with installation occurring in 2011. Three model codes were used to simulate groundwater flow and contaminant transport: leachate percolation and aquifer recharge was modeled using the Hydrologic Evaluation of Landfill Performance (HELP) model; groundwater flow was modeled using MODFLOW; and contaminant transport was modeled using MT3DMS. The model was calibrated to simulate observed groundwater head data, and then to observed concentration data and trends from 2000 to 2009. Boron was modeled for the reasons cited previously. The model was configured to simulate the fluctuations in groundwater elevation and flow direction caused by changes in Mississippi River stage. The model predicts that groundwater quality will improve over time, as leachate percolation from the impoundments is reduced following installation of the geosynthetic cover. Under the Base Case scenario the model suggests that concentrations in all monitoring wells will stabilize below the 2 mg/l Class I boron standard within 13 to 20 years, with the sole exception of on-site well MW-6. Concentrations on-site at MW-6 were slowly decreasing at the end of the 20 year period and a linear interpolation of the trend suggests that concentrations will be lower than the Class I standard at this location after approximately 28 years.

Finally, Ameren's proposed Closure Plan will ensure that the synthetic cap is effective and will not result in further degradation of groundwater quality by requiring ongoing groundwater monitoring obligations based on the results of trend analyses. The Plan would require investigation of increasing trends and if a trend is determined to be statistically significant and attributable to the ash pond system, it will require Ameren to take corrective action. The groundwater monitoring data and analyses will be submitted to the Agency on an ongoing basis throughout the closure and post-closure care periods.

VII. REQUESTED AGENCY ACTIONS

Following Agency review of this submittal, and assuming that you concur with the proposed remedy as described above, we understand that you will issue a public notice regarding your intent to establish a GMZ for the Venice site. At that time, we would forward both the Agency notice, and a copy of this request to the Corps of Engineers, to initiate substantive discussions regarding the cap and cover design to evaluate and resolve any concerns the Corps may have regarding the levee. Again, assuming comments from both the public and the Corps can be addressed, we ask that a final decision be reached to establish the GMZ.

VIII. AMEREN'S RESPONSE TO THE ESTABLISHMENT OF A GMZ

Upon establishment of the GMZ, Ameren will finalize and submit a Closure Plan and Completion of Closure Report and Post-Closure Care Plan, for review and approval by the Agency. The principal components of these plans are outlined below:

1) Closure Plan

- a) Summary of Supporting Documents (i.e. Technical Memorandums including the Supplemental Hydrogeologic Assessment, Predicted Change in Percolation Rates, Boron Loading to the Mississippi River, and the Modeled Change in Contaminant concentrations Following Closure)
- b) Final Delineation of the GMZ
- c) Groundwater Monitoring Plan
  - i) Monitoring Well System
  - ii) Monitoring Program
    - (1) Parameters
    - (2) Monitoring intervals
    - (3) Reporting
    - (4) Analytical and Quality Assurance/Quality Control methods

- d) Performance Assessment Plan (trend analyses methodology)
- e) Final Cover System Design (60%)
- f) Construction Quality Assurance Plan
- g) Final Slope and Berm Stability Analysis

2) Completion of Closure Report and Post Closure Care Plan

- a) Report/Certification of Completion (of final cover installation)
- b) Post Closure Care Plan
  - i) Maintenance of the Cover System
  - ii) Inspections and Corrective Actions
  - iii) Groundwater Monitoring Program
  - iv) Performance Assessment Plan

IX. CONCULSIONS

We believe the discussion above in conjunction with the technical documents contained in the appendices, adequately and appropriately characterize the groundwater contamination associated with the historic operation of the AmerenUE's Venice Power Plant. As replacement water treatment facilities for the Plant are in-place and fully functioning, Ameren is proposing to close in-place the old ash ponds, utilizing a final cover consisting of a geosynthetic membrane, overlain by three feet of soils, and followed by establishment of vegetation. Ameren believes that the proposed closure plan constitutes "an adequate corrective action, equivalent to a corrective action process approved by the Agency" (in accordance with 35 Ill. Adm. Code 620.Appendix D). We therefore request the Agency to establish a Groundwater Management Zone to facilitate implementation of this remedy. Finally, we note that as part of the *Missouri-Illinois Bridge Project*, the Illinois Department of Transportation ("IDOT") has requested an easement along the eastern and southern edge of the ash impoundments system to construct an access road for bridge construction and/or maintenance. The final closure plan proposed by Ameren and approved by the Agency must therefore allow for modifications to accommodate any future IDOT requests. Please do not hesitate to call me or Michael Bollinger at 314-554-3652, if you have any question or comments this proposal, or believe a meeting to discuss our request would be helpful.

Sincerely,

Michael F. Bollinger for/

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References

EPRI (2006, November) Characterization of Field Leachates at Coal Combustion Product Management Sites - Arsenic, Selenium, Chromium, and Mercury Speciation

EPRI | ELECTRIC POWER RESEARCH INSTITUTE

Characterization of Field Leachates at Coal Combustion Product Management Sites

Arsenic, Selenium, Chromium, and Mercury Speciation

Technical Report

Characterization of Field Leachates at Coal Combustion Product Management Sites

Arsenic, Selenium, Chromium, and Mercury Speciation

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REPORT SUMMARY

A large amount of laboratory-generated leachate data has been produced over the last two decades to estimatecoal combustion product (CCP) leachate concentrations, and a variety of leaching methods have been used. No one method, however, has been shown to accurately represent field leaching conditions. In fact, little work has been performed to systematically evaluate field-generated leachates representative of a range of coal types, combustion systems, and management methods, and only limited work has been conducted to determine the species of key constituents in CCP field leachates. For this project, field leachate samples were collected from a wide variety of CCP management sites distributed throughout the United States in order to provide a broad characterization of major and trace constituents in the leachate. Speciation of arsenic, selenium, chromium, and mercury in the leachates was also determined. This report presents an evaluation of analytical results as a function of CCP type, management method, and source coal.

Background

The leachability CCPs can vary widely based on factors such as coal type and combustion/collection processes. CCP leachates commonly have neutral to alkaline pH, and as a result, the mobility of heavy metal cations such as lead and cadmium is limited. However, other constituents typically occur as oxyanions, which are more mobile than metal cations under alkaline pH conditions. Arsenic, selenium, and chromium are of particular interest due to the multiple species that may be present in CCP leachate, and because the speciation of these elements affects both mobility and toxicity. Mercury is also of interest due to the expected increase in future concentrations as well as the toxicity of organic species at low concentrations. EPRI and the U.S. Department of Energy (DOE) cosponsored this project to characterize field leachates at CCP management sites.

Objectives

To broadly characterize CCP leachate samples, collected in the field from a wide variety of CCP management settings, including speciation of arsenic, selenium, chromium, and, in some cases, mercury.

Approach

Eighty-one field leachate samples were collected from 29 CCP management facilities. Samples were collected from leachate wells, leachate collection systems, drive-point piezometers, lysimeters, the ash/water interface at impoundments, impoundment outfalls and inlets, and seeps. All samples—collected using uniform sampling procedures and analyzed by a single laboratory for over 30 constituents—were intended to represent CCP leachate in actual management settings. Arsenic, chromium, and selenium speciation samples were collected at all sites, and mercury speciation samples were collected at 15 sites. Mercury samples were collected using

ultraclean methods. Total and monomethylmercury were preserved using HCl, while dimethylmercury was purged from the collected water samples with an argon stream in the field, and collected on Carbotrap™ adsorbent tubes. Laboratory analytical methods were selected to provide detection limits of less than one part per billion for most trace elements, and less than 1 part per trillion for mercury and its species.

Results

Results showed that

- Sulfate was the dominant anion in coal ash leachate samples, the only constituent in the leachate with a median concentration greater than 100 mg/L. Major cations in bituminous coal ash leachate were calcium and magnesium, while ash leachate derived from subbituminous/lignite coal was dominated by sodium.
- Silicon and boron had the highest median concentrations (greater than 1000 µg/L) in ash among the minor and trace constituents. Median concentrations of strontium, molybdenum, lithium, aluminum, and barium were greater than 100 µg/L. Conversely, median concentrations of chromium, beryllium, thallium, silver, lead, and mercury were lower than 1 µg/L; silver, beryllium, and lead were rarely detected.
- Most constituents (22 out of the 34 analyzed) had higher concentrations in ash landfill leachate samples than in ash impoundment leachate samples. Concentrations of most major constituents were higher in flue gas desulfurization (FGD) leachate than in ash leachate.
- Arsenic concentrations in ash leachate ranged from 1.4 to 1380 µg/L, with a median of 25 µg/L. The dominant arsenic species was As(V). As(III) was only dominant in four samples from impoundments where bituminous coal ash was managed.
- Selenium concentration in ash leachate ranged from 0.07 to 1760 µg/L, with a median of 19 µg/L. Se(IV) was the dominant species in ash ponds and for bituminous coal ash, while Se(VI) was predominant in landfill settings and for subbituminous/lignite coal ash.
- Mercury concentrations were very low, with a median concentration of 3.8 ng/L and maximum of 61 ng/L in coal ash leachate, and a median concentration of 8.3 ng/L and maximum of 79 ng/L in FGD leachate. The concentration of organic mercury species was almost always less than 1 ng/L.

EPRI Perspective

There has been a long running debate regarding the validity of the many lab leaching tests used in CCP studies. This research provides a broad leachate database that can be used to bracket expected leachate concentrations in actual field settings, and to evaluate differences among CCP types and management methods. In related research, this database will be used for improving leachate prediction models. Knowledge of leaching behavior is critical in accurately evaluating the long-term risks associated with CCP management sites.

Keywords

Coal Combustion Products; Leachate; Arsenic; Chromium; Mercury; Selenium

ABSTRACT

Field leachate samples were collected from 29 coal combustion product (CCP) management sites from several geographic locations in the United States to provide a broad characterization of major and trace constituents in the leachate. In addition, speciation of arsenic, selenium, chromium, and mercury in the leachates was determined. A total of 81 samples were collected representing a variety of CCP types, management approaches, and source coals. Samples were collected from leachate wells, leachate collection systems, drive-point piezometers, lysimeters, the ash/water interface at impoundments, impoundment outfalls and inlets, and seeps.

Results suggest distinct differences in the chemical composition of leachate from coal ash and flue gas desulfurization (FGD) sludge, landfills and impoundments, and from bituminous and subbituminous/lignite coals. Concentrations of many constituents were higher in landfill leachate than in impoundment leachate. Furthermore, aluminum, carbonates, chloride, chromium, copper, mercury, sodium, and sulfate concentrations were higher in leachates for ash from subbituminous/lignite coal; while antimony, calcium, cobalt, lithium, magnesium, manganese, nickel, thallium, and zinc concentrations were higher in leachate from bituminous coal ash.

FGD leachate had a different chemical signature than ash leachate. Concentrations of most major constituents in FGD leachate were higher than in ash leachate; this is particularly true for chloride and potassium. In addition, median concentrations of boron, strontium, and lithium were higher in FGD leachate than in ash leachate, while concentrations of selenium, vanadium, uranium, and thallium were lower.

Analysis of speciation samples indicated that ash leachate is usually dominated by As(V) and Cr(VI). Selenium was mostly in the form of Se(IV), although there were a significant number of samples dominated by Se(VI). Se(IV) dominated in impoundment settings when the source coal was bituminous or a mixture of bituminous and subbituminous, while Se(VI) was predominant in landfill settings and when the source coal was subbituminous/lignite. Mercury concentrations were very low in all samples, with a median of 3.8 ng/L in ash leachate and 8.3 ng/L in FGD leachate. The organic species of mercury always had low concentration, usually less than 5 percent of the total mercury concentration.

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1

INTRODUCTION

Background

Coal combustion products (CCPs)—fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) solids—are derived primarily from incombustible mineral matter in coal and sorbents used to capture gaseous components from the flue gas, and as such contain a wide range of inorganic constituents. Concentrations of these constituents in CCPs and their leachability can vary widely by coal type and combustion/collection processes. Since CCP leachates commonly have neutral to alkaline pH, mobility of heavy metal cations such as lead and cadmium is limited. Other constituents, such as arsenic and selenium, typically occur as oxyanions, which are more mobile than metal cations under alkaline pH conditions. Knowledge of factors controlling the leachability and mobility in groundwater of the different constituents is critical to development of appropriate CCP management practices, including treatment of ash ponds and groundwater management at dry disposal sites and large scale land application uses.

There has been a large amount of laboratory-generated leachate data produced over the last two decades to estimate CCP leachate concentrations. A wide variety of leaching methodologies have been used, and it is difficult to compare results across test methods. There has been little work done to systematically evaluate field-generated leachates representative of a range of coal types, combustion systems, and management methods.

Arsenic, selenium, chromium, and mercury are of particular interest due to the multiple species that may be present in CCP leachate. The speciation affects both mobility and toxicity. Previous research has indicated that arsenic and selenium concentrations in laboratory-generated ash leachates generally range from less than 1 µg/L to about 800 µg/L (EPRI, 2003a). Arsenic concentrations higher than 1,000 µg/L in ash porewater have been associated with pyrite oxidation in areas where coal mill rejects are concentrated (EPRI, 2003b). Only limited work has been performed to determine the species of arsenic and selenium present in field leachates. The species of arsenic and selenium present in the leachate will have a significant effect on their release from the ash and mobility in groundwater (EPRI, 1994; EPRI, 2000a; EPRI, 2004).

Speciation of chromium and mercury are also important considerations with respect to mobility and toxicity. Hexavalent chromium (Cr(VI)) is more mobile and more toxic then trivalent chromium (Cr(III)), which has relatively low solubility. Mercury may be present in CCP leachates in very low concentrations, on the order of parts per trillion; there are few measurements of mercury species present in field leachates using ultra clean sampling methods.

Objectives

The objective of this research was to characterize CCP leachate samples collected in the field from a wide variety of CCP management settings. Characterization included speciation of arsenic, selenium, chromium, and, in some cases, mercury. This research provides field-scale data that can be compared to laboratory-generated data, and that can be used to model and predict the effects of CCP management methods on leachate quality and the long-term fate of inorganic constituents at CCP management sites.

2

METHODS

Site Selection

Preliminary information on power plant configurations, emission controls, and CCP management methods was assembled for 274 power plants operated by 32 utilities. A subset of management sites was selected from this list, based on individual site considerations as well as development of a range of site types representative of the industry.

A distribution of sites was selected to encompass:

- a broad geographic distribution;
- a range of CCP types (fly ash, bottom ash, flue gas desulfurization solids);
- a representative distribution of CCP management methods (landfills and impoundments, active and inactive);
- coal types from various coal source regions;
- varying plant characteristics
  - boiler types;
  - particulate controls;
  - NOx controls;
  - SO_2 controls;
  - units with and without flue gas conditioning.

Individual sites were evaluated based on:

- availability of leachate sampling points;
- whether or not the site was believed to have leachate in sufficient quantities for sampling (i.e., wet CCP).
- utility interest in participation;

Based on these criteria, 33 CCP sites in 15 states were selected for sampling.

Sample Collection

Leachate samples were collected from several access points, including leachate wells, lysimeters, leachate collection systems, sluice lines, direct push drive-points, core samples, and ponds. The goal was to obtain undiluted samples representative of CCP leachate. Samples were collected by a variety of methods, depending on sample type and accessibility. In all cases, the samples were filtered in-line and collected directly into bottles containing appropriate preservatives. Sample collection is described below, and a comparison of analytical results for samples collected from different sample points is provided in Appendix B.

Direct Push Samples

Shallow porewater samples were collected from within the CCP using two direct-push methods: drive-point piezometers and t-handle probes. The drive-point sampler consisted of a ¾-inch stainless steel drive-point piezometer driven into the CCP to the desired sampling depth using a slide hammer (Figure 2-1). A ½-inch plastic tube was attached to the drive-point and threaded through ¾-inch steel riser pipe. The sample was extracted by sliding chemically-inert ¼-inch FEP tubing through the ½ -inch tubing down the riser pipe and into the screened portion of the stainless steel drive-point. The FEP tubing was then attached to a peristaltic pump via a short length of clean flexible silicone pump tubing.

Figure 2-1
Direct Push Sample Collection Using a Drive Point Piezometer

The t-handle probe is composed of a single, thin-diameter stainless steel tube that has small manufactured slots cut into the tip for sample collection (Figure 2-2). A short plastic netting was placed over the tip of the probe just prior to installation to reduce intake of fine-grained sediments. Each t-handle probe was hand-driven into the CCP to a depth of as much as six feet. The top of the t-handle was then connected to a plastic syringe to initiate water flow. Once water flow was established, a short piece of silicone tubing was used to connect ¼-inch FEP tubing to the top of the probe. The ¼-inch FEP tubing was then connected to a peristaltic pump via a short length of clean flexible silicone pump tubing.

Figure 2-2
Direct-Push Sample Collection Using a T-Handled Probe

Leachate Wells, Lysimeters, and Leachate Collection Systems

Leachate wells, lysimeters, and leachate collection systems collect deep porewater within or immediately beneath the CCP. The leachate wells sampled for this study were installed by the utilities for the purpose of monitoring leachate quality. These wells, which consist of small-diameter (2- to 4-inch) polyvinylchloride (PVC) or stainless steel pipe with slotted screens at the bottom, are installed vertically in the CCP. Lysimeters[1] were also installed to monitor leachate quality, and differ from leachate wells in that they collect porewater beneath the CCP. Lysimeters are large collection devices, usually lined with plastic and filled with sand or gravel. Leachate percolates through the CCP and into the lysimeter, where it is removed from the sand or gravel through piping that extends to land surface. Leachate collection systems are installed to drain leachate from a CCP management unit, thus preventing head build-up on the liner. These systems typically consist of large-diameter (at least 4 inch) slotted plastic pipe embedded in a sand or gravel layer above the liner. Samples may be collected at clean-out ports where the pipes emerge from beneath the fill deposit, or at the tanks where the collected leachate is stored prior to processing.

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[1] In a typical installation, lysimeters are installed beneath liners to monitor liner performance. However, the lysimeters monitored for this study were installed immediately beneath the CCP.

Whenever possible, low-flow methods were employed while sampling leachate wells to minimize disturbances within the sampling zone. Low-flow sampling is accomplished by pumping water at a rate that is compatible with the rate of recovery for the well (or similar sample point) and the matrix being sampled, using methods that do not cause water surging within the well (Puls and Barcelona, 1995). Purging and sampling were performed with a peristaltic pump or, for deeper wells, a bladder pump. In a few cases with restricted access, a hand-operated Waterra™ pump or bailer was used to retrieve samples.

When low-flow sampling methods could not be performed, either "minimum purge" sampling or "maximum purge" sampling was used. Minimum purge sampling was used in a few instances where CCP surrounding the well had relatively low permeability and would not achieve a stable drawdown during low-flow pumping. This method was only used on wells that were constructed of PVC. Maximum purge sampling was used in the few instances where an existing well was constructed of stainless steel or any other metal, which may have influenced the water sample, if the well could not support low-flow sampling flow rates. In these instances, the well was completely purged the day before sampling.

Lysimeters and leachate collection systems were sampled by lowering the peristaltic pump FEP tubing to the water surface. However, in some cases, the depth to water was too great for sampling with a peristaltic pump, in which case the Waterra pump or a bladder pump connected to Teflon™ tubing was used to withdraw the sample.

Surface Water and Sluice Samples

Surface water samples were collected from ash or FGD ponds. Typically, the pond samples were accessed from structures that extended above the water, or by boat. In either case, ¼-inch FEP tubing was lowered into the water and connected to a peristaltic pump via a short length of clean flexible silicone tubing. Samples were collected from different depths by attaching the FEP tubing to a clean water level indicator and lowering the tubing to the desired depth. In most cases, samples were collected from as near the ash/water interface as possible. Seep, sluice, and outfall samples were collected directly from the sluice pipe or outfall structure in a clean plastic container or plastic dip cup sampler (Figure 2-3). FEP tubing connected to a peristaltic pump via a short length of clean flexible silicone tubing was lowered into the container and the sample was collected.

Figure 2-3
Seep Sampling

Core Samples

Core samples were collected at selected sites where porewater samples could not otherwise be obtained. A hollow-stem auger drill rig was used to advance a lined split-spoon sampler or core barrel sampler into the CCP deposit. Typically, a preliminary borehole was drilled in advance of the sample borehole in order to log the intervals where the wettest CCP was encountered, and the sampler was then advanced in a second, adjacent borehole to the selected depth. Porewater was then extracted from the core in the laboratory.

Sample Preservation

Core Samples

Core samples for leachate analyses were collected in clear, large-diameter, plastic or Teflon liners. After the liner tubes were recovered, the ends were cut so that no air volume or disturbed sample was included in the tube, and the ends of the tubes were sealed with Parafilm™, plastic end caps, and tape. Tubes were stored in coolers with dry ice for shipment to the laboratory via overnight delivery. Leachate was extracted from wet ash samples in the laboratory by centrifuge, then filtered and preserved as described below for liquid samples.

Liquid Samples

Liquid leachate samples were filtered in the field and then split for the individual analyses. A 0.45 μm filter was used for all liquid samples, and turbid samples were prefiltered using either a 1.0 or 5.0 μm filter.

There are two general approaches for preservation of speciation samples: acid preservation and cryofreezing, each with drawbacks. Acid preservation approaches have limited holding times, and require prior knowledge of redox conditions at the sample point for selection of the appropriate preservation fluid—reducing conditions are particularly problematic. Cryofreezing is not commonly used and there may be nuances to this method that have not been explored. Since prior data on redox conditions were typically not available for this sampling, the freezing approach was employed. Samples for arsenic, selenium, and chromium speciation were immediately cryofrozen in the field using liquid nitrogen (Figure 2-4), and then kept frozen on dry ice with minimal air contact until analysis to prevent changes in speciation by oxidation.

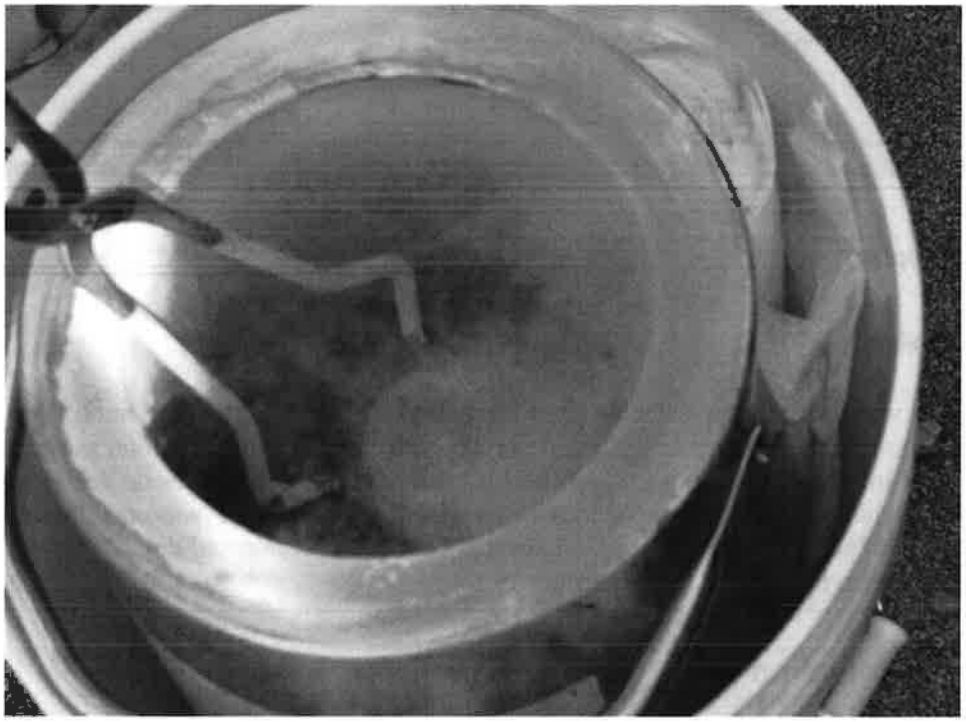


Figure 2-4
Cryofreezing a Leachate Sample in Liquid Nitrogen

Separate water samples were collected for the determination of dissolved mercury (Hg_{diss}), dissolved methyl mercury ($MeHg_{diss}$), and dimethyl mercury (DMM). New tubing, filter materials, and sampling containers were used to prevent sample contamination. Samples for Hg_{diss} and $MeHg_{diss}$ were collected using in-line filtration of a defined sample volume (40 mL for Hg_{diss} and 250 mL for $MeHg_{diss}$) and preserved immediately with HCl. The fresh filters used for each of these filtration steps were collected and stored in Petri dishes for the determination of particulate mercury (Hg_{part}) and particulate methyl mercury ($MeHg_{part}$). DMM was purged from the collected water samples with an argon stream (30 min at 1 L/min) in the field, and collected on Carbotrap™ adsorbent tubes (Figure 2-5). These tubes were dried with an argon stream opposite to the adsorption direction (10 min at 1 L/min), sealed, and kept cold and dark until analysis. All collected samples were double-bagged to prevent contamination, and clean sampling protocols (consistent with USEPA method 1631) were followed.

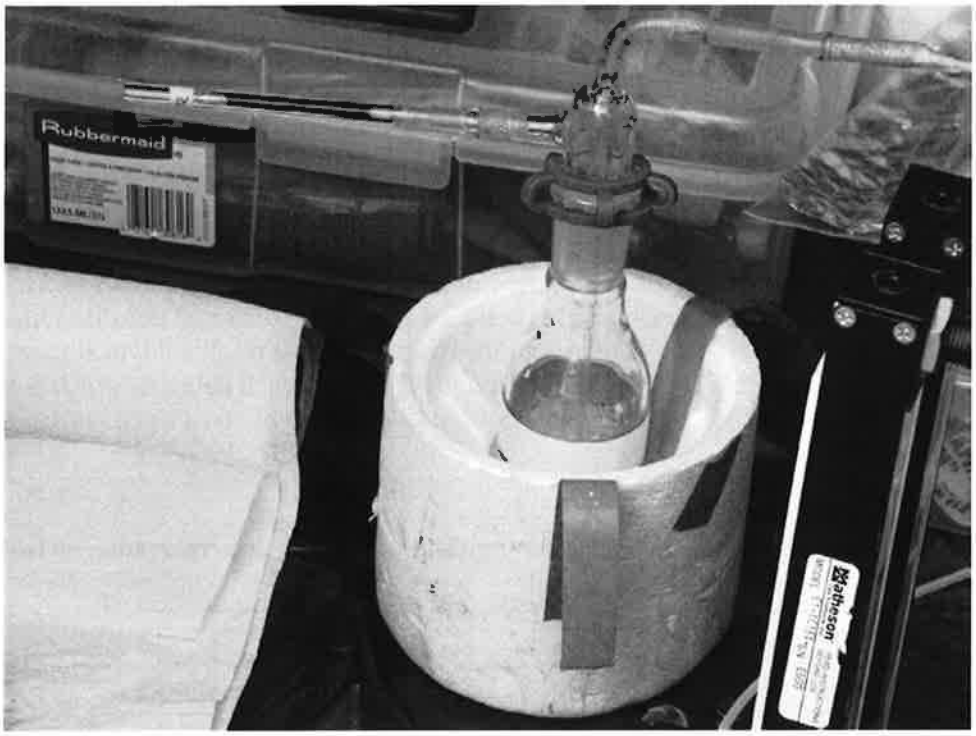


Figure 2-5
Argon Bubbling Through a Leachate Sample to Vaporize DMM

Field parameters including pH, conductivity, redox potential, and temperature were measured using an in-line flow cell and/or multi-probe sample collected during sampling.

Quality Control

A suite of quality control (QC) samples were analyzed for most sample trips, which consisted of sample and matrix spike duplicates, blanks, and reference materials as appropriate and available. Final data reported may be corrected to reflect the results of the QC samples to yield the most accurate and precise result possible.

Laboratory Preparation and Analysis

Determination of Dissolved Arsenic and Selenium by Dynamic Reaction Cell-ICP-MS (DRC-ICP-MS)

Dissolved arsenic and selenium were determined by a Perkin-Elmer DRC II ICP-MS in dynamic reaction cell (DRC) mode using ammonia as the reaction gas for the determination of arsenic, and a methane/ammonia mixture for selenium. Chromium was also determined together with selenium (under the same conditions), and the obtained results were in good agreement with the DF-ICP-MS results, which were reported in the final data set. Instrument settings and monitored isotopes are reported in Table 2-1, which also contains typical instrumental detection limits (IDLs) for each element. These IDLs represent the overall average of all analytical runs throughout the project, and are comprised of individual IDLs for each data set, which were calculated as three times the standard deviation of four instrument blanks (1 percent HNO_3) in each instrument run.

Table 2-1
Method Parameters for Total Arsenic, Selenium, and Chromium Determinations by DRC-ICP-MS

	As	Se + Cr
Measured masses	^{75}As	^{80}Se, ^{52} Cr
Monitor masses	^{77}Se, ^{78}Se, ^{82}Se	^{78}Se, ^{82}Se, ^{53}Cr
Dwell time	200 ms/isotope	200 ms/isotope
Reaction gas	NH_3 = 0.35 mL/min	NH_3 = 0.3 mL/min CH_4 = 0.45 mL/min
Bandpass	RPq = 0.6	RPq = 0.6
Typical IDL [ppb]	0.01	0.01(^{80}Se), 0.01 (^{52}Cr)

Arsenic is monoisotopic and therefore has no confirmation isotope; however, ^{77}Se was measured to compensate for the potential interference of ^{40}Ar^{35}Cl on ^{75}As. The major isotope ^{80}Se was used for quantification of selenium. In the absence of interferences, all isotopes of an element should yield the same result, and for most of the samples this was achieved with the selected instrument settings. However in the case of low selenium and high salt concentrations, the three measured selenium isotopes showed different results. In these cases, the result was flagged in the results table (Appendix A). ^{53}Cr was measured as a control isotope for ^{52}Cr, and the two chromium isotopes generally agreed very well. Rhodium and indium were used as internal standards. A certified reference material was analyzed with each analytical run to confirm accurate calibration, and a matrix duplicate, a matrix spike, and a matrix spike duplicate were analyzed with each batch.

Arsenic and Selenium Speciation by Ion-Chromatography Anion Self-Regenerating Suppressor ICP-MS (IC-ASRS-ICP-MS)

As(III), As(V), Se(IV), and Se(VI) were determined simultaneously by IC-ASRS-ICP-MS (Wallschläger and Roehl, 2001; Wallschläger et al., 2005) using a Dionex ion-chromatography system with anion self-regenerating suppressor (ASRS) coupled to a Perkin-Elmer DRC II (Figures 2-6 and 2-7). Method parameters are listed in Table 2-2. The ICP-MS was used in standard mode as the interfering anions are chromatographically separated in time from the analytes. Typical achieved MDLs were 0.1 ppb per species. In addition to the species mentioned above, any other unidentified anionic species such as soluble As-S compounds can be determined by this method.

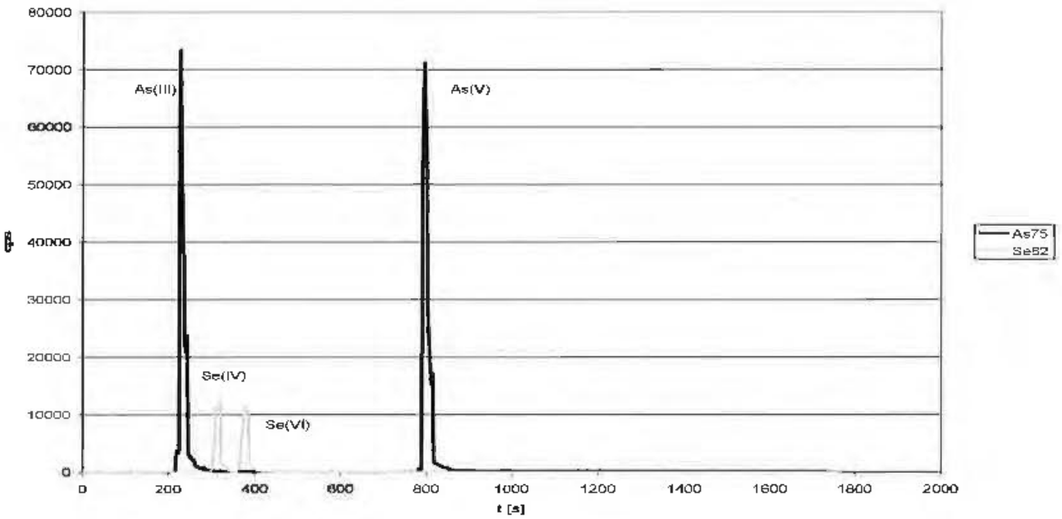


Figure 2-6
Chromatogram Showing 5 ppb Each for As(III), As(V), Se(IV), and Se(VI)

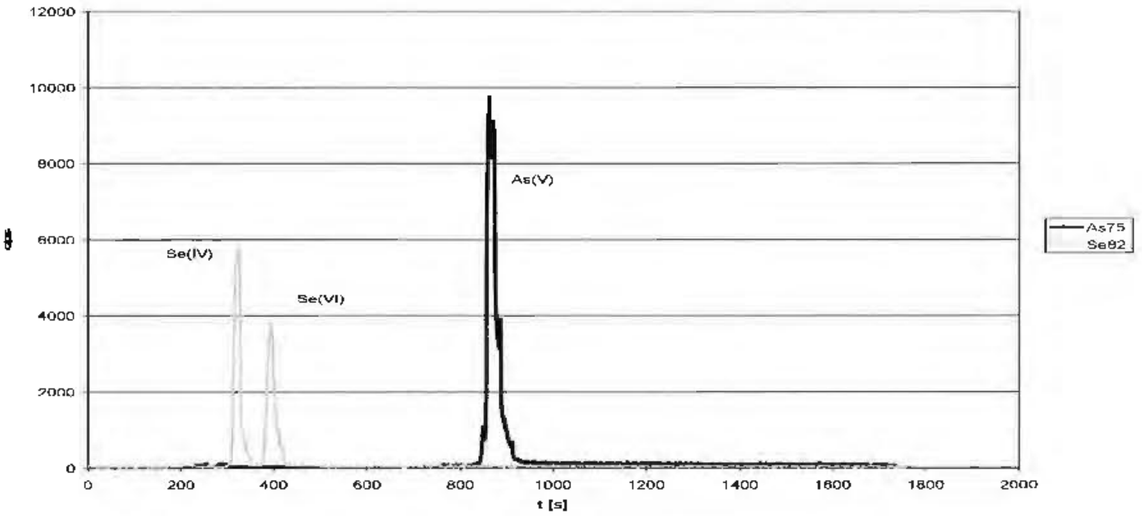


Figure 2-7
Chromatogram Showing Selenium and Arsenic Species for a Real Sample (10x dilution)

Table 2-2
Method Parameters for Arsenic, Selenium, and Chromium Speciation by IC-ASRS-DRC-ICP-MS

	Arsenic and Selenium Species	Chromium Species
Column	Dionex AS-16 4-mm + AG-16 4-mm	Dionex AS-16 4-mm + AG-16 4-mm
Eluent	sulfate in 3 mmol/L NaOH with 2 mmol/L oxalate 0→3 min: 1 mM SO_4^{2-} 3→4 min: 1→10 mM SO_4^{2-} 4→14 min: 10 mM SO_4^{2-} 14→16 min: 10→30 mM SO_4^{2-} 16→30 min: 30 mM SO_4^{2-} 30→35 min: 1 mM SO_4^{2-}	20 mM NaOH
Injection volume	1 mL	1 mL
Flow rate	1.2 mL/min	1.5 mL/min
Reaction gas	none	NH_3 = 0.3 mL/min
Bandpass	none	RPq = 0.3
Typical IDL [ppb]	0.1 As(III), 0.4 As(V), 0.05 Se(IV), 0.05 Se(VI)	0.01 Cr(III), 0.01 Cr(VI)

Determination of Dissolved Arsenic, Selenium, and Speciation in Sample Splits

A subset of the CCP leachate samples were split and forwarded to a separate laboratory for arsenic and selenium speciation analysis. These samples were field preserved using hydrochloric acid, rather than cryofreezing, and speciation analysis was performed within 48 hours of collection.

Total arsenic and selenium results were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using scandium and niobium as internal standards. Due to the relatively high concentration of chloride present in the samples, an interference correction was employed for total arsenic during analysis.

Speciation for As(III), As(V), Se(IV), and Se(VI) was achieved by coupling a Hamilton PRP-X100 anion exchange column to the front end (sample introduction) of the ICP-MS instrument operated in a time domain mode. Lab Alliance pumps were used in conjunction with a gradient phosphate buffer mobile phase to elute and separate the compounds. Peak areas were used to quantitate species. Quality control measures performed during these analysis included reanalysis with greater elution times for samples where the sum of species was considerably different from the total concentration, review of chromatograms for unidentified species spikes, analytical sample duplicates, and analytical spike samples.

Chromium Speciation by Ion-Chromatography Anion Self-Regenerating Suppressor DRC-ICP-MS (IC-ASRS-DRC-ICP-MS)

Cr(III) and Cr(VI) were determined by IC-ASRS-DRC-ICP-MS using a Dionex ion-chromatography system with ASRS coupled to a Perkin-Elmer DRC II in DRC mode. This analysis was performed separately from the arsenic and selenium species determination, because Cr(III) must first be derivatized off-line to $(EDTA\text{-}Cr)^-$ before it can be determined together with Cr(VI) by anion-exchange chromatography prior to ICP-MS detection (Gürleyük and Wallschläger, 2001) (Figures 2-8 and 2-9). Modifications from the originally published method are listed in Table 2-2.

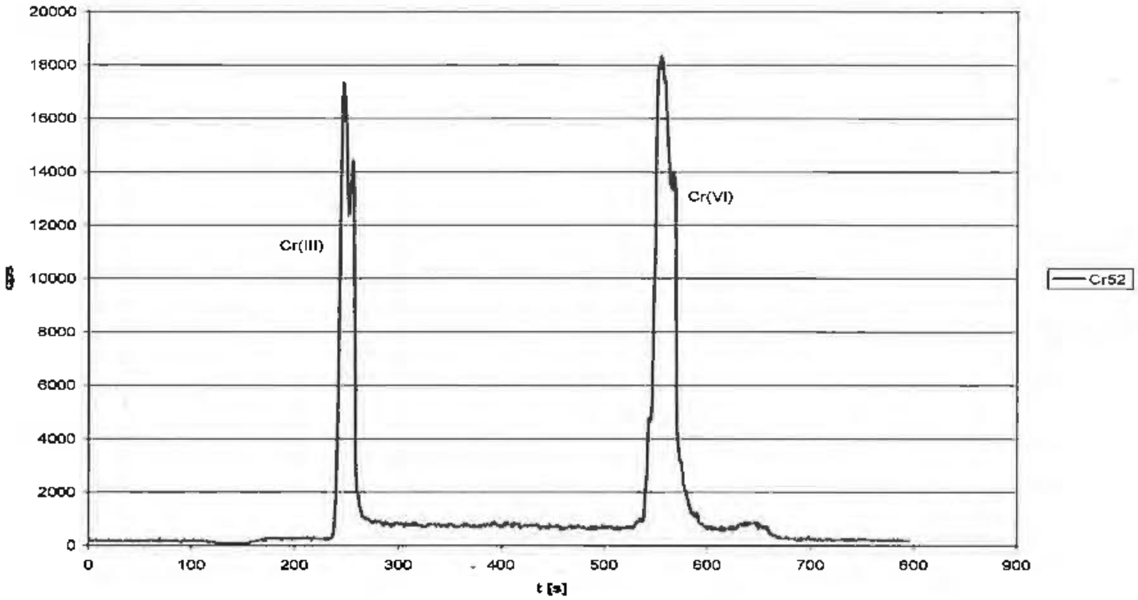


Figure 2-8
Chromatogram Showing 0.5 ppb Each for Cr(III) and Cr(VI)

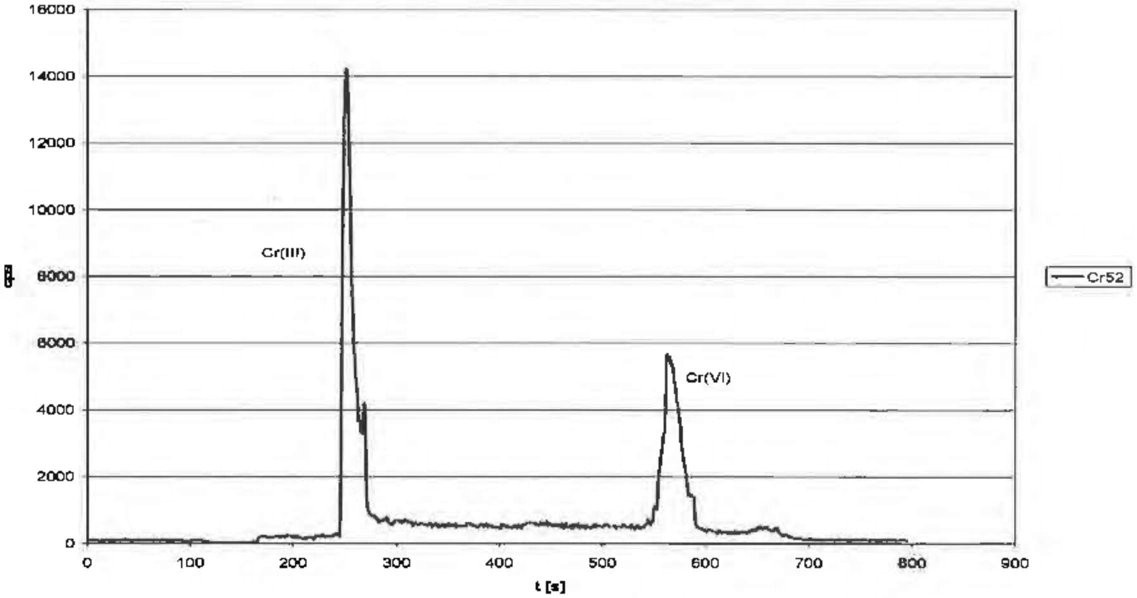


Figure 2-9
Chromatogram for Sample 034 Analyzed at a 2x Dilution

Mercury Speciation Methods

Dimethyl Mercury (DMM): DMM was purged from the collected water samples with an argon stream in the field, and collected on Carbotrap™ adsorbent tubes. These tubes were dried with an argon stream opposite to the adsorption direction, sealed, and kept cold and dark until analysis. DMM was desorbed thermally from the adsorbent trap onto an analytical trap, from which DMM was thermo-desorbed and analyzed by gas chromatography–ICP-MS (GC-ICP-MS) (similar to Lindberg et al., 2004). Figure 2-10 shows a typical chromatogram obtained by this technique: the first peak (around 70 s) is caused by elemental mercury (not quantified in this project), while the second peak (around 120 s) is DMM. The retention time of DMM is determined by analysis of DMM standards, and quantification is achieved by injecting gaseous Hg^0 standards (which is permissible, because the response of ICP-MS to mercury is species-independent).

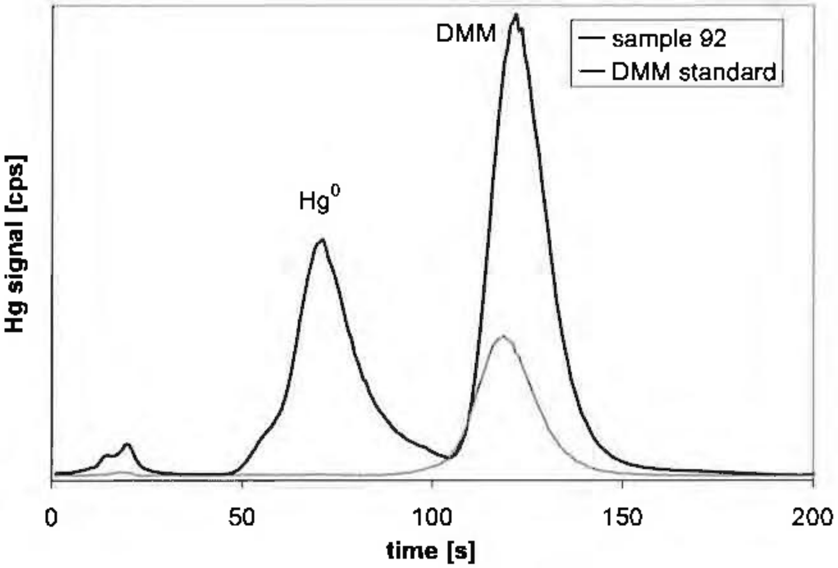


Figure 2-10
GC-ICP-MS Chromatogram for the Determination of DMM

Monomethyl Mercury (MeHg): MeHg was determined by GC-ICP-MS after derivatization to methylethyl mercury with sodium tetraethylborate. MeHg was isolated from filtered waters and particulate matter (yielding dissolved and particulate MeHg) by steam distillation as methyl mercury chloride (MeHgCl), and determined using isotope dilution with isotopically-enriched MeHg. For this purpose, each sample is spiked with a known amount of MeHg labeled with the isotope ^{201}Hg prior to the steam distillation process. The result is a GC-ICP-MS chromatogram (Figure 2-11) in which the MeHg signal (around 110 s) shows an altered isotope ratio (compared to the natural isotope abundance) reflecting the added spike. From the change in isotope ratio (in this case: $^{201}Hg/^{202}Hg$), the concentration of MeHg in the native sample is calculated. This isotope dilution technique is used routinely at Trent University for $MeHg_{diss}$ and Hg_{diss} determinations (see below), because it effectively corrects for variable procedural recoveries encountered when normal external calibration methods are used (Hintelmann & Ogrinc, 2003). Figure 2-11 shows a second peak (around 50 s), which represents some unspecific source of mercury in the instrumental setup; this signal has the "normal" mercury isotope ratio, proving that it's not MeHg.

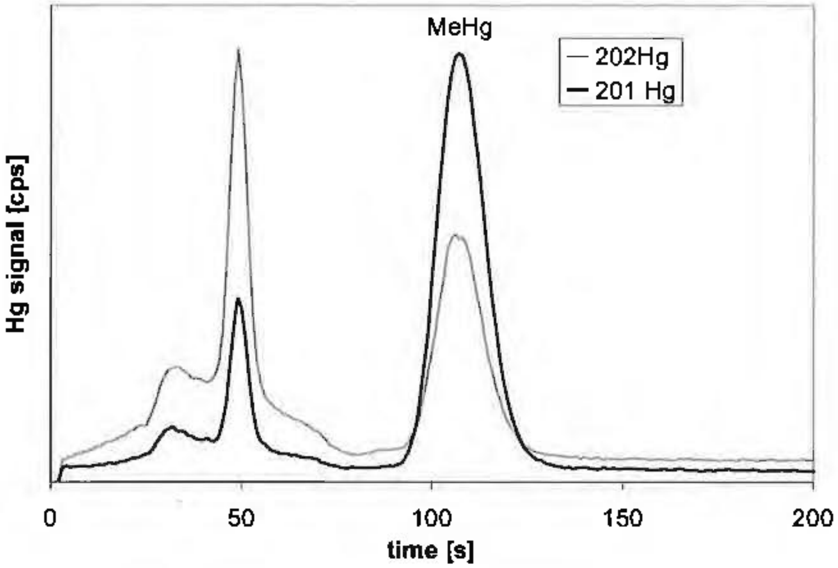


Figure 2-11
GC-ICP-MS Chromatogram for the Determination of MeHg by Isotope Dilution

<u>Mercury (Hg):</u> Total mercury in filtered waters and on filters with particulate matter (yielding dissolved and particulate mercury, Hg_{diss} and Hg_{part}) was determined by cold vapor-ICP-MS (CV-ICP-MS), also using an analog isotope dilution approach with ^{201}Hg for quantification. Samples for Hg_{diss} analysis were digested with BrCl and pre-reduced with $NH_2OH{\bullet}HCl$ prior to the CV-ICP-MS measurement (Hintelmann and Ogrinc, 2003). Table 2-3 summarizes the different analytical methods used to measure mercury speciation in the collected water samples and their typical performance characteristics. It is noteworthy that the blanks for Hg_{diss} and Hg_{part} are typically larger than many of the analyzed samples; however, since blanks are fairly constant, they can be subtracted.

Table 2-3
Mercury Speciation Methods

Parameter	Analyzed sample Volume (mL)	Typical Detection Limit (ng/L)	Typical Analytical Blank (ng/L)
DMM	105	0.005	none
$MeHg_{diss}$	50	0.02	0.02
$MeHg_{part}$	250	0.01	0.01
Hg_{diss}	n/a	0.2	1
Hg_{part}	40	1	5

Trace Element Determinations by Double-Focusing ICP-MS (DF-ICP-MS)

A Thermo Finnigan ELEMENT2 double-focusing inductively coupled plasma-mass spectrometer (DF-ICP-MS) was used in medium resolution mode to determine 22 elements of interest (Table 2-4). Each sample was analyzed at three different dilutions (500x, 100x, and 20x) to cover the different concentration ranges of the elements. Due to the high salt load of the samples, a dilution factor of less than 20x might lead to instrument damage and was therefore avoided; however, all field blanks and equipment blanks were analyzed undiluted because they did not contain salts. According to the typical concentrations encountered for different elements, the 500x diluted samples were analyzed for Li, B, Al, Si, Fe, Sr, and Mo; the 100x diluted samples for Li, Be, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Mo, Ag, Cd, Sb, Ba, Tl, Pb, and U; and the 20x diluted samples for Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sb, Ba, Tl, Pb, and U. If one element was analyzed at more than one dilution, the result obtained with the lowest dilution factor under consideration of the calibrated range was reported.

Table 2-4
Trace Metals by DF-ICP-MS

Element	Measured Isotope	Control Isotope	Isotopes Agree?	Typical IDL [ppb]
Aluminum	^{27}Al	monoisotopic		0.1
Antimony	^{121}Sb	^{123}Sb	Y	0.004
Barium	^{136}Ba	^{137}Ba	Y	0.06
Beryllium	^{9}Be	monoisotopic		0.01
Boron	^{10}B	^{11}B	Y	0.2
Cadmium	^{110}Cd	^{111}Cd, ^{114}Cd	N	0.004
Chromium	^{53}Cr	^{52}Cr	Y	0.01
Cobalt	^{59}Co	monoisotopic		0.002
Copper	^{65}Cu	^{63}Cu	Y	0.01
Iron	^{56}Fe	^{57}Fe	Y	0.1
Lead	^{208}Pb	^{206}Pb, ^{207}Pb	Y	0.003
Lithium	^{7}Li	not measurable		0.04
Manganese	^{55}Mn	monoisotopic		0.009
Molybdenum	^{98}Mo	^{95}Mo	Y	0.04
Nickel	^{60}Ni	^{58}Ni	Y (except in samples with high Fe concentrations)	0.03
Silica	^{28}Si	^{30}Si	Y	0.3
Silver	^{107}Ag	^{109}Ag	Y? (concentrations close to MDL)	0.005
Strontium	^{88}Sr	^{87}Sr	Y (after Rb correction of ^{87}Sr)	0.05
Thallium	^{205}Tl	^{203}Tl	Y? (concentrations close to MDL)	0.002
Uranium	^{238}U	not available	no interferences	0.001
Vanadium	^{51}V	^{50}V	N	0.004
Zinc	^{66}Zn	^{68}Zn	Y? (concentrations close to MDL)	0.09

At least two isotopes for each element were measured (if possible) to verify the absence of spectrometric interferences. Scandium, indium, rhodium, and germanium were used as internal standards to monitor and correct instrument drift and sample uptake effects. All measured and control isotopes are listed in Table 2-4. Typically, the results obtained for the measured and the control isotope were identical (within the analytical uncertainty); however, some exceptions are explained below. Average IDLs are also listed in Table 2-4. The method detection limit (MDL) was estimated as the IDL times the applicable dilution factor of the analyzed sample. The IDL/MDL was determined with each analytical run and varied slightly depending on the instrument performance on that day. All data reported were instrument-blank corrected. For quality control purposes, a certified reference material (CRM) was analyzed at two different dilutions per analytical run to confirm an accurate calibration. For each sample batch (usually one per sampling trip) one randomly selected sample was analyzed in duplicate and spiked and analyzed in duplicate to assess accuracy and reproducibility.

For some of the elements listed in Table 2-4, the results obtained for the measured and the control isotope did not match. Several elements (e.g., Ag, Zn, Tl) are present in most samples at concentrations of only 5-10 times the detection limit, so that analytical uncertainty and/or insufficient number of samples with detectable concentrations prevented a meaningful isotope comparison. In other cases, the control isotope had a very low abundance and although the sample concentration was very well detectable for the main isotope, the quantification by the minor isotope was impaired by low signal intensities (e.g., ^{50}V; natural abundance 0.25 percent). Also, in the used concentration range, ^{6}Li was not detected in medium resolution mode by the instrument; therefore, it was not used for confirming ^{7}Li.

In medium (or even high) resolution mode, some isobaric and polyatomic interferences could not be resolved: ^{58}Ni was not separated from ^{58}Fe in medium resolution mode (required resolution ~30,000; available resolution ~ 10,000). As the ^{58}Fe abundance is only 0.28 percent, the associated error is normally negligible; however, if the iron concentrations are extremely high, as in some of the analyzed samples, ^{58}Ni will be affected. Also, ^{87}Sr was also not separated from ^{87}Rb in medium resolution mode (required resolution ~300,000); however, the error in this case is not negligible as ^{87}Rb has an abundance of 27.8 percent. If ^{87}Sr is corrected for ^{87}Rb, both ^{87}Sr and ^{88}Sr yield identical results. For cadmium, both ^{111}Cd and ^{114}Cd were interfered with by MoO (required resolution ~100K and ~80K, respectively); in addition, ^{114}Cd was also affected by an isobaric interference of ^{114}Sn. Based on those considerations, ^{110}Cd was used for quantification. Generally, as spectroscopic interferences are normally positive, in the event that two isotopes yield a different result, the lower concentration will most likely be the uninterfered and therefore deliver the correct result.

Ancillary Parameters

Redox potential, pH, conductivity, dissolved oxygen, and temperature were determined in the field on the filtered samples with a YSI multiprobe (for wells, this measurement was made immediately after the low-flow conditions had stabilized; for all other types of water samples, this was done prior to collecting all other aliquots). Separate aliquots were used for these analyses and discarded afterwards.

Methods

Sodium, potassium, magnesium, and calcium were determined by cation-exchange chromatography with suppressed conductivity detection, and chloride and sulfate were determined by anion-exchange chromatography using the same detection principle, following standard methods. Total carbon (TC) and total inorganic carbon (TIC) were determined by flow injection-infrared spectrometry (Shimadzu Total Organic Carbon Analyzer) following standard methods, where TIC is liberated from the sample by addition of HCl, while TC is liberated by oxygen combustion; total organic carbon (TOC) is then determined by difference TC-TIC, which may lead to imprecise results in samples with low TOC content.

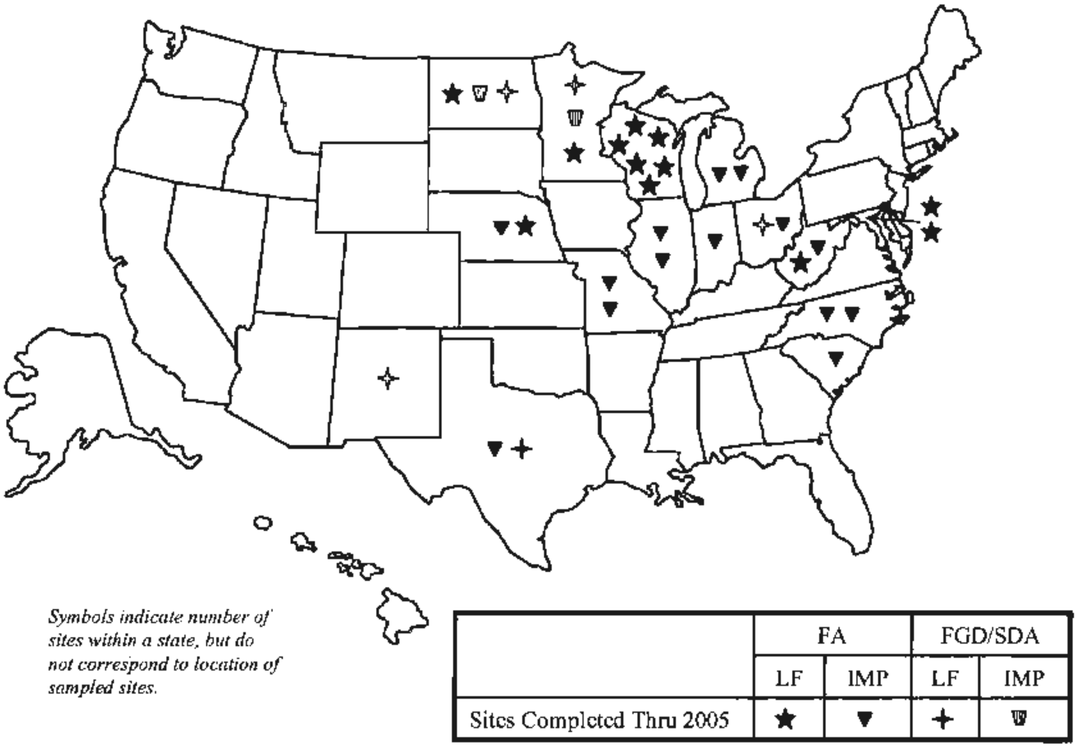
3

SAMPLE SUMMARY

Site and Sample Attributes

Location

The 33 sample sites are concentrated in the eastern United States where coal-fired power plants predominate (Figure 3-1). Attributes of sampled sites are listed in Table 3-1, and leachate sample attributes are listed in Table 3-2.



Symbols indicate number of sites within a state, but do not correspond to location of sampled sites.

	FA		FGD/SDA	
	LF	IMP	LF	IMP
Sites Completed Thru 2005	★	▼	+	▽

Figure 3-1
Sample Site Locations by State

Facility Type

Samples were collected at 15 impoundments and 17 landfills (Table 3-1). One of the sites counted as an impoundment is the 14093 site. This site is a landfill that receives ash originally sluiced to an impoundment. Washing of ash during sluicing is believed to have an effect on ash leachate concentration; therefore, this site was counted as an impoundment.

The 27413 site is not classified as a landfill or impoundment. Ash was originally sluiced to this site, and later it was managed dry. There were no data to indicate whether the samples were collected in areas where ash was sluiced or managed dry; therefore, this site was not used in comparisons of landfill and impoundment ash.

Sample Methods

Landfill Samples

All of the 29 landfill leachate samples represent interstitial water. Three samples were collected from wells screened in the CCP, two samples were collected from lysimeters screened immediately beneath the CCP, one was collected from a surface seep, and 19 were collected from leachate collection systems (Table 3-3). The remaining four samples were core samples from soil borings; however, these samples did not yield sufficient water for analysis when centrifuged in the laboratory. As a result, 25 landfill leachate samples were analyzed.

The four dry cores were each collected from different sites, and, in each case, the dry core was the only sample collected at that site. These samples and sites are not included in the discussions that follow. As a result, for the remainder of this report, only 29 of the 33 sites will be referenced.

Impoundment Samples

Twenty-seven of the 53 impoundment samples represent interstitial water. These include eight samples collected from wells screened in the CCP, 13 samples collected from drive-point piezometers or push point samplers, three seep samples, and three core extracts (Table 3-3). The remaining 26 leachate samples include 12 collected from impoundments near the ash-water interface, and 14 samples collected from sluice lines or at impoundment outfalls.

Other Samples

The three leachate samples from site 27413 are interstitial water collected from temporary leachate wells.

Source Power Plant Attributes

Boiler Type

The majority of sites (24 of 29) sampled received CCP from pulverized coal (PC) plants with dry-bottom boilers (Table 3-1), representing 71 of the 81 leachate samples (Table 3-2). One site (one sample) received CCP from a wet-bottom PC boiler, and three sites (four samples) received CCP from cyclone boilers. The remaining site (five samples) received CCP from a plant that has both dry-bottom PC boilers and cyclones.

A variety of firing configurations are represented in the PC boilers including:

- Tangential: 10 sites, 34 samples
- Wall-fired (mostly opposed): 7 sites, 18 samples
- Multiple configurations: 9 sites, 25 samples

Source Coal

Most sites (11 sites, 48 samples) received CCP from power plants that burned bituminous coal (Tables 3-1 and 3-2). The power plant feeding one of these 11 sites (23214) also burns 5 percent petroleum coke.

Seven sites (13 samples) received CCP from plants that burn subbituminous coal, and four sites (five samples) received CCP from lignite-burning plants. The subbituminous and lignite samples will be grouped together in discussions that follow.

Four sites (seven samples) received CCP from plants that burn a blend of fuels:

- 22346: formerly bituminous, coal units burned a blend of 80 percent subbituminous and 20 percent bituminous coal at the time of sampling. This site also received oil ash.
- 22347: formerly bituminous, coal units burned a blend of 80 percent subbituminous and 20 percent bituminous coal at the time of sampling.
- 25410A and 25410B: an undetermined blend of subbituminous and bituminous coals, plus used tires and petroleum coke.

Three sites (eight samples) have CCP derived from a mixture of sources:

- 50183 received CCP from three different power plants burning bituminous and subbituminous coal.
- 27413 and 50210 received CCP from power plants that switched from bituminous to subbituminous coal.

Emission Controls

Six of the 29 sites received CCP from flue gas desulfurization (FGD) systems, the remaining sites received coal ash, either from plants without FGD systems or that was collected prior to the FGD system (Tables 3-1 and 3-2).

Fly Ash

Most fly ash samples came from plants (17 plants, 48 samples) with cold-side electrostatic precipitators (ESPs). Two sites (7 samples) received CCP from plants with hot-side ESPs and one site (1 sample) received CCP from a plant with a fabric filter. Three sites (11 samples) received CCP from multiple sources:

- 50183 received CCP from three plants, two have cold-side precipitators, and one has a hot-side ESP.
- 33104 received CCP from one plant with cold-side and hot-side ESPs on different units.
- 50213 received CCP from a plant with a cold-side ESP on two units, and a hot-side ESP and fabric filter on another unit.

Thirteen of the ash sample sites (41 samples) received CCP from units with flue gas conditioning to improve precipitator performance. NOx controls included low-NOx burners (12 samples), overfired air (5 samples), selective catalytic reduction (5 samples), and multiple types.

FGD

Five of the six FGD sites, representing 13 samples, received CCP from wet FGD systems. Four of these systems were coupled with cold-side ESPs; three of the four systems with ESPs systems used natural oxidation while the other used inhibited oxidation. The other wet FGD system was not coupled with an ESP or fabric filter, and used forced air oxidation. The FGD systems feeding three of these sites used magnesium-lime sorbent, one used lime, and one used limestone.

One site (1 sample) received CCP from a spray dryer system coupled with a fabric filter. The FGD sorbent used in this system was lime.

At one of the six FGD units, flue gas conditioning was used to improve precipitator performance. That unit also had a low-NOx burner.

Table 3-1
Attributes of Sample Sites and Source Power Plants

Site	Source Fuel Type	Source Plant Boiler Type	PC Boiler Firing	Source Plant Particulate Collection	Source Plant SO2 Control	Source Plant SO2 Sorbent	Source Plant Flue Gas Cond.	Source Plant NOx Control	Byproducts Managed	DUP	IMP	LF	QC
23214	Subbit	Cyclone		ESP cold-side	None	None	None	Combustion-OFA	FA Class C			1	
50183	Mix	Dry Bottom PC Boiler	multiple types	Multiple types	None	None	Yes	Multiple types	FA, BA			4	1
33106	Bit	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types	FA, BA	1	7		3
20094A	Bit	Dry Bottom PC Boiler	wall-fired opposed	ESP multiple	None	None	None	Multiple types	FA, BA			1*	
20094B	Bit	Dry Bottom PC Boiler	wall-fired opposed	ESP multiple	None	None	None	Multiple types	FA, BA			1*	
34186A	Lig	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	None	Multiple types	FA			1	
34186B	Lig	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	None	Multiple types	FGD, BA		2		2
34186C	Lig	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	None	Multiple types	FGD, FA, BA	1		1	
33104	Bit	Dry Bottom PC Boiler	tangential	Multiple types	None	None	None	Postcombustion SCR	FA, BA	1	5		1
50408	Bit	Dry Bottom PC Boiler	wall-fired	ESP cold-side	None	None	None	Combustion-none	FA, BA			1	
35015A	Bit	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	Yes	Combustion-LNB	FGD, FA			6	
35015B	Bit	Multiple types	multiple types	ESP cold-side	None	None	None	Combustion-LNB	FA	1	5		1
31192	Subbit	Dry Bottom PC Boiler	tangential	Fabric filter	Wet-natural	Limestone	None	Other	FA, FGD, BA			1*	
13115A	Subbit	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types	BA, FA		3		
13115B	Bit	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Other	FA, BA		3		

Table 3-1
Attributes of Sample Sites and Source Power Plants (continued)

Site	Source Fuel Type	Source Plant Boiler Type	PC Boiler Firing	Source Plant Particulate Collection	Source Plant SO2 Control	Source Plant SO2 Sorbent	Source Plant Flue Gas Cond.	Source Plant NOx Control	Byproducts Managed	DUP	IMP	LF	QC
49003A	Bit	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	Yes	Multiple types	FA		8		
49003B	Bit	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	None	Combustion-LNB	FA			4	2
22346	Blend	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Yes	Multiple types	FA, OA	1	3		3
22347	Blend	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Other	FA		1		
40109	Bit	Dry Bottom PC Boiler	tangential	ESP hot-side	None	None	None	Multiple types	FA, BA	1	5		1
27412	Subbit	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	None	Combustion-OFA	FA, BA			1^{*}	
27413	Mix	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Yes	Multiple types	FA				3
50210	Mix	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	None	Multiple types	FA, BA			1	
43034	Lig	Wet Bottom PC Boiler	wall-fired	ESP cold-side	Wet-inhib	Limestone	None	Multiple types	FGD,FA			1	
50212	Subbit	Dry Bottom PC Boiler	wall-fired	ESP cold-side	None	None	Yes	Multiple types	FA	1		2	2^{+}
23223A	Subbit	Dry Bottom PC Boiler	multiple types	Fabric filter	Spray Dryer	Lime	no data	Multiple types	SDA			1	
23223B	Subbit	Dry Bottom PC Boiler	multiple types		Wet-FO	Lime	no data	Multiple types	FGD		3		
25410A	Blend	Cyclone		ESP cold-side	None	None	Yes	Combustion-OFA	FA, BA		2		
25410B	Blend	Cyclone		ESP cold-side	None	None	Yes	Combustion-OFA	FA		1		
50211	Bit	Dry Bottom PC Boiler	wall-fired front	Fabric filter	None	None	no data	Combustion-LNB	FA			1	
14093	Bit	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Multiple	Multiple types	FA (sluiced)	1	3		2

Table 3-1
Attributes of Sample Sites and Source Power Plants (continued)

Site	Source Fuel Type	Source Plant Boiler Type	PC Boiler Firing	Source Plant Particulate Collection	Source Plant SO2 Control	Source Plant SO2 Sorbent	Source Plant Flue Gas Cond.	Source Plant NOx Control	Byproducts Managed	DUP	IMP	LF	QC
43035	Subbit	Dry Bottom PC Boiler	wall-fired opposed	ESP hot-side	None	None	None	Combustion-LNB	FA,BA,EA (sluiced)	1	2		1
50213	Subbit	Dry Bottom PC Boiler	multiple types	Multiple types	None	None	Multiple	Multiple types	FA			2	

Notes:

Ash at site 27413 was first sluiced, then managed dry.

* indicates that core sample collected at this site did not yield sufficient water for analysis.

˙ one of the two leachate samples collected at site 50212 was treated with CO_2

Abbreviations:

Bit = bituminous; Subbit = Subbituminous; Mix = CCP from different units burning different coals; Blend = CCP from a single unit burning two different fuels

PC = pulverized coal; ESP = electrostatic precipitator; OFA = overfired air; LNB = low-NOx burner

FA = fly ash; BA = bottom ash; EA = economizer ash; FGD = flue gas desulfurization sludge; OA = oil ash

LF = landfill; IMP = impoundment; DUP = duplicate sample; QC = quality control sample

Table 3-2
Leachate Sample Attributes

Sample ID	Source	Byproduct	Source Fuel Type	Site	Source Plant PC Boiler Type	PC Boiler Firing	Source Plant Particulate Collection	Source Plant SO2 Control	Source Plant SO2 Sorbent	Source Plant Flue Gas Cond.	Source Plant NOx Control
001	Landfill	FA,BA	Mix	50210	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	None	Multiple types
002	Landfill	FA	Subbit	50213	Dry Bottom PC Boiler	multiple types	Multiple types	None	None	Multiple	Multiple types
003	Landfill	FA	Subbit	50213	Dry Bottom PC Boiler	multiple types	Multiple types	None	None	Multiple	Multiple types
004	Landfill	FA,BA	Mix	50183	Dry Bottom PC Boiler	multiple types	Multiple types	None	None	Yes	Multiple types
005	Landfill	FA,BA	Mix	50183	Dry Bottom PC Boiler	multiple types	Multiple types	None	None	Yes	Multiple types
006	Landfill	SDA	Subbit	23223A	Dry Bottom PC Boiler	multiple types	Fabric filter	Spray Dryer	Lime	no data	Multiple types
007	Impoundment	FGD	Subbit	23223B	Dry Bottom PC Boiler	multiple types		Wet-FO	Lime	no data	Multiple types
008	Impoundment	FGD	Subbit	23223B	Dry Bottom PC Boiler	multiple types		Wet-FO	Lime	no data	Multiple types
009	Impoundment	FGD	Subbit	23223B	Dry Bottom PC Boiler	multiple types		Wet-FO	Lime	no data	Multiple types
010	Landfill	FA	Subbit	23214	Cyclone		ESP cold-side	None	None	None	Combustion-OFA
012	Impoundment	FA	Bit	14093	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Multiple	Multiple types
013	Impoundment	FA	Bit	14093	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Multiple	Multiple types
014	Impoundment	FA	Bit	14093	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Multiple	Multiple types
015	Impoundment	FA,BA	Blend	25410A	Cyclone		ESP cold-side	None	None	Yes	Combustion-OFA
016	Impoundment	FA,BA	Blend	25410A	Cyclone		ESP cold-side	None	None	Yes	Combustion-OFA
017	Impoundment	FA,BA	Subbit	13115A	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
018	Impoundment	FA,BA	Bit	13115B	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Other
019	Impoundment	FA	Subbit	13115A	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
020	Impoundment	FA,BA	Subbit	13115A	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
021	Impoundment	FA	Bit	49003A	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	Yes	Multiple types
022	Impoundment	FA	Bit	49003A	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	Yes	Multiple types
023	Impoundment	FA	Bit	49003A	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	Yes	Multiple types
024	Landfill	FA	Bit	49003B	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	None	Combustion-LNB
025	Landfill	FA	Bit	49003B	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	None	Combustion-LNB
026	Impoundment	FA	Bit	49003A	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	Yes	Multiple types
027	Landfill	FGD, FA	Bit	35015A	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	Yes	Combustion-LNB
028	Landfill	FGD, FA	Bit	35015A	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	Yes	Combustion-LNB
029	Landfill	FGD, FA	Bit	35015A	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	Yes	Combustion-LNB

Table 3-2
Leachate Sample Attributes (continued)

Sample ID	Source	Byproduct	Source Fuel Type	Site	Source Plant PC Boiler Type	PC Boiler Firing	Source Plant Particulate Collection	Source Plant SO2 Control	Source Plant SO2 Sorbent	Source Plant Flue Gas Cond.	Source Plant NOx Control
030	Impoundment	FA	Bit	35015B	Multiple types	multiple types	ESP cold-side	None	None	None	Combustion-LNB
031	Impoundment	FA	Bit	35015B	Multiple types	multiple types	ESP cold-side	None	None	None	Combustion-LNB
032	Impoundment	FA,BA	Bit	35015B	Multiple types	multiple types	ESP cold-side	None	None	None	Combustion-LNB
037	Impoundment	FA	Bit	33106	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
038	Impoundment	FA	Bit	33106	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
039	Impoundment	FA	Bit	33106	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
042	Impoundment	FA	Bit	33106	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
043	Impoundment	FA	Bit	33106	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
044	Impoundment	FA	Bit	33106	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
049	Impoundment	FA,BA	Bit	33106	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Multiple types
051	Impoundment	FA	Bit	40109	Dry Bottom PC Boiler	tangential	ESP hot-side	None	None	None	Multiple types
052	Impoundment	FA	Bit	40109	Dry Bottom PC Boiler	tangential	ESP hot-side	None	None	None	Multiple types
053	Impoundment	FA	Bit	40109	Dry Bottom PC Boiler	tangential	ESP hot-side	None	None	None	Multiple types
057	Impoundment	FA,BA	Bit	40109	Dry Bottom PC Boiler	tangential	ESP hot-side	None	None	None	Multiple types
059	Impoundment	FA,BA	Bit	40109	Dry Bottom PC Boiler	tangential	ESP hot-side	None	None	None	Multiple types
061	Impoundment	FA	Bit	33104	Dry Bottom PC Boiler	tangential	Multiple types	None	None	None	Postcombustion SCR
062	Impoundment	FA	Bit	33104	Dry Bottom PC Boiler	tangential	Multiple types	None	None	None	Postcombustion SCR
064	Impoundment	FA	Bit	33104	Dry Bottom PC Boiler	tangential	Multiple types	None	None	None	Postcombustion SCR
069	Impoundment	FA,BA	Bit	33104	Dry Bottom PC Boiler	tangential	Multiple types	None	None	None	Postcombustion SCR
070	Impoundment	FA,BA	Bit	33104	Dry Bottom PC Boiler	tangential	Multiple types	None	None	None	Postcombustion SCR
079	Impoundment	FA,OA	Blend	22346	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Yes	Multiple types
082	Impoundment	FA,OA	Blend	22346	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Yes	Multiple types
083	Impoundment	FA	Blend	22347	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Other
084	Impoundment	FA,OA	Blend	22346	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Yes	Multiple types
090	See Notes	FA	Mix	27413	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Yes	Multiple types
091	See Notes	FA	Mix	27413	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Yes	Multiple types
092	See Notes	FA	Mix	27413	Dry Bottom PC Boiler	multiple types	ESP cold-side	None	None	Yes	Multiple types

Table 3-2
Leachate Sample Attributes (continued)

Sample ID	Source	Byproduct	Source Fuel Type	Site	Source Plant PC Boiler Type	PC Boiler Firing	Source Plant Particulate Collection	Source Plant SO2 Control	Source Plant SO2 Sorbent	Source Plant Flue Gas Cond.	Source Plant NOx Control
093	Landfill	FA,BA	Subbit	27412	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	None	Combustion-OFA
097	Landfill	FA	Subbit	50212	Dry Bottom PC Boiler	wall-fired	ESP cold-side	None	None	Yes	Multiple types
098	Landfill	FA,BA	Mix	50183	Dry Bottom PC Boiler	multiple types	Multiple types	None	None	Yes	Multiple types
099	Landfill	FA,BA	Mix	50183	Dry Bottom PC Boiler	multiple types	Multiple types	None	None	Yes	Multiple types
101	Landfill	FA,BA	Bit	50408	Dry Bottom PC Boiler	wall-fired	ESP cold-side	None	None	None	Combustion-none
102	Landfill	FA	Bit	50211	Dry Bottom PC Boiler	wall-fired front	Fabric filter	None	None	no data	Combustion-LNB
105	Impoundment	FGD	Lig	34186B	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	None	Multiple types
106	Landfill	FGD,FA,BA	Lig	34186C	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	None	Multiple types
107	Impoundment	FGD	Lig	34186B	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	None	Multiple types
108	Landfill	FA	Lig	34186A	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	None	Multiple types
111	Landfill	FA	Bit	49003B	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	None	Combustion-LNB
112	Landfill	FA	Bit	49003B	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	None	Combustion-LNB
113	Impoundment	FA	Bit	49003A	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	Yes	Multiple types
114	Impoundment	FA	Bit	49003A	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	Yes	Multiple types
115	Impoundment	FA	Bit	49003A	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	Yes	Multiple types
116	Impoundment	FA	Bit	49003A	Dry Bottom PC Boiler	wall-fired opposed	ESP cold-side	None	None	Yes	Multiple types
118	Impoundment	FA,BA	Bit	35015B	Multiple types	multiple types	ESP cold-side	None	None	None	Combustion-LNB
119	Impoundment	FA,BA	Bit	35015B	Multiple types	multiple types	ESP cold-side	None	None	None	Combustion-LNB
120	Landfill	FGD, FA	Bit	35015A	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	Yes	Combustion-LNB
121	Landfill	FGD, FA	Bit	35015A	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	Yes	Combustion-LNB
122	Landfill	FGD, FA	Bit	35015A	Dry Bottom PC Boiler	tangential	ESP cold-side	Wet-natural	Mg-Lime	Yes	Combustion-LNB
123	Landfill	FA	Bit	20094A	Dry Bottom PC Boiler	wall-fired opposed	ESP multiple	None	None	None	Multiple types
124	Landfill	FA,BA	Bit	20094B	Dry Bottom PC Boiler	wall-fired opposed	ESP multiple	None	None	None	Multiple types
126	Impoundment	FA,BA	Subbit	43035	Dry Bottom PC Boiler	wall-fired opposed	ESP hot-side	None	None	None	Combustion-LNB
127	Impoundment	FA,BA	Subbit	43035	Dry Bottom PC Boiler	wall-fired opposed	ESP hot-side	None	None	None	Combustion-LNB
128	Landfill	FGD,FA	Lig	43034	Wet Bottom PC Boiler	wall-fired	ESP cold-side	Wet-inhib	Limestone	None	Multiple types
ES-1	Landfill	FGD,FA	Subbit	31192	Dry Bottom PC Boiler	tangential	Fabric filter	Wet-natural	Limestone	None	Other

Table 3-2
Leachate Sample Attributes (continued)

Sample ID	Source	Byproduct	Source Fuel Type	Site	Source Plant PC Boiler Type	PC Boiler Firing	Source Plant Particulate Collection	Source Plant SO2 Control	Source Plant SO2 Sorbent	Source Plant Flue Gas Cond.	Source Plant NOx Control
HN-1	Impoundment	FA,BA	Bit	13115B	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Other
HN-2	Impoundment	FA,BA	Bit	13115B	Dry Bottom PC Boiler	tangential	ESP cold-side	None	None	Yes	Other
SX-1	Impoundment	FA	Blend	25410B	Cyclone		ESP cold-side	None	None	Yes	Combustion-OFA

Notes:

Ash at site 27413 (samples 090, 091, 092) was first sluiced, then managed dry.

QC and duplicate samples not listed

Abbreviations:

Bit = bituminous; Subbit = Subbituminous; Mix = CCP from different units burning different coals; Blend = CCP from a single unit burning two different fuels

PC = pulverized coal; ESP = electrostatic precipitator; OFA = overfired air; LNB = low-NOx burner

FA = fly ash; BA = bottom ash; EA = economizer ash; FGD = flue gas desulfurization sludge;

Table 3-3
Sample Collection Methods

Sample ID	Site	Source	Byproduct	Point	Method
001	50210	Landfill	FA,BA	Leachate Well	Waterra Pump to Peristaltic
002	50213	Landfill	FA	Lysimeter	Bladder Pump
003	50213	Landfill	FA	Lysimeter	Bladder Pump
004	50183	Landfill	FA,BA	Leachate Collection System	Peristaltic Pump
005	50183	Landfill	FA,BA	Leachate Well	Waterra Pump to Peristaltic
006	23223A	Landfill	SDA	Leachate Collection System	Peristaltic Pump
007	23223B	Impoundment	FGD	Leachate Well	Bladder Pump
008	23223B	Impoundment	FGD	Leachate Well	Bladder Pump
009	23223B	Impoundment	FGD	Ash/Water Interface	Peristaltic Pump
010	23214	Landfill	FA	Leachate Collection System	Bailer to Peristaltic
012	14093	Impoundment	FA	Leachate Well	Waterra Pump to Peristaltic
013	14093	Impoundment	FA	Leachate Well	Peristaltic Pump
014	14093	Impoundment	FA	Leachate Well	Peristaltic Pump
015	25410A	Impoundment	FA,BA	Ash/Water Interface	Peristaltic Pump
016	25410A	Impoundment	FA,BA	Drive Point Piezometer	Peristaltic Pump
017	13115A	Impoundment	FA,BA	Ash/Water Interface	Peristaltic Pump
018	13115B	Impoundment	FA,BA	Leachate Well	Peristaltic Pump
019	13115A	Impoundment	FA	Sluice Line	Dip Sampler to Peristaltic Pump
020	13115A	Impoundment	FA,BA	Outfall	Peristaltic Pump
021	49003A	Impoundment	FA	Drive Point Piezometer	Peristaltic Pump
022	49003A	Impoundment	FA	Ash/Water Interface	Peristaltic Pump
023	49003A	Impoundment	FA	Drive Point Piezometer	Peristaltic Pump
024	49003B	Landfill	FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
025	49003B	Landfill	FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
026	49003A	Impoundment	FA	Outfall	Dip Sampler to Peristaltic Pump
027	35015A	Landfill	FGD, FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
028	35015A	Landfill	FGD, FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
029	35015A	Landfill	FGD, FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
030	35015B	Impoundment	FA	Seep	Dip Sampler to Peristaltic Pump
031	35015B	Impoundment	FA	Drive Point Piezometer	Peristaltic Pump
032	35015B	Impoundment	FA,BA	Outfall	Peristaltic Pump
037	33106	Impoundment	FA	Drive Point Piezometer	Peristaltic Pump
038	33106	Impoundment	FA	T-Handle Probe	Peristaltic Pump
039	33106	Impoundment	FA	Drive Point Piezometer	Peristaltic Pump
042	33106	Impoundment	FA	Sluice Line	Peristaltic Pump
043	33106	Impoundment	FA	Sluice Line	Peristaltic Pump
044	33106	Impoundment	FA	Outfall	Peristaltic Pump
049	33106	Impoundment	FA,BA	Ash/Water Interface	Peristaltic Pump
051	40109	Impoundment	FA	Sluice Line	Peristaltic Pump
052	40109	Impoundment	FA	Drive Point Piezometer	Peristaltic Pump
053	40109	Impoundment	FA	T-Handle Probe	Peristaltic Pump
057	40109	Impoundment	FA,BA	Ash/Water Interface	Peristaltic Pump
059	40109	Impoundment	FA,BA	Outfall	Peristaltic Pump

Table 3-3
Sample Collection Methods (continued)

Sample ID	Site	Source	Byproduct	Point	Method
061	33104	Impoundment	FA	Drive Point Piezometer	Peristaltic Pump
062	33104	Impoundment	FA	Drive Point Piezometer	Peristaltic Pump
064	33104	Impoundment	FA	Sluice Line	Peristaltic Pump
069	33104	Impoundment	FA,BA	Ash/Water Interface	Peristaltic Pump
070	33104	Impoundment	FA,BA	Outfall	Peristaltic Pump
079	22346	Impoundment	FA,OA	Leachate Well	Peristaltic Pump
082	22346	Impoundment	FA,OA	Ash/Water Interface	Peristaltic Pump
083	22347	Impoundment	FA	Ash/Water Interface	Peristaltic Pump
084	22346	Impoundment	FA,OA	Leachate Well	Peristaltic Pump
090	27413	See Notes	FA	Leachate Well	Peristaltic Pump
091	27413	See Notes	FA	Leachate Well	Peristaltic Pump
092	27413	See Notes	FA	Leachate Well	Peristaltic Pump
093	27412	Landfill	FA,BA	Soil Boring	Core Extract
097	50212	Landfill	FA	Leachate Collection System	Peristaltic Pump
098	50183	Landfill	FA,BA	Leachate Collection System	Peristaltic Pump
099	50183	Landfill	FA,BA	Leachate Well	Waterra Pump to Peristaltic
101	50408	Landfill	FA,BA	Leachate Collection System	Peristaltic Pump
102	50211	Landfill	FA	Leachate Collection System	Peristaltic Pump
105	34186B	Impoundment	FGD	Ash/Water Interface	Peristaltic Pump
106	34186C	Landfill	FGD,FA,BA	Leachate Collection System	Dip Sampler to Peristaltic Pump
107	34186B	Impoundment	FGD	Sluice Line	Peristaltic Pump
108	34186A	Landfill	FA	Seep	Peristaltic Pump
111	49003B	Landfill	FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
112	49003B	Landfill	FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
113	49003A	Impoundment	FA	T-Handle Probe	Peristaltic Pump
114	49003A	Impoundment	FA	T-Handle Probe	Peristaltic Pump
115	49003A	Impoundment	FA	Ash/Water Interface	Peristaltic Pump
116	49003A	Impoundment	FA	Outfall	Dip Sampler to Peristaltic Pump
118	35015B	Impoundment	FA,BA	Ash/Water Interface	Peristaltic Pump
119	35015B	Impoundment	FA,BA	Outfall	Peristaltic Pump
120	35015A	Landfill	FGD, FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
121	35015A	Landfill	FGD, FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
122	35015A	Landfill	FGD, FA	Leachate Collection System	Dip Sampler to Peristaltic Pump
123	20094A	Landfill	FA	Soil Boring	Core Extract
124	20094B	Landfill	FA,BA	Soil Boring	Core Extract
126	43035	Impoundment	FA,BA	Seep	Dip Sampler to Peristaltic Pump
127	43035	Impoundment	FA,BA	Seep	Dip Sampler to Peristaltic Pump
128	43034	Landfill	FGD,FA	Leachate Collection System	Peristaltic Pump
ES-1	31192	Landfill	FGD,FA	Soil Boring	Core Extract

Table 3-3
Sample Collection Methods (continued)

Sample ID	Site	Source	Byproduct	Point	Method
HN-1	13115B	Impoundment	FA,BA	Soil Boring	Core Extract
HN-2	13115B	Impoundment	FA,BA	Soil Boring	Core Extract
SX-1	25410B	Impoundment	FA	Soil Boring	Core Extract

Notes:

Ash at site 27413 (samples 090, 091, 092) was first sluiced, then managed dry.

QC and duplicate samples not listed

Abbreviations:

FA = fly ash; BA = bottom ash; EA = economizer ash; FGD = flue gas desulfurization sludge; OA = oil ash

4

LEACHATE QUALITY AT CCP MANAGEMENT FACILITIES

Analytical data were entered in a database and reviewed for outliers; anomalous values were checked and corrected, if appropriate, by the Trent University laboratory. Data are summarized in this section; all results are listed in Appendix A.

Many of the data summaries that follow are based on box-whisker plots, which graphically show the distribution of concentrations for a given group of data (Figure 4-1). Non-detect values were plotted at their detection limit.

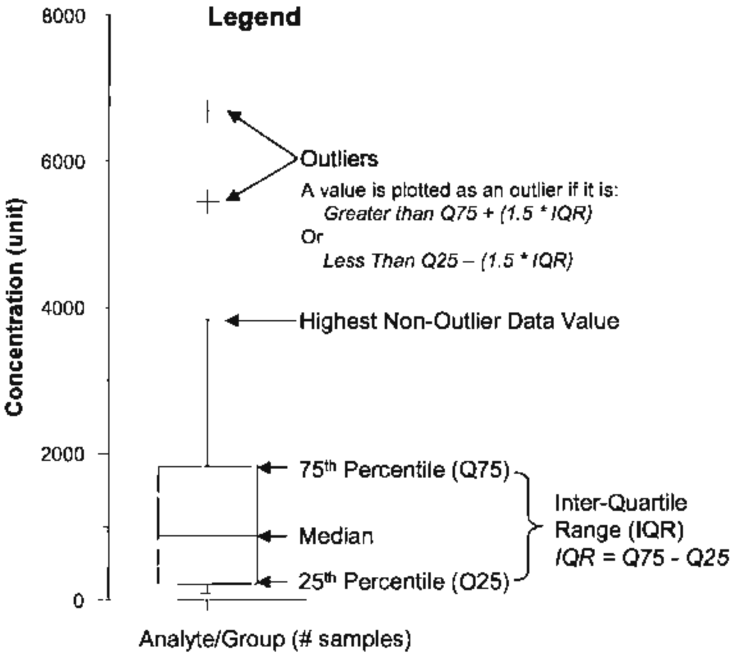


Figure 4-1
Legend for Box-Whisker Plots

Major Constituents

Ash Leachate

The collected leachate samples were generally moderately to strongly oxidizing (positive Eh compared to the standard hydrogen electrode) and moderately to strongly alkaline (Figure 4-2). The subbituminous/lignite ash samples had a slightly higher median pH than bituminous ash, and the highest pH values were from sites receiving subbituminous/lignite ash. The lowest Eh and lowest pH samples were from impoundments.

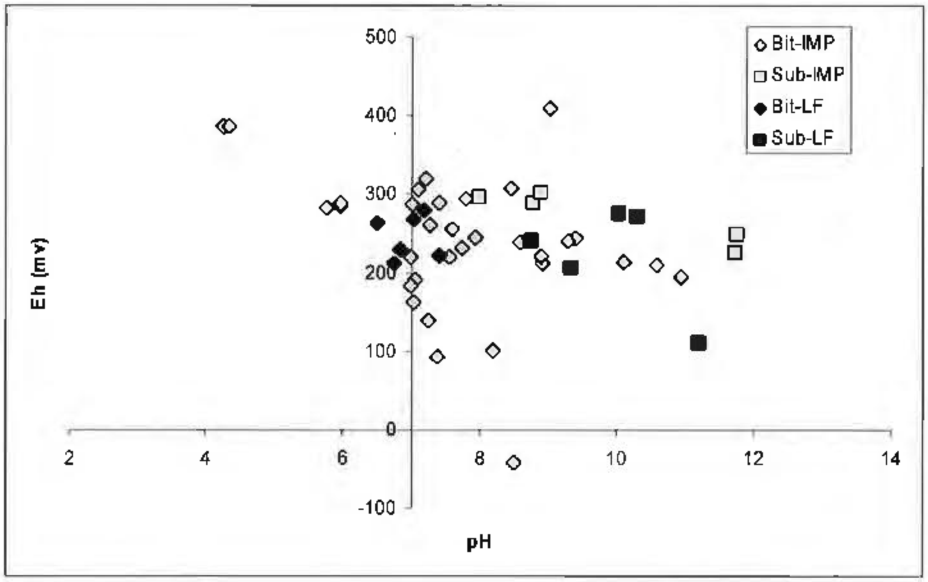


Figure 4-2
Eh-pH Diagram for Ash Samples

Sulfate was the only constituent in the ash leachate samples with a median concentration greater than 100 mg/L (339 mg/L; Figure 4-3, Table 4-1). Most samples had concentrations greater than 100 mg/L, and more than 25 percent of the samples had concentrations greater than 1,000 mg/L. The highest concentration for any constituent in ash leachate was for sulfate in sample 002 (6,690 mg/L; Table 4-1), a leachate sample collected from a landfill receiving subbituminous coal ash.

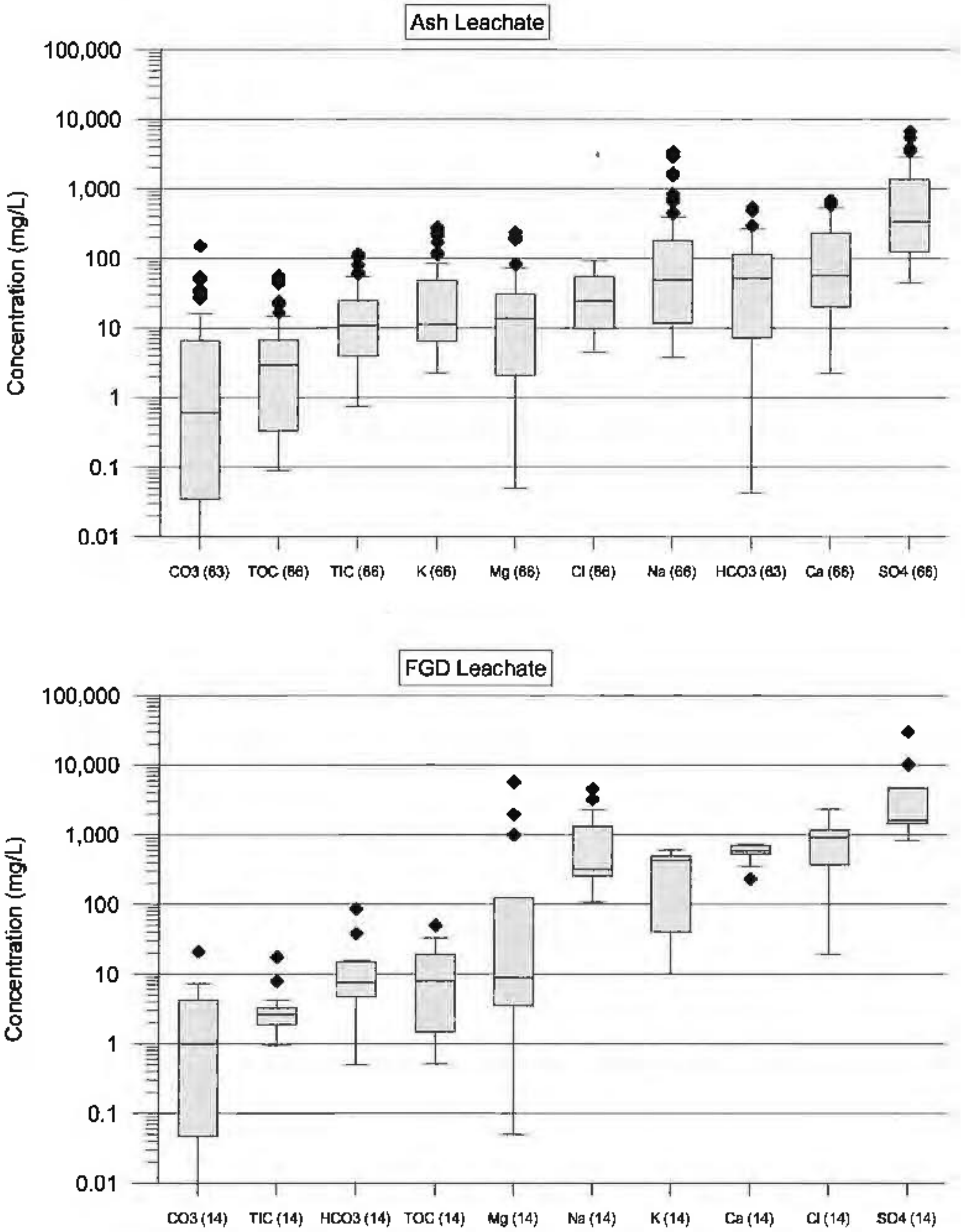


Figure 4-3
Ranges for Major Constituents in CCP Leachate

Table 4-1
Summary Statistics of CCP Leachate Analytical Results

	Ash Leachate Samples					FGD Leachate Samples				
	Count	**Min**	**Median**	**Max**	**% BDL**	**Count**	**Min**	**Median**	**Max**	**% BDL**
Ag (ug/L)	67	<0.2	<0.2	2.0	93%	14	<0.20	<0.20	<0.20	100%
Al (ug/L)	67	<2.0	114	44,400	16%	14	<24	179	890	14%
As (ug/L)	67	1.4	25	1,380	0%	14	11	28	230	0%
As(III)	67	<0.04	0.37	859	40%	14	<0.3	2.1	197	21%
As(V)	67	<0.08	18	534	8%	14	<0.5	5.4	63	21%
B (ug/L)	67	207	2,160	112,000	0%	14	1,450	9,605	98,500	0%
Ba (ug/L)	67	<18	108	657	4%	14	<30	73	158	7%
Be (ug/L)	67	<0.2	<0.4	8.6	94%	14	<0.20	<0.80	1.5	93%
Ca (mg/L)	66	<2.2	55	681	2%	14	234	589	730	0%
Cd (ug/L)	67	<0.2	1.5	65	12%	14	0.50	1.8	13	0%
Cl (mg/L)	66	4.5	25	92	0%	14	19	921	2,330	0%
Co (ug/L)	67	<0.04	1.0	133	31%	14	<0.028	1.0	78	36%
CO_3 (mg/L)	63	<0.01	0.60	152	13%	14	<0.010	1.0	21	21%
Cr (ug/L)	67	<0.2	0.60	5,100	45%	14	<0.20	<0.50	53	64%
Cr(III)	41	<0.01	0.16	340	34%	4	<0.1	0.082	1.3	50%
Cr(VI)	53	<0.006	0.7	5090	36%	5	<0.02	2.9	47	40%
Cu (ug/L)	67	<0.2	3.0	494	19%	14	<0.26	2.6	44	14%
Fe (ug/L)	67	<3	<50	25,600	52%	14	<4.6	<50	1,200	71%
H_2CO_3 (mg/L)	63	<0.01	<0.01	3.4	87%	14	<0.010	<0.010	0.041	93%
HCO_3 (mg/L)	63	0.042	53	535	0%	14	0.50	7.5	87	0%
Hg (ng/L)	22	0.25	3.8	61	0%	8	0.82	8.3	79	0%
K (mg/L)	66	<2.2	11	277	3%	14	10	425	609	0%
Li (ug/L)	67	<1.0	129	23,600	13%	14	<20	3,055	7,070	14%
Mg (mg/L)	66	<0.05	13	236	8%	14	<0.050	8.9	5,810	14%
Mn (ug/L)	67	<0.1	55	4,170	21%	14	<0.10	113	1,170	14%
Mo (ug/L)	67	<8.2	405	39,600	3%	14	164	341	60,800	0%
Na (mg/L)	66	3.8	52	3,410	0%	14	108	322	4,630	0%
Ni (ug/L)	67	<0.6	5.8	189	13%	14	<2.0	3.4	597	36%
Pb (ug/L)	67	<0.1	<0.20	8.0	73%	14	<0.14	<0.20	3.5	64%
Sb (ug/L)	67	<0.1	2.4	59	3%	14	<0.10	1.00	22	29%
Se (ug/L)	67	0.071	19	1,760	0%	14	1.1	6.2	2,360	0%
Se(IV)	67	<0.1	5.3	217	21%	14	<0.1	<2.0	79	64%
Se(VI)	67	<0.1	1.5	1300	34%	14	<0.3	2.2	1660	21%
Si (ug/L)	67	221	4,645	19,000	0%	14	400	2,480	45,400	0%
SO_4 (mg/L)	66	45	339	6,690	0%	14	836	1,615	30,500	0%
Sr (ug/L)	67	<30	829	12,000	1%	14	1,500	5,230	16,900	0%
TIC (mg/L)	66	0.75	11	115	0%	14	0.95	2.6	18	0%
Tl (ug/L)	67	<0.1	0.36	18	46%	14	<0.10	<0.22	2.9	86%
TOC (mg/L)	66	<0.09	3.3	57	24%	14	0.51	8.0	50	0%
U (ug/L)	67	<0.01	1.2	61	19%	14	<0.010	0.20	16	36%
V (ug/L)	67	<0.42	45	5,020	3%	14	<0.69	4.1	400	21%
Zn (ug/L)	67	<1.5	5.0	289	46%	14	<2.0	<5.0	68	57%
DO (%)	61	0.10	35	165	0%	14	0.20	14	95	0%
ORP (mV)	63	-41	241	411	2%	14	1.5	201	356	0%
pH (SU)	64	4.3	7.9	12	0%	14	6.2	9.0	12	0%
EC (µmho/cm)	64	174	990	12,760	0%	14	2,190	6,461	26,140	0%
Temp (ºC)	64	10	21	36	0%	14	9.9	17	27	0%

Notes:

Dissolved oxygen (DO) is percent saturation

More than 25 percent of the calcium, bicarbonate, and sodium concentrations in ash leachate were greater than 100 mg/L, and several sodium concentrations were greater than 1,000 mg/L, with the highest being 3,410 mg/L in sample 002.

Most of the ash leachate sample anion concentrations were dominated by sulfate (Figure 4-4). All of the exceptions were impoundment samples, three of which were porewater (samples 018, 061, and 084) while the other seven samples were pond, sluice, or outfall water. All except one of the exceptions had relatively low sulfate concentrations (two less than 200 mg/L and seven less than 100 mg/L), while sample 018 had a close to median sulfate concentration (339 mg/L) and a relatively high bicarbonate concentration (535 mg/L). All of the exceptions tended toward carbonate/bicarbonate type.

Cation concentrations in the leachate samples were usually dominated by calcium or calcium with varying percentages of sodium and magnesium when the source coal was bituminous, and by sodium when the source coal was subbituminous/lignite. Samples 017, 019, and 020 were exceptions to this relationship, having roughly equal percentages of the cations. The sodium-dominated subbituminous/lignite samples were collected from landfills, while samples 017, 019, and 020 were collected from an impoundment that receives more bottom ash than fly ash.

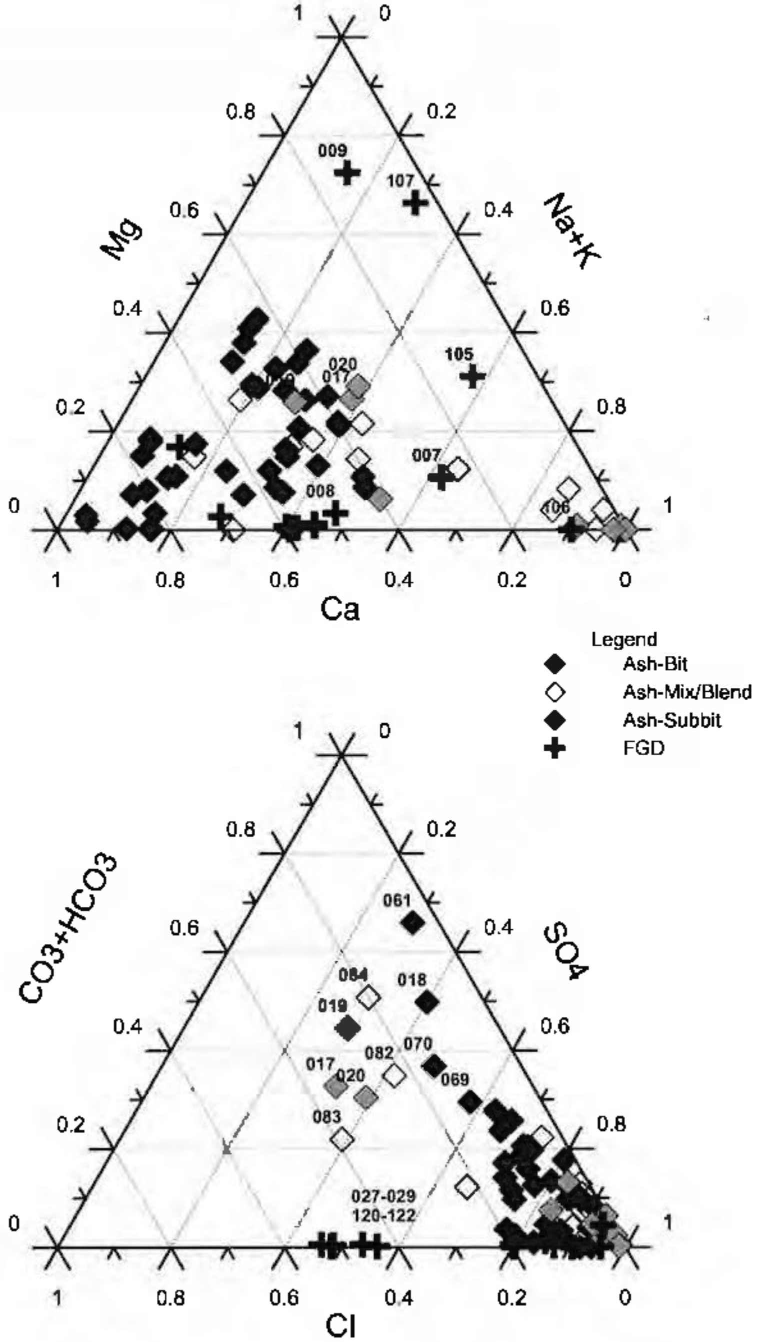


Figure 4-4
Ternary Plots Showing Relative Percentages of Major Constituents in Ash Leachate

FGD Leachate

Leachate samples collected from FGD product management sites (FGD leachates) were moderately to strongly oxidizing (positive Eh compared to the standard hydrogen electrode) and moderately to strongly alkaline (Figure 4-5). Landfill samples, as a group, were less oxic and more alkaline than impoundment samples, although the lowest Eh value was for an impoundment.

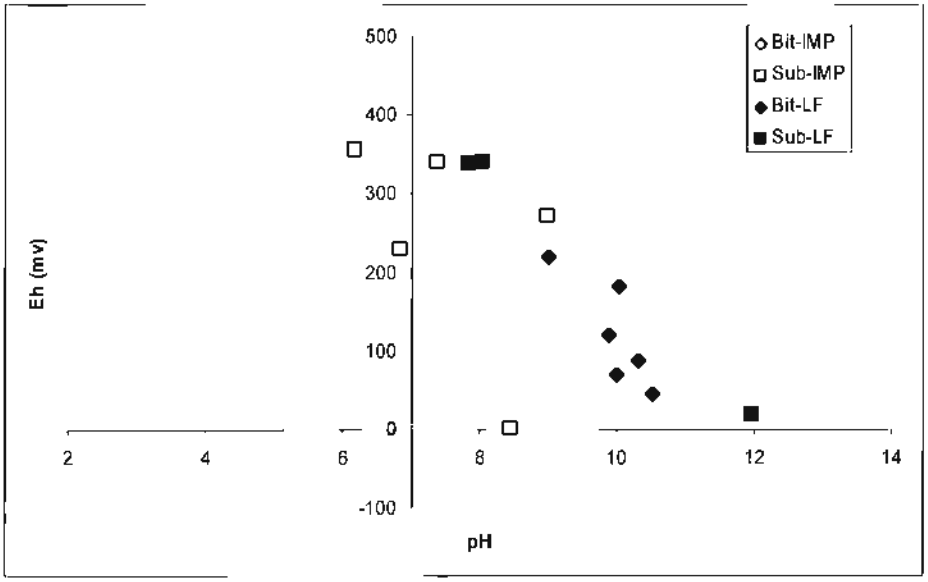


Figure 4-5
Eh-pH Diagram for FGD Leachate Samples

Concentrations of most major constituents (specifically, calcium, chloride, potassium, sodium, and sulfate) in FGD leachate were higher than in ash leachate (Figure 4-3). The median sulfate concentrations was 1,615 mg/L, and the maximum sulfate concentration was 30,500 mg/L, which was the highest single analytical result returned from the field leachate sampling. The high sulfate concentration was obtained from an impoundment where sluice water is recirculated.[2]

More than 25 percent of the chloride and sodium concentrations were greater than 1,000 mg/L, and median concentrations of chloride, calcium, potassium, and sodium were greater than 100 mg/L. Overall, the FGD leachate samples have higher concentrations of chloride and potassium, relative to the other major constituents, than ash leachate.

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[2] Two of the 14 FGD leachate samples were from impoundments where sluice water is recirculated; however, the median concentrations from FGD sites without recirculation are also significantly higher than the ash leachate medians.

All of the FGD leachate samples from plants burning subbituminous/lignite coal were dominated by sulfate (Figure 4-4), while the six samples (027-029, 120-122) from a plant that burned bituminous coal had equal percentages of sulfate and chloride—sulfate concentrations were relatively low in these samples.[3] This plant (35015A) has a wet FGD system that uses magnesium-lime as sorbent, similar to some of the other FGD systems from which leachate samples were collected (Table 3-1).

Cation ratios in FGD leachate samples varied considerably, even among samples collected from the same site, largely due to varying magnesium concentrations. For example, samples 007, 008, and 009, all from the 23223B site, ranged from calcium-sodium to magnesium-sodium, primarily based on a variation in magnesium concentrations. Samples 105 and 107, both from the 34186B site, exhibited a similar range in cation ratios, which was also based on varying magnesium concentrations. However, there was no clear relationship between FGD sorbent, coal type, and cation chemistry in the FGD leachate samples.

Minor and Trace Elements

Box-whisker plots of minor and trace elements in ash and FGD leachate are sorted by median concentration, from highest concentration on the right to lowest concentration on the left.

Ash Leachate

Silica and boron had median concentrations higher than 1,000 μg/L in the ash leachate field samples (Figure 4-6). Median concentrations of strontium, molybdenum, lithium, aluminum, and barium were greater than 100 μg/L (Figure 4-6), while median concentrations of chromium, beryllium, thallium, silver, lead, and mercury were lower than 1 μg/L (Figure 4-7). Silver, beryllium, and lead were rarely detected (26 percent of the samples or less).

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[3] Due to the low number of samples, the FGD leachate results were not differentiated by source coal in Figure 4-4.

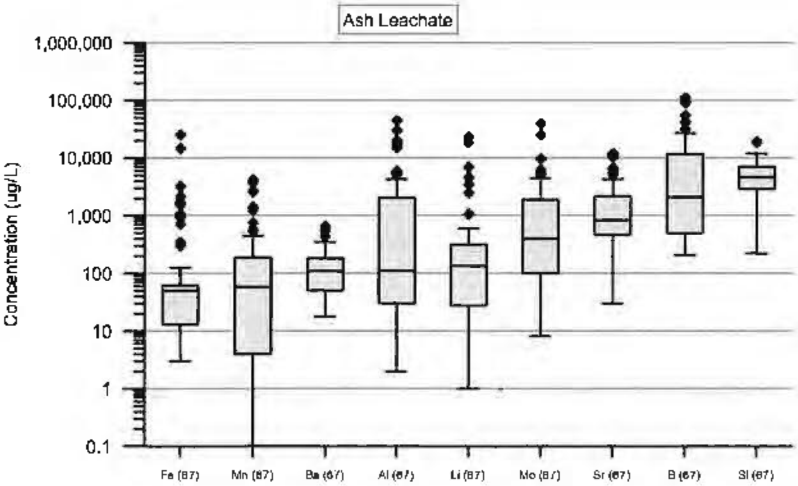

Figure 4-6
Ranges of Minor Constituents In Ash Leachate

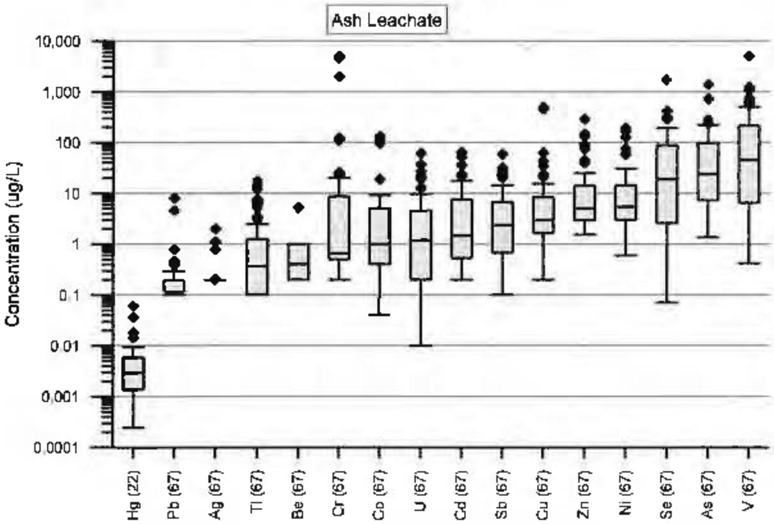

Figure 4-7
Ranges of Trace Constituents in Ash Leachate

FGD Leachate

Boron, strontium, lithium, and silica had median concentrations greater than 1,000 µg/L in the FGD field leachate samples (Figure 4-8). Median concentrations of molybdenum, aluminum, and manganese were greater than 100 µg/L (Figure 4-8), while median concentrations of chromium, beryllium, thallium, silver, lead, and mercury were lower than 1 µg/L (Figure 4-9).

Silver was not detected in the 14 FGD leachate samples, and beryllium, chromium, iron, lead, and thallium, were detected in less than 40 percent of the samples (Table 4-1).

The relative concentrations of minor and trace elements in FGD leachate were somewhat different than in ash leachate. Median concentrations of boron, strontium, and lithium in FGD leachate were a factor of 3 or more higher than in ash leachate, while concentrations of selenium and vanadium were a factor of 3 or more higher in ash leachate than in FGD leachate (Figure 4-10). Median concentrations of uranium and thallium were also a factor of 3 or more higher in the ash leachate, but the concentrations were very low (1 µg/L or less) in both leachates.

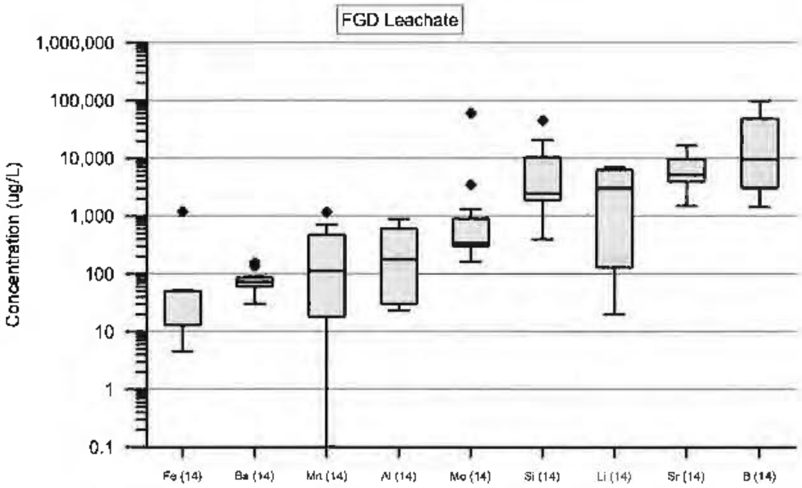

Figure 4-8
Ranges of Minor Constituents in FGD Leachate

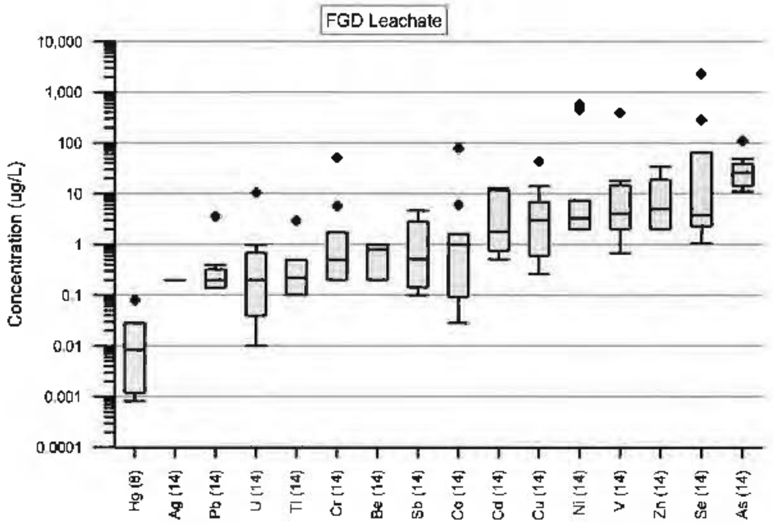

Figure 4-9
Ranges of Trace Constituents in FGD Leachate

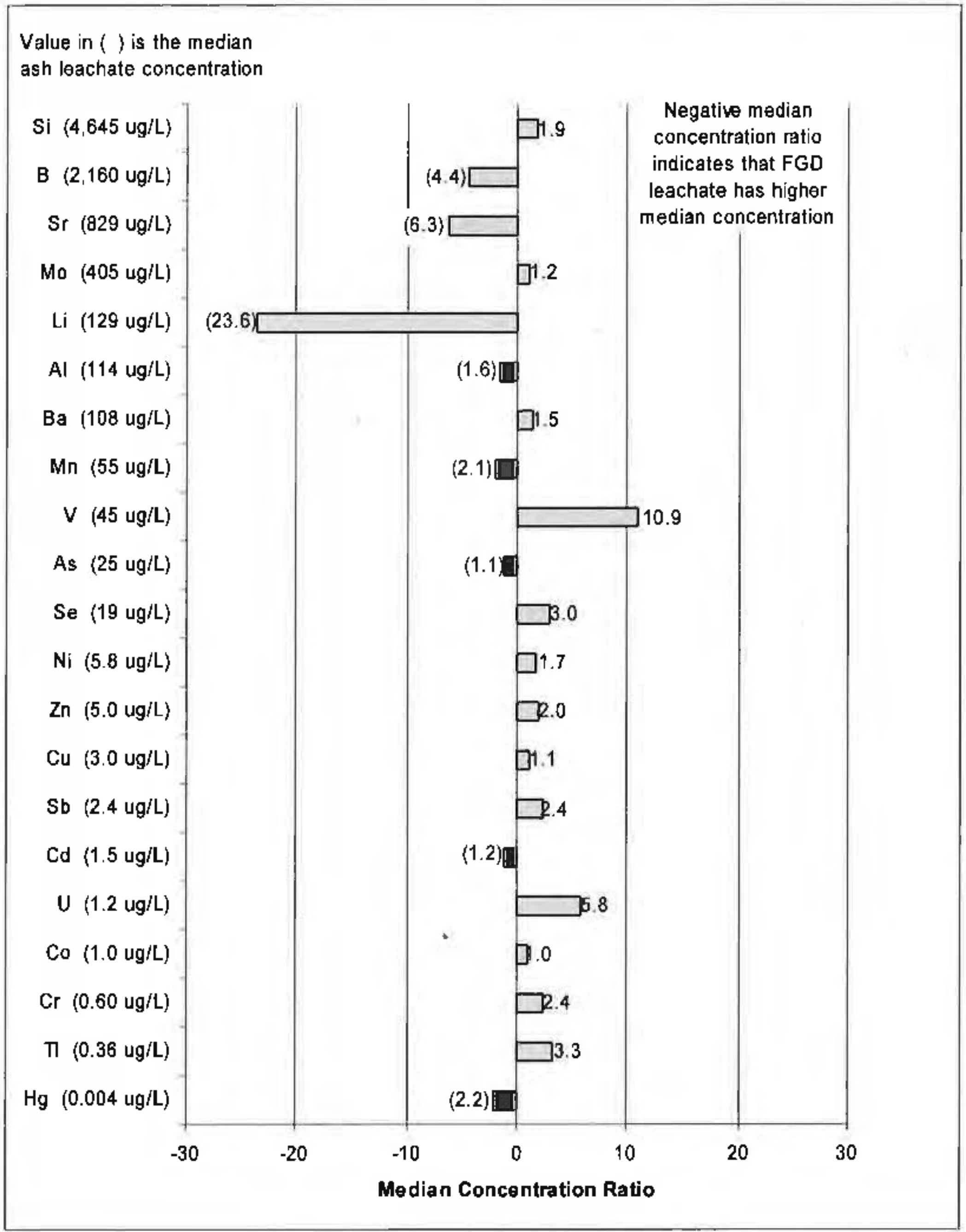

Figure 4-10
Comparison of Median Concentrations of Minor and Trace Elements in Ash and FGD Leachate

Comparison of Ash Leachate Concentrations to Site and Plant Attributes

Leachate concentrations were compared as a function of source coal type and management method in order to evaluate the differences in leachate quality. Samples from multiple sites are required for such a comparison to be meaningful. As a result, this comparison focused on ash samples because five or more samples from two or more sites were available for each comparison (Table 4-2). Summary statistics listing the count, minimum, median, and maximum concentration of each analyte by management type (landfill, impoundment), and source coal (bituminous, subbituminous/lignite) are listed in Table 4-3 for ash leachate and Table 4-4 for FGD leachate.

Table 4-2
Sample (A) and Site (B) Categories

A. Sample Count		**Source Coal**					
		Bit	**Blend**	**Lig**	**Mix**	**Subbit**	**total**
Ash	Impoundment	36	7	0	0	5	48
	Landfill	6	0	1	5	4	16
	Other	0	0	0	3	0	3
	total	42	7	1	8	9	67
FGD	Impoundment	0	0	2	0	3	5
	Landfill	6	0	2	0	1	9
	total	6	0	4	0	4	14
	All	**48**	**7**	**5**	**8**	**13**	**81**

B. Site Count		**Source Coal**					
		Bit	**Blend**	**Lig**	**Mix**	**Subbit**	**total**
Ash	Impoundment	7	4	0	0	2	13
	Landfill	3	0	1	2	3	9
	Other	0	0	0	1	0	1
	total	10	4	1	3	5	23
FGD	Impoundment	0	0	1	0	1	2
	Landfill	1	0	2	0	1	4
	total	1	0	3	0	2	6
	All	**11**	**4**	**4**	**3**	**7**	**29**

Table 4-3
Statistical Summary of Ash Leachate Samples by Management Method and Coal Type

	Landfill				Landfill				Impoundment				Impoundment			
	Bituminous				Subbituminous/Lignite				Bituminous				Subbituminous/Lignite			
	Count	min	med	max	Count	min	med	max	Count	min	med	max	Count	min	med	max
Ag (ug/L)	6	<0.2	<0.2	<0.2	5	<0.2	<0.2	0.78	36	<0.2	<0.2	2.0	5	<0.2	<0.2	<0.2
Al (ug/L)	6	<2	7.5	52	5	81	2,680	17,500	36	<5.9	62	15,100	5	730	4,190	5,920
As (ug/L)	6	1.4	6.2	11	5	4.1	45	84	36	5.1	58	1,380	5	4.1	5.1	6.4
B (ug/L)	6	11,100	23,050	89,500	5	6,080	18,400	41,500	36	207	1,085	112,000	5	470	860	3,890
Ba (ug/L)	6	23	45	50	5	<18	18	63	36	<30	141	545	5	36	140	350
Be (ug/L)	6	<0.2	<0.2	<0.8	5	<0.2	<1	<1	36	<0.2	<0.4	8.6	5	<0.2	<1	<1
Ca (mg/L)	5	235	405	431	5	6.3	19	596	36	12	51	681	5	<2.5	43	81
Cd (ug/L)	6	4.6	10	36	5	7.6	11	52	36	<0.2	1.2	21	5	<0.3	<0.3	2.1
Cl (mg/L)	5	15	29	73	5	11	28	92	36	4.5	15	87	5	31	72	85
Co (ug/L)	6	0.072	9.1	113	5	<0.42	3.3	133	36	<0.2	1.5	22	5	<0.04	<1	1.1
CO_3 (mg/L)	5	0.025	0.11	0.18	5	2.5	50	152	34	<0.01	0.13	16	5	1.1	4.4	36
Cr (ug/L)	6	<0.2	0.17	20	5	0.48	2,000	5,100	36	<0.2	<0.5	29	5	0.66	2.8	108
Cu (ug/L)	6	<0.91	1.1	2.8	5	1.6	43	494	36	<0.38	1.9	452	5	2.4	7.1	12
Fe (ug/L)	6	<8	34	90	5	<3.0	<50	46	36	<5	10	14,700	5	<25	<50	<50
H_2CO_3 (mg/L)	5	<0.01	<0.01	0.020	5	<0.01	<0.01	<0.01	34	<0.01	<0.01	3.4	5	<0.01	<0.01	<0.01
HCO_3 (mg/L)	5	100	229	265	5	1.0	108	481	34	0.042	28	535	5	1.1	110	241
Hg (ng/L)	2	2.1	3.0	3.8	3	14	18	37	7	0.38	1.4	5.2	2	5.4	7.4	9.4
K (mg/L)	5	23	170	219	5	73	80	120	36	<2.2	9.2	277	5	5.5	7.7	40
Li (ug/L)	6	431	5,740	23,600	5	<4.4	<20	27	36	30	213	1,060	5	<7.0	<20	16
Mg (mg/L)	5	69	188	236	5	0.53	6.7	57	36	0.080	6.8	72	5	<0.05	21	28
Mn (ug/L)	6	72	2,060	4,110	5	<1.5	1.5	7.7	36	<0.2	72	4,170	5	<0.2	<4	14
Mo (ug/L)	6	751	3,280	9,630	5	2,680	5,720	25,400	36	8.2	214	6,030	5	<30	80	524
Na (mg/L)	5	80	188	455	5	840	1,700	3,410	36	3.8	19	72	5	53	56	653
Ni (ug/L)	6	3.0	18	189	5	2.2	8.0	75	36	<0.6	7.1	72	5	<0.6	3.7	7.1
Pb (ug/L)	6	<0.12	<0.14	0.12	5	<0.2	0.29	0.29	36	<0.1	<0.15	8.0	5	<0.14	<0.2	0.21
Sb (ug/L)	6	0.14	2.5	9.1	5	0.67	0.90	5.2	36	0.29	6.1	59	5	0.24	0.48	0.62
Se (ug/L)	6	0.67	49	91	5	6.6	413	1,760	36	0.071	13	283	5	1.8	2.5	181
Si (ug/L)	6	2,300	6,075	9,400	5	221	1,540	9,900	36	700	4,715	18,500	5	2,200	3,400	10,300

Table 4-3
Statistical Summary of Ash Leachate Samples by Management Method and Coal Type (continued)

	Landfill				Landfill				Impoundment				Impoundment			
	Bituminous				Subbituminous/Lignite				Bituminous				Subbituminous/Lignite			
	Count	min	med	max	Count	min	med	max	Count	min	med	max	Count	min	med	max
SO_4 (mg/L)	5	845	2,350	2,440	5	2,870	3,830	6,690	36	45	171	1,830	5	91	131	1.120
Sr (ug/L)	6	1,320	4,600	10,300	5	<30	303	12,000	36	170	671	5,610	5	530	649	1,830
TIC (mg/L)	5	24	55	80	5	1.7	32	105	36	0.75	5.5	115	5	5.9	22	49
Tl (ug/L)	6	<0.1	0.47	5.3	5	<0.1	<0.1	<0.5	36	<0.1	0.68	18	5	<0.1	<0.1	<0.1
TOC (mg/L)	5	1.3	4.1	4.6	5	5.3	49	55	36	<0.09	0.64	22	5	0.40	6.0	7.9
U (ug/L)	6	7.4	19	37	5	0.22	5.7	21	36	<0.1	0.70	61	5	<0.02	1.1	1.2
V (ug/L)	6	<0.83	3.1	44	5	3.6	635	5,020	36	2.6	39	754	5	10	17	236
Zn (ug/L)	6	<2	45	289	5	<2	<5	12	36	<2	8.7	90	5	<2	8.4	11
DO (%)	6	16	53	95	5	0.20	14	87	34	2.9	40	165	5	1.6	4.5	35
ORP (mV)	6	213	247	280	5	111	240	276	33	41	240	409	5	225	289	303
pH (SU)	6	6.5	6.9	7.4	5	8.8	10	11	34	4.3	7.6	11	5	8.0	8.9	12
EC (umho/cm)	6	2,000	3,682	4,915	5	6,174	7,690	12,760	34	174	578	2,980	5	680	990	4,020
Temp (°C)	6	14	15	17	5	11	17	22	34	10	22	32	5	16	30	36

Table 4-4
Statistical Summary of FGD Leachate Samples by Management Method and Coal Type

	Landfill				Landfill				Impoundment*			
	Bituminous				Subbituminous/Lignite				Subbituminous/Lignite			
	Count	min	med	max	Count	min	med	max	Count	min	med	max
Ag (ug/L)	6	<0.2	<0.2	<0.2	3	<0.2	<0.2	<0.2	5	<0.2	<0.2	<1
Al (ug/L)	6	<24	149	229	3	<26	26	608	5	31	610	890
As (ug/L)	6	11	28	49	3	12	14	110	5	17	29	230
B (ug/L)	6	1,450	2,950	3,260	3	7,310	11,900	15,600	5	26,800	50,200	98,500
Ba (ug/L)	6	58	63	80	3	70	86	134	5	<30	75	158
Be (ug/L)	6	<0.2	<0.5	<0.8	3	<0.2	<0.2	<1	5	<0.2	<1	1.5
Ca (mg/L)	6	669	704	730	3	234	351	528	5	524	570	600
Cd (ug/L)	6	0.51	0.83	1.9	3	0.75	3.8	13	5	0.50	6.6	12
Cl (mg/L)	6	911	1,170	1,260	3	19	98	859	5	345	572	2,330
Co (ug/L)	6	<0.028	<0.55	0.093	3	<0.11	0.11	1.6	5	<0.092	6.1	78
CO_3 (mg/L)	6	0.73	2.9	7.3	3	0.047	0.44	21	5	<0.01	<0.01	1.7
Cr (ug/L)	6	<0.2	<0.35	<0.5	3	0.46	0.91	5.7	5	<0.4	<1.7	53
Cu (ug/L)	6	<0.26	0.34	3.5	3	0.60	1.5	3.6	5	0.41	6.9	44
Fe (ug/L)	6	<13	<31.5	<50	3	<4.6	<25	4.6	5	<4.7	4.7	1,200
H_2CO_3 (mg/L)	6	<0.01	<0.01	<0.01	3	<0.01	<0.01	<0.01	5	<0.01	<0.01	0.041
HCO_3 (mg/L)	6	3.4	5.9	16	3	0.50	15	87	5	4.9	7.9	38
Hg (ng/L)	3	1.2	12	21	2	0.82	40	79	3	1.9	4.2	28
K (mg/L)	6	470	500	609	3	10	30	350	5	20	80	500
Li (ug/L)	6	5,890	6,415	7,070	3	<20	33	130	5	<20	1,050	3,390
Mg (mg/L)	6	<2.5	4.3	9.6	3	<0.05	8.2	77	5	23	1,000	5,810
Mn (ug/L)	6	16	50	202	3	<0.1	<4	197	5	113	564	1,170
Mo (ug/L)	6	180	316	368	3	310	910	3,520	5	164	570	60,800
Na (mg/L)	6	247	291	341	3	108	141	2,310	5	606	1,330	4,630
Ni (ug/L)	6	<2	<3	3.5	3	<2	4.3	7.5	5	3.3	153	597
Pb (ug/L)	6	<0.14	<0.17	<0.2	3	<0.14	<0.2	0.39	5	<0.2	0.32	3.5
Sb (ug/L)	6	<0.1	<0.22	0.14	3	1.3	2.3	4.7	5	0.72	4.6	22
Se (ug/L)	6	1.1	2.4	3.9	3	17	51	65	5	3.7	159	2,360
Si (ug/L)	6	1,810	1,950	3,000	3	2,600	3,940	21,000	5	400	10,500	45,400

Table 4-4
Statistical Summary of FGD Leachate Samples by Management Method and Coal Type (continued)

	Landfill				Landfill				Impoundment*			
	Bituminous				Subbituminous/Lignite				Subbituminous/Lignite			
	Count	min	med	max	Count	min	med	max	Count	min	med	max
SO_4 (mg/L)	6	1,350	1,510	1,620	3	836	1,450	4,710	5	2,080	10,200	30,500
Sr (ug/L)	6	3,520	4,095	4,500	3	5,960	9,140	9,730	5	1,500	11,700	16,900
TIC (mg/L)	6	0.95	2.5	3.3	3	3.0	4.3	18	5	1.7	2.4	7.9
Tl (ug/L)	6	<0.1	<0.42	0.34	3	<0.1	<0.1	<0.1	5	<0.1	<0.5	2.9
TOC (mg/L)	6	0.51	1.4	2.4	3	7.9	8.1	19	5	9.9	21	50
U (ug/L)	6	<0.022	<0.15	0.097	3	<0.01	0.97	10	5	<0.2	0.68	16
V (ug/L)	6	<0.69	0.98	4.5	3	4.0	6.8	400	5	<1.8	15	103
Zn (ug/L)	6	<2	<3.5	12	3	<2	5.4	19	5	<2	23	68
DO (%)	6	11	23	81	3	0.40	65	95	5	0.20	0.30	36
ORP (mV)	6	46	104	220	3	18	339	341	5	1.5	271	356
pH (SU)	6	9.0	10.0	10.5	3	7.8	8.0	12.0	5	6.2	7.4	9.0
EC (umho/cm)	6	5,550	6,211	6,897	3	2,190	2,870	11,560	5	4,770	12,950	26,140
Temp (°C)	6	12	16	16	3	19	19	21	5	9.9	19	27

* Impoundment category includes two samples from impoundments where water is recirculated

Management in Impoundments Versus Landfills

Concentration ranges for ash leachate in impoundments and landfills are compared in Table 4-5, and selected constituents are graphically illustrated in Figure 4-11 for ash from bituminous coal, and Figure 4-12 for ash from subbituminous/lignite coal. Graphical comparisons for all analyzed constituents are presented in Appendix C, Figures C-1 and C-2.

Table 4-5
Comparison of Ash Leachate Concentrations From Landfills and Impoundments

	Landfill Concentration Higher			Impoundment Concentration Higher	
	Strongly	**Moderately**	**No Difference**	**Moderately**	**Strongly**
Ca (mg/L)	◆		○		
Cl (mg/L)		◆	○		
CO$_3$ (mg/L)		○	◆		
HCO$_3$ (mg/L)	◆	○			
K (mg/L)	◆○				
Mg (mg/L)	◆		○		
Na (mg/L)	◆○				
SO$_4$ (mg/L)	◆○				
Ag (ug/L)			◆○		
Al (ug/L)			○		◆
As (ug/L)	○				◆
B (ug/L)	◆○				
Ba (ug/L)					○◆
Be (ug/L)			◆○		
Cd (ug/L)	◆○				
Co (ug/L)	◆○				
Cr (ug/L)	○		◆		
Cu (ug/L)	○			◆	
Fe (ug/L)			○	◆	
Hg (ng/L)	◆○				
Li (ug/L)	◆		○		
Mn (ug/L)	◆		○		
Mo (ug/L)	◆○				
Ni (ug/L)		◆○			
Pb (ug/L)		○		◆	
Sb (ug/L)	○			◆	
Se (ug/L)	○	◆			
Si (ug/L)			◆	○	
Sr (ug/L)	◆		○		
Tl (ug/L)			○	◆	
U (ug/L)	◆	○			
V (ug/L)	○				◆
Zn (ug/L)		◆	○		

Notes:

◆ = bituminous source coal ○ = subbituminous/lignite source coal

Strongly indicates that interquartile range of one dataset is higher than the other dataset, or median is one order of magnitude higher in one dataset

Moderately indicates that a portion of the interquartile range, and the median, of one dataset is higher than the other dataset.

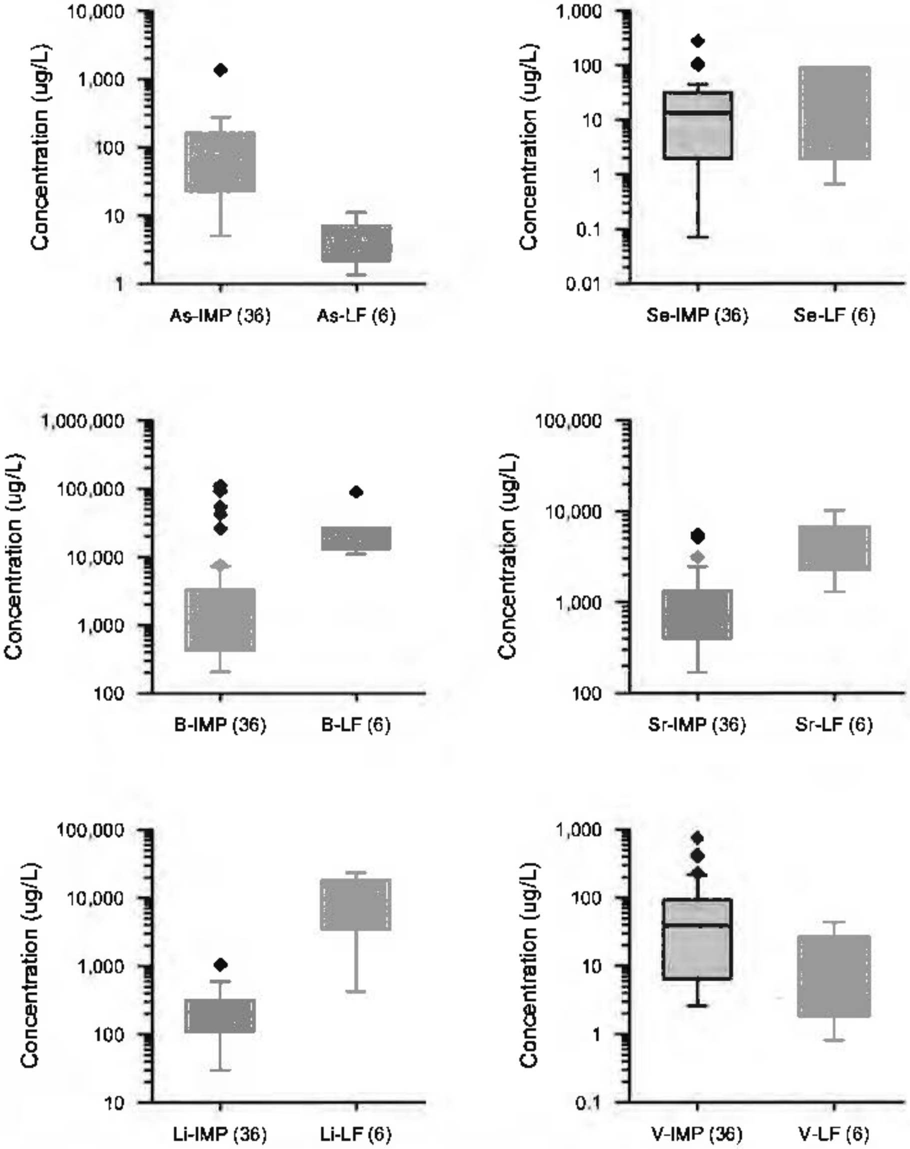

Figure 4-11
Comparison of Field Leachate Concentrations for Selected Constituents: Bituminous Coal Ash, Landfill versus Impoundment (See Appendix C for other parameters)

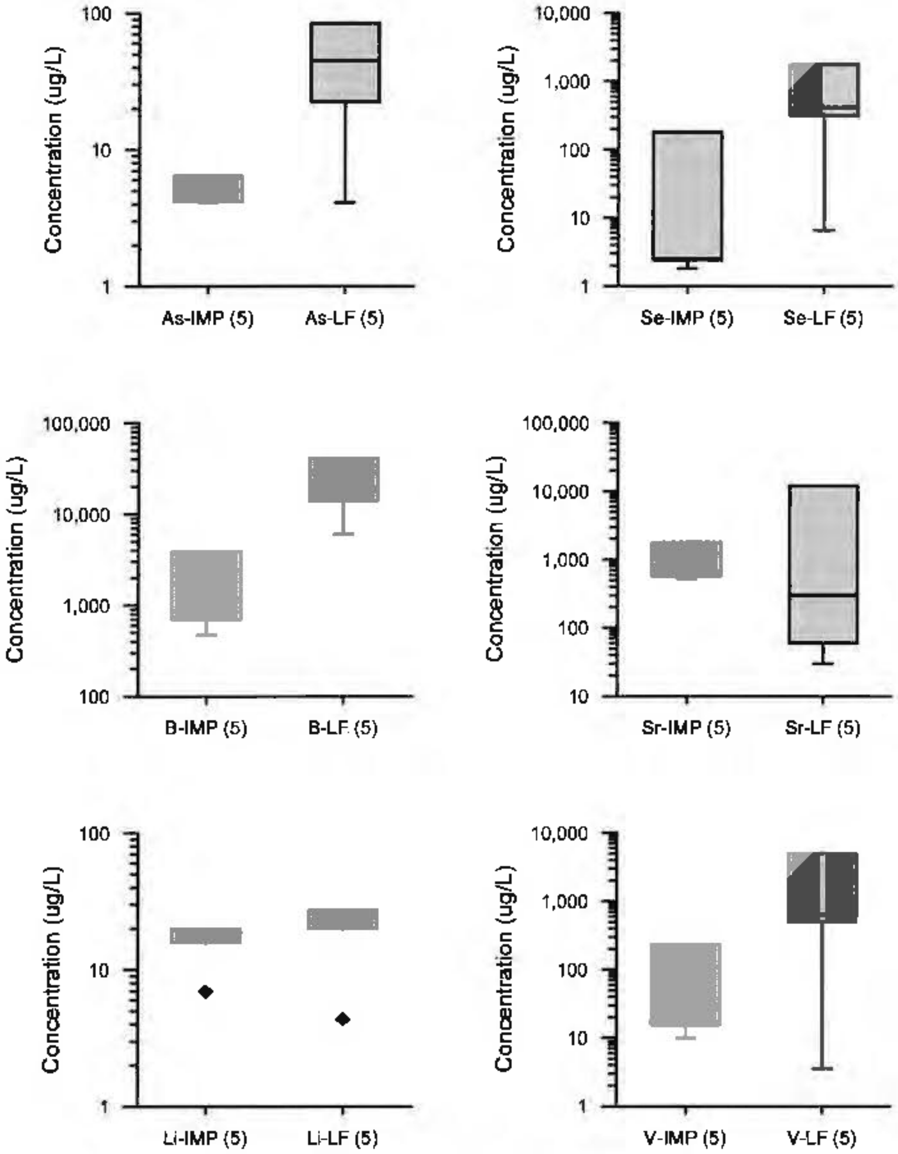

Figure 4-12
Comparison of Field Leachate Concentrations for Selected Constituents: Subbituminous/ Lignite Coal Ash, Landfill versus Impoundment (See Appendix C for other parameters)

Most constituents (22 out of the 34 analyzed) had higher concentration in the landfill leachate samples than in the impoundment leachate samples. The most significant factor contributing to this result is that the leachate in impoundments has a higher water to solid ratio than leachate in landfills, and is, in essence, more dilute. The pond water is more dilute due to the volume of water required to hydraulically transport ash, and the porewater in impoundments is often more dilute because constituents that are easily leached from the surface of the ash particles are washed off during sluicing.

Bituminous versus Subbituminous and Lignite Source Coal

Concentration ranges for ash leachate in impoundments and landfills are compared in Table 4-6, and selected constituents are graphically illustrated in Figure 4-13 for landfill leachate, and Figure 4-14 for impoundment leachate. All analyzed constituents are graphically illustrated in Appendix C, Figures C-3 and C-4.

The field leachate data demonstrate the dependence of several individual constituents on the source coal type. For major ions, leachate from bituminous coal ash had higher concentrations of calcium in both landfill and impoundment settings, while leachate from subbituminous/lignite coal had higher concentrations of carbonate and sodium in both management settings.

Minor and trace constituents for which concentrations in leachate from bituminous coal ash are higher than in leachate from subbituminous/lignite coal, regardless of management environment, are cobalt, lithium, manganese, nickel, antimony, thallium, and zinc (Table 4-6). The difference for lithium is particularly strong. This non-reactive element had a concentration range of 3,400 to 23,600 µg/L in landfill leachate from bituminous coal versus 5 to 27 µg/L in landfill leachate from subbituminous/lignite coal, and 30-1,060 µg/L (bituminous) versus 7 to 20 µg/L (subbituminous/lignite) in impoundment leachate (Figures 4-13 and 4-14). Manganese had similarly large concentration differences, particularly in the landfill environment. Thallium was only detected in leachate from bituminous coal ash (31 of 42 samples, 74 percent), and was not detected in leachate from subbituminous/lignite coal ash (0 of 10 samples).

Minor and trace constituents for which concentrations in leachate from subbituminous/lignite coal ash were higher than in leachate from bituminous coal, regardless of management environment, are aluminum, chromium, copper, and mercury (Table 4-6). The difference is most notable for aluminum and mercury, where the concentrations are an order of magnitude or more higher for both landfill and impoundment leachate.

Table 4-6
Comparison of Ash Leachate Concentrations for Bituminous and Lignite/Subbituminous Source Coal

	Bituminous Concentration Higher			Lig/Subbit Concentration Higher	
	Strongly	Moderately	No Difference	Moderately	Strongly
Ca (mg/L)	◆	○			
Cl (mg/L)			◆		○
CO_3 (mg/L)					○◆
HCO_3 (mg/L)			◆	○	
K (mg/L)		◆	○		
Mg (mg/L)	◆		○		
Na (mg/L)					○◆
SO_4 (mg/L)			○		◆
Ag (ug/L)			◆○		
Al (ug/L)					○◆
As (ug/L)	○				◆
B (ug/L)			○◆		
Ba (ug/L)			◆○		
Be (ug/L)			◆○		
Cd (ug/L)		○	◆		
Co (ug/L)		◆○			
Cr (ug/L)				○	◆
Cu (ug/L)				○	◆
Fe (ug/L)			◆○		
Hg (ng/L)					◆○
Li (ug/L)	◆○				
Mn (ug/L)	◆○				
Mo (ug/L)		○		◆	
Ni (ug/L)		◆○			
Pb (ug/L)			○	◆	
Sb (ug/L)	○	◆			
Se (ug/L)			○		◆
Si (ug/L)		◆	○		
Sr (ug/L)		◆	○		
Tl (ug/L)	○	◆			
U (ug/L)		◆	○		
V (ug/L)			○		◆
Zn (ug/L)	◆	○			

Notes:

◆ = Landfills ○ = Impoundments

Strongly indicates that interquartile range of one dataset is higher than the other dataset, or median is one order of magnitude higher in one dataset

Moderately indicates that a portion of the interquartile range, and the median, of one dataset is higher than the other dataset.

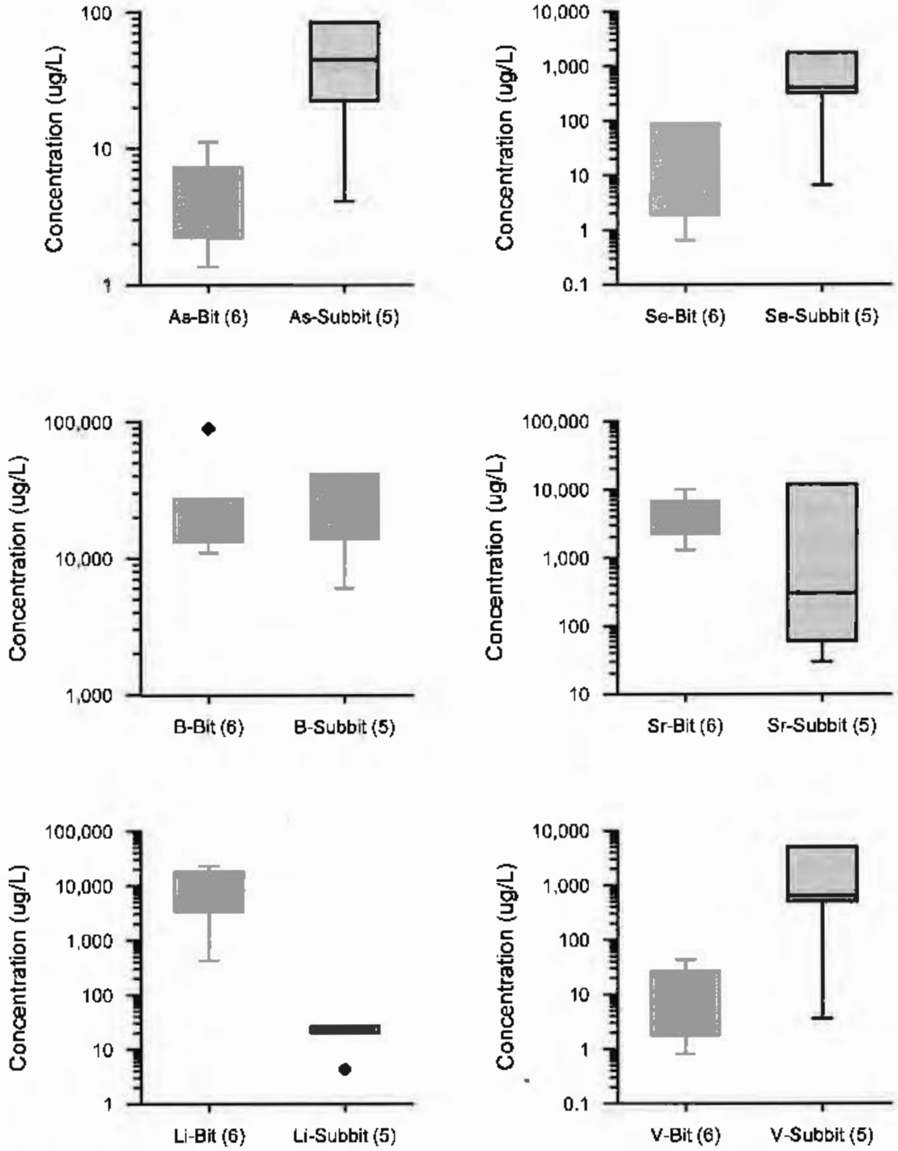

Figure 4-13
Comparison of Field Leachate Concentrations for Selected Constituents: Bituminous vs Subbituminous/Lignite Coal Ash, Landfills (See Appendix C for other parameters)

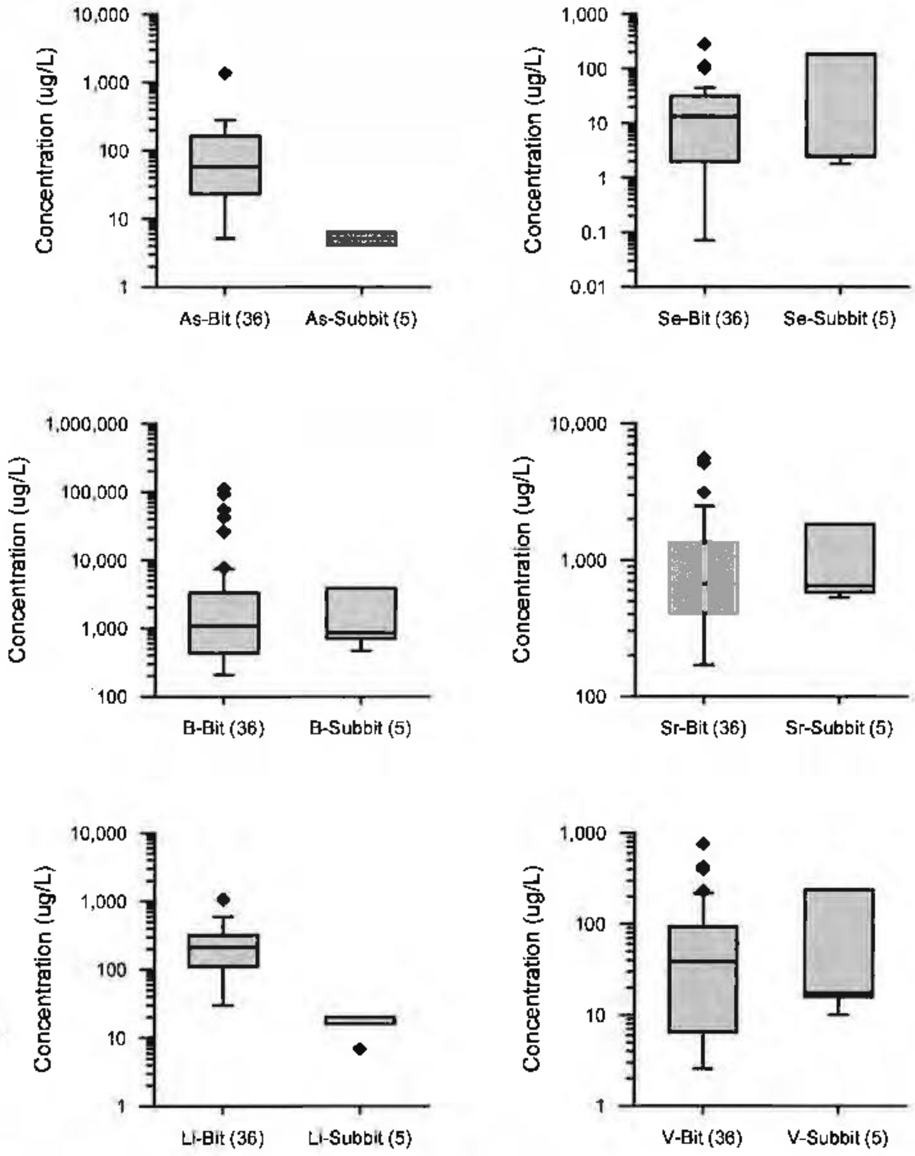

Figure 4-14
Comparison of Field Leachate Concentrations for Selected Constituents: Bituminous vs Subbituminous/Lignite Coal Ash, Impoundments (See Appendix C for other parameters)

Key constituents for which a consistent difference between bituminous and subbituminous/lignite leachate were not found included:

- Arsenic: Concentrations in impoundments were significantly higher when the source coal was subbituminous/lignite, and concentrations in landfills were significantly higher when the source coal was bituminous. Site-specific pH and redox conditions play a significant role in arsenic leaching.
- Boron: The highest boron concentrations (50,000 to 112,000 µg/L) were in leachate from bituminous coal ash, while the highest subbituminous/lignite concentration was 41,000 µg/L. However, there were numerous samples from bituminous ash leachate with considerably lower concentration, and as a result, the medians and interquartile ranges for boron were similar for the two coal types.
- Selenium and Vanadium: Concentrations of these two elements were, for the most part, higher in leachate from subbituminous/lignite coal ash than in leachate from bituminous coal ash. However, there were several relatively high concentrations in bituminous ash impoundments that increased the median sufficiently so that there were no significant differences in the interquartile ranges.
- Strontium and Uranium: For landfill leachate, these elements had significantly higher concentration when the source coal was bituminous than when the source coal was subbituminous/lignite. In impoundment leachate, the bituminous median values were lower than the subbituminous/lignite median values, although the maximum concentrations were significantly higher in the bituminous samples.

Evaluation of Unique Samples

Several samples stand out as unique either due to relatively high concentrations of selected constituents or power plant attributes. Table 4-7 and Table 4-8, respectively, list the maximum concentration of each constituent analyzed in ash and FGD leachate, and whether or not this concentration is significantly higher than the next highest concentration from another site. Table 4-8 excludes samples 106 and 107, which are from an FGD impoundment where concentrations of most constituents are very high because sluice water is recirculated.

For ash leachates, samples from three sites had four to seven constituents with the highest concentration: 50213 (7), 25410A (4), and 49003B (4). 50213 site had the highest concentrations of Co, CO_3, Cr, Cu, Na, Se, and SO_4. The 50213 site is a landfill with pH range from 10.0 to 10.3. The power plant units associated with the 50213 site are dry-bottom PC boilers that have burned subbituminous coal during the active life of the site. Two smaller units have cold-side electrostatic precipitators, while a larger unit utilized a hot-side precipitator for most of the active life of the 50213 site and a fabric filter for the last two years. The larger unit has a low-NOx burner. Leachate was collected in two lysimeters that directly underlie the ash. The leachate at this site was alkaline, with a pH higher than 10. Relatively high ORP values, low iron concentrations, and oxidized forms of arsenic, selenium, and chromium indicate that redox conditions at this site were oxidizing. The only uncommon attributes of this site are the lysimeters used to collect the leachate and the hot-side precipitator. Two other sites received ash from hot-side precipitators (40109 and 43035). These sites did not have similarly high leachate concentrations, however they are both impoundments that receive ash derived from bituminous coal.

Table 4-7
Ash Leachate Samples With Maximum Concentrations

	Count	Max	Sample	Site	Next*	Comment
Ag (ug/L)	67	2.0	HN-1	13115B	1.1	The three highest silver concentrations came from core samples.
Al (ug/L)	67	44,400	016	25410A	30,000	This sample also had relatively high concentrations of B, Cd, K, Mo, Pb, Si, V, and Zn.
As (ug/L)	67	1,380	061	33104	727	No consistent correlations to site/plant attributes.
B (ug/L)	67	112,000	013	14093	109,000	Concentration not significantly higher than other samples.
Ba (ug/L)	67	657	092	27413	545	Concentration not significantly higher than other samples.
Be (ug/L)	67	8.6	043	33106	5.2	Only four beryllium detects; these occurred in four of the five samples with pH lower than 6.0.
Ca (mg/L)	66	681	012	14093	665	Concentration not significantly higher than other samples.
Cd (ug/L)	67	65	016	25410A	52	Two highest concentrations in samples from plants with cyclone boilers, both burn petroleum coke, 25410A also burns used tires.
Cl (mg/L)	66	92	097	50212	87	Concentration not significantly higher than other samples.
Co (ug/L)	67	133	002	50213	113	No consistent correlations to site/plant attributes.
CO_3 (mg/L)	63	152	003	50213	53	No consistent correlations to site/plant attributes.
Cr (ug/L)	67	5,100	002	50213	2,000	May be partially due to erosion of balls (30% Cr) that are used when pulverizing the coal at 50213 plant.
Cu (ug/L)	67	494	002	50213	452	Second lysimeter (003) at this site had a concentration of 62 µg/L.
Fe (ug/L)	67	25,600	079	22346	14,700	No consistent correlations to site/plant attributes.
H_2CO_3 (mg/L)	63	3.4	043	33106	2.8	Highest at sites with low pH.
HCO_3 (mg/L)	63	535	097	50212	535	Concentration not significantly higher than other samples.
Hg (ng/L)	22	61	098	50183	37	Resample concentration at this point was 6 ng/L.
K (mg/L)	66	277	HN-1	13115B	255	Concentration not significantly higher than other samples.
Li (ug/L)	67	23,600	111	49003B	6,940	Two leachate collection system points were sampled twice et this site. For both sample events, one returned high lithium concentration and one returned lower, although still high lithium concentrations. Similar pH, ORP and DO values.
Mg (mg/L)	66	236	111	49003B	188	Concentration not significantly higher than other samples.
Mn (ug/L)	67	4,170	018	13115B	4,110	Concentration not significantly higher than other samples.
Mo (ug/L)	67	39,600	016	25410A	25,400	Two highest concentrations in samples from plants with Cyclone boilers, both burn petroleum coke, 25410A also burns used tires.
Na (mg/L)	66	3,410	002	50213	1,700	Two highest concentrations in samples from this site.
Ni (ug/L)	67	189	111	49003B	128	Two leachate collection system points were sampled twice at this site. For both sample events, one returned high nickel concentration and one returned low nickel concentrations. Similar pH, ORP and DO values.
Pb (ug/L)	67	8.0	051	40109	4.6	Two of three samples with lead higher than 1 µg/L were also the only two samples with pH < 5. Other sample (016) had pH of 11.5.
Sb (ug/L)	67	59	023	49003A	27	Antimony concentrations at this site are unusually high.
Se (ug/L)	67	1,760	003	50213	428	Two highest concentrations in samples from this site.

Table 4-7
Ash Leachate Samples With Maximum Concentrations (continued)

	Count	Max	Sample	Site	Next*	Comment
Si (ug/L)	67	19,000	016	25410A	18,500	Concentration not significantly higher than other samples.
SO_4 (mg/L)	66	6,690	002	50213	3,830	Two highest concentrations in samples from this site
Sr (ug/L)	67	12,000	108	34186A	11,100	Concentration not significantly higher than other samples.
TIC (mg/L)	66	115	18	13115B	105	Concentration not significantly higher than other samples.
Tl (ug/L)	67	18	032	35015B	12	Concentration not significantly higher than other samples.
TOC (mg/L)	66	57	098	50183	55	Concentration not significantly higher than other samples.
U (ug/L)	67	61	023	49003A	37	Several other elements relatively high in this sample.
V (ug/L)	67	5,020	010	23214	1,230	Two highest concentrations in samples from plants with Cyclone boilers, both burn petroleum coke.
Zn (ug/L)	67	289	111	49003B	130	Two leachate collection system points were sampled twice at this site twice. For both sample events, one returned high zinc concentration and one returned low zinc concentrations. Similar pH, ORP and DO values.

* next highest concentration from a different site.

The high chromium concentrations at 50213 were attributed by the utility to high chromium concentration in the flue gas as a result of erosion of the balls used to pulverize the coal. Chromium volatilized in the flue gas may condense on the ash particles and then readily leach from the particles in the landfill environment. High concentrations of other elements may be due to limited dilution. The ash is not saturated at this site; instead, the lysimeters collect porewater that was in tight contact with the ash particles.

The 49003B site is also a landfill and had the highest concentrations of Li, Mg, Ni, and Zn, and a pH range from 6.5 to 7.0. The 49003B source power plant has no unusual attributes, yet concentrations of most elements at one of the two leachate collection system sample points were higher than median concentrations for the whole sample set.

The 25410A site is an impoundment and had the highest concentrations of Al, Cd, Mo, and Si, and a pH of 11.7. The 25410A plant is different from most plants in the study in that it burns a blend of fuels including pet coke and tires in a cyclone boiler. The elevated concentrations at the 25410A site may to be associated with either the cyclone boiler or the fuel mixture, or both.

Table 4-8 lists maximum concentrations in FGD leachate samples. In general, there were too few samples to conclusively correlate high or low concentrations to plant and site attributes.

Table 4-8
FGD Leachate Samples With Maximum Concentrations

	Count	Max.	Sample	Site	Next*	Comment
Ag (ug/L)	12	50183L ND				All values below detection limits,
Al (ug/L)	12	890	008	23223B	608	No consistent correlations to site/plant attributes.
As (ug/L)	12	110	106	34186C	49	High DO (95%), low ORP (18 mV), pH 12.
B (ug/L)	12	98,500	009	23223B	15,600	No consistent correlations to site/plant attributes.
Ba (ug/L)	12	134	106	34186C	90	Concentration not significantly higher than other samples.
Be (ug/L)	12	50183L ND				All values below detection limits,
Ca (mg/L)	12	730	029	35015A	577	Concentration not significantly higher than other samples.
Cd (ug/L)	12	13	106	34186C	12	No consistent correlations to site/plant attributes.
Cl (mg/L)	12	1,260	028	35015A	859	No consistent correlations to site/plant attributes.
Co (ug/L)	12	78	009	23223B	1.6	No consistent correlations to site/plant attributes.
CO_3 (mg/L)	12	21	106	34186C	7.3	High value pH related.
Cr (ug/L)	12	53	009	23223B	5.7	No consistent correlations to site/plant attributes.
Cu (ug/L)	12	44	008	23223B	3.6	No consistent correlations to site/plant attributes.
Fe (ug/L)	12	1,200	007	23223B	4.6	Only sample with pH below 7 (6.2)
H_2CO_3 (mg/L)	12	0.041	007	23223B	<0.01	Only sample with pH below 7 (6.2)
HCO_3 (mg/L)	12	87	006	23223A	16	No consistent correlations to site/plant attributes.
Hg (ng/L)	8	79	128	43034	28	Most oxidized FGD sample collected.
K (mg/L)	12	609	121	35015A	350	No consistent correlations to site/plant attributes.
Li (ug/L)	12	7,070	122	35015A	2,720	No consistent correlations to site/plant attributes.
Mg (mg/L)	12	1,990	009	23223B	77	No consistent correlations to site/plant attributes.
Mn (ug/L)	12	704	007	23223B	202	No consistent correlations to site/plant attributes.
Mo (ug/L)	12	60,800	007	23223B	3,520	No consistent correlations to site/plant attributes.
Na (mg/L)	12	2,310	106	34186C	1,330	No consistent correlations to site/plant attributes.
Ni (ug/L)	12	597	007	23223B	7.5	No consistent correlations to site/plant attributes.
Pb (ug/L)	12	3.5	007	23223B	0.39	Detects only for with lignite/subbituminous ash.
Sb (ug/L)	12	4.7	006	23223A	4.6	No consistent correlations to site/plant attributes.
Se (ug/L)	12	2,360	009	23223B	65	No consistent correlations to site/plant attributes.
Si (ug/L)	12	21,000	106	34186C	12,700	No consistent correlations to site/plant attributes.
SO_4 (mg/L)	12	10,400	009	23223B	4,710	No consistent correlations to site/plant attributes.
Sr (ug/L)	12	16,900	007	23223B	9,730	No consistent correlations to site/plant attributes.
TIC (mg/L)	12	18	006	23223A	4.3	No consistent correlations to site/plant attributes.
Tl (ug/L)	12	2.9	009	23223B	0.34	No consistent correlations to site/plant attributes.
TOC (mg/L)	12	21	007	23223B	19	No consistent correlations to site/plant attributes.
U (ug/L)	12	10	006	23223A	0.97	No consistent correlations to site/plant attributes.
V (ug/L)	12	400	106	34186C	18	No consistent correlations to site/plant attributes.
Zn (ug/L)	12	34	009	23223B	23	No consistent correlations to site/plant attributes.

* next highest concentration from a different site.

Typical plant components in this study included wet-bottom coal-fired PC units, cold-side ESPs, and wet FGD systems. Less common were plants with cyclone boilers, non-coal fuel sources, hot-side ESPs, and dry FGD systems. Results for these less common configurations are discussed below:

- Cyclone Boilers: The power plants associated with 23214, 25410A, and 25410B use cyclone boilers. Cyclone boilers tend to burn hotter than PC boilers, and also burn a wider variety of fuels. These plants are the only ones sampled that burn petroleum coke, and the fuel burned at 25410A and 25410B also includes used tires. Leachate sampled at these sites had higher than median concentrations of most elements, and the highest concentrations of cadmium, molybdenum, and vanadium. Vanadium is often associated with petroleum coke. The relatively high concentrations from these samples may reflect the effect of the cyclone boiler, or the fuel. Concentrations at one of the sample locations from 25410A and 25410B were often higher than at 23214, but not sufficiently so to indicate any effects from the tires on ash leachate composition.
- Hot-Side ESPs: The plants associated with the 40109, 43035, and 50213 sites have hot-side ESP's, while the other plants with ESPs are cold-side. The 40109 and 43035 samples did not stand out in terms of high or low concentration. These sites are impoundments and receive bituminous coal ash. As previously discussed, the 50213 site is a landfill and received subbituminous ash, and had relatively high concentrations of several constituents, including selenium. The high selenium concentration is unusual in that less selenium capture in ash is expected from plants with hot-side ESPs, due to the higher temperatures at the collection point. Presence in the leachate may indicate that the selenium captured in the hot-side is present in a relatively soluble form for the subbituminous coal ash. Similarly, the relatively high concentrations at the 50213 site may indicate increased leachability for the subbituminous ash collected at the hotter temperatures. However, this is only one site and more data from plants burning subbituminous coal with hot-side ESPs are needed to confirm this observation. The relatively low concentrations seen at the 40109 and 43035 sites may suggest that the 50213 data are specific to the particular plant, fuel, or management setting.
- Oil Ash: 22346 is the only site sampled where oil ash was managed with coal ash. The leachate from the ash sampled at this site did not stand out in terms of low or high concentration. Since oil ash is generally high in vanadium and nickel, this result suggests that either the effect of the oil ash is not appreciable due to its volume relative to the coal ash, or that the coal ash geochemically mitigates releases from the oil ash.
- Wet-Bottom PC Boiler: 43034 is the only plant that has a wet-bottom PC boiler. The leachate from the FGD byproduct sampled at this site did not stand out in terms of low or high concentration.
- Dry FGD System: 23223A is associated with the only power plant that used a spray dryer system; all other FGD samples came from power plants with wet FGD systems. With a few exceptions, the leachate from this site tended to have relatively low concentrations. The most notable exception was uranium, which had a concentration of 10 μg/L at this site and less than 1 μg/L at the other FGD sites.

5

SPECIATION OF ARSENIC, SELENIUM, CHROMIUM, AND MERCURY AT CCP MANAGEMENT FACILITIES

The mobility and toxicity of inorganic constituents is sometimes strongly dependent on their aqueous speciation. This is particularly true for arsenic, selenium, and chromium, which can be present at elevated concentrations in CCP leachate. Important species in leachate and groundwater are As(III) and As(V), Se (IV) and Se(VI), and Cr(III) and Cr(VI). Organic species for the other constituents (e.g., methylarsenic acid) were not considered in this study. Generally speaking, As(III) and Cr(VI) are more toxic and more mobile than As(V) and Cr(III); and Se(IV) is more toxic to most terrestrial and aquatic wildlife than the more mobile Se(VI). It is important to know the species present in leachate in order to assess potential impacts associated with these constituents. Although mercury is generally present only at very low concentrations in ash leachate and is very immobile in groundwater, the organic mercury species (monomethyl mercury) can bioaccumulate to toxic levels in the surface water environment and is therefore of interest.

Evaluation of Speciation Sample Preservation Methods

Speciation of arsenic and selenium in field samples with widely varying matrix characteristics such as the CCP leachate is challenging because preservation techniques and analytical interferences can have a significant impact on the results. Several preservation methods (HCl, cryofreezing, EDTA, HNO_3, none) were compared on sample splits from one site, and a comparison of speciation results for 32 split samples from several sites using two preservation methods (HCl and cryofreezing) are presented in Appendix D.

Results varied by sample, and suggested that, regardless of preservation method, a critically important factor was minimizing hold times. Species recovery was poorest for the samples collected in 2003 (samples 001 through 032) due to longer holding times for the frozen samples. Importantly, the split sample data collected during this study indicated that, even when overall species recovery was low, the relative predominance of reduced or oxidized species of arsenic and selenium were similar regardless of preservation method or laboratory used. Speciation results presented in the following sections are for samples that were preserved by cryofreezing in the field with liquid nitrogen.

Arsenic

Overview of Results

Total arsenic was detected at concentrations well above the detection limit in all collected water samples (n = 81 after removing all QA samples)[4], and at least one species was detected in all except two samples. Review of duplicate samples indicated that analytical results were usually reproducible, particularly when concentrations were greater than 1 µg/L (Table 5-1).

Excluding duplicates, 51 of the 81 samples contained detectable concentrations of arsenite, 73 samples had detectable concentrations of arsenate, and 30 samples contained detectable concentrations of arsenic species other than arsenite or arsenate. These other species are either monomethyl arsenate or soluble arsenic-sulfur (As-S) compounds. Both types of other arsenic species are technically As(V) compounds (i.e., they contain arsenic in the +5 oxidation state); although they were not grouped with As(V) because they potentially have different chemical and environmental characteristics.

Monomethyl arsenate is either formed by microbial methylation of inorganic arsenic or used as a biocide. However, contrary to the case of mercury, the methylated (i.e., organic) forms of arsenic are less toxic than the inorganic forms, and are therefore generally not regarded as a source of concern. The soluble As-S compounds are formed by reaction of arsenite and free sulfide in reducing waters, and there are also some studies suggesting that these species are less toxic than arsenite and arsenate. In all except two samples (which had relatively low total arsenic concentration), the other arsenic species constituted the minority of all arsenic present (<20 percent).

The arsenic speciation mass balance (the sum of all individual species determined in a given sample divided by the independently-determined total arsenic concentration) varied strongly, and was not always satisfactory. Less than half (35 of 81 samples) had a recovery greater than 80 percent (Figure 5-1). Reasons for this somewhat disappointing performance likely originate from the complexity of the studied samples. Species recovery for the 2004/2005 samples was better than for the 2003 samples due to reduced holding times and other laboratory refinements (Appendices D and E).

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[4] QA samples include blanks and duplicates.

Table 5-1
Arsenic Speciation Data

Site	Sample	Source	CCP	Coal	Total As (ug/L)	As(III) (ug/L)	As(V) (ug/L)	As, other species (ug/L)	Sum of Species	% Recovery	% As(III)	% As(V)	% As (other)
50210	001	LF	FA,BA	Mix	20	<0.3	9.5	2.1	11.6	57%			
50213	002	LF	FA	Subbit	48	<6	47	<6	47.2	**98%**	0.0%	100.0%	0.0%
50213	003	LF	FA	Subbit	84	<6	69	<6	68.8	**82%**	0.0%	100.0%	0.0%
50183	004	LF	FA,BA	Mix	19	8.4	5.2	<0.3	13.5	73%			
50183	005	LF	FA,BA	Mix	3.0	<0.2	1.3	<0.2	1.3	45%			
23223A	006	LF	SDA	Subbit	12	<0.3	0.94	<0.3	0.9	8%			
23223B	007	IMP	FGD	Subbit	20	<2	<2	<2	0.0	0%			
23223B	008	IMP	FGD	Subbit	17	0.75	<0.5	<0.3	0.7	4%			
23223B	009	IMP	FGD	Subbit	29	<6	<10	<6	0.0	0%			
23214	010	LF	FA	Subbit	22	1.5	10	<0.6	11.5	52%			
14093	012	IMP	FA	Bit	238	97	66	<0.6	163.3	69%			
14093	013	IMP	FA	Bit	22	3.7	<0.5	<0.3	3.7	17%			
14093	*013D*	*Dup*	*FA*	*Bit*	*22*	*1.9*	*<0.5*	*<0.3*	*1.9*	*9%*			
14093	014	IMP	FA	Bit	163	1.9	86	0.86	88.6	54%			
25410A	015	IMP	FA,BA	Blend	24	<0.6	24	<0.6	23.6	**99%**	0.0%	100.0%	0.0%
25410A	016	IMP	FA,BA	Blend	69	<0.6	25	<0.6	24.7	36%			
13115A	017	IMP	FA,BA	Subbit	4.1	0.88	<0.08	0.069	1.0	23%			
13115B	018	IMP	FA,BA	Bit	23	0.42	5.2	<0.06	5.6	24%			
13115A	019	IMP	FA	Subbit	5.1	0.57	<0.08	<0.06	0.6	11%			
13115A	020	IMP	FA,BA	Subbit	4.2	1.0	0.53	0.15	1.7	40%			
49003A	021	IMP	FA	Bit	194	2.1	208	<0.3	210.0	**108%**	1.0%	99.0%	0.0%
49003A	022	IMP	FA	Bit	11	13	0.49	<0.06	13.0	**118%**	96.3%	3.7%	0.0%
49003A	023	IMP	FA	Bit	218	0.79	189	<0.3	189.5	**87%**	0.4%	99.6%	0.0%
49003B	024	LF	FA	Bit	11	0.36	<0.2	<0.2	0.4	3%			
49003B	025	LF	FA	Bit	6.5	1.4	<0.08	<0.06	1.4	21%			
49003A	026	IMP	FA	Bit	11	11	0.40	<0.2	11.6	**107%**	96.5%	3.5%	0.0%
35015A	027	LF	FGD, FA	Bit	39	13	4.8	1.3	19.4	49%			
35015A	028	LF	FGD, FA	Bit	30	2.4	1.7	0.20	4.3	14%			
35015A	029	LF	FGD, FA	Bit	49	1.7	8.9	0.35	10.9	22%			

Table 5-1
Arsenic Speciation Data (continued)

Site	Sample	Source	CCP	Coal	Total As (ug/L)	As(III) (ug/L)	As(V) (ug/L)	As, other species (ug/L)	Sum of Species	% Recovery	% As(III)	% As(V)	% As (other)
35015B	030	IMP	FA	Bit	43	3.5	29	0.35	33.4	79%			
35015B	031	IMP	FA	Bit	221	201	24	0.69	225.5	**102%**	89.2%	10.5%	0.3%
35015B	032	IMP	FA,BA	Bit	25	17	17	0.074	34.5	136%	50.8%	49.0%	0.2%
33106	037	IMP	FA	Bit	56	0.30	34		34.3	61%			
33106	038	IMP	FA	Bit	123	2.6	53		56.0	46%			
33106	039	IMP	FA	Bit	42	1.4	53		54.2	128%	2.6%	97.4%	ND
33106	042	IMP	FA	Bit	24	<0.1	19		19.2	**81%**	0.0%	100.0%	ND
33106	043	IMP	FA	Bit	75	<0.05	28		27.6	37%			
33106	044	IMP	FA	Bit	5.1	0.39	2.5		2.9	57%			
33106	*044D*	*Dup*	*FA*	*Bit*	*4.9*	*<0.04*	*2.3*		*2.3*	*48%*			
33106	049	IMP	FA,BA	Bit	5.4	<0.04	2.3	<0.04	2.3	43%			
40109	051	IMP	FA	Bit	38	0.70	15		15.7	41%			
40109	052	IMP	FA	Bit	164	23	7.7		30.5	19%			
40109	053	IMP	FA	Bit	279	108	82	0.70	191.0	68%			
40109	057	IMP	FA,BA	Bit	99	<0.2	93		92.5	**94%**	0.0%	100.0%	ND
40109	059	IMP	FA,BA	Bit	124	<0.2	127		126.6	**102%**	0.0%	100.0%	ND
40109	*059D*	*Dup*	*FA,BA*	*Bit*	*125*	*<0.2*	*119*		*118.5*	**95%**	0.0%	100.0%	ND
33104	061	IMP	FA	Bit	1,380	859	519		1,377.4	**100%**	62.4%	37.6%	ND
33104	062	IMP	FA	Bit	62	<0.2	37		37.5	61%			
33104	064	IMP	FA	Bit	178	<0.4	150		150.2	**84%**	0.0%	100.0%	ND
33104	069	IMP	FA,BA	Bit	100	<0.2	94		93.6	**94%**	0.0%	100.0%	ND
33104	070	IMP	FA,BA	Bit	143	<0.2	136		135.7	**95%**	0.0%	100.0%	ND
33104	*070D*	*Dup*	*FA,BA*	*Bit*	*144*	*<0.2*	*137*	*0.53*	*137.6*	**96%**	0.0%	99.6%	0.4%
22346	079	IMP	FA,OA	Blend	99	9.5	104		113.8	**115%**	8.3%	91.7%	ND
22346	*079D*	*Dup*	*FA,OA*	*Blend*	*97*	*9.9*	*73*		*82.5*	**85%**	12.0%	88.0%	ND
22346	082	IMP	FA,OA	Blend	23	0.21	15		14.7	64%			
22347	083	IMP	FA	Blend	6.2	0.23	2.4		2.6	43%			
22346	084	IMP	FA,OA	Blend	727	71	535		606.0	**83%**	11.8%	88.2%	ND

Table 5-1
Arsenic Speciation Data (continued)

Site	Sample	Source	CCP	Coal	Total As (ug/L)	As(III) (ug/L)	As(V) (ug/L)	As, other species (ug/L)	Sum of Species	% Recovery	% As(III)	% As(V)	% As (other)
27413	090	See Notes	FA	Mix	23	0.28	18	0.67	18.9	**84%**	1.5%	95.0%	3.5%
27413	091	See Notes	FA	Mix	11	<0.05	9.4	0.15	9.6	**89%**	0.0%	98.4%	1.6%
27413	092	See Notes	FA	Mix	3.3	<0.05	0.49	0.10	0.6	18%			
50212	097	LF	FA	Subbit	45	<0.1	36	<0.1	36.3	**81%**	0.0%	100.0%	0.0%
50183	098	LF	FA,BA	Mix	77	0.66	60	0.29	60.5	79%			
50183	099	LF	FA,BA	Mix	4.8	0.10	3.7	0.19	4.0	**84%**	2.6%	92.7%	4.7%
50408	101	LF	FA,BA	Bit	2.2	<0.1	0.23	0.62	0.9	38%			
50211	102	LF	FA	Bit	7.2	<0.05	6.3	<0.05	6.3	**88%**	0.0%	100.0%	0.0%
34186B	105	IMP	FGD	Lig	230	197	50	3.8	250.6	**109%**	78.4%	20.1%	1.5%
34186C	106	LF	FGD,FA,BA	Lig	110	16	63	5.8	84.7	77%			
34186C	*106D*	*Dup*	*FGD,FA,BA*	*Lig*	*112*	*14*	*77*	*5.2*	*96.3*	**86%**	14.3%	80.2%	5.4%
34186B	107	IMP	FGD	Lig	31	0.95	15	<0.2	16.1	52%			
34186A	108	LF	FA	Lig	4.1	0.37	2.3	<0.05	2.7	65%			
49003B	111	LF	FA	Bit	5.9	<0.1	3.4	<0.1	3.4	58%			
49003B	112	LF	FA	Bit	1.4	0.68	0.95	0.20	1.8	133%	37.1%	52.1%	10.8%
49003A	113	IMP	FA	Bit	102	0.75	118	0.17	118.7	**116%**	0.6%	99.2%	0.1%
49003A	114	IMP	FA	Bit	24	<0.1	20	<0.1	20.5	**87%**	0.0%	100.0%	0.0%
49003A	115	IMP	FA	Bit	8.3	3.1	5.3	<0.05	8.3	**100%**	36.7%	63.3%	0.0%
49003A	116	IMP	FA	Bit	8.2	1.0	7.4	0.083	8.5	**103%**	11.9%	87.2%	1.0%
35015B	118	IMP	FA,BA	Bit	41	0.66	45	0.15	46.3	**114%**	1.4%	98.3%	0.3%
35015B	*118D*	*Dup*	*FA,BA*	*Bit*	*40*	*0.18*	*46*	*0.11*	*45.9*	**116%**	0.4%	99.4%	0.2%
35015B	119	IMP	FA,BA	Bit	30	<0.05	31	0.29	30.8	**102%**	0.0%	99.1%	0.9%
35015A	120	LF	FGD, FA	Bit	27	7.2	11	9.3	27.9	**104%**	25.7%	41.0%	33.2%
35015A	121	LF	FGD, FA	Bit	11	1.3	6.0	0.57	7.9	72%			
35015A	122	LF	FGD, FA	Bit	26	7.6	8.3	6.0	21.9	**86%**	34.8%	37.8%	27.4%
43035	126	IMP	FA,BA	Subbit	5.2	<0.1	3.6	<0.1	3.6	69%			
43035	*126D*	*Dup*	*FA,BA*	*Subbit*	*4.9*	*<0.1*	*3.2*	*<0.1*	*3.2*	*66%*			
43035	127	IMP	FA,BA	Subbit	6.4	<0.2	4.0	<0.2	4.0	63%			
43034	128	LF	FGD,FA	Lig	14	10	2.8	0.45	13.3	**94%**	75.4%	21.2%	3.4%

Table 5-1
Arsenic Speciation Data (continued)

Site	Sample	Source	CCP	Coal	Total As (ug/L)	As(III) (ug/L)	As(V) (ug/L)	As, other species (ug/L)	Sum of Species	% Recovery	% As(III)	% As(V)	% As (other)
13115B	HN-1	IMP	FA,BA	Bit	60	<0.1	34	0.23	33.8	57%			
13115B	HN-2	IMP	FA,BA	Bit	21	<0.1	6.9	0.14	7.1	34%			
25410B	SX-1	IMP	FA	Blend	72	0.88	47	<0.1	47.8	66%			

Notes:

Ash at site 27413 (samples 090, 091, 092) was first sluiced, then managed dry.

Abbreviations:

Bit = bituminous; Subbit = Subbituminous; Mix = CCP from different units burning different coals; Blend = CCP from a single unit burning two different fuels

FA = fly ash; BA = bottom ash; EA = economizer ash; FGD = flue gas desulfurization sludge; OA = oil ash

LF = landfill; IMP = impoundment; DUP = duplicate sample

ND = not determined

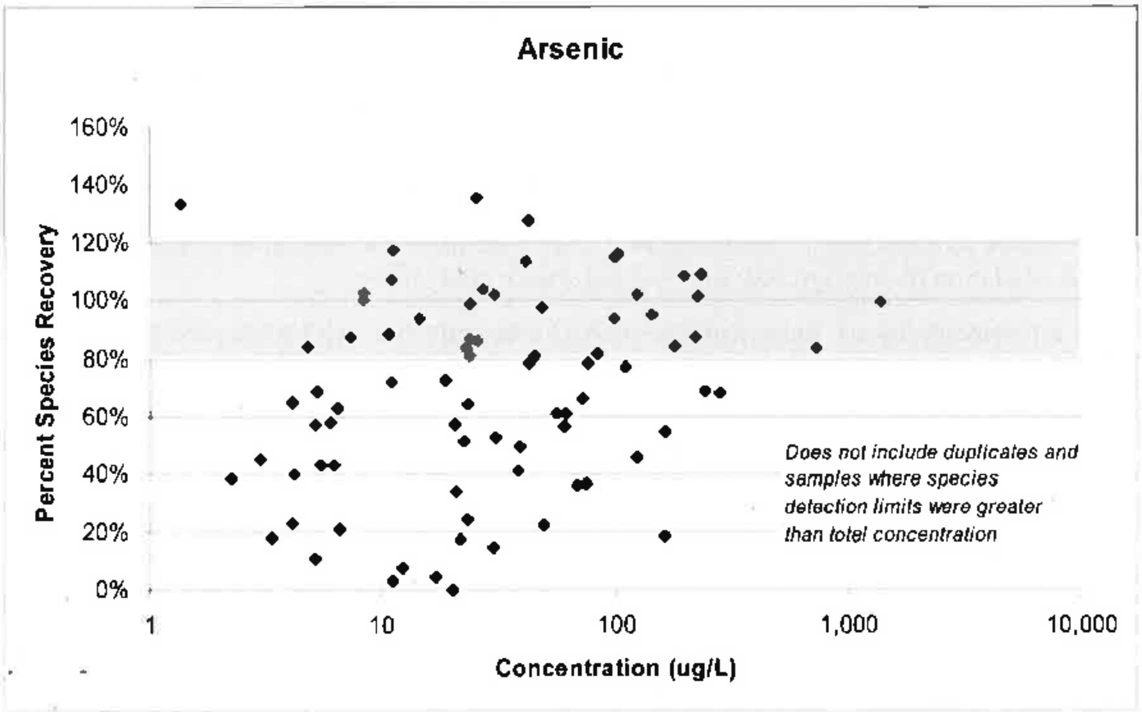

Figure 5-1
Arsenic Species Recovery

Comparison of Speciation to Site and Plant Attributes

Dominant species and relative percentages of the species were tabulated as a function of management method (landfill or impoundment) and source coal type. Relative species percentage was calculated for samples with greater than 80 percent recovery. The dominant species was determined based on the following criteria:

- For species recovery greater than 80 percent, a species was identified as dominant if its concentration was 60 percent or more of the sum of species.
- If species recovery was greater than 80 percent, and no species concentration was greater than 60 percent of the sum of species, then the sample was listed as "neutral".
- For species recovery less than 80 percent, a species was identified as dominant if its concentration was greater than 50 percent of the total concentration.[5]
- Samples with less than 80 percent species recovery in which no species concentration was greater than 50 percent of the total concentration were not tabulated.

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[5] If the sum of species is 80 percent, and the species concentration is 50 percent of the total concentration, then that species accounts for at least 62.5 percent of the sum of species.

The relative percent of species recovery was tabulated for the 35 individual samples (not counting duplicates) in which the sum of species was greater than 80 percent of the total arsenic concentration (Table 5-1). For ash management sites (31 samples), the percentage of As(V) ranged from 3 to 100 percent with a median of 99 percent, the percentage of As(III) ranged from 0 to 96 percent with a median of 0.6 percent, and the percentage of other species ranged from 0 to 11 percent with a median of 0 percent. For FGD management sites (4 samples), the percentage of As(V) ranged from 20 to 41 percent with a median of 30 percent, the percentage of As(III) ranged from 26 to 78 percent with a median of 55 percent, and the percentage of other species ranged from 2 to 33 percent with a median of 15 percent. A more detailed tabulation by management method and source coal yields:

- For ash impoundments, the percentage of As(V) ranged from 3 to 100 percent for plants burning bituminous coal (20 samples), no samples from lignite/subbituminous plants had sufficient species recovery to calculate a ratio, and the percentage of As(V) ranged from 88 to 100 percent for sites receiving ash from units that burn a blend of bituminous and subbituminous coal (3 samples) (Figure 5-2).
- For ash landfills, the percentage of As(V) was 52 to 100 percent for plants burning bituminous coal (2 samples), 100 percent for plants burning lignite/subbituminous coal (3 samples), and 93 percent for a site that received ash from multiple units burning different coals (1 sample).
- One other ash management site (27413) where ash was originally sluiced, then landfilled, and where a mixture of coal sources were used, had 95 to 98 percent As(V) (2 samples).
- For FGD landfills, samples with greater than 80 percent species recovery had roughly equal percentages of As(III), As(V), and other arsenic species at sites receiving bituminous coal ash (2 samples), and a site receiving lignite ash had 72 percent As(III) (1 sample) (Figure 5-2).
- Similarly, an FGD impoundment/lignite sample had 72 percent As(III) (1 sample). There were no FGD impoundment/bituminous samples.

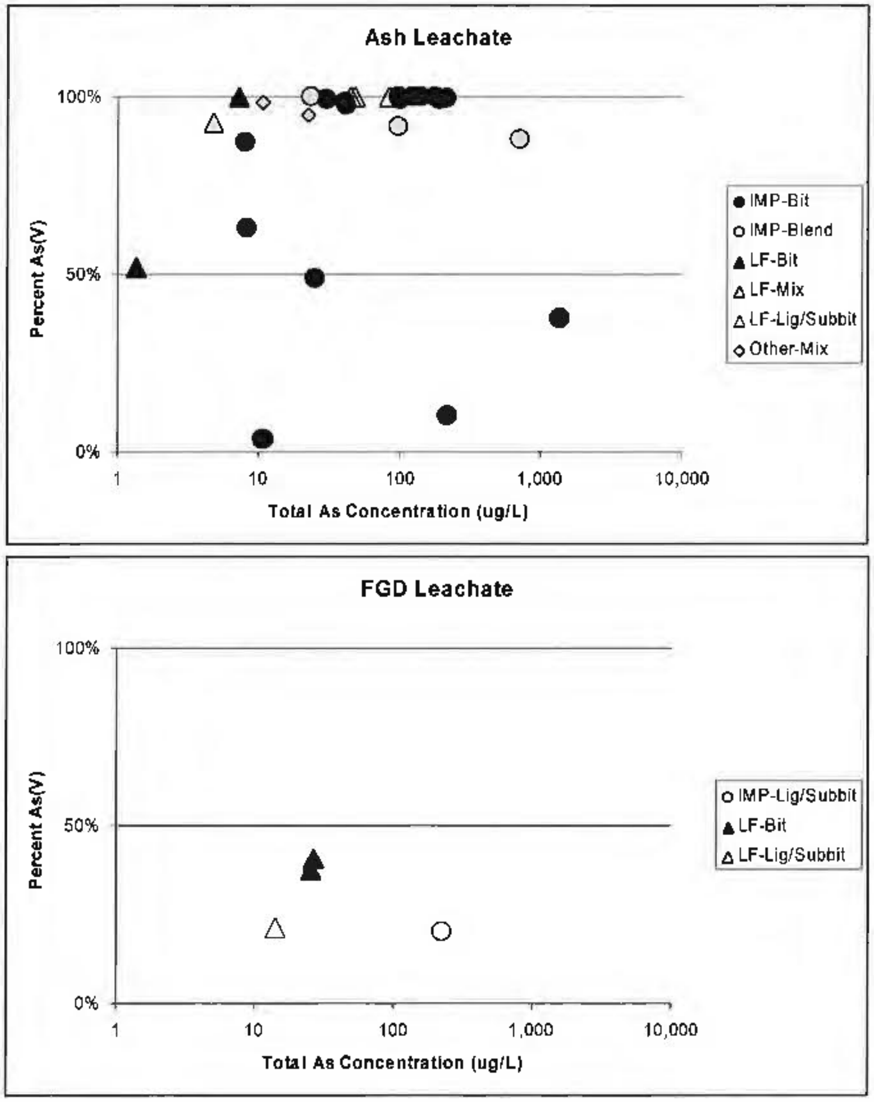

Figure 5-2
Relative Percent of As(V) vs Total As Concentration

Results of the dominant species analysis corroborates the results of the relative species analysis, and indicates that ash leachate is dominated by As(V) (Table 5-2). As(III) is only dominant in four samples from ash impoundment environments at sites where bituminous coal was burned, and in FGD leachate when bituminous coal was burned.

Table 5-2
Tabulation of Dominant Arsenic Species by Sample

Ash Samples	**Impoundment**	**Landfill**	***Total***
Ash – Bituminous	4 – 1 – 20 (36)	0 – 1 – 2 (6)	*4 – 2 – 22* *(42)*
Ash – Blend/Mix	0 – 0 – 5 (7)	0 – 0 – 2 (5)	*0 – 0 – 9** *(15*)*
Ash – Subbituminous/Lignite	0 – 0 – 2 (5)	0 – 0 – 4 (5)	*0 – 0 – 6* *(10)*
Total	*4 – 1 – 27* *(48)*	*0 – 1 – 8* *(16)*	*4 – 2 – 37** *(67*)*
FGD Samples	**Impoundment**	**Landfill**	***Total***
FGD – Bituminous		0 – 2 – 1 (6)	*0 – 2 – 1* *(6)*
FGD – Blend/Mix			
FGD – Subbituminous/Lignite	1 – 0 – 0 (5)	1 – 0 – 1 (3)	*2 – 0 – 1* *(8)*
Total	*1 – 0 – 0* *(5)*	*1 – 2 – 2* *(9)*	*2 – 2 – 2* *(14)*

Legend: number of samples in which → As(III) dominant - Neutral - As(V) dominant
(Total number of samples in group)

* Tabulation includes the samples from the 27413 site, which could not be characterized as landfill or impoundment.

The four ash leachate samples dominated by As(III) (022, 026, 031, and 061) came from three different sites (49003A, 35015B, and 33104), indicating that it is not a site-specific occurrence. Furthermore, other samples from each of the three sites were dominated by As(V), indicating that it is not a site-wide occurrence. Total arsenic concentration in the four samples dominated by As(III) ranged from 11 to 1,380 µg/L (Figure 5-3). The pH values of these samples were neutral to slightly alkaline (7.1 to 8.5 SU). Sample 031 had only 6 percent dissolved oxygen and a negative ORP value, indicative of reducing conditions. Most of the other samples with dissolved oxygen concentrations lower than 10 percent were not evaluated because species recovery was too low, and no other sample had a negative ORP value. Sample 061 had abundant dissolved oxygen (65 percent), although it also had a relatively low ORP value of 140 mV and a dissolved iron concentration of 2,170 µg/L, which may be indicative of reducing conditions. The total arsenic concentration for samples 031 and 061 were an order of magnitude or more higher than the other samples collected at these sites. Samples 022 and 026, both collected from the 49003A impoundment had field measurements indicative of oxic conditions, and total arsenic concentrations were at the low end of the range for samples collected at this site.

FGD leachate samples were evenly split between the reduced and oxidized species of arsenic. There was no correlation with pH, dissolved oxygen, or ORP. In fact, the two samples clearly dominated by As(V) (106 and 121) had lower ORP values than the two samples dominated by As(III) (105 and 128).

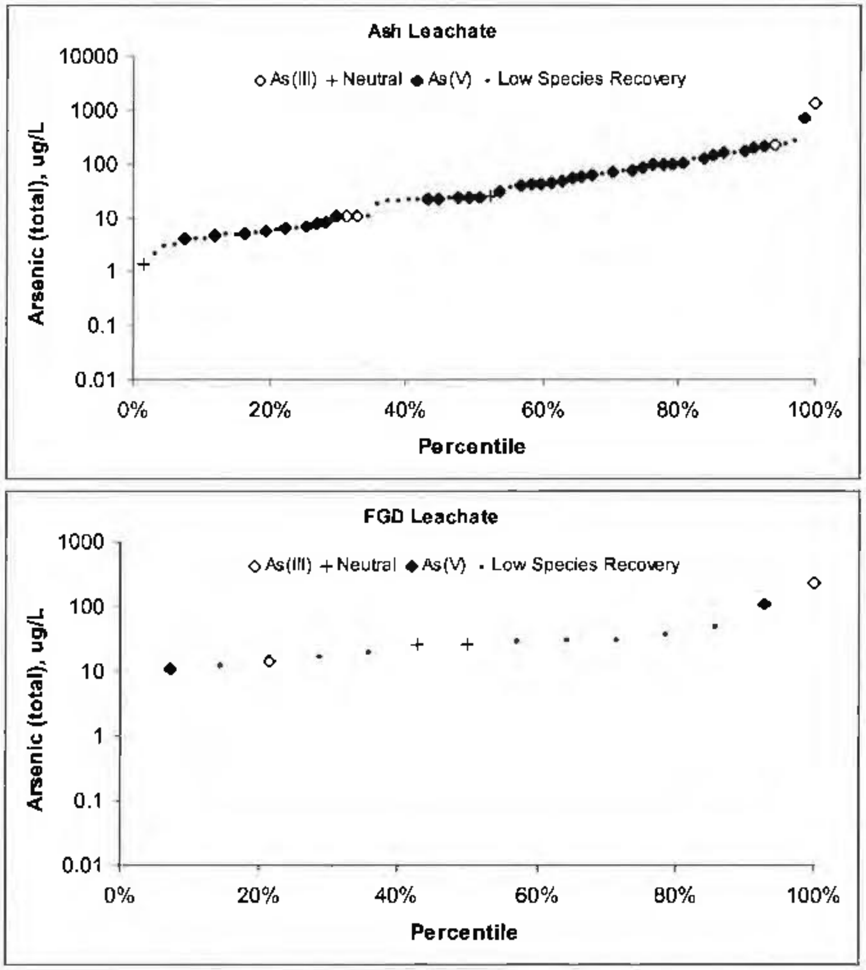

Figure 5-3
Species Predominance as a Function of Total Arsenic Concentration in Leachate.

Selenium

Overview of Results

Detectable concentrations of selenium were present in all 81 samples (Table 5-3). Review of duplicate sample results indicated that results were highly reproducible across the entire concentration range.

Selenite was detected in 58 of the 81 samples, and selenate was detected in 55 of the 81 samples. Two samples (107 and 128) contained other selenium species, which were theorized to be selenium-sulfur compounds.

Like arsenic, the selenium speciation mass balance varied strongly, and was not always satisfactory. Selenium had the same number of samples (35 of 81 samples) as arsenic with greater than 80 percent recovery (Figure 5-4); although the samples with poor species recovery were not always the same as arsenic.

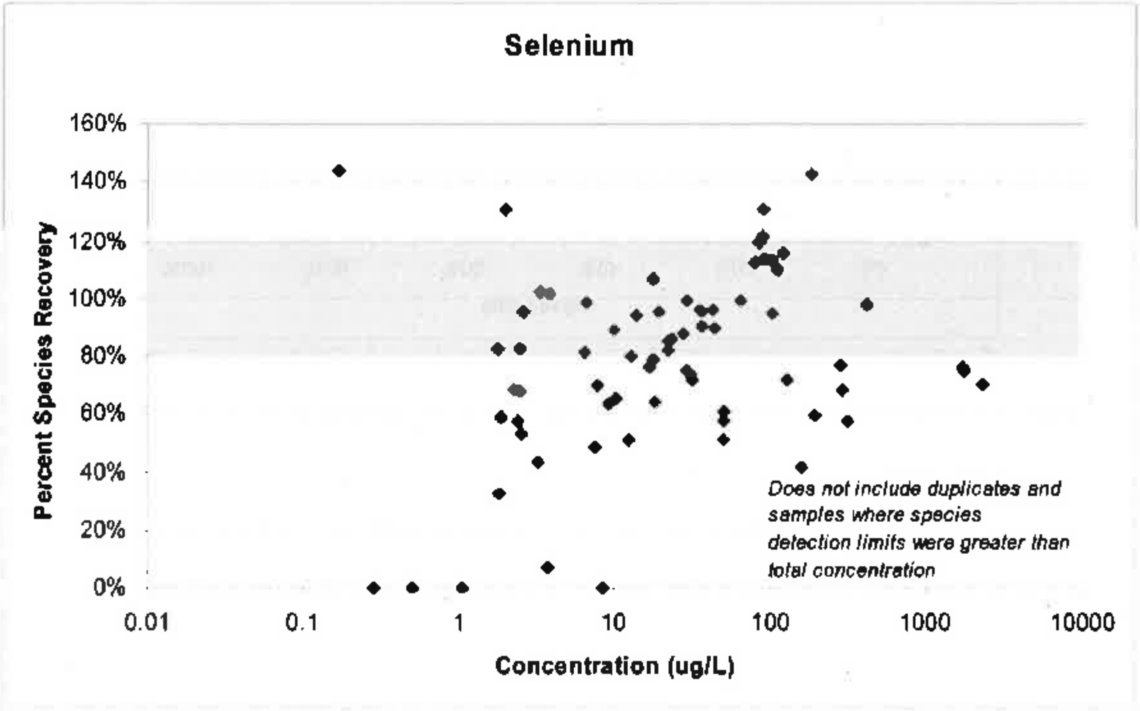

Figure 5-4
Selenium Species Recovery

Table 5-3
Selenium Speciation Data

Site	Sample	Source	CCP	Coal	Total Se (ug/L)	Se(IV) (ug/L)	Se(VI) (ug/L)	Se, other (ug/L)	Sum of Species	% Recovery	% Se(IV)	% Se(VI)	% Se (other)
50210	001	LF	FA,BA	Mix	127	8.3	83		91.3	72%			
50213	002	LF	FA	Subbit	1,730	19	1,300		1,318.6	76%			
50213	003	LF	FA	Subbit	1,760	76	1,240		1,315.9	75%			
50183	004	LF	FA,BA	Mix	50	8.1	22		30.3	61%			
50183	005	LF	FA,BA	Mix	7.6	3.1	0.57		3.7	49%			
23223A	006	LF	SDA	Subbit	17	1.6	11		12.8	76%			
23223B	007	IMP	FGD	Subbit	289	79	119		198.2	69%			
23223B	008	IMP	FGD	Subbit	3.7	<0.1	0.27		0.3	7%			
23223B	009	IMP	FGD	Subbit	2,360	<2	1,660		1,660.0	70%			
23214	010	LF	FA	Subbit	318	24	158		182.3	57%			
14093	012	IMP	FA	Bit	3.2	1.4	<0.2		1.4	43%			
14093	013	IMP	FA	Bit	0.28	<0.1	<0.1		0.0	0%			
14093	*013D*	*dup*	*FA*	*Bit*	*0.38*	*<0.1*	*<0.1*		*0.0*	*0%*			
14093	014	IMP	FA	Bit	1.8	0.59	<0.2		0.6	33%			
25410A	015	IMP	FA,BA	Blend	22	15	3.4		18.3	**82%**	81.2%	18.8%	ND
25410A	016	IMP	FA,BA	Blend	193	101	14		115.4	60%			
13115A	017	IMP	FA,BA	Subbit	2.4	0.26	1.1		1.4	57%			
13115B	018	IMP	FA,BA	Bit	0.50	<0.1	<0.2		0.0	0%			
13115A	019	IMP	FA	Subbit	1.8	0.14	1.3		1.5	**82%**	9.5%	90.5%	ND
13115A	020	IMP	FA,BA	Subbit	2.5	0.90	0.79		1.7	68%			
49003A	021	IMP	FA	Bit	6.5	5.3	<0.6		5.3	**81%**	100.0%	0.0%	ND
49003A	022	IMP	FA	Bit	31	20	2.2		22.7	74%			
49003A	023	IMP	FA	Bit	283	217	1.5		218.2	77%			
49003B	024	LF	FA	Bit	18	5.3	6.3		11.6	64%			
49003B	025	LF	FA	Bit	1.9	<0.1	1.1		1.1	59%			
49003A	026	IMP	FA	Bit	32	20	2.2		22.6	72%			
35015A	027	LF	FGD, FA	Bit	1.1	<0.3	<0.3		0.0	0%			
35015A	028	LF	FGD, FA	Bit	2.6	<0.3	1.4		1.4	53%			
35015A	029	LF	FGD, FA	Bit	2.3	<0.3	1.6		1.6	69%			

Table 5-3
Selenium Speciation Data (continued)

Site	Sample	Source	CCP	Coal	Total Se (ug/L)	Se(IV) (ug/L)	Se(VI) (ug/L)	Se, other (ug/L)	Sum of Species	% Recovery	% Se(IV)	% Se(VI)	% Se (other)
35015B	030	IMP	FA	Bit	44	27	12		39.5	**90%**	68.3%	31.7%	ND
35015B	031	IMP	FA	Bit	13	0.92	5.5		6.4	51%			
35015B	032	IMP	FA,BA	Bit	18	13	0.75		14.2	79%			
33106	037	IMP	FA	Bit	2.0	2.6	<1		2.6	131%	100.0%	0.0%	ND
33106	038	IMP	FA	Bit	0.13	<0.5	<1		0.0	0%			
33106	039	IMP	FA	Bit	0.17	0.24	<0.4		0.2	144%	100.0%	0.0%	ND
33106	042	IMP	FA	Bit	43	39	1.9		41.0	**96%**	95.3%	4.7%	ND
33106	043	IMP	FA	Bit	24	20	<1		20.2	**86%**	100.0%	0.0%	ND
33106	044	IMP	FA	Bit	14	11	1.7		13.1	**94%**	86.7%	13.3%	ND
33106	*044D*	*dup*	*FA*	*Bit*	*14*	*12*	*1.8*		*13.3*	***98%***	86.7%	13.3%	ND
33106	049	IMP	FA,BA	Bit	10	8.3	0.64		8.9	**89%**	92.8%	7.2%	ND
40109	051	IMP	FA	Bit	0.45	<0.5	<1		0.0	0%			
40109	052	IMP	FA	Bit	10	6.7	<4		6.7	65%			
40109	053	IMP	FA	Bit	1.2	<2	<4		0.0	0%			
40109	057	IMP	FA,BA	Bit	2.4	2.0	<1		2.0	**83%**	100.0%	0.0%	ND
40109	059	IMP	FA,BA	Bit	2.6	2.5	<1		2.5	**95%**	100.0%	0.0%	ND
40109	*059D*	*dup*	*FA,BA*	*Bit*	*2.6*	*2.2*	*<1*		*2.2*	***87%***	100.0%	0.0%	ND
33104	061	IMP	FA	Bit	4.3	<10	<20		0.0	0%			
33104	062	IMP	FA	Bit	112	90	32		122.5	**110%**	73.8%	26.2%	ND
33104	064	IMP	FA	Bit	103	97	<4		97.1	**95%**	100.0%	0.0%	ND
33104	069	IMP	FA,BA	Bit	36	33	1.7		34.8	**96%**	95.1%	4.9%	ND
33104	070	IMP	FA,BA	Bit	29	29	<4		28.8	**99%**	100.0%	0.0%	ND
33104	*070D*	*dup*	*FA,BA*	*Bit*	*29*	*28*	*<4*		*27.9*	***95%***	100.0%	0.0%	ND
22346	079	IMP	FA,OA	Blend	0.16	<0.2	<0.3		0.0	0%			
22346	*079D*	*dup*	*FA,OA*	*Blend*	*0.16*	*<0.2*	*<0.3*		*0.0*	*0%*			
22346	082	IMP	FA,OA	Blend	19	18	0.26		18.1	**95%**	98.6%	1.4%	ND
22347	083	IMP	FA	Blend	13	8.7	1.5		10.2	80%			
22346	084	IMP	FA,OA	Blend	0.57	<2	<3		0.0	0%			
27413	090	See Notes	FA	Mix	86	5.2	97		102.3	**120%**	5.1%	94.9%	ND
27413	091	See Notes	FA	Mix	122	3.6	138		141.9	**116%**	2.5%	97.5%	ND
27413	092	See Notes	FA	Mix	103	0.56	116		117.0	**113%**	0.5%	99.5%	ND

Table 5-3
Selenium Speciation Data (continued)

Site	Sample	Source	CCP	Coal	Total Se (ug/L)	Se(IV) (ug/L)	Se(VI) (ug/L)	Se, other (ug/L)	Sum of Species	% Recovery	% Se(IV)	% Se(VI)	% Se (other)
50212	097	LF	FA	Subbit	413	38	366		404.2	**98%**	9.4%	90.6%	ND
50183	098	LF	FA,BA	Mix	51	29	<2		29.3	58%			
50183	099	LF	FA,BA	Mix	2.0	<0.8	<2		0.0	0%			
50408	101	LF	FA,BA	Bit	91	<0.8	104		103.6	**114%**	0.0%	100.0%	ND
50211	102	LF	FA	Bit	80	5.3	85		90.8	**113%**	5.9%	94.1%	ND
34186B	105	IMP	FGD	Lig	8.5	<2	<4	<2	0.0	0%			
34186C	106	LF	FGD,FA,BA	Lig	65	<2	64	<2	64.4	**99%**	0.0%	100.0%	0.0%
34186C	*106D*	*dup*	*FGD,FA,BA*	*Lig*	*65*	*<2*	*65*	*<2*	*65.1*	***100%***	0.0%	100.0%	0.0%
34186B	107	IMP	FGD	Lig	159	<2	16	51	66.5	42%			
34186A	108	LF	FA	Lig	6.6	2.6	3.9	<0.5	6.5	**98%**	39.6%	60.4%	0.0%
49003B	111	LF	FA	Bit	91	39	72		110.3	122%	35.1%	64.9%	ND
49003B	112	LF	FA	Bit	0.67	<0.5	<1		0.0	0%			
49003A	113	IMP	FA	Bit	29	19	2.6		21.8	75%			
49003A	114	IMP	FA	Bit	0.071	<0.5	<1		0.0	0%			
49003A	115	IMP	FA	Bit	36	30	3.1		32.7	**90%**	90.7%	9.3%	ND
49003A	116	IMP	FA	Bit	35	31	3.3		34.0	**96%**	90.2%	9.8%	ND
35015B	118	IMP	FA,BA	Bit	18	18	1.3		18.9	**107%**	93.0%	7.0%	ND
35015B	*118D*	*dup*	*FA,BA*	*Bit*	*18*	*16*	*1.3*		*17.7*	***96%***	92.9%	7.1%	ND
35015B	119	IMP	FA,BA	Bit	28	23	1.7		24.4	**87%**	93.1%	6.9%	ND
35015A	120	LF	FGD, FA	Bit	3.3	1.8	1.5		3.4	**102%**	54.7%	45.3%	ND
35015A	121	LF	FGD, FA	Bit	3.9	1.1	2.8		3.9	**102%**	28.2%	71.8%	ND
35015A	122	LF	FGD, FA	Bit	1.1	<0.5	<1		0.0	0%			
43035	126	IMP	FA,BA	Subbit	89	13	103	<0.3	115.9	131%	10.8%	89.2%	0.0%
43035	*126D*	*dup*	*FA,BA*	*Subbit*	*88*	*13*	*104*	*<0.3*	*116.9*	*132%*	11.1%	88.9%	0.0%
43035	127	IMP	FA,BA	Subbit	181	12	245	<0.3	257.5	143%	4.8%	95.2%	0.0%
43034	128	LF	FGD,FA	Lig	51	17	6.7	1.8	25.9	51%			

Table 5-3
Selenium Speciation Data (continued)

Site	Sample	Source	CCP	Coal	Total Se (ug/L)	Se(IV) (ug/L)	Se(VI) (ug/L)	Se, other (ug/L)	Sum of Species	% Recovery	% Se(IV)	% Se(VI)	% Se (other)
13115B	HN-1	IMP	FA,BA	Bit	22	2.6	16		19.0	85%	13.9%	86.1%	ND
13115B	HN-2	IMP	FA,BA	Bit	9.2	<1	5.8		5.8	64%			
25410B	SX-1	IMP	FA	Blend	7.8	1.8	3.6		5.4	70%			

Notes:

Ash at site 27413 (samples 090, 091, 092) was first sluiced, then managed dry.

Abbreviations:

Bit = bituminous; Subbit = Subbituminous; Mix = CCP from different units burning different coals; Blend = CCP from a single unit burning two different fuels

FA = fly ash; BA = bottom ash; EA = economizer ash; FGD = flue gas desulfurization sludge; OA = oil ash

LF = landfill; IMP = impoundment; DUP = duplicate sample

ND = not determined

Comparison of Speciation to Site and Plant Attributes

Dominant species and relative percentages of the species were tabulated using the same procedure as for arsenic. For ash management sites (32 samples), the percentage of Se(IV) ranged from 0 to 100 percent with a median of 88 percent, the percentage of Se(VI) ranged from 0 to 100 percent with a median of 12 percent, and the percentage of other species was 0 percent for samples with greater than 80 percent species recovery. For FGD management sites (3 samples), the percentage of Se(IV) ranged from 0 to 55 percent with a median of 28 percent, the percentage of Se(VI) ranged from 45 to 100 percent with a median of 72 percent, and the percentage of other species was 0 percent. A more detailed tabulation by management method and source coal yields:

- For ash impoundments, the percentage of Se(VI) ranged from 0 to 86 percent for plants burning bituminous coal (19 samples), 89 to 95 percent for plants burning lignite/subbituminous coal (3 samples), and 1 to 19 percent for sites receiving ash from units that burn a blend of bituminous and subbituminous coal (2 samples) (Figure 5-5).
- For ash landfills, the percentage of Se(VI) was 65 to 100 percent for plants burning bituminous coal (3 samples), and 60 to 91 percent for plants burning lignite/subbituminous coal (2 samples).
- One other ash management site (27413) where ash was originally sluiced, then landfilled, and where a mixture of coal sources were used, had 95 to 99 percent Se(VI) (3 samples).
- For FGD landfills, the percentage of Se(VI) was 45 to 72 percent for plants burning bituminous coal (2 samples), and 100 percent for plants burning lignite/subbituminous coal (1 sample) (Figure 5-5).
- No FGD impoundment samples had greater than 80 percent species recovery.

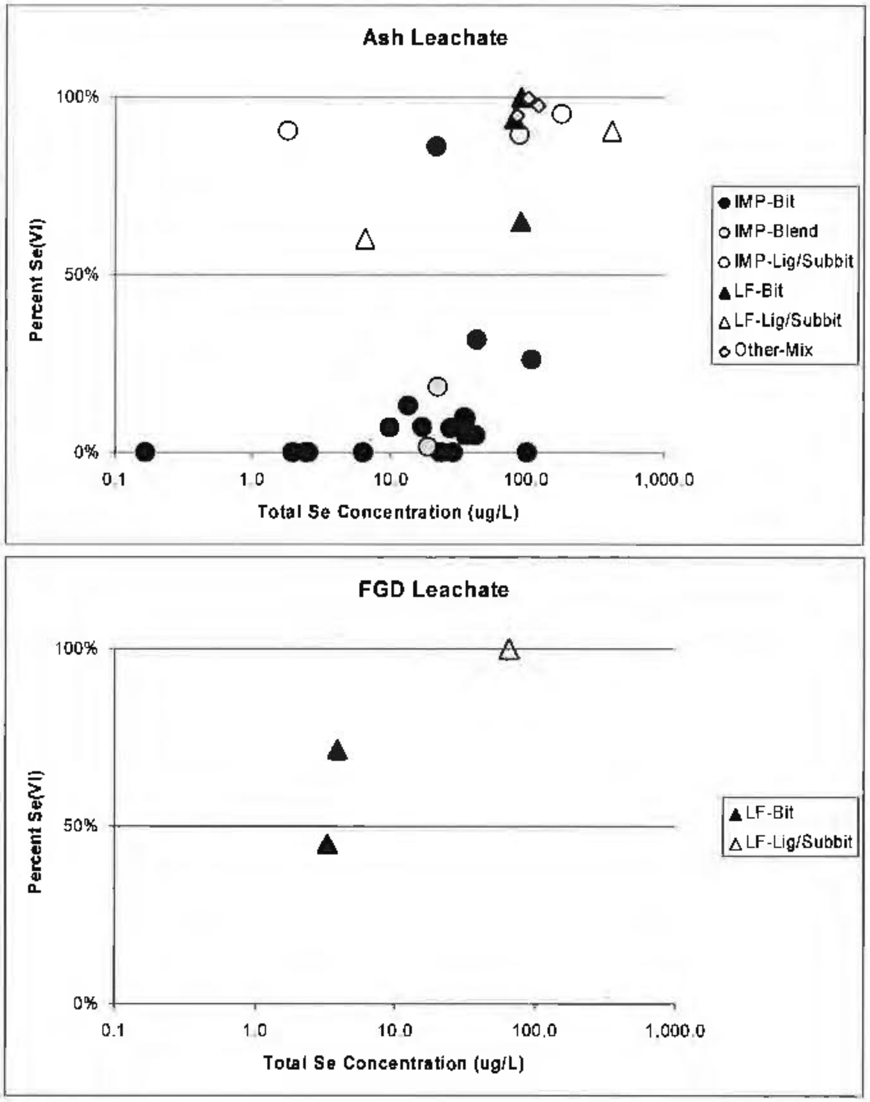

Figure 5-5
Relative Percent of Se(VI) versus Total Se Concentration

Results of the dominant species analysis corroborates the relative percentage analysis and indicates that ash leachate is dominated by Se(IV) in impoundment settings when the source coal is bituminous or a mixture of bituminous and subbituminous, while Se(VI) is predominant in landfill settings and when the source coal is subbituminous/lignite (Table 5-4). Most samples with relatively high concentration (>80 µg/L) were dominated by Se(VI) while samples with concentrations lower than 50 µg/L were mostly dominated by Se(IV) (Figure 5-6).

Table 5-4
Tabulation of Dominant Selenium Species by Sample

Ash Samples	**Impoundment**	**Landfill**	***Total***
Ash – Bituminous	24 – 0 – 2 (36)	0 – 0 – 4 (6)	*24 – 0 – 6* *(42)*
Ash – Blend/Mix	4 – 0 – 0 (7)	1 – 0 – 1 (5)	*5 – 0 – 4** *(15*)*
Ash – Subbituminous/Lignite	0 – 0 – 3 (5)	0 – 0 – 4 (5)	*0 – 0 – 7* *(10)*
Total	*28 – 0 – 5* *(48)*	*1 – 0 – 9* *(16)*	*29 – 0 – 17** *(67*)*
FGD Samples	**Impoundment**	**Landfill**	***Total***
FGD – Bituminous		0 – 1 – 3 (6)	*0 – 1 – 3* *(6)*
FGD – Blend/Mix			
FGD – Subbituminous/Lignite	0 – 0 – 1 (5)	0 – 0 – 2 (3)	*0 – 0 – 3* *(8)*
Total	*0 – 0 – 1* *(5)*	*0 – 1 – 5* *(9)*	*0 – 1 – 6* *(14)*

Legend: number of samples in which → Se(IV) dominant - Neutral - Se(VI) dominant

(Total number of samples in group)

* Tabulation includes the samples from the 27413 site, which could not be characterized as landfill or impoundment.

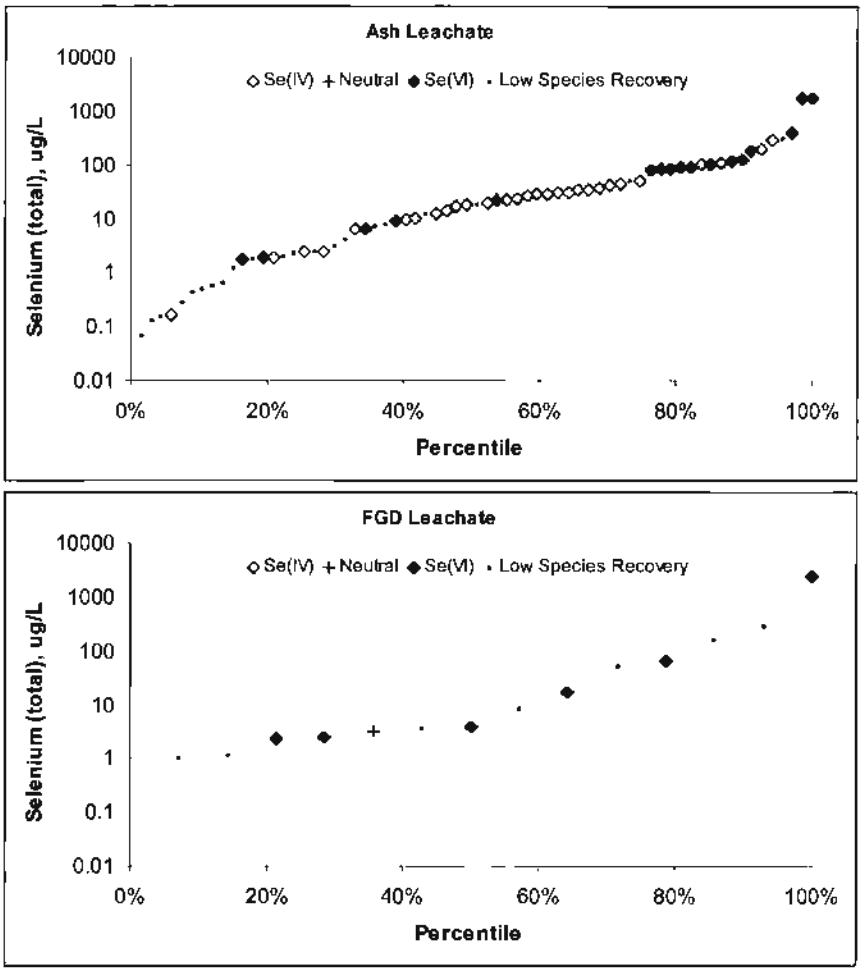

Figure 5-6
Species Predominance as a Function of Total Selenium Concentration in Leachate.

Chromium

Overview of Results

Chromium was detected in 42 of the 81 samples (Table 5-5). Chromium speciation was not always determined in samples for which total concentrations were non-detect or lower than 1 µg/L. Cr(III) analysis was performed for 45 samples, and 29 had detectable concentrations. Cr(VI) was analyzed in 58 samples and 37 had detectable concentrations. Review of duplicate samples indicated that chromium results were reproducible.

The speciation mass balance was good for total chromium concentrations greater than 5 µg/L: 16 of 19 samples with concentration greater than 5 µg/L had species recovery greater than 80 percent (Figure 5-7). The three other samples from this group had greater than 65 percent recovery.

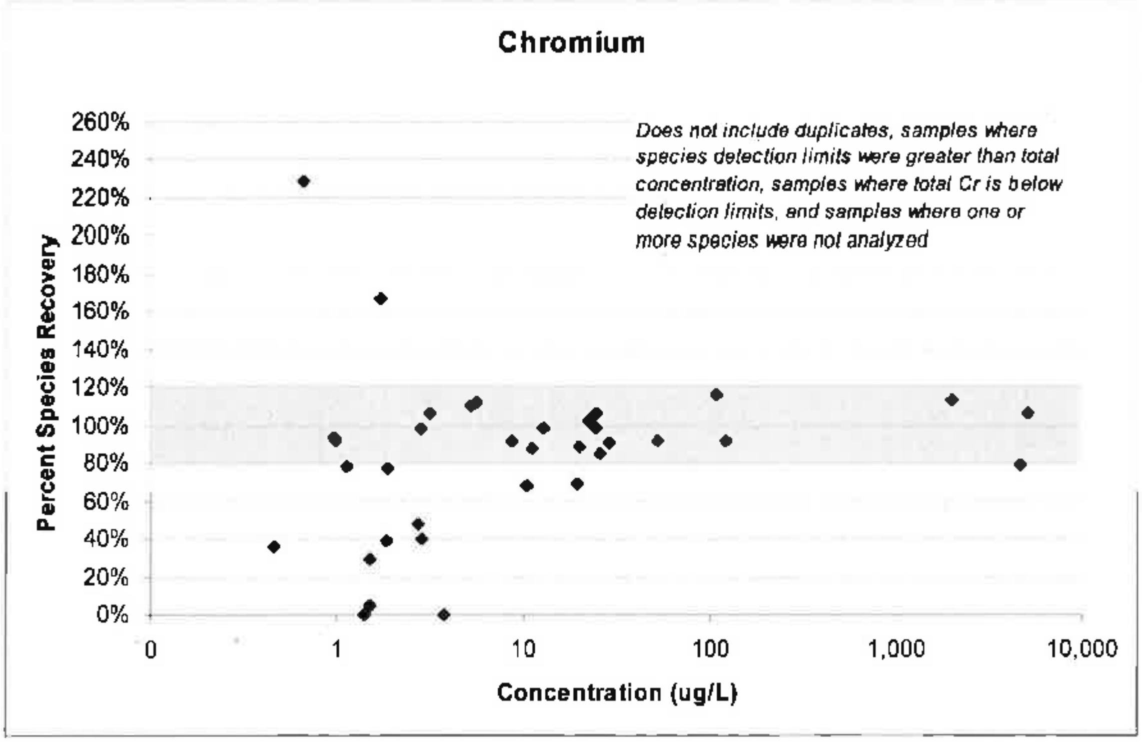

Figure 5-7
Chromium Species Recovery

Table 5-5
Chromium Speciation Data

Site	Sample	Source	Byproduct	Coal	Total Cr (ug/L)	Cr(III) (ug/L)	Cr(VI) (ug/L)	Sum of Species	% Recovery	% Cr(III)	% Cr(VI)
50210	001	LF	FA,BA	Mix	<0.5		2.2	2.20	*		
50213	002	LF	FA	Subbit	5,100	340	5,090	5,430.00	**106%**	6%	94%
50213	003	LF	FA	Subbit	4,670	190	3,530	3,720.00	80%		
50183	004	LF	FA,BA	Mix	8.8	<0.1	8.1	8.10	**92%**	0%	100%
50183	005	LF	FA,BA	Mix	0.66		1.5	1.50	229%	0%	100%
23223A	006	LF	SDA	Subbit	5.7	<0.1	6.4	6.40	**113%**	0%	100%
23223B	007	IMP	FGD	Subbit	1.7	<0.1	2.9	2.90	167%	0%	100%
23223B	008	IMP	FGD	Subbit	<0.5		<0.1	*	*		
23223B	009	IMP	FGD	Subbit	53	1.3	47	48.53	**92%**	3%	97%
23214	010	LF	FA	Subbit	26	<0.4	22	22.00	**85%**	0%	100%
14093	012	IMP	FA	Bit	<0.5		1.9	1.90	*		
14093	013	IMP	FA	Bit	<0.5		0.70	0.70	*		
14093	*013D*	*dup*	*FA*	*Bit*			*0.70*	*0.70*	*		
14093	014	IMP	FA	Bit	<0.5		0.50	0.50	*		
25410A	015	IMP	FA,BA	Blend	13	<0.4	13	12.80	**99%**	0%	100%
25410A	016	IMP	FA,BA	Blend	3.8	<0.1	<0.5	*	0%		
13115A	017	IMP	FA,BA	Subbit	2.8	<0.04	2.8	2.80	**98%**	0%	100%
13115B	018	IMP	FA,BA	Bit	<0.5		1.3	1.30	*		
13115A	019	IMP	FA	Subbit	0.96	<0.1	0.90	0.90	**94%**	0%	100%
13115A	020	IMP	FA,BA	Subbit	0.66		<0.05	*	0%		
49003A	021	IMP	FA	Bit	<0.5		<0.05	*	*		
49003A	022	IMP	FA	Bit	0.98	<0.04	0.90	0.90	**92%**	0%	100%
49003A	023	IMP	FA	Bit	<0.5		<0.5	*	*		
49003B	024	LF	FA	Bit	<0.5			*	*		
49003B	025	LF	FA	Bit	<0.5			*	*		
49003A	026	IMP	FA	Bit	1.1	<0.04	0.90	0.90	78%		
35015A	027	LF	FGD, FA	Bit	<0.5			*	*		
35015A	028	LF	FGD, FA	Bit	<0.5			*	*		
35015A	029	LF	FGD, FA	Bit	<0.5			*	*		

Table 5-5
Chromium Speciation Data (continued)

Site	Sample	Source	Byproduct	Coal	Total Cr (ug/L)	Cr(III) (ug/L)	Cr(VI) (ug/L)	Sum of Species	% Recovery	% Cr(III)	% Cr(VI)
35015B	030	IMP	FA	Bit	<0.5		<0.05	*	*		
35015B	031	IMP	FA	Bit	<0.5		<0.1	*	*		
35015B	032	IMP	FA,BA	Bit	1.4	<0.1	<0.05	*	0%		
33106	037	IMP	FA	Bit	<0.4	<0.01	<0.01	*	*		
33106	038	IMP	FA	Bit	<0.4	<0.01	<0.01	*	*		
33106	039	IMP	FA	Bit	<0.4	<0.01	<0.01	*	*		
33106	042	IMP	FA	Bit	<0.4	0.17	0.029	0.20	*		
33106	043	IMP	FA	Bit	29	26	<0.1	26.42	**91%**	100%	0%
33106	044	IMP	FA	Bit	<0.4	0.25	<0.01	0.25	*		
33106	*044D*	*dup*	*FA*	*Bit*	*<0.4*	*0.12*	*<0.01*	*0.12*	*		
33106	049	IMP	FA,BA	Bit	<0.4	0.074	<0.01	0.07	*		
40109	051	IMP	FA	Bit	11	9.9	<0.05	9.92	**88%**	100%	0%
40109	052	IMP	FA	Bit	<0.4	0.16	0.064	0.22	*		
40109	053	IMP	FA	Bit	<0.4	0.050	<0.01	0.05	*		
40109	057	IMP	FA,BA	Bit	1.9	1.1	0.41	1.47	77%		
40109	059	IMP	FA,BA	Bit	2.7	0.011	1.3	1.29	48%		
40109	*059D*	*dup*	*FA,BA*	*Bit*	*2.5*	*<0.01*	*1.2*	*1.23*	*49%*		
33104	061	IMP	FA	Bit	<0.4	0.27	<0.01	0.27	*		
33104	062	IMP	FA	Bit	10	0.95	6.2	7.19	69%		
33104	064	IMP	FA	Bit	22	0.044	23	23.02	**103%**	0%	100%
33104	069	IMP	FA,BA	Bit	3.2	0.46	3.0	3.44	**107%**	13%	87%
33104	070	IMP	FA,BA	Bit	5.3	0.63	5.3	5.91	**111%**	11%	89%
33104	*070D*	*dup*	*FA,BA*	*Bit*	*5.4*	*0.62*	*5.2*	*5.78*	***106%***	*11%*	*89%*
22346	079	IMP	FA,OA	Blend	<0.2	<0.02	<0.006	*	*		
22346	*079D*	*dup*	*FA,OA*	*Blend*	*<0.2*	*<0.02*	*<0.006*	*	*		
22346	082	IMP	FA,OA	Blend	25	1.2	23	24.19	**98%**	5%	95%
22347	083	IMP	FA	Blend	20	2.4	15	17.66	**89%**	14%	86%
22346	084	IMP	FA,OA	Blend	<0.2	0.039	<0.006	0.04	*		
27413	090	See Notes	FA	Mix	0.75			*	*		
27413	091	See Notes	FA	Mix	<0.2			*	*		
27413	092	See Notes	FA	Mix	122	2.8	109	111.61	**91%**	2%	98%

Table 5-5
Chromium Speciation Data (continued)

Site	Sample	Source	Byproduct	Coal	Total Cr (ug/L)	Cr(III) (ug/L)	Cr(VI) (ug/L)	Sum of Species	% Recovery	% Cr(III)	% Cr(VI)
50212	097	LF	FA	Subbit	2,000	40	2,230	2,270.00	**114%**	2%	98%
50183	098	LF	FA,BA	Mix	2.8	0.16	0.99	1.15	40%		
50183	099	LF	FA,BA	Mix	<0.2			*	*		
50408	101	LF	FA,BA	Bit	1.5	<0.08	0.075	0.07	5%		
50211	102	LF	FA	Bit	20	0.42	13	13.70	70%		
34186B	105	IMP	FGD	Lig	<0.4			*	*		
34186C	106	LF	FGD,FA,BA	Lig	0.91			*	*		
34186C	*106D*	*dup*	*FGD,FA,BA*	*Lig*	*0.88*			*	*		
34186B	107	IMP	FGD	Lig	<2			*	*		
34186A	108	LF	FA	Lig	0.48			*	*		
49003B	111	LF	FA	Bit	0.54			*	*		
49003B	112	LF	FA	Bit	<0.2			*	*		
49003A	113	IMP	FA	Bit	<0.2			*	*		
49003A	114	IMP	FA	Bit	0.31			*	*		
49003A	115	IMP	FA	Bit	1.5	0.34	0.092	0.43	29%		
49003A	116	IMP	FA	Bit	1.8	0.40	0.31	0.71	39%		
35015B	118	IMP	FA,BA	Bit	<0.2			*	*		
35015B	*118D*	*dup*	*FA,BA*	*Bit*	*<0.2*			*	*		
35015B	119	IMP	FA,BA	Bit	0.23			*	*		
35015A	120	LF	FGD, FA	Bit	<0.2			*	*		
35015A	121	LF	FGD, FA	Bit	<0.2			*	*		
35015A	122	LF	FGD, FA	Bit	<0.2			*	*		
43035	126	IMP	FA,BA	Subbit	108	4.1	121	125.04	**116%**	3%	97%
43035	*126D*	*dup*	*FA,BA*	*Subbit*	*109*	*2.1*	*122*	*124.39*	***114%***	*2%*	*98%*
43035	127	IMP	FA,BA	Subbit	24	0.53	26	26.03	**107%**	2%	98%
43034	128	LF	FGD,FA	Lig	0.46	0.16	<0.02	0.16	36%		

Table 5-5
Chromium Speciation Data (continued)

Site	Sample	Source	Byproduct	Coal	Total Cr (ug/L)	Cr(III) (ug/L)	Cr(VI) (ug/L)	Sum of Species	% Recovery	% Cr(III)	% Cr(VI)
13115B	HN-1	IMP	FA,BA	Bit	<0.5			*	*		
13115B	HN-2	IMP	FA,BA	Bit	<0.5			*	*		
25410B	SX-1	IMP	FA	Blend	<0.5		<0.1	*	*		

Notes:

Ash at site 27413 (samples 090, 091, 092) was first sluiced, then managed dry.

* indicates that sum of species was not calculated because individual species were not analyzed or not detected, or % recovery was not calculated because the total chromium concentration was below detection limits or individual species were not analyzed.

Abbreviations:

Bit = bituminous; Subbit = Subbituminous; Mix = CCP from different units burning different coals; Blend = CCP from a single unit burning two different fuels

FA = fly ash; BA = bottom ash; EA = economizer ash; FGD = flue gas desulfurization sludge; OA = oil ash

LF = landfill; IMP = impoundment; DUP = duplicate sample

ND = not determined

Comparison of Speciation to Site and Plant Attributes

For ash leachate samples with greater than 80 percent species recovery (20 samples), the percentage of Cr(III) ranged from 0 to 100 percent, with a median of 2 percent and the range of Cr(VI) was 0 to 100 percent with a median of 98 percent. For FGD leachate (3 samples), Cr(III) ranged from 0 to 3 percent with a median of 0 percent and Cr(VI) ranged from 97 to 100 percent with a median of 100 percent (Figure 5-8).

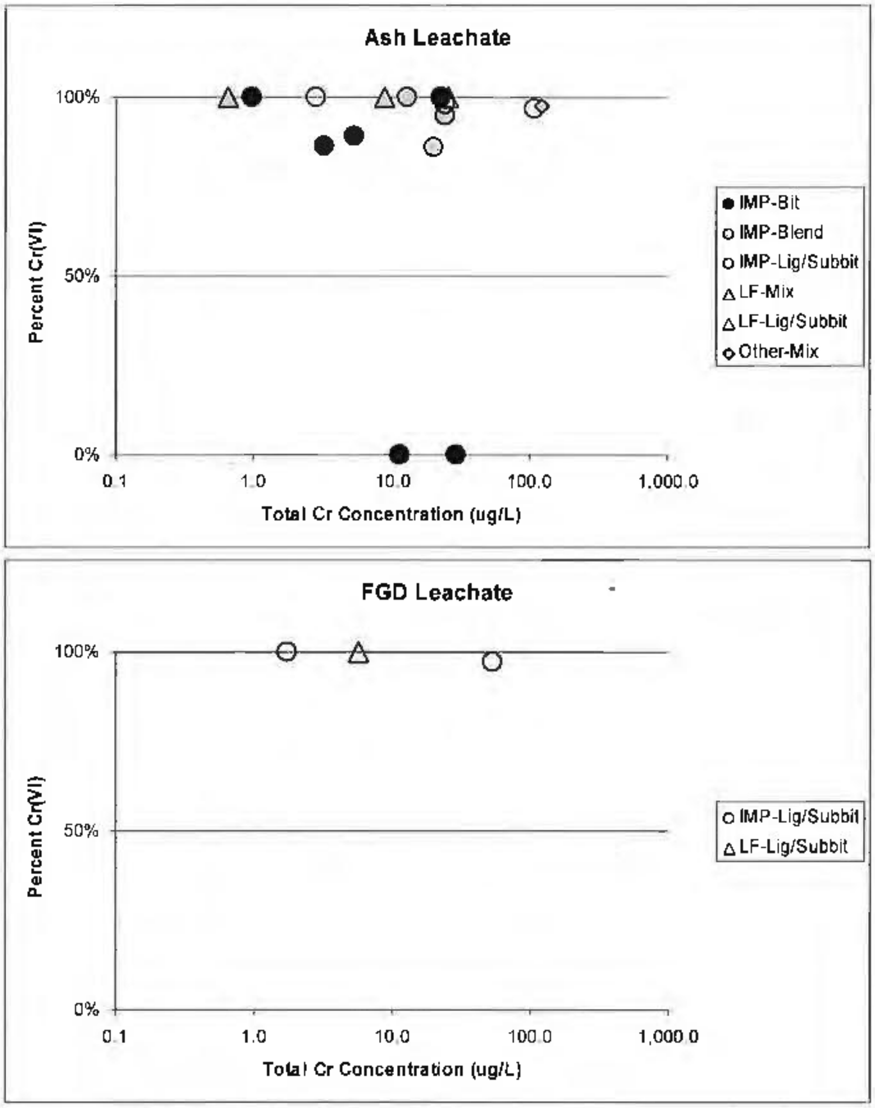

Figure 5-8
Percent Cr(VI) versus Total Cr Concentration

Using the same approach as for arsenic and selenium, the dominant chromium species was determined in 27 samples, and 24 of these were dominated by Cr(VI). The only samples dominated by Cr(III) were obtained from impoundments where the source coal was bituminous (Table 5-6). Two of these samples had very low pH (<4.5) and the other had relatively low concentration. There was no apparent relationship of between chromium speciation and total concentration (Figure 5-9).

The predominance of Cr(VI) matches geochemical expectations, because nearly all leachate samples are neutral to alkaline, and Cr(VI) is very soluble under such conditions, while Cr(III) would precipitate or bind strongly to mineral surfaces. The notable exceptions were samples 043 and 051, which only contained soluble Cr(III), and sample 057 which had a mixture of Cr(III) and Cr(V)), but also had a relatively low total concentration (1.9 µg/L). Samples 043 and 051 had the lowest pH values measured in the study (4.26 and 4.35, respectively; 1.5 pH units lower than the next lowest sample). Under the strongly acidic pH of these samples, the solubility of Cr(III) and Cr(VI) is reversed.

Five samples (002, 003, 092, 097, and 126) had Cr(VI) concentrations greater than 100 µg/L, and three of those samples (002, 003, and 097) had concentrations > 1,000 µg/L. All five samples were strongly alkaline (pH > 9.4) and oxidizing (Eh > 200 mV), and four are known to have had subbituminous coal as the CCP source (the coal source for sample 092 was uncertain).

Table 5-6
Tabulation of Dominant Selenium Species by Sample

Ash Samples	**Impoundment**	**Landfill**	_**Total**_**
Ash – Bituminous	3 – 0 – 6 (15)	0 – 0 – 1 (3)	_3 – 0 – 7_ _(18)_
Ash – Blend/Mix	0 – 0 – 3 (4)	0 – 0 – 2 (3)	_0 – 0 – 6*_ _(9*)_
Ash – Subbituminous/Lignite	0 – 0 – 4 (5)	0 – 0 – 4 (5)	_0 – 0 – 8_ _(10)_
Total	_3 – 0 – 13_ _(24)_	_0 – 0 – 7_ _(11)_	_3 – 0 – 21*_ _(37*)_
FGD Samples	**Impoundment**	**Landfill**	_**Total**_**
FGD – Bituminous			
FGD – Blend/Mix			
FGD – Subbituminous/Lignite	0 – 0 – 2 (2)	0 – 0 – 1 (3)	_0 – 0 – 3_ _(5)_
Total	0 – 0 – 2 (2)	0 – 0 – 1 (3)	_0 – 0 – 3_ _(5)_

Legend: number of samples in which → Cr(III) dominant - Neutral - Cr(VI) dominant

(Total number of samples in group)

* Tabulation includes two samples from the 27413 site, which could not be characterized as landfill or impoundment.

** Sum of total ash and FGD samples is less than 81 because only 42 samples had detectable chromium concentrations.

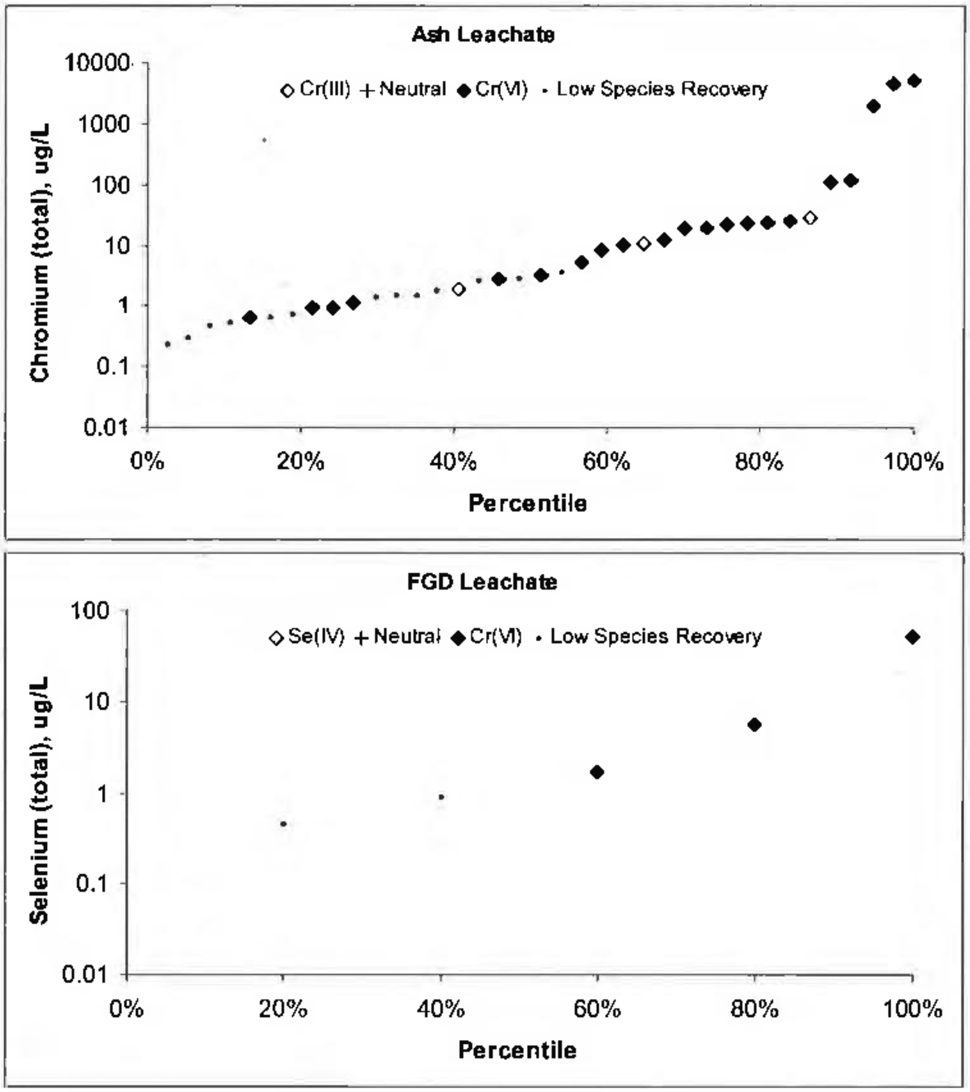

Figure 5-9
Species Predominance as a Function of Total Chromium Concentration in Leachate.

Mercury

Mercury speciation was determined on 31 samples, not counting duplicates (Table 5-7). Dimethyl mercury (DMM) was not determined on four of these samples, either because no sample was collected (due to logistic issues) or because the sample was lost during analysis (due to the fact that the employed analytical technique only allows one analysis attempt per sample). In addition, there was no particulate methyl mercury ($MeHg_{part}$) for one sample due to a field equipment problem; and dissolved methyl mercury and particulate mercury were not analyzed in another sample due to insufficient sample volume. The two duplicate samples showed poor reproducibility of results.

Table 5-7
Mercury Species Data

Site	Sample	Source	CCP	Coal	Hg_{diss} (ng/L)	DMM (ng/L)	$\text{MeHg}_{\text{diss}}$ (ng/L)	Hg_{part} (ng/L)	$\text{MeHg}_{\text{part}}$ (ng/L)
50210	001	LF	FA,BA	Mix		0.055			0.028
50213	002	LF	FA	Subbit	14	0.0051	0.11	254	0.032
50213	003	LF	FA	Subbit	18	<0.005	0.091	26	<0.01
50183	004	LF	FA,BA	Mix	5.9	<0.005	0.26	<1	0.036
50183	005	LF	FA,BA	Mix	2.1	0.0097	0.12	44	0.086
23223A	006	LF	SDA	Subbit	0.82	<0.005	0.54	25	0.092
23223B	007	IMP	FGD	Subbit	1.9	0.0074	<0.02	16	0.022
23223B	008	IMP	FGD	Subbit	4.2	<0.005	0.068	<1	0.013
23223B	009	IMP	FGD	Subbit	28		<0.02	121	0.015
49003A	021	IMP	FA	Bit	1.4	<0.005	0.034	155	0.020
49003A	022	IMP	FA	Bit	1.00	<0.005	0.027	53	0.027
49003A	023	IMP	FA	Bit	1.4	<0.005	<0.02	14	0.026
49003A	026	IMP	FA	Bit	0.38	<0.005	<0.02	17	<0.01
35015A	027	LF	FGD, FA	Bit	21	<0.005	1.6	4.3	<0.01
35015A	028	LF	FGD, FA	Bit	1.2	<0.005	0.18	13	<0.01
35015A	029	LF	FGD, FA	Bit	12	<0.005	0.70	59	0.011
35015B	030	IMP	FA	Bit	0.80	0.022	0.063	<1	0.11
35015B	031	IMP	FA	Bit	5.2	0.050	6.7	30	
35015B	032	IMP	FA,BA	Bit	1.4	0.032	0.047	186	0.055
22346	079	IMP	FA,OA	Blend	0.25	<0.005	<0.02	5.8	0.058
22346	*079D*	*dup*	*FA,OA*	*Blend*	*0.48*	*<0.005*	*0.053*	*3.0*	*0.052*
22346	082	IMP	FA,OA	Blend	5.9	<0.005	0.046	18	0.027
22347	083	IMP	FA	Blend	2.1	0.040	0.17	22	0.16
22346	084	IMP	FA,OA	Blend	0.58	<0.005	0.056	4.6	0.027
50212	097	LF	FA	Subbit	37	*	0.22	16	0.054
50183	098	LF	FA,BA	Mix	61	*	0.76	11	0.015
50183	099	LF	FA,BA	Mix	5.7	*	0.033	13	<0.01
50408	101	LF	FA,BA	Bit	2.1	*	<0.02	3.0	0.010
50211	102	LF	FA	Bit	3.8	*	0.12	52	<0.01
43035	126	IMP	FA,BA	Subbit	9.4		0.17	3.1	0.024
43035	*126D*	*dup*	*FA,BA*	*Subbit*	*2.0*		*0.21*	*6.1*	*0.024*
43035	127	IMP	FA,BA	Subbit	5.4		0.028	3.0	0.018
43034	128	LF	FGD,FA	Lig	79		6.4	100	0.059

Notes:

* Failed QC due to high concentration in the equipment blank sample.

Abbreviations:

Bit = bituminous; Subbit = Subbituminous; Mix = CCP from different units burning different coals; Blend = CCP from a single unit burning two different fuels

FA = fly ash; BA = bottom ash; EA = economizer ash; FGD = flue gas desulfurization sludge; OA = oil ash

LF = landfill; IMP = impoundment; DUP = duplicate sample

Total Hg_{diss} was detected in all 30 samples where collected, with concentrations ranging from 0.25 to 79 ng/L. Particulate mercury was detected in 27 of 30 samples.

DMM results were detectable in only 8 of the 22 samples that passed QC, and detected concentrations were lower than 0.06 ng/L. Samples 097 through 102 reported considerably higher DMM concentrations than the other samples; however, the second highest concentration was from equipment blank sample 084 (0.81 ng/L). As a result, DMM samples 097 through 102, which were collected on a single trip, failed to meet QC criteria, and were not reported here. There was no apparent difference in DMM concentration by coal type or management method.

$MeHg_{diss}$ was detected in 24 of 30 samples where analyzed, and concentrations ranged from non-detect to 6.7 ng/L. Only three samples had a $MeHg_{diss}$ concentration greater than 1 ng/L. The site with the highest concentration, 35015A, yielded two other samples with concentrations lower than 0.1 ng/L. There was no clear difference in $MeHg_{diss}$ concentrations by coal type, but there was a tendency for landfill leachate to yield higher concentrations than impoundment leachate.

Methylated vs. Inorganic Mercury

The relative methyl mercury fraction of the total mercury concentration was calculated as:

$$f(MeHg)\ [\%] = 100 \bullet [MeHg_{diss} + DMM)]/Hg_{diss}$$

DMM was added to the $MeHg_{diss}$ concentrations, because it is likely that any DMM present in the collected MeHg samples would have been volatilized by the time the samples were analyzed. There was no apparent correlation between the concentrations of total mercury and methylated mercury compounds (Figure 5-10). Furthermore, methylated mercury compounds constitute only a small fraction of the total mercury concentration in the studied waters, usually less than 5 percent (Figure 5-10). This is in agreement with most previous environmental mercury speciation studies. Only samples 006 and 031 had more than 15.2 percent $MeHg_{diss}$. Sample 006 had extremely low (<1 ng/L) Hg_{diss} and $MeHg_{diss}$ concentrations, while the $MeHg_{diss}$ concentration in sample 031 is suspect because: 1) it is higher than the total mercury (Hg_{diss}) concentration; and 2) it is two orders of magnitude higher than in two other samples (030 and 032) collected at that site on the same day (Table 5-7).

Dissolved vs. Particulate Mercury

Particulate mercury (Hg_{part} and $MeHg_{part}$) is a measure of the mercury on colloids in the water, which accumulate on the filter during sampling. As such, the particulate concentrations are dependent both on the mass of mercury on the particles and the mass of solids collected on the filters. It is of interest because mercury bound to colloids, which can move with groundwater, may be transported more quickly than mercury dissolved in water, which may sorb to the soil under the pH range typical of most groundwater.

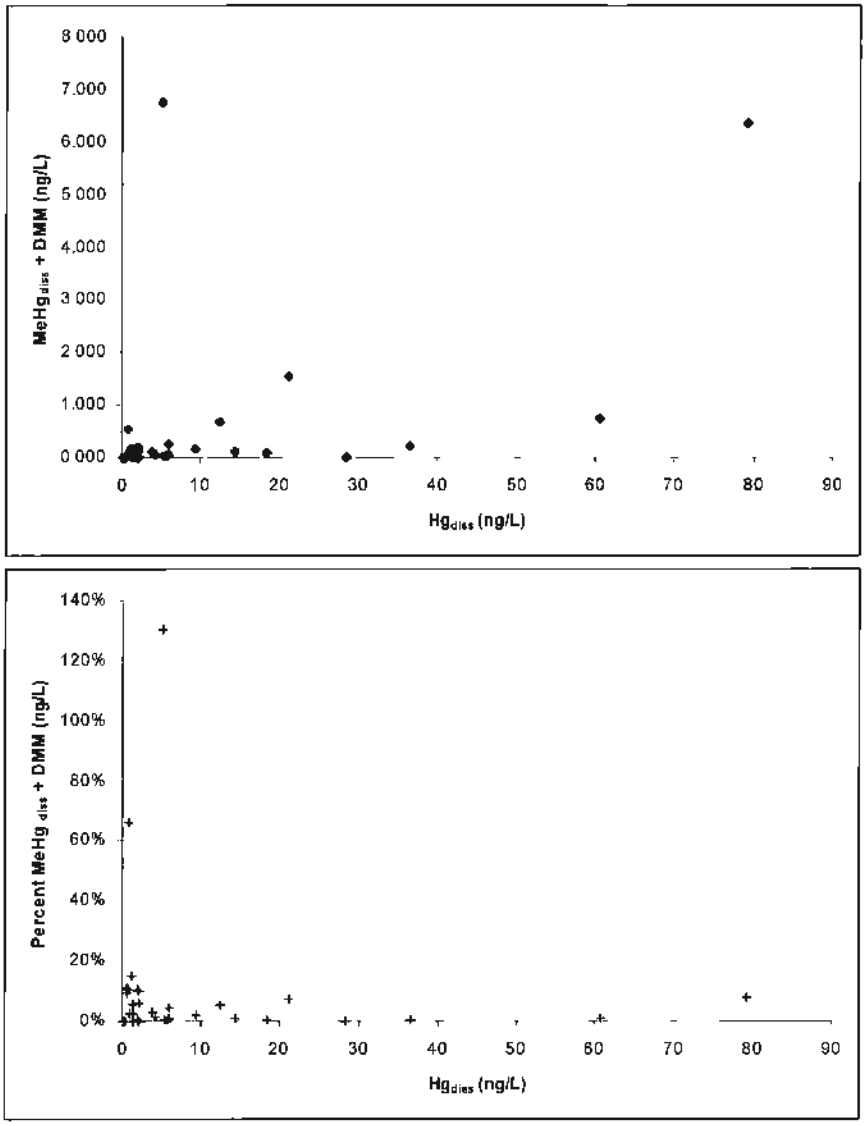

Figure 5-10
Comparison of Organic and Inorganic Mercury Concentrations

The Hg_{part} concentrations in the field leachate samples were low, ranging from <1 to 254 ng/L (Table 5-7). The highest concentration (sample 002) was obtained from a lysimeter at Site 50213, where subbituminous fly ash was managed. A second lysimeter at the same site had a particulate concentration of 26 ng/L. Conversely, the Hg_{diss} concentration associated with these two samples did not exhibit the variability of the particulate concentrations. There was no overall relationship between Hg_{part} and Hg_{diss} concentration (Figure 5-11), nor was there a relationship between $MeHg_{part}$ and $MeHg_{diss}$ (Figure 5-12).

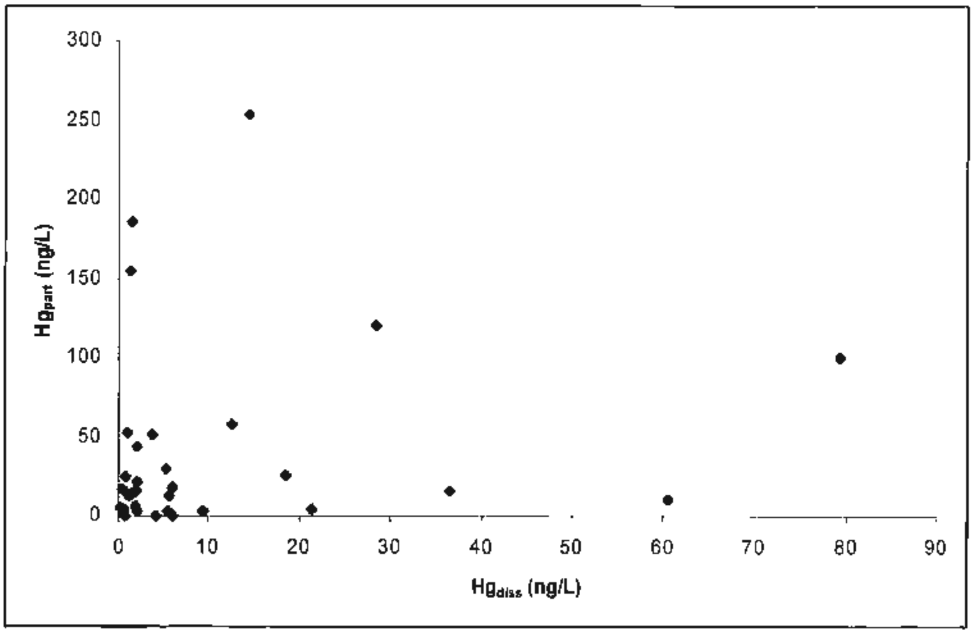

Figure 5-11
Dissolved versus Particulate Mercury Concentrations

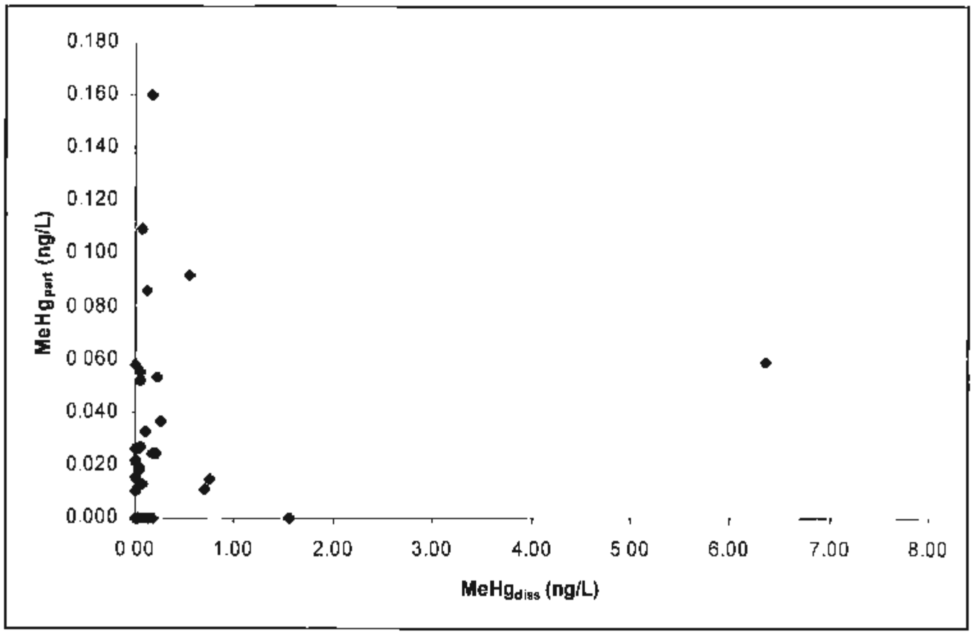

Figure 5-12
Dissolved versus Particulate Methyl Mercury Concentrations

6
CONCLUSIONS

The following conclusions are based on 81 field leachate samples collected at 29 CCP management sites. Due to their unique characteristics, coal ash leachate (67 samples) and FGD leachate (14 samples) were treated separately.

Chemical Composition of Coal Ash Field Leachate Samples

- Most leachate samples were moderately to strongly oxidizing and moderately to strongly alkaline. The subbituminous/lignite ash samples had higher median pH (10.0) than bituminous ash (6.9). Several samples with relatively low Eh and pH were collected from impoundments.
- The anion chemistry of coal ash leachate samples is dominated by sulfate. The median concentration of this constituent was 339 mg/L; this was the only constituent in the leachate with a median concentration greater than 100 mg/L.
- Major cation chemistry was strongly influenced by the type of coal burned at the power plant. Ash leachate derived from bituminous coal was dominated by calcium and magnesium, while ash leachate derived from subbituminous/lignite coal was dominated by sodium.
- Silica and boron had the highest median concentrations (4,645 and 2,160 µg/L, respectively) of the minor and trace constituents. Median concentrations of strontium, molybdenum, lithium, aluminum, and barium were greater than 100 µg/L. Conversely, median concentrations of chromium, beryllium, thallium, silver, lead, and mercury were lower than 1 µg/L; with silver, beryllium, and lead being rarely detected (detected in 7, 6, and 27 percent of the samples, respectively).
- Most constituents (22 out of the 34 analyzed) had higher concentrations in landfill leachate samples than in impoundment leachate samples.
- Leachate samples derived from bituminous coal ash had higher concentrations of calcium, magnesium, cobalt, lithium, manganese, nickel, antimony, thallium, and zinc than leachate from subbituminous coal ash. Lithium and manganese had concentrations an order of magnitude higher in the bituminous ash leachate samples, while thallium was only detected in leachate from bituminous ash.
- Leachate from subbituminous/lignite coal ash had higher concentrations of carbonates, chloride, sodium, sulfate, aluminum, chromium, copper, and mercury than leachate from bituminous coal. The difference was most notable for aluminum and mercury, where the concentrations were higher by an order of magnitude or more.

Chemical Composition of FGD Leachate Field Samples

- The FGD leachate samples were moderately to strongly oxidizing, and moderately to strongly alkaline. Landfill samples, as a group, were less oxic and more alkaline than impoundment samples, although the lowest Eh value was for an impoundment.
- Concentrations of most major constituents (specifically, calcium, chloride, potassium, sodium, and sulfate) in FGD leachate were higher than in ash leachate. The median sulfate concentration was 1,615 mg/L, and the maximum sulfate concentration was 30,500 mg/L, which was the highest single analytical result returned from the field leachate sampling. The high sulfate concentration was obtained from an impoundment where sluice water is recirculated.
- More than 25 percent of the chloride and sodium concentrations were greater than 1,000 mg/L, and median concentrations of chloride, calcium, potassium, and sodium were greater than 100 mg/L.
- The FGD leachate samples had higher percentages of chloride and potassium than the ash leachate samples.
- Anion concentrations were largely dominated by sulfate. Major cation concentrations (calcium, magnesium, potassium, sodium) were variable, with samples from the same site having different cation chemistry.
- The relative concentrations of minor and trace elements in FGD leachate were somewhat different than in ash leachate. Median concentrations of boron, strontium, and lithium in FGD leachate were a factor of 3 or more higher than in ash leachate, while concentrations of selenium, vanadium, uranium, and thallium in ash leachate were higher than in FGD leachate by a factor of 3 or more.
- Boron (9,605 µg/L), strontium (5,230 µg/L), lithium (3,055 µg/L), and silica (2,480 µg/L) had median concentrations greater than 1,000 µg/L in the FGD field leachate samples. Median concentrations of molybdenum, aluminum, and manganese were greater than 100 µg/L, while median concentrations of chromium, heryllium, thallium, silver, lead, and mercury were lower than 1 µg/L. Silver was not detected in the 14 FGD leachate samples, while beryllium (7 percent detects), chromium (36 percent), iron (29 percent), lead (36 percent), and thallium (14 percent), were usually not detected.

Speciation Analysis in Field Leachate Samples

Arsenic

- Arsenic concentrations in ash leachate ranged from 1.4 to 1,380 µg/L, with a median of 25 µg/L.
- The dominant arsenic species was determined in 43 samples. Most ash leachate samples (37) were dominated by As(V). As(III) was only dominant in four samples from impoundments where bituminous coal ash was managed. Two samples had equal amounts of arsenic species.

- Arsenic concentration in FGD leachate ranged from 11 to 230 μg/L, with a median of 28 μg/L.
- The dominant arsenic species was determined in 6 FGD leachate samples. Two were dominated by As(V), two were dominated by As(III), and two samples had equal amounts of the species.

Selenium

- Selenium concentration in ash leachate ranged from 0.07 to 1,760 μg/L, with a median of 19 μg/L.
- The dominant selenium species was determined in 46 leachate samples. Most ash leachate samples (29) were dominated by Se(IV). Se(VI) was dominant in 17 samples. Se(IV) dominated in impoundment settings when the source coal was bituminous or a mixture of bituminous and subbituminous, while Se(VI) was predominant in landfill settings and when the source coal was subbituminous/lignite. Most samples with relatively high concentration (>80 μg/L) were dominated by Se(VI) while samples with concentrations lower than 50 μg/L were mostly dominated by Se(IV).
- Selenium concentration in FGD leachate ranged from 1.1 to 2,360 μg/L, with a median of 6.2 μg/L.
- The dominant selenium species was determined in 7 FGD leachate samples. Six were dominated by Se(VI), one had similar percentages of both species, and none were dominated by Se(IV).

Chromium

- Chromium concentration in ash leachate ranged from <0.2 to 5,100 μg/L, with a median of 0.60 μg/L.
- The dominant chromium species was determined in 27 ash leachate samples. Most ash leachate samples (24) were dominated by Cr(VI). Cr(III) was dominant in three samples, two of which had acidic pH.
- Chromium concentration in FGD leachate ranged from <0.2 to 53 μg/L, with a median concentration below detection limits.
- The dominant chromium species was determined in three FGD leachate samples, and all three were dominated by Cr(VI).

Mercury

- Mercury concentrations in 22 ash leachate samples were very low, ranging from 0.25 to 61 ng/L, with a median concentration of 3.8 ng/L. Mercury concentrations in 8 FGD leachate samples were also very low, ranging from 0.82 to 79 ng/L, with a median concentration of 8.3 ng/L.
- The organic species of mercury always had low concentration, usually less than 5 percent of the total mercury concentration. Monomethyl mercury concentrations ranged from <0.02 to

6.7 ng/L, with a median concentration of 0.08 ng/L. Dimethyl mercury concentrations ranged from <0.02 to 0.06 ng/L, with a median concentration of <0.02 ng/L. There was no relationship between inorganic and organic mercury concentrations.

- There was no clear relationship between organic mercury concentrations and coal type, although there was a tendency for landfill leachate to yield slightly higher concentrations than impoundment leachate.

Effects of Power Plant Attributes on CCP Leachate Composition

- Power plants that have cyclone boilers and burn petroleum coke produced leachate samples with higher than median concentrations of most elements, and the highest concentrations of cadmium, molybdenum, and vanadium.
- There was no definitive relationship on leachate quality associated with hot-side and cold-side ESPs. Three sites receiving ash from hot-side ESPs were sampled. A landfill yielded the highest concentrations of Co, CO_3, Cr, Cu, Na, Se, and SO_4 of the sampled ash sites. However two impoundments did not show evidence of high concentrations.
- Oil ash was managed with coal ash at one site. The leachate from the ash sampled at this site did not show any evidence of low or high concentration for any elements.
- Most constituents in leachate from the single plant with a spray-dryer FGD system had lower concentration than leachate samples from the wet FGD systems used at other plants.

7
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A

ANALYTICAL RESULTS

Table A-1
Hydrochemistry and Trace Elements

		001	002	003	004	005	006	007	008	009	010	012	QA-1	013
Chloride	mg/L	86.2	25	11	26	6.5	19	572	371	345	28	9	< 0.01	27.3
Sulfate	mg/L	909	6,690	5,450	1,960	350	1,450	3,150	2,080	10,400	3,830	1,650	0.47	1,700
Sodium	mg/L	443	3,410	2,910	672	93	108	1,330	606	743	1,700	30	0.4	55
Potassium	mg/L	255	80	80	20	< 5	10	80	20	40	118	< 20	< 0.2	75
Magnesium	mg/L	< 1	0.59	0.53	70	15	77	125	23	1,990	8	13	0.10	36
Calcium	mg/L	10	19	9	218	70	528	524	563	577	139	681	0.53	584
TOC	mg/L	13.9	55.1	49.8	43.9	4.5	8.1	20.5	16.2	9.9	5.3	1.9	0.4 (a)	6.3
TIC	mg/L	6.9	32.2	63.1	29.7	11.9	17.5	2.4	2.7	1.7	1.7	2.0	1.56	16.6
Temperature	°C	20.2	21.5	15.4	14.9	21.3	18.7	17.6	26.9	25.6	17.3	22.6	n/a	21.3
Spec. Cond.	mS/cm	3.5	12.8	11.2	3.8	0.8	2.9	8.3	4.8	13.0	7.7	2.7	n/a	2.9
Diss. Oxygen	% sat.	0.1	0.2	0.2	0.2	0.2	0.4	0.2	0.3	0.3	14	5	n/a	4
pH	pH	11.6	10.0	10.3	9.3	7.4	8.0	6.2	8.4	7.4	11.2	9.4	n/a	8.2
ORP (corr.)	mV	209	276	271	276	411	341	356	1	342	111	245	n/a	102
Lithium	ug/L	2,460	< 20	< 20	< 20	< 20	< 20	170	< 20	2,720	< 20	80	< 20	100
Beryllium	ug/L	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 4	< 1
Boron	ug/L	2,120	18,400	31,900	10,800	1,410	15,600	81,500	49,000	98,500	14,000	93,400	< 50	112,000
Aluminum	ug/L	18,100	2,680	17,500	< 30	< 30	< 30	610	890	190	980	530	< 30	< 30
Silicon	ug/L	6,900	5,800	1,200	6,100	6,400	2,600	10,500	400	12,700	9,900	1,500	< 100	18,500
Vanadium	ug/L	373	1,070	635	45	< 2	4	15	< 2	18	5,020	195	< 2	4
Manganese	ug/L	< 4	7	< 4	751	577	< 4	704	113	564	< 4	22	< 4	2,560
Iron	ug/L	< 50	< 50	< 50	< 50	< 50	< 50	1,200	< 50	< 50	< 50	< 50	< 50	14,700
Cobalt	ug/L	< 1	133	9	< 1	< 1	< 1	6	< 1	78	< 1	< 1	< 1	7
Nickel	ug/L	< 3	75	8	14	4	4	597	5	463	8	4	< 20	15
Copper	ug/L	11	494	62	6	3	4	14	44	7	15	< 3	< 3	< 3
Zinc	ug/L	< 5	< 5	< 5	< 5	6	19	23	< 5	34	12	12	< 30	45
Strontium	ug/L	800	60	< 30	930	80	9,140	16,900	14,900	11,700	3,900	2,250	< 30	1,260
Molybdenum	ug/L	9,740	5,720	6,200	1,200	440	310	60,800	570	320	25,400	740	< 30	100
Silver	ug/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 1	0.2
Cadmium	ug/L	17.7	8.8	7.6	1.9	0.8	0.7	12.3	11.8	4.2	51.9	1.5	< 2	0.4
Antimony	ug/L	0.9	0.8	0.7	0.6	< 0.3	4.7	2.8	0.7	4.6	1.0	6.7	< 3	0.7
Barium	ug/L	50	< 30	< 30	110	40	70	50	< 30	90	50	40	< 30	< 30
Thallium	ug/L	< 0.1	< 0.5	< 0.5	< 0.1	< 0.1	< 0.1	< 0.5	< 0.1	2.9	< 0.1	< 0.1	<0.01	0.6
Lead	ug/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.5	0.3	< 0.2	0.3	< 0.2	< 1	< 0.2
Uranium	ug/L	< 0.2	0.2	9.8	1.3	< 0.2	10.4	0.7	< 0.2	0.7	0.3	1.8	< 1	3.3

Table A-1
Hydrochemistry and Trace Elements (continued)

		013D	014	QA-2	015	016	SX-1	017	018	019	020	HN-1	HN-2	021
Chloride	mg/L	27.5	32.8	0.05	25.3	54.8	22.2	72.0	63.4	84.8	75.9	29.2	45.4	18.0
Sulfate	mg/L	1,610	1,370	0.40	782	910	1,530	91.4	339	124	131	1,260	810	193
Sodium	mg/L	56	17	0.9	60	731	52	53	57	56	54	72	53	31
Potassium	mg/L	74	26	< 0.2	20	229	38	8	9	6	6	277	48	11
Magnesium	mg/L	39	7	0.63	33	20	7	21	36	28	23	3	21	13
Calcium	mg/L	544	591	1.34	255	15	529	46	231	81	43	302	291	48
TOC	mg/L	6.2	3.9	0.6 (a)	5.3	24.0	16.6	6.7	14.2	6.0	0.4 (a)	21.5	22.5	1.2 (a)
TIC	mg/L	16.7	35.1	1.47	15.4	5.60	11.3	22.4	115.0	48.7	24.8	2.48	2.94	8.03
Temperature	°C	n/a	20.5	32	31.7	30.6	n/a	29.7	18.3	35.5	29.6	n/a	n/a	20.8
Spec. Cond.	mS/cm	n/a	2.6	0.0	1.6	5.1	n/a	0.7	1.6	1.0	0.7	n/a	n/a	0.6
Diss. Oxygen	% sat.	n/a	5.5	3	3.7	2.9	n/a	1.6	2.9	3.4	4.5	n/a	n/a	29.5
pH	pH	n/a	9.3	5.3	9.3	11.7	n/a	8.8	7.4	8.0	8.9	n/a	n/a	7.9
ORP (corr.)	mV	n/a	240	515	339	124	n/a	289	94	296	303	n/a	n/a	245
Lithium	ug/L	n/a	110	< 20	100	60	50	< 20	30	< 20	< 20	1,060	60	310
Beryllium	ug/L	n/a	< 1	< 4	< 1	< 1	< 0.8	< 1	< 1	< 1	< 1	< 0.8	< 0.8	< 0.8
Boron	ug/L	n/a	54,900	< 50	3,890	109,000	24,200	860	26,300	470	700	2,350	42,700	850
Aluminum	ug/L	n/a	300	< 30	100	44,400	< 150	1,920	80	4,190	730	< 150	< 150	80
Silicon	ug/L	n/a	1,500	< 100	8,800	19,000	2,400	3,000	10,300	3,400	2,200	3,400	3,300	5,400
Vanadium	ug/L	n/a	36	< 2	550	1,230	11	16	6	10	17	206	41	217
Manganese	ug/L	n/a	25	< 4	< 4	8	52	< 4	4,170	14	< 4	< 4	< 4	67
Iron	ug/L	n/a	< 50	< 50	< 50	1,530	< 50	< 50	3,190	< 50	< 50	< 50	< 50	300
Cobalt	ug/L	n/a	< 1	< 1	3	2	< 1	< 1	2	1	< 1	< 1	< 1	< 1
Nickel	ug/L	n/a	5	< 20	16	128	< 3	5	8	7	4	10	7	4
Copper	ug/L	n/a	< 3	< 3	< 3	21	< 3	12	35	8	7	7	5	6
Zinc	ug/L	n/a	40	< 30	< 5	130	25	8	7	9	11	16	< 5	6
Strontium	ug/L	n/a	3,140	< 30	4,300	1,200	2,690	530	640	580	720	930	680	730
Molybdenum	ug/L	n/a	6,030	< 30	420	39,600	3,010	80	100	< 30	< 30	1,910	500	710
Silver	ug/L	n/a	< 0.2	< 1	< 0.2	< 0.2	1.1	< 0.2	< 0.2	< 0.2	< 0.2	2.0	0.8	< 0.2
Cadmium	ug/L	n/a	21.2	< 2	1.0	64.7	14.0	< 0.3	0.4	< 0.3	< 0.3	8.5	1.5	1.2
Antimony	ug/L	n/a	2.0	< 3	1.4	2.4	1.3	0.5	0.6	0.6	0.5	3.4	1.6	31.4
Barium	ug/L	n/a	40	< 30	350	140	80	140	100	350	220	80	60	240
Thallium	ug/L	n/a	< 0.1	<0.01	2.5	0.3	3.1	< 0.1	0.1	< 0.1	< 0.1	< 0.5	< 0.5	1.5
Lead	ug/L	n/a	< 0.2	< 1	< 0.2	4.6	0.8	< 0.2	< 0.2	0.21	< 0.2	0.4	0.4	< 0.2
Uranium	ug/L	n/a	1.1	< 1	3.7	0.7	12.5	1.1	4.6	1.2	1.2	< 0.2	0.7	2.7

Table A-1
Hydrochemistry and Trace Elements (continued)

		022	023	024	025	026	027	028	029	030	031	032	034	035
Chloride	mg/L	17.8	28.4	23	15.3	17.9	932	1,260	1,200	33.8	87	55.9	< 0.01	< 0.01
Sulfate	mg/L	217	248	2,350	845	219	1,620	1,610	1,510	948	1,830	386	< 0.05	< 0.05
Sodium	mg/L	42	33	188	80	43	285	341	297	25	60	32	< 0.1	< 0.1
Potassium	mg/L	9	8	170	40	9	470	580	500	20	50	10	< 0.2	< 0.2
Magnesium	mg/L	14	28	203	82	14	3	10	4	39	35	50	< 0.05	< 0.05
Calcium	mg/L	43	79	405	235	43	671	722	730	332	665	124	< 0.05	< 0.05
TOC	mg/L	0.5 (a)	2.2	1.3 (a)	4.1	0.9 (a)	1.9	0.5 (a)	1.4 (a)	0.5 (a)	11.0	0.6 (a)	0.1 (a)	0.1 (a)
TIC	mg/L	2.49	27.3	54.5	79.9	1.04	1.00	3.25	0.95	10.4	1.53	12.9	0.43 (a)	0.46 (a)
Temperature	°C	21.6	17.4	15.6	15.2	22.2	16.3	16.1	15.5	15.4	15.6	13.9	23.0	23.6
Spec. Cond.	mS/cm	0.6	0.7	4.0	2.0	0.6	5.6	6.6	6.1	1.8	3.0	1.0	0.003	0.002
Diss. Oxygen	% sat.	39.1	17.6	16	15.8	22.4	11.8	10.6	17.1	29.6	6.1	14.5	84.7	71.1
pH	pH	7.1	7.0	7.0	6.5	7.2	10.0	9.0	9.9	8.5	8.5	7.8	5.67	5.40
ORP (corr.)	mV	307	287	268	264	319	71	220	121	308	-41	295	335	306
Lithium	ug/L	360	120	18,600	3,430	320	6,920	5,890	6,260	100	410	240	<0.1	<0.1
Beryllium	ug/L	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	< 0.8	<0.04	<0.04
Boron	ug/L	430	1,970	22,400	11,100	420	1,450	3,260	2,820	3,280	7,610	2,210	0.9	1.4
Aluminum	ug/L	40	90	< 30	< 30	40	190	< 30	130	190	140	< 30	0.4	0.8
Silicon	ug/L	3,600	3,400	9,400	5,400	3,300	3,000	1,900	2,000	700	3,700	5,400	6.7	18.4
Vanadium	ug/L	70	427	4	< 2	63	< 2	< 2	4	18	4	12	0.10	0.06
Manganese	ug/L	104	149	3,650	4,110	104	18	202	62	41	269	92	<0.02	0.05
Iron	ug/L	< 50	120	80	90	< 50	< 50	< 50	< 50	< 50	< 50	< 50	0.4	0.4
Cobalt	ug/L	8	2	96	8	8	< 1	< 1	< 1	< 1	1	3	<0.02	<0.02
Nickel	ug/L	19	9	167	6	21	3	< 3	< 3	3	8	17	0.08	0.09
Copper	ug/L	8	8	< 3	< 3	< 3	< 3	3	< 3	16	< 3	24	0.46	0.47
Zinc	ug/L	21	11	148	< 5	14	< 5	12	< 5	90	13	15	<0.3	0.7
Strontium	ug/L	430	1,990	6,460	2,290	400	3,520	3,980	4,300	990	2,480	360	<0.4	<0.4
Molybdenum	ug/L	410	500	3,870	2,420	400	180	350	300	140	210	120	<0.1	<0.1
Silver	ug/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	<0.02	<0.02
Cadmium	ug/L	1.1	1.0	9.1	5.1	1.6	0.5	0.8	0.6	< 0.3	0.5	1.2	<0.02	<0.02
Antimony	ug/L	24.3	59.1	4.9	0.5	23.5	< 0.3	< 0.3	< 0.3	5.0	2.7	3.8	<0.02	<0.02
Barium	ug/L	190	110	50	50	190	60	60	80	80	60	160	<0.2	<0.2
Thallium	ug/L	12.0	1.3	1.5	0.4	12.3	< 0.5	< 0.5	< 0.5	3.4	< 0.1	17.6	<0.02	<0.02
Lead	ug/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.03	<0.02
Uranium	ug/L	< 0.2	60.8	13.0	19.3	< 0.2	< 0.2	< 0.2	< 0.2	5.3	2.0	1.0	<0.01	<0.01

Table A-1
Hydrochemistry and Trace Elements (continued)

		036	037	038	039	042	043	044	044D	049	050	051	052	053
Chloride	mg/L	< 0.01	8.8	9.7	9.4	9.7	7.1	9.8	9.1	9.8	< 0.01	5.3	7.6	8.1
Sulfate	mg/L	< 0.05	123	121	101	57	111	70	70	53	< 0.05	111	128	176
Sodium	mg/L	< 0.1	3.8	3.9	4.7	8.6	8.5	8.3	8.3	7.0	0.1	11.8	6.8	5.6
Potassium	mg/L	< 0.2	2.2	2.3	5.3	5.2	7.0	5.0	5.0	4.0	< 0.2	13.6	11.1	9.2
Magnesium	mg/L	< 0.05	6.91	6.61	3.08	2.06	2.58	2.66	2.67	2.53	< 0.05	1.81	0.08	0.12
Calcium	mg/L	< 0.05	45.8	45.3	36.1	12.4	19.9	15.4	15.5	13.2	0.09	14.4	58.4	69.5
TOC	mg/L	0.1 (a)	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	0.1 (a)	< 0.09	0.8 (a)	0.7 (a)
TIC	mg/L	0.48 (a)	10.4	10.5	6.66	2.01	1.03	0.75 (a)	0.68 (a)	2.18	0.44 (a)	0.92	3.30	4.96
Temperature	°C	23.6	22	22.7	24.2	29.4	32	32	31.5	25.8	24.5	26.5	27.1	26.7
Spec. Cond.	mS/cm	0.001	0.379	0.381	0.317	0.178	0.293	0.209	0.210	0.174	0.009	0.287	0.588	0.468
Diss. Oxygen	% sat.	77	35	27.6	33.5	84.1	75.7	67.9	80.2	77.6	72	82.4	56	40.6
pH	pH	5.66	7.05	7.04	6.98	5.79	4.26	5.97	6.03	5.97	4.92	4.35	10.59	8.92
ORP (corr.)	mV	299	192	163	184	283	388	285	289	290	300	387	211	212
Lithium	ug/L	<0.1	82	81	125	179	239	146	145	99	<0.1	520	561	595
Beryllium	ug/L	<0.04	<0.4	<0.4	<0.4	1.6	8.6	0.8	1.3	<0.4	<0.04	5.2	<0.4	<0.4
Boron	ug/L	3.1	1390	1240	917	426	838	429	489	265	43.3	272	4620	7370
Aluminum	ug/L	1.0	15	14	6	148	3730	66	72	14	3.5	2150	15100	2010
Silicon	ug/L	21.5	7960	7660	7000	4700	5780	4730	5100	4670	15.3	5840	1890	1030
Vanadium	ug/L	0.10	13.8	6.9	2.6	70.8	35.6	9.6	9.5	5.6	0.21	4.7	754.4	62.4
Manganese	ug/L	0.67	248	244	261	42.7	77.5	86.1	88.6	79.4	23.4	113	0.4	5.9
Iron	ug/L	1.0	921	1700	1070	6	722	18	28	7	8.2	3240	16	30
Cobalt	ug/L	<0.02	1.7	0.7	<0.2	11.5	21.6	8.7	9.0	5.2	0.05	18.9	<0.2	0.2
Nickel	ug/L	0.45	7.2	4.2	2.4	37.8	71.9	26.7	27.5	13.6	2.98	58.2	<0.6	1.5
Copper	ug/L	0.55	0.5	1.0	<0.4	8.7	152	12.0	11.2	1.9	1.13	452	1.8	8.4
Zinc	ug/L	0.7	<3	<3	<3	58.1	80.4	35.6	32.9	18.3	5.6	74.6	<3	5.7
Strontium	ug/L	<0.4	1350	1360	1120	170	247	272	262	209	<0.4	806	5150	5610
Molybdenum	ug/L	<0.1	1110	1060	287	127	35	54	54	60	0.2	8	246	360
Silver	ug/L	<0.02	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.02	<0.2	<0.2	<0.2
Cadmium	ug/L	<0.02	4.6	4.1	1.2	1.3	1.9	0.7	0.8	0.5	<0.02	2.4	0.8	2.3
Antimony	ug/L	<0.02	4.6	2.4	0.3	13.9	17.8	8.7	8.8	7.1	<0.02	5.9	14.4	2.6
Barium	ug/L	<0.2	125	169	77	75	131	180	181	195	<0.2	545	250	87
Thallium	ug/L	<0.02	<0.2	<0.2	<0.2	0.7	4.2	1.6	1.5	0.7	<0.02	6.3	0.4	0.3
Lead	ug/L	<0.02	<0.1	<0.1	<0.1	0.2	1.9	0.2	<0.1	<0.1	<0.02	8.0	<0.1	0.5
Uranium	ug/L	<0.01	0.2	0.1	<0.1	<0.1	0.5	<0.1	<0.1	<0.1	<0.01	1.0	0.1	1.7

Table A-1
Hydrochemistry and Trace Elements (continued)

		057	059	059D	060	061	062	064	069	070	070D	077	078	079
Chloride	mg/L	5.6	4.5	4.6	< 0.01	7.1	15.8	5.0	7.3	12.1	9.7	< 0.01	< 0.01	77.2
Sulfate	mg/L	52	55	55	< 0.05	61	117	150	45	50	51	< 0.05	< 0.05	315
Sodium	mg/L	8.1	8.5	8.5	< 0.1	9.5	11.4	7.3	6.0	10.8	10.8	< 0.1	< 0.1	63
Potassium	mg/L	5.8	6.4	6.4	< 0.2	6.4	9.6	9.4	3.6	5.0	4.9	< 0.2	< 0.2	13
Magnesium	mg/L	1.53	1.37	1.43	< 0.05	4.97	0.11	1.49	2.16	1.78	1.81	< 0.05	< 0.05	19.5
Calcium	mg/L	16.8	16.8	16.5	0.20	55.1	76.5	58.1	19.0	26.0	26.3	< 0.05	< 0.05	95.3
TOC	mg/L	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	0.4 (a)	0.2 (a)	0.3 (a)
TIC	mg/L	6.02	5.07	4.99	0.43 (a)	38.3	3.98	3.92	6.04	9.44	9.55	0.34 (a)	0.28 (a)	20.6
Temperature	°C	28.5	31.2	n/a	25.7	27.6	29	30	27.7	29.4	28.9	28.6	27.0	19.5
Spec. Cond.	mS/cm	0.189	0.195	n/a	0.003	0.433	0.765	0.455	0.182	0.244	0.247	0.001	0.002	1.076
Diss. Oxygen	% sat.	89.2	165.1	n/a	90.2	65.3	37.9	67.7	63.5	67.9	68.3	64.3	74.3	28.0
pH	pH	7.66	9.04	n/a	5.4	7.25	10.95	10.12	7.57	8.91	9.1	5.07	5.58	6.75
ORP (corr.)	mV	n/a	409	na	277	140	196	214	220	223	220	263	236	114
Lithium	ug/L	267	293	288	<0.1	155	243	430	140	160	167	<0.05	<0.05	134
Beryllium	ug/L	<0.4	<0.4	<0.4	<0.04	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.01	<0.01	<0.2
Boron	ug/L	300	351	309	1.2	2600	494	476	231	207	236	7.1	6.8	1110
Aluminum	ug/L	111	356	366	1.8	58	3900	2310	29	468	519	2.3	2.3	<2
Silicon	ug/L	5120	5010	5190	8.6	11100	6870	4760	7450	7190	6920	509	513	10100
Vanadium	ug/L	31.3	34.4	34.6	0.18	5.6	176.9	229.6	61.3	93.1	94.2	0.22	0.21	0.4
Manganese	ug/L	1.6	0.6	0.8	0.04	395	<0.2	<0.2	22.0	0.4	0.7	7.50	4.84	190
Iron	ug/L	6	26	25	0.7	2170	17	13	<5	27	46	12.9	2.28	25600
Cobalt	ug/L	<0.2	<0.2	<0.2	<0.02	0.3	<0.2	<0.2	1.3	<0.2	<0.2	0.007	0.003	0.18
Nickel	ug/L	2.3	1.7	1.4	<0.6	4.0	<0.6	0.9	5.4	0.6	<0.6	<0.03	<0.03	<0.6
Copper	ug/L	1.3	2.0	1.8	0.5	<0.4	1.2	0.5	0.7	1.8	2.1	0.30	0.27	<0.2
Zinc	ug/L	<3	4.0	<3	0.4	<3	<3	<3	<3	<3	<3	0.4	0.4	1.5
Strontium	ug/L	545	547	576	<0.4	1840	1010	478	340	258	263	3.37	3.39	2190
Molybdenum	ug/L	62	63	61	<0.1	95	173	217	78	61	63	<0.02	<0.02	135
Silver	ug/L	<0.2	<0.2	<0.2	<0.02	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.01	<0.01	<0.2
Cadmium	ug/L	<0.2	0.4	<0.2	<0.02	0.3	0.6	0.6	0.3	<0.2	<0.2	<0.01	<0.01	<0.2
Antimony	ug/L	6.2	5.6	5.5	<0.02	0.7	8.2	27.4	9.5	7.6	7.9	<0.005	0.005	<0.1
Barium	ug/L	182	171	166	<0.2	226	194	319	156	124	132	<0.1	<0.1	99.2
Thallium	ug/L	1.0	0.9	0.9	<0.02	0.5	<0.2	0.3	1.0	0.4	0.4	<0.005	<0.005	<0.1
Lead	ug/L	<0.1	<0.1	<0.1	<0.02	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.04	0.02	<0.1
Uranium	ug/L	0.5	1.2	1.3	<0.01	1.4	<0.1	0.7	0.3	2.2	2.2	<0.001	<0.001	1.91

Table A-1
Hydrochemistry and Trace Elements (continued)

		079D	082	083	084	088	089	090	091	092	TEB	094	095	096 (1)
Chloride	mg/L	77.9	72.0	68.4	67.9	< 0.01	0.37	11.8	5.35	4.67	0.22	0.06	0.04	92.4
Sulfate	mg/L	315	174	92.8	135	< 0.05	1.50	324	393	448	0.65	< 0.05	< 0.05	2,850
Sodium	mg/L	63	68	45	38	0.7	0.9	182	277	109	0.6	< 0.1	< 0.1	1,560
Potassium	mg/L	14	5	4	6	< 0.2	0.2	113	84	67	1.2	< 0.2	< 0.2	74
Magnesium	mg/L	19.4	19.1	12.6	30.8	< 0.05	0.35	0.15	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	9
Calcium	mg/L	98.0	79.1	34.4	105	< 0.05	0.72	11.9	2.22	287	1.30	< 0.05	< 0.05	9
TOC	mg/L	0.8 (a)	2.6	4.7	< 0.09	0.4 (a)	0.5 (a)	12.8	4.3	3.4	0.4 (a)	0.3 (a)	0.3 (a)	49.8
TIC	mg/L	19.7	35.9	11.9	60.5	0.28 (a)	1.20	13.8	7.62	0.85	1.37	0.21 (a)	0.23 (a)	128
Temperature	°C	18.0	30.2	25.9	19.2	n/a	n/a	17.2	16.8	15.9	n/a	12.4	13.7	16.1
Spec. Cond.	mS/cm	1.068	0.911	0.547	0.927	n/a	n/a	1.59	2.33	1.427	n/a	0.002	0.005	7.295
Diss. Oxygen	% sat.	21.0	65.1	100.0	40.7	n/a	n/a	n/a	n/a	n/a	n/a	84	73.3	67
pH	pH	6.84	8.64	9.36	7.78	n/a	n/a	10.86	11.52	11.17	n/a	6.2	5.44	7.29
ORP (corr.)	mV	87	241	217	198	n/a	n/a	246	288	346	n/a	227	261	223
Lithium	ug/L	134	60	27	139	<0.05	4	2	5	11	1.25	<0.05	<0.05	5
Beryllium	ug/L	<0.2	<0.2	<0.2	<0.2	<0.01	0.011	<0.2	<0.2	<0.2	<0.01	<0.01	<0.01	<0.2
Boron	ug/L	1200	442	1020	4310	89.6	215	1800	495	1080	240	1.1	0.7	5650
Aluminum	ug/L	<2	1080	2030	41	1.1	92.9	19900	30000	5140	38.6	7.8	1.3	1700
Silicon	ug/L	9970	4210	1050	2300	3780	6740	4200	4390	2460	7100	11.5	9.2	1400
Vanadium	ug/L	0.5	103	49.3	11.5	0.09	1.23	365	562	156	1.07	0.13	0.15	473
Manganese	ug/L	191	2.0	1.0	91.1	1.50	9.97	0.9	<0.1	<0.1	6.1	0.5	0.22	1.5
Iron	ug/L	25200	<3	<3	62.0	52.7	271	29.7	<8	<8	140	5.4	0.51	25.3
Cobalt	ug/L	0.18	0.80	0.53	0.81	<0.001	0.17	0.12	0.04	0.40	0.301	<0.001	<0.001	3.27
Nickel	ug/L	<0.6	3.6	4.4	4.6	<0.05	6.29	14	4	<1	12	0.06	0.08	7
Copper	ug/L	1.4	3.8	2.1	<0.2	0.33	2.02	1.4	0.5	1.4	1.2	1.4	2.5	30.0
Zinc	ug/L	2.5	<2	3.0	<2	<0.1	6.9	<2	<2	<2	2.9	3.3	4.3	<2
Strontium	ug/L	2140	828	1010	2520	9.48	82.6	830	1610	11100	135	0.31	0.11	311
Molybdenum	ug/L	132	21.9	27.7	283	0.04	0.83	1890	1390	658	0.75	0.02	<0.01	4510
Silver	ug/L	<0.2	<0.2	<0.2	<0.2	<0.01	<0.01	<0.2	<0.2	<0.2	<0.01	<0.01	<0.01	<0.2
Cadmium	ug/L	<0.2	<0.2	0.3	0.7	<0.005	0.037	6.1	4.8	2.8	0.04	0.02	0.01	15.0
Antimony	ug/L	<0.1	1.1	2.9	1.1	0.021	0.074	2.3	0.5	0.2	0.082	0.007	<0.005	0.8
Barium	ug/L	93.6	434	294	176	<0.2	10.7	89.3	259	657	29.7	0.6	<0.2	20
Thallium	ug/L	<0.1	0.5	<0.1	0.4	<0.005	<0.005	<0.1	<0.1	<0.1	0.021	<0.005	<0.005	<0.1
Lead	ug/L	<0.1	<0.1	0.2	<0.1	0.01	0.17	<0.1	<0.1	<0.1	0.03	0.09	0.06	<0.1
Uranium	ug/L	1.95	2.66	1.23	26.8	<0.0005	0.17	0.39	<0.01	0.01	0.02	<0.0005	<0.0005	5.53

Table A-1
Hydrochemistry and Trace Elements (continued)

		096D (1)	097	098	099	100	101	102	103	104	105	106	106D	107
Chloride	mg/L	92.5	91.7	38.7	27.3	0.07	37.2	73.0	0.01	0.02	1,080	859	715	2,330
Sulfate	mg/L	2,870	2,870	1,800	1,510	0.08	1,610	2,410	< 0.05	0.12	10,200	4,710	4,430	30,500
Sodium	mg/L	1,560	1,560	837	651	1.3	117	455	0.2	0.1	3,270	2,310	2,210	4,630
Potassium	mg/L	77	73	31	6	< 0.2	23	219	< 0.2	< 0.2	380	350	350	500
Magnesium	mg/L	10	7	44	16	< 0.05	188	69	< 0.05	< 0.05	1,000	< 0.05	< 0.05	5,810
Calcium	mg/L	11	6	52	73	0.17	392	431	< 0.05	< 0.05	600	234	228	570
TOC	mg/L	50.1	48.7	56.8	14.7	0.4 (a)	4.6	3.3	0.1 (a)	0.1 (a)	33.1	19.1	18.6	50.1
TIC	mg/L	128	105	39.7	14.1	0.28 (a)	27.8	24.3	0.16 (a)	0.27 (a)	7.88	4.27	4.36	1.85
Temperature	°C	16.5	17.4	12.9	15.1	13.4	16.9	15.8	n/a	6.6	9.94	19.0	19.0	19.18
Spec. Cond.	mS/cm	7.379	7.340	4.282	3.451	0.003	3.363	4.915	n/a	0.072	18.85	11.56	11.56	26.14
Diss. Oxygen	% sat.	61.1	69.4	27.5	37	81.1	86.1	94.7	n/a	64.5	36	95	95	2
pH	pH	7.71	9.35	8.58	7.91	5.94	6.74	7.41	n/a	9.54	8.99	11.96	11.96	6.83
ORP (corr.)	mV	224	206	39	103	238	213	222	n/a	288	271	18	18	230
Lithium	ug/L	5	4	63	<1	<0.05	431	6940	<0.05	<0.05	1050	130	132	3390
Beryllium	ug/L	<0.2	<0.2	<0.2	<0.2	<0.01	<0.2	<0.2	<0.01	<0.01	<0.2	<0.2	<0.2	1
Boron	ug/L	5950	6080	11700	2590	0.8	89500	23700	<0.1	0.2	26800	7310	7460	50200
Aluminum	ug/L	1700	4300	117	42	3	52	<2	2.3	2.7	31	608	618	708
Silicon	ug/L	1340	1540	4620	4410	25.7	6750	3940	5.9	17.9	2280	21000	22000	45400
Vanadium	ug/L	477	500	159	3.8	0.10	0.8	44.3	0.25	0.33	1.8	400	403	103
Manganese	ug/L	1.4	1.5	59.8	1230	0.39	1420	72.3	0.33	2.32	473	<0.1	0.1	1170
Iron	ug/L	20.1	46.3	<8	126	0.52	12.1	<8	2.05	1.36	4.7	4.6	6.6	52.4
Cobalt	ug/L	3.31	3.28	0.88	0.29	<0.001	9.19	0.07	<0.001	0.008	0.09	0.11	0.07	13.0
Nickel	ug/L	7	8	9	2	0.18	31	3	<0.03	0.25	3.3	7.5	8.0	153
Copper	ug/L	29.9	42.8	1.7	1.5	1.60	2.8	1.6	0.51	0.55	0.4	0.6	0.5	2
Zinc	ug/L	<2	<2	<2	<2	5	86	<2	0.2	0.7	<2	<2	<2	68
Strontium	ug/L	293	303	1700	93	0.72	1320	10300	0.67	3.88	6980	9730	10000	1500
Molybdenum	ug/L	4450	4480	2580	2070	0.05	751	9630	<0.04	<0.04	164	3520	3560	1320
Silver	ug/L	<0.2	<0.2	<0.2	<0.2	<0.01	<0.2	<0.2	<0.01	<0.01	<0.2	<0.2	<0.2	<1
Cadmium	ug/L	13.1	13.0	7.7	6.1	0.028	4.6	35.9	0.005	<0.005	0.5	12.8	11.8	6.6
Antimony	ug/L	0.8	0.9	0.7	0.2	0.013	0.1	4.4	0.013	<0.005	9.4	2.3	2.2	22.3
Barium	ug/L	16	18	34	66	0.7	23	48	<0.1	0.2	75	134	138	158
Thallium	ug/L	<0.1	<0.1	<0.1	<0.1	<0.005	<0.1	<0.1	<0.005	<0.005	<0.1	<0.1	<0.1	<0.5
Lead	ug/L	0.2	0.3	0.3	0.2	<0.1	0.1	0.1	0.017	<0.005	0.2	0.4	0.5	0.8
Uranium	ug/L	5.41	5.66	1.87	0.19	<0.0005	36.6	7.38	<0.0007	<0.0007	6.47	<0.01	0.04	16.0

Table A-1
Hydrochemistry and Trace Elements (continued)

		108	109	110	111	112	113	114	115	116	117	118	118D	119
Chloride	mg/L	84	0.29	0.17	28.5	n/a	13.4	19.6	16.9	16.8	< 0.01	66.2	66.3	64.8
Sulfate	mg/L	3,490	< 0.05	0.10	2,440	n/a	203	210	166	163	< 0.05	462	467	441
Sodium	mg/L	840	0.2	< 0.1	190	n/a	21	28	31	32	0.3	36	37	36
Potassium	mg/L	120	< 0.2	< 0.2	210	n/a	11	11	9	10	< 0.2	13	13	9
Magnesium	mg/L	57	< 0.05	< 0.05	236	n/a	22	20	17	16	< 0.05	72	74	67
Calcium	mg/L	596	< 0.05	< 0.05	405	n/a	49	53	45	38	< 0.05	121	123	123
TOC	mg/L	10.3	0.4 (a)	0.2 (a)	4.1	n/a	1.8	1.4 (a)	1.4 (a)	1.5	0.3 (a)	3.9	4.3	4.1
TIC	mg/L	18.8	0.86	0.73 (a)	59.9	n/a	14.2	16.7	1.57	2.48	0.75 (a)	19.2	19.4	21.6
Temperature	°C	10.6	n/a	n/a	15.05	14.2	20.98	22.03	16.0	15.5	n/a	14.65	14.4	10.48
Spec. Cond.	mS/cm	6.174	n/a	n/a	4.529	2.765	0.643	0.673	0.567	0.564	n/a	1.348	1.355	1.319
Diss. Oxygen	% sat.	87	n/a	n/a	58.7	46.7	28.4	15.1	87	98.4	n/a	80.7	120	122.8
pH	pH	8.76	n/a	n/a	7.18	6.83	7.74	6.99	7.28	7.41	n/a	7.6	7.49	8.6
ORP (corr.)	mV	240	n/a	n/a	280	229	231	220	261	289	n/a	257	244	240
Lithium	ug/L	27	<0.05	<0.05	23600	4540	347	187	318	312	<0.05	253	264	162
Beryllium	ug/L	<0.2	<0.01	<0.01	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.01	<0.2	<0.2	<0.2
Boron	ug/L	41500	0.9	2.0	27200	13300	1480	931	444	450	0.7	2200	2120	1700
Aluminum	ug/L	81	3.5	3.4	27	17	42	51	17	25	4.3	18	13	28
Silicon	ug/L	221	26.1	42.2	7440	2300	2840	12000	2890	2970	42.4	3710	3840	2870
Vanadium	ug/L	3.6	0.14	0.14	26.9	1.8	402	45.2	53.6	54.3	0.18	3.8	3.5	6.5
Manganese	ug/L	7.7	0.57	4.48	2700	531	147	445	59.3	58.1	0.40	155	167	59.6
Iron	ug/L	3.0	3.7	0.9	<13	55.4	<13	349	<13	<13	0.4	<13	<13	<13
Cobalt	ug/L	0.42	<0.001	0.039	113	8.91	1.76	5.36	7.15	7.05	0.039	3.76	3.53	1.58
Nickel	ug/L	2.2	<0.1	0.2	189	5	<2	6	14	14	<0.1	15	14	8
Copper	ug/L	1.6	0.64	0.96	1.3	0.9	0.4	1.6	9.8	8.8	0.53	2.5	3.0	1.9
Zinc	ug/L	<2	0.7	1.0	289	4	<2	6	16	13	0.8	11	9	<2
Strontium	ug/L	12000	0.59	40.5	6750	2740	662	771	405	411	0.61	507	513	465
Molybdenum	ug/L	2680	0.02	0.11	5100	2690	1280	264	340	336	0.02	131	128	88.7
Silver	ug/L	0.8	<0.01	<0.01	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.01	<0.2	<0.2	<0.2
Cadmium	ug/L	10.6	0.02	0.01	23.6	11.8	5.6	1.4	2.0	2.0	<0.005	1.4	1.0	0.6
Antimony	ug/L	5.2	<0.005	0.006	9.1	0.6	58.5	4.4	20.0	20.7	<0.005	3.1	2.8	2.5
Barium	ug/L	63	<0.1	0.6	40	43	105	62	182	177	0.6	150	153	118
Thallium	ug/L	<0.1	<0.005	<0.005	5.3	0.6	0.8	0.3	7.6	7.3	<0.005	14.2	11.0	6.8
Lead	ug/L	0.3	0.028	0.008	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	0.013	<0.14	<0.14	<0.14
Uranium	ug/L	21.1	<0.0008	0.001	18.9	21.8	7.91	0.20	0.15	0.17	<0.0008	1.75	1.73	2.02

Table A-1
Hydrochemistry and Trace Elements (continued)

		120	121	122	125	126	126D	127	128
Chloride	mg/L	1,150	1,190	911	0.09	42.5	42.7	31	98
Sulfate	mg/L	1,350	1,510	1,430	< 0.05	507	509	1,120	836
Sodium	mg/L	255	303	247	0.1	393	393	653	141
Potassium	mg/L	500	609	486	< 0.2	20	20	40	30
Magnesium	mg/L	5	6	< 2.5	< 0.05	< 0.05	< 0.05	< 0.05	8
Calcium	mg/L	710	698	669	< 0.05	< 2.5	< 2.5	13	351
TOC	mg/L	1.5	1.3 (a)	2.4	0.6 (a)	6.0	5.8	7.9	7.9
TIC	mg/L	2.81	2.53	2.37	0.39 (a)	5.90	5.89	7.40	3.03
Temperature	°C	16.16	13.65	12.02	12.08	16.75	17.02	16.4	20.5
Spec. Cond.	mS/cm	6.322	6.897	5.906	0.013	2.57	2.76	4.02	2.19
Diss. Oxygen	% sat.	81.3	29.8	77.8	46	35	35	13.1	65
pH	pH	10.33	10.04	10.53	6.04	11.75	11.75	11.74	7.84
ORP (corr.)	mV	87	181	46	373	249	241	225	339
Lithium	ug/L	6470	6360	7070	<0.05	7	8	16	33
Beryllium	ug/L	<0.2	<0.2	<0.2	<0.01	<0.4	<0.4	<0.2	<0.2
Boron	ug/L	3080	3160	1560	2.7	3070	2890	3890	11900
Aluminum	ug/L	167	24	229	4.2	5590	5620	5920	26
Silicon	ug/L	1890	1810	2360	1.1	9450	8860	10300	3940
Vanadium	ug/L	4.5	0.7	1.3	0.29	122	120	236	6.8
Manganese	ug/L	38.1	113	15.5	0.14	<0.4	<0.4	<0.2	197
Iron	ug/L	<13	<13	<13	0.3	<25	<25	<25	<25
Cobalt	ug/L	0.05	0.09	0.03	0.022	<0.04	<0.04	0.20	1.61
Nickel	ug/L	3	<2	<2	<0.1	<0.6	<0.6	<2	<2
Copper	ug/L	0.3	0.4	1.4	0.04	4.2	3.9	2.4	1.5
Zinc	ug/L	<2	<2	<2	0.2	<2	<2	<2	5
Strontium	ug/L	4500	4210	3860	0.63	649	648	1630	5960
Molybdenum	ug/L	333	368	223	0.02	220	223	524	910
Silver	ug/L	<0.2	<0.2	<0.2	<0.01	<0.2	<0.2	<0.2	<0.2
Cadmium	ug/L	1.9	1.6	0.8	<0.005	1.0	1.0	2.1	3.8
Antimony	ug/L	0.1	0.1	<0.1	<0.005	0.4	0.4	0.2	1.3
Barium	ug/L	78	65	58	0.4	36	34	64	86
Thallium	ug/L	0.3	<0.1	<0.1	<0.005	<0.1	<0.1	<0.1	<0.1
Lead	ug/L	<0.14	<0.14	<0.14	<0.007	<0.14	<0.14	<0.14	<0.14
Uranium	ug/L	0.02	0.10	0.04	<0.0008	<0.02	<0.02	<0.02	0.97

Table A-1
Hydrochemistry and Trace Elements (continued)

Footnotes:

(1) = Samples 096 and 096D are samples of leachate that were treated with CO2 prior to analysis.
(a) = sample concentration less than 5 times blank
n/a = not analyzed

Table A-2
Speciation

	Sample ID	001	002	003	004	005	006	007	008	009	010	012	QA-1
As, diss.	ug/L	20.4	48.4	84	18.6	3.0	12.2	20.1	16.9	28.9	22.3	238	0.11
As(III), diss.	ug/L	< 0.3	< 6	< 6	8.4	< 0.2	< 0.3	< 2	0.7 (a)	< 6	1.5 (a)	97.0	< 0.02
As(V), diss.	ug/L	9.5	47	69	5.2	1.3	0.9 (a)	< 2	< 0.5	< 10	10	66	< 0.03
As, other	ug/L	2.1	< 6	< 6	< 0.3	< 0.2	< 0.3	< 2	< 0.3	< 6	< 0.6	< 0.6	< 0.02
Cr, diss.	ug/L	< 0.5	5,100	4,670	8.8	0.7	5.7	2	< 0.5	52.9	25.8	< 0.5	< 3
Cr(III), diss.	ug/L	n/a	340	190	< 0.1	n/a	< 0.1	< 0.1	n/a	1	< 0.4	n/a	n/a
Cr(VI), diss.	ug/L	2.2	5,090	3,530	8.1	1.5	6.4	2.9	< 0.1	47	22	1.9	< 0.05
Se, diss.	ug/L	127	1,730	1,760	49.9	7.6	16.8 (b)	289	3.7 (b)	2,360	318	3.24	0.10 (a)
Se(IV), diss.	ug/L	8.3	19	76	8.1	3.15	1.6	79.5	< 0.1	< 2	24.4	1.4	< 0.02
Se(VI), diss.	ug/L	83.0	1,300	1,240	22.1	0.57	11.2	119	0.27 (a)	1,660	158	< 0.2	< 0.03
Se, other	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$\mathrm{Hg}_{\mathrm{diss.}}$	ng/L	n/a	14.4	18.4	5.9	2.1 (a)	0.8 (a)	1.9 (a)	4.2 (a)	28.4	n/a	n/a	n/a
$\mathrm{Hg}_{\mathrm{part.}}$	ng/L	n/a	254	26	< 1	44	25 (a)	16 (a)	< 1	121	n/a	n/a	n/a
$\mathrm{MeHg}_{\mathrm{diss.}}$	ng/L	n/a	0.11	0.09 (a)	0.26	0.12	0.54	< 0.02	0.07 (a)	< 0.02	n/a	n/a	n/a
$\mathrm{MeHg}_{\mathrm{part.}}$	ng/L	0.03 (a)	0.03 (a)	< 0.01	0.04 (a)	0.09	0.09	0.02 (a)	0.01 (a)	0.02 (a)	n/a	n/a	n/a
DMM	ng/L	0.055	0.005	< 0.005	< 0.005	0.010	< 0.005	0.007	< 0.005	n/a	n/a	n/a	n/a

Table A-2
Speciation (continued)

	Sample ID	013	013D	014	QA-2	015	016	SX-1	017	018	019	020	HN-1	HN-2
As, diss.	ug/L	21.6	22	163	0.12	23.8	68.6	72.0	4.11	23.1	5.11	4.19	59.8	20.6
As(III), diss.	ug/L	3.7	1.9	1.9	0.02 (a)	< 0.6	< 0.6	0.9	0.88	0.42	0.57	1.00	< 0.1	< 0.1
As(V), diss.	ug/L	< 0.5	< 0.5	86	< 0.03	24	25	46.9	<0.08	5.22	<0.08	0.53	33.6	6.9
As, other	ug/L	< 0.3	< 0.3	0.9 (a)	< 0.02	< 0.6	< 0.6	< 0.1	0.1	< 0.06	< 0.06	0.1	0.2	0.1
Cr, diss.	ug/L	< 0.5	n/a	< 0.5	< 3	12.9	3.8	< 0.5	3	< 0.5	1.0	0.7	< 0.5	< 0.5
Cr(III), diss.	ug/L	n/a	n/a	n/a	n/a	< 0.4	< 0.1	n/a	< 0.04	n/a	< 0.1	n/a	n/a	n/a
Cr(VI), diss.	ug/L	0.7	0.7	0.5	< 0.05	12.8	< 0.5	< 0.1	2.8	1.3	0.9	< 0.05	n/a	n/a
Se, diss.	ug/L	0.28 (b)	0.38 (b)	1.81 (b)	0.10 (a)	22.4	193	7.77	2.4	0.50 (b)	1.8	2.5	22.2	9.15
Se(IV), diss.	ug/L	< 0.1	< 0.1	0.6 (a)	< 0.02	14.9	101	2 (a)	0.3 (a)	< 0.1	0.1 (a)	0.9	3 (a)	< 1
Se(VI), diss.	ug/L	< 0.1	< 0.1	< 0.2	< 0.03	3.4	14.3	4 (a)	1.1	< 0.2	1.3	0.8	16	6
Se, other	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$Hg_{diss.}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$Hg_{part.}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$MeHg_{diss.}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$MeHg_{part.}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
DMM	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Table A-2
Speciation (continued)

	Sample ID	021	022	023	024	025	026	027	028	029	030	031	032	034
As, diss.	ug/L	194	11.1	218	11.2	6.47	10.8	39.1	30.0	48.9	42.5	221	25.4	< 0.02
As(III), diss.	ug/L	2.1	12.5	0.8 (a)	0.4 (a)	1.35	11.2	13.2	2.4	1.7	3.5	201	17.5	< 0.01
As(V), diss.	ug/L	208	0.49	189	<0.2	<0.08	0.4 (a)	4.8	1.7	8.9	29.5	23.6	16.9	< 0.8
As, other	ug/L	< 0.3	< 0.06	< 0.3	< 0.2	< 0.06	< 0.2	1.3	0.2	0.3	0.4	0.7	0.1	n/a
Cr, diss.	ug/L	< 0.5	1.0	< 0.5	< 0.5	< 0.5	1.1	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.4	0.08
Cr(III), diss.	ug/L	n/a	< 0.04	n/a	n/a	n/a	< 0.04	n/a	n/a	n/a	n/a	n/a	< 0.1	0.06
Cr(VI), diss.	ug/L	< 0.05	0.9	< 0.5	n/a	n/a	0.9	n/a	n/a	n/a	< 0.05	< 0.1	< 0.05	< 0.01
Se, diss.	ug/L	6.5	30.7	283	18.2	1.9 (b)	31.5	1.05 (b)	2.56 (b)	2.29	44.1	12.5	18.0	< 0.02
Se(IV), diss.	ug/L	5.3	20.5	217	5.3	< 0.1	20.4	< 0.3	< 0.3	< 0.3	27.0	0.9 (a)	13.5	< 0.1
Se(VI), diss.	ug/L	< 0.6	2.2	1.5	6.3	1.1	2.2	< 0.3	1.4	1.6	12.5	5.5	0.7	< 0.2
Se, other	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$Hg_{diss.}$	ng/L	1.4 (a)	1.0 (a)	1.4 (a)	n/a	n/a	0.4 (a)	21.3	1.2 (a)	12.4	0.8 (a)	5.2	1.4 (a)	n/a
$Hg_{part.}$	ng/L	155	53	14 (a)	n/a	n/a	17 (a)	4 (a)	13 (a)	59	< 1	30	186	n/a
$MeHg_{diss.}$	ng/L	0.03 (a)	0.03 (a)	< 0.02	n/a	n/a	< 0.02	1.56	0.18	0.70	0.06 (a)	6.71	0.05 (a)	n/a
$MeHg_{part.}$	ng/L	0.02 (a)	0.03 (a)	0.03 (a)	n/a	n/a	< 0.01	< 0.01	< 0.01	0.01 (a)	0.11	n/a	0.05	n/a
DMM	ng/L	< 0.005	< 0.005	< 0.005	n/a	n/a	< 0.005	< 0.005	< 0.005	< 0.005	0.022	0.050	0.032	n/a

Table A-2
Speciation (continued)

	Sample ID	035	036	037	038	039	042	043	044	044D	049	050	051	052
As, diss.	ug/L	< 0.02	0.03 (a)	56.0	123	42.3	23.7	75.2	5.1	4.9	5.4	0.12	38.1	164
As(III), diss.	ug/L	< 0.01	< 0.01	0.30	2.63	1.39	< 0.1	< 0.05	0.39	< 0.04	< 0.04	< 0.01	0.70 (a)	22.8
As(V), diss.	ug/L	< 0.8	< 0.8	34	53	53	19 (a)	28	3 (a)	2 (a)	2 (a)	< 0.8	15	8 (a)
As, other	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	< 0.04	n/a	n/a	n/a
Cr, diss.	ug/L	0.07	0.14	< 0.4	< 0.4	< 0.4	< 0.4	29.2	< 0.4	< 0.4	< 0.4	0.80	11.3	< 0.4
Cr(III), diss.	ug/L	0.07	0.07	< 0.01	< 0.01	< 0.01	0.17	26.4	0.25	0.12	0.07	0.84	9.92	0.16
Cr(VI), diss.	ug/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.03 (a)	< 0.1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05	0.06
Se, diss.	ug/L	< 0.02	0.02 (a)	1.98 (b)	0.13 (a)	0.17 (a)	42.6	23.5 (b)	13.9	13.6	10.0	0.02 (a)	0.45 (b)	10.2
Se(IV), diss.	ug/L	< 0.1	< 0.1	2.6	< 0.5	0.2 (a)	39.1	20.2	11.4	11.5	8.3	< 0.1	< 0.5	7
Se(VI), diss.	ug/L	< 0.2	< 0.2	< 1	< 1	< 0.4	1.9	< 1	1.7	1.8	0.6 (a)	< 0.2	< 1	< 4
Se, other	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$\mathrm{Hg}_{\mathrm{diss.}}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$\mathrm{Hg}_{\mathrm{part.}}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$\mathrm{MeHg}_{\mathrm{diss.}}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$\mathrm{MeHg}_{\mathrm{part.}}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
DMM	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Table A-2
Speciation (continued)

	Sample ID	053	057	059	059D	060	061	062	064	069	070	070D	077	078
As, diss.	ug/L	279	98.6	124	125	< 0.02	1,380	61.5	178	99.5	143	144	< 0.008	0.017 (a)
As(III), diss.	ug/L	108	< 0.2	< 0.2	< 0.2	< 0.01	859	< 0.2	< 0.4	< 0.2	< 0.2	< 0.2	< 0.04	< 0.04
As(V), diss.	ug/L	82	93	127	119	< 0.8	519	37	150	94	136	137	< 0.8	< 0.8
As, other	ug/L	0.7	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.53	n/a	n/a
Cr, diss.	ug/L	< 0.4	1.9	2.7	2.5	0.10	< 0.4	10.5	22.4	3.2	5.3	5.4	0.02	0.02
Cr(III), diss.	ug/L	0.05	1.06	0.01 (a)	< 0.01	0.05	0.27	0.95	0.04 (a)	0.46	0.63	0.62	<0.02	0.02
Cr(VI), diss.	ug/L	< 0.01	0.41	1.28	1.23	< 0.01	< 0.01	6.24	23.0	2.98	5.28	5.17	<0.006	<0.006
Se, diss.	ug/L	1.24 (b)	2.44	2.58 (b)	2.55	< 0.02	4.31	112	103	36.4	29.1	29.4	< 0.008	< 0.008
Se(IV), diss.	ug/L	< 2	2.0	2.5	2.2	< 0.1	<10	90.4	97	33.1	29	28	< 0.04	< 0.04
Se(VI), diss.	ug/L	< 4	< 1	< 1	< 1	< 0.2	<20	32.1	< 4	1.7 (a)	< 4	< 4	< 0.06	< 0.06
Se, other	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Hg_{diss}.	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	1.9 (a)	2.5 (a)
Hg_{part}.	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3 (a)	4 (a)
$MeHg_{diss}$.	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	< 0.02	0.06 (a)
$MeHg_{part}$.	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.15	0.09
DMM	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	< 0.005	< 0.005

Table A-2
Speciation (continued)

Sample ID		079	079D	082	083	084	088	089	090	091	092	TEB	094	095
As, diss.	ug/L	99.1	97.0	23.0	6.19	727	0.076 (a)	0.896	22.6	10.8	3.33	0.922	0.035 (a)	0.046 (a)
As(III), diss.	ug/L	9.5	9.9	0.2 (a)	0.23	71	n/a	n/a	0.28	< 0.05	< 0.05	0.01 (a)	< 0.01	< 0.01
As(V), diss.	ug/L	104	73	15	2.4 (a)	535	n/a	n/a	18.0	9.4	0.5	0.09	< 0.02	< 0.02
As, other	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.67	0.15 (a)	0.10 (a)	n/a	n/a	n/a
Cr, diss.	ug/L	< 0.2	< 0.2	24.6	19.9	< 0.2	0.22	1.22	0.7	< 0.2	122	0.49	0.03	< 0.01
Cr(III), diss.	ug/L	<0.02	<0.02	1.25	2.43	0.04 (a)	n/a	n/a	n/a	n/a	3 (a)	n/a	n/a	n/a
Cr(VI), diss.	ug/L	<0.006	<0.006	22.9	15.2	<0.006	n/a	n/a	n/a	n/a	109	n/a	n/a	n/a
Se, diss.	ug/L	0.16 (a)	0.16 (a)	19.1	12.8	0.57 (b)	0.010 (a)	0.194 (b)	85.5	122	103	0.094 (a)	0.037 (a)	0.063 (a)
Se(IV), diss.	ug/L	< 0.2	< 0.2	17.9	8.72	< 2	n/a	n/a	5.2	3.6	0.6 (a)	< 0.05	< 0.05	< 0.05
Se(VI), diss.	ug/L	< 0.3	< 0.3	0.3 (a)	1.5 (a)	< 3	n/a	n/a	97	138	116	< 0.05	< 0.05	< 0.05
Se, other	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Hg_{diss}.	ng/L	0.2 (a)	0.5 (a)	5.9	2.1 (a)	0.6 (a)	n/a	n/a	n/a	n/a	n/a	n/a	1.9 (a)	0.9 (a)
Hg_{part}.	ng/L	6 (a)	3 (a)	18 (a)	22 (a)	5 (a)	n/a	n/a	n/a	n/a	n/a	n/a	15 (a)	6 (a)
$MeHg_{diss}$.	ng/L	< 0.02	0.05 (a)	0.05 (a)	0.17	0.06 (a)	n/a	n/a	n/a	n/a	n/a	n/a	0.03 (a)	0.06 (a)
$MeHg_{part}$.	ng/L	0.06	0.05	0.03 (a)	0.16	0.03 (a)	n/a	n/a	n/a	n/a	n/a	n/a	< 0.01	0.02 (a)
DMM	ng/L	< 0.005	< 0.005	< 0.005	0.040	< 0.005	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.808

Table A-2
Speciation (continued)

	Sample ID	096 (1)	096D (1)	097	098	099	100	101	102	103	104	105	106	106D
As, diss.	ug/L	38.3	37.8	44.9	76.9	4.80	0.200	2.23	7.24	0.009 (a)	0.031 (a)	230	110	112
As(III), diss.	ug/L	< 0.1	< 0.1	< 0.1	0.66	0.10 (a)	< 0.01	< 0.1	< 0.05	< 0.01	< 0.01	197	15.9	13.8
As(V), diss.	ug/L	28.2	28.4	36.3	59.5	3.7	< 0.02	0.2 (a)	6.3	0.11	0.08	50.3	63.0	77.3
As, other	ug/L	< 0.1	< 0.1	< 0.1	0.29	0.19	n/a	0.62	< 0.05	n/a	n/a	3.83	5.78	5.22
Cr, diss.	ug/L	1,990	1,980	2,000	2.8	< 0.2	0.03	1.5	19.6	< 0.02	< 0.02	< 0.4	0.9	0.9
Cr(III), diss.	ug/L	120	140	40 (a)	0.2	n/a	n/a	< 0.08	0.4 (a)	n/a	n/a	n/a	n/a	n/a
Cr(VI), diss.	ug/L	2,050	2,030	2,230	0.99	n/a	n/a	0.07	13.3	n/a	n/a	n/a	n/a	n/a
Se, diss.	ug/L	428	427	413	50.7	2.04 (b)	0.047 (a)	91.0	80.5	0.008 (a)	0.008 (a)	8.5 (b)	64.8	65.1
Se(IV), diss.	ug/L	37.3	37.6	38.2	29.3	< 0.8	< 0.05	< 0.8	5.3	< 0.05	< 0.05	< 2	< 2	< 2
Se(VI), diss.	ug/L	363	367	366	< 2	< 2	< 0.05	104	85	< 0.05	< 0.05	< 4	64	65
Se, other	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	< 0.05	< 0.05	< 2	< 2	< 2
$Hg_{diss.}$	ng/L	29.5	32.2	36.5	60.6	5.7	1.5 (a)	2.1 (a)	3.8 (a)	n/a	n/a	n/a	n/a	n/a
$Hg_{part.}$	ng/L	23 (a)	10 (a)	16 (a)	11 (a)	13 (a)	3 (a)	3 (a)	52	n/a	n/a	n/a	n/a	n/a
$MeHg_{diss.}$	ng/L	0.22	0.20	0.22	0.76	0.03 (a)	< 0.02	< 0.02	0.12	n/a	n/a	n/a	n/a	n/a
$MeHg_{part.}$	ng/L	0.03 (a)	0.03 (a)	0.05	0.01 (a)	< 0.01	0.01 (a)	0.01 (a)	< 0.01	n/a	n/a	n/a	n/a	n/a
DMM	ng/L	0.216	0.335	0.262	0.035	0.265	n/a	0.565	2.47	n/a	n/a	n/a	n/a	n/a

Table A-2
Speciation (continued)

	Sample ID	107	108	109	110	111	112	113	114	115	116	117	118	118D
As, diss.	ug/L	30.6	4.09	0.014 (a)	0.055 (a)	5.94	1.36	102	23.5	8.32	8.24	0.015 (a)	40.8	39.5
As(III), diss.	ug/L	1.0	0.37	< 0.01	< 0.01	< 0.1	0.7	0.8	< 0.1	3.05	1.01	< 0.01	0.66	0.18
As(V), diss.	ug/L	15.1	2.3	< 0.02	0.05 (a)	3.4	0.9	118	20.5	5.3	7.4	< 0.02	45.5	45.6
As, other	ug/L	< 0.2	< 0.05	n/a	n/a	< 0.1	0.2	0.2	< 0.1	< 0.05	0.08	n/a	0.15	0.11
Cr, diss.	ug/L	<2	0.5	0.02	0.03	0.5	< 0.2	< 0.2	0.3	1.5	1.8	0.03	< 0.2	< 0.2
Cr(III), diss.	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.34	0.40	n/a	n/a	n/a
Cr(VI), diss.	ug/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.09	0.31	n/a	n/a	n/a
Se, diss.	ug/L	159	6.56 (b)	0.013 (a)	0.021 (a)	90.5	0.67 (b)	29.3	0.07 (a)	36.1	35.4	0.010 (a)	17.6	18.5
Se(IV), diss.	ug/L	< 2	2.6	< 0.05	< 0.05	38.7	< 0.5	19.2	< 0.5	29.6	30.7	< 0.05	17.5	16.5
Se(VI), diss.	ug/L	16	3.9	< 0.05	< 0.05	72	< 1	3 (a)	< 1	3	3	< 0.05	1.3 (a)	1.3 (a)
Se, other	ug/L	51	< 0.5	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$Hg_{diss.}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$Hg_{part.}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$MeHg_{diss.}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$MeHg_{part.}$	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
DMM	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Table A-2
Speciation (continued)

	Sample ID	119	120	121	122	125	126	126D	127	128
As, diss.	ug/L	30.2	26.8	11.0	25.5	< 0.009	5.20	4.86	6.42	14.3
As(III), diss.	ug/L	< 0.05	7.2	1.3	7.6	< 0.02	< 0.1	< 0.1	< 0.2	10.1
As(V), diss.	ug/L	30.5	11.4	6.0	8.3	< 0.4	4 (a)	3 (a)	4 (a)	3 (a)
As, other	ug/L	0.29	9.3	0.6	6.0	< 0.02	< 0.1	< 0.1	< 0.2	0.4
Cr, diss.	ug/L	0.2	< 0.2	< 0.2	< 0.2	0.05	108	109	24.4	0.5
Cr(III), diss.	ug/L	n/a	n/a	n/a	n/a	0.04	4.15 (a)	2.13 (a)	0.5 (a)	0.16
Cr(VI), diss.	ug/L	n/a	n/a	n/a	n/a	0.02 (a)	121	122	25.5	< 0.02
Se, diss.	ug/L	27.9	3.30 (b)	3.86 (b)	1.13 (b)	< 0.005	88.7	88.3	181	50.9
Se(IV), diss.	ug/L	22.8	1.8	1.1 (a)	< 0.5	< 0.06	12.5	13.0	12.3	17.4
Se(VI), diss.	ug/L	1.7	2 (a)	3 (a)	< 1	< 0.3	103	104	245	7
Se, other	ug/L	n/a	n/a	n/a	n/a	< 0.3	< 0.3	< 0.3	< 0.3	1.8
$\mathrm{Hg}_{\mathrm{diss.}}$	ng/L	n/a	n/a	n/a	n/a	3.1 (a)	9.4	2.0 (a)	5.4	79.3
$\mathrm{Hg}_{\mathrm{part.}}$	ng/L	n/a	n/a	n/a	n/a	3 (a)	3 (a)	6 (a)	3 (a)	100
$\mathrm{MeHg}_{\mathrm{diss.}}$	ng/L	n/a	n/a	n/a	n/a	0.16	0.17	0.21	0.03 (a)	6.36
$\mathrm{MeHg}_{\mathrm{part.}}$	ng/L	n/a	n/a	n/a	n/a	0.02 (a)	0.02 (a)	0.02 (a)	0.02 (a)	0.06
DMM	ng/L	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Footnotes:
(1) = Samples 096 and 096D are samples of leachate that were treated with CO_2 prior to analysis.
(a) sample concentration less than 5 times blank
(b) isotope ratios do not match
n/a = not analyzed

B
LEACHATE VARIABILITY AS A FUNCTION OF SAMPLE POINT

Leachate samples were collected from a variety of sample points representing interstitial (porewater) and surface water matrices. Interstitial water from pores of the CCP was collected using leachate wells, lysimeters, drive-point piezometers, and t-handle probes. Seeps and leachate collection systems provided interstitial water that was potentially exposed to the atmosphere. Surface water samples were collected from the ash/water interface in impoundments and from impoundment outfalls. Ash handling waters were collected from sluice pipes.

To evaluate the significance of the type of sample point on the leachate quality results, different sampling points within the same site were compared. Nine sites had multiple sample points for the same CCP management unit. Seven of the sites were impoundments (Table B-1), one site was an impoundment with recirculated water (Table B-2), and one site was a landfill (Table B-3). Indicator parameters, concentrations of reactive constituents (arsenic, chromium, selenium), and non-reactive constituents (boron, sulfate) were compared.

For the seven impoundments, several different methods of sampling were available for comparison of interstitial water, surface water, and sluice water (Table B-1). Comparing different sampling points within a single site yielded the following general observations:

- Field-measured oxidation-reduction potential (ORP) was always higher in surface water samples than interstitial samples. Sluice water ORP was similar to the surface water.
- The pH of interstitial water tended to be higher than surface water samples. Sluice water pH was variable, and in one case was significantly lower than either the interstitial water or surface water.
- Total dissolved solids concentration in interstitial waters were higher than surface waters, suggesting either increased dilution in the pond or higher equilibrium concentrations in the ash sediments due to increased proximity or contact time. Sluice pipe inlet samples were collected at three of the impoundment sites, and in each case, the TDS concentration in the sluice sample was higher than the pond and outfall concentrations, but lower than the interstitial water samples, which suggests that both dilution in the pond and additional leaching in the sediments is occurring.

Table B-1
Comparison of Leachate Samples From Different Collection Points at Impoundments

Site	Analyte	Interstitial				Surface Water		Other
		Drive Point Piez.	**Leachate Well**	**T-Handle Probe**	**Seep**	**Ash / Water Interface**	**Outfall**	**Sluice Line**
33106	ORP (mV)	188		163		**290**	**285**	**335**
	pH (STD)	**7.0**		**7.0**		6.0	6.0	5.0
	TDS	**223**		**247**		99	119	136
	As (ug/L)	49		**123**		5.4	5.1	49
	Cr (ug/L)	<0.40		<0.40		<0.40	<0.40	**14**
	Se (ug/L)	1.1		0.13		**10**	**14**	**33**
	B (ug/L)	**1,154**		**1,240**		265	429	632
	SO4 (mg/L)	**112**		**121**		53	70	84
49003A	ORP (mV)	266		225		284	304	
	pH (STD)	7.5		7.4		7.2	7.3	
	TDS	**455**		**411**		328	325	
	As (ug/L)	**206**		**63**		9.7	9.5	
	Cr (ug/L)	<0.50		0.053		**1.2**	**1.5**	
	Se (ug/L)	145		15		33	33	
	B (ug/L)	**1,410**		**1,205**		437	435	
	SO4 (mg/L)	221		207		192	191	
33104	ORP (mV)	168				220	223	214
	pH (STD)	9.1				7.6	8.9	10
	TDS	**300**				120	163	260
	As (ug/L)	**721**				100	143	178
	Cr (ug/L)	5.0				3.2	5.3	**22**
	Se (ug/L)	58				36	29	**103**
	B (ug/L)	**1,547**				231	207	**476**
	SO4 (mg/L)	89				45	50	**150**
35015B	ORP (mV)	<41			**308**	**257**	**267**	
	pH (STD)	8.5			8.5	7.6	8.2	
	TDS	**2,750**			1,456	870	793	
	As (ug/L)	**221**			43	41	28	
	Cr (ug/L)	<0.50			<0.50	<0.20	0.82	
	Se (ug/L)	13			**44**	18	23	
	B (ug/L)	**7,610**			3,280	2,200	1,955	
	SO4 (mg/L)	**1,830**			948	462	414	
22346	ORP (mV)		156			**241**		
	pH (STD)		7.3			**8.8**		
	TDS		694			606		
	As (ug/L)		**413**			23		
	Cr (ug/L)		<0.20			**25**		
	Se (ug/L)		0.37			**19**		
	B (ug/L)		**2,710**			442		
	SO4 (mg/L)		**225**			174		

Table B-1
Comparison of Leachate Samples From Different Collection Points at Impoundments (continued)

		Interstitial				**Surface Water**		**Other**
Site	**Analyte**	**Drive Point Piez.**	**Leachate Well**	**T-Handle Probe**	**Seep**	**Ash / Water Interface**	**Outfall**	**Sluice Line**
40109	ORP (mV)	211		212			**409**	**387**
	pH (STD)	**11**		**8.9**		7.7	9.0	4.4
	TDS	**258**		**311**		126	125	172
	As (µg/L)	**164**		**279**		99	124	38
	Cr (µg/L)	<0.40		<0.40		**1.9**	**2.7**	**11**
	Se (µg/L)	**10**		1.2		2.4	2.6	0.45
	B (µg/L)	**4,620**		**7,370**		300	351	272
	SO4 (mg/L)	**128**		**176**		52	55	111
25410A	ORP (mV)	124				**339**		
	pH (STD)	**12**				9.3		
	TDS	**2,205**				1,273		
	As (µg/L)	**69**				24		
	Cr (µg/L)	3.8				**13**		
	Se (µg/L)	**193**				22		
	B (µg/L)	**109,000**				3,890		
	SO4 (mg/L)	**910**				782		

In some cases, multiple samples were taken from a sample point; these results were averaged.
Bold indicates that these concentrations are significantly higher than concentrations observed in samples from the other matrix.

- Arsenic concentrations were always significantly higher in interstitial waters than in surface waters. Sluice water arsenic showed no consistent trend relative to the interstitial water and surface water.
- Chromium concentrations were always highest in the sluice water samples, variable in the surface water samples, and always low in the interstitial water. This may suggest that chromium initially leached from fly ash in the sluice line was later removed from solution at these sites (all fly ash from bituminous coal).
- Selenium concentrations were variable, sometimes highest in the interstitial water, sometimes highest in the surface water, and sometimes highest in the sluice water.
- Boron and sulfate are highly soluble constituents. Boron concentrations were always significantly higher in the interstitial water than the surface water or the sluice water, suggesting either dilution by transport water and pond water, or increased leaching in the interstitial waters, or both. Sulfate was similar to boron, although the relative difference between the sampling points was not as great.

One impoundment site (23223B) utilized recirculated pond water. At this site, surface water concentrations of all constituents were much higher than the interstitial water, reflecting the concentration build-up due to surface water reuse (Table B-2).

Table B-2
Comparison of Leachate Samples From Different Collection Points at an Impoundment With Recirculated Water

		Interstitial	Surface Water
Site	**Analyte**	**Leachate Well**	**Ash / Water Interface**
23223B	ORP (mV)	179	**342**
	pH (STD)	7.3	7.4
	TDS	4,851	**14,233**
	As (µg/L)	18	**29**
	Cr (µg/L)	0.62	**53**
	Se (µg/L)	146	**2,360**
	B (µg/L)	65,250	**98,500**
	SO4 (mg/L)	2,615	**10,400**

In some cases, multiple samples were taken from a sample point; these results were averaged.
Bold indicates that these concentrations are significantly higher than concentrations observed in samples from the other matrix.

One landfill site (50183) had samples collected from a leachate collection system and a leachate well (Table B-3). Both provide samples of interstitial water, the difference being that the leachate collection system provides an opportunity for exposure to atmospheric conditions that does not exist in a leachate well when properly sampled. In this case, the sample from the leachate collection system had a lower ORP, and had much higher concentrations of all constituents than the leachate well sample. The large difference in water quality at this site may reflect heterogeneity at the site rather than a systematic difference in sampling location. The landfill receives fly ash from three different plants, and the plants burn different coal types.

Exposure to atmospheric conditions, particularly oxygen, may be particularly important when measuring species concentrations in the leachate. Speciation by sample point was compared for the nine sites with multiple sample points. These data indicated wide variability in some cases, but no clear pattern of speciation change was associated with sample points (see Tables 5-1, 5-3, and 5-5).

Table B-3
Comparison of Leachate Samples From Different Collection Points at a Landfill

		Interstitial	
Site	**Analyte**	**Leachate Well**	**Leachate Collection System**
50183	ORP (mV)	**257**	158
	pH (STD)	7.7	**9.0**
	TDS	1,479	**3,080**
	As (µg/L)	3.9	**48**
	Cr (µg/L)	0.23	**5.8**
	Se (µg/L)	4.8	**50**
	B (µg/L)	2,000	**11,250**
	SO4 (mg/L)	930	**1,880**

In some cases, multiple samples were taken from a sample point; these results were averaged.
Bold indicates that these concentrations are significantly higher than concentrations observed in samples from the other matrix.

In summary, this analysis suggests that there were some systematic patterns to variation among sampling points at impoundment sites. Concentrations of non-reactive elements, sulfate and particularly boron, were significantly higher in interstitial leachate than in surface water leachate. Concentrations of arsenic were also consistently higher in interstitial water. Conversely, Chromium concentration tended to be slightly higher in sluice water and surface water samples.

C

BOX PLOTS COMPARING ASH LEACHATE CONCENTRATIONS BY SITE AND PLANT ATTRIBUTES

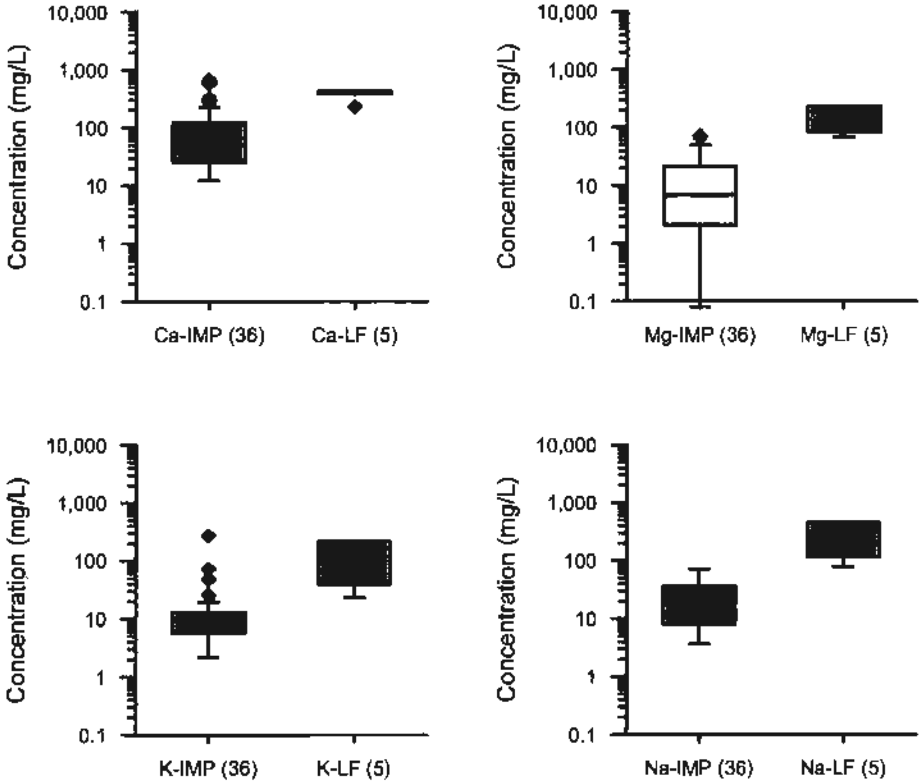

Figure C-1
Comparison of Field Leachate Concentrations: Bituminous Coal Ash, Landfill versus Impoundment

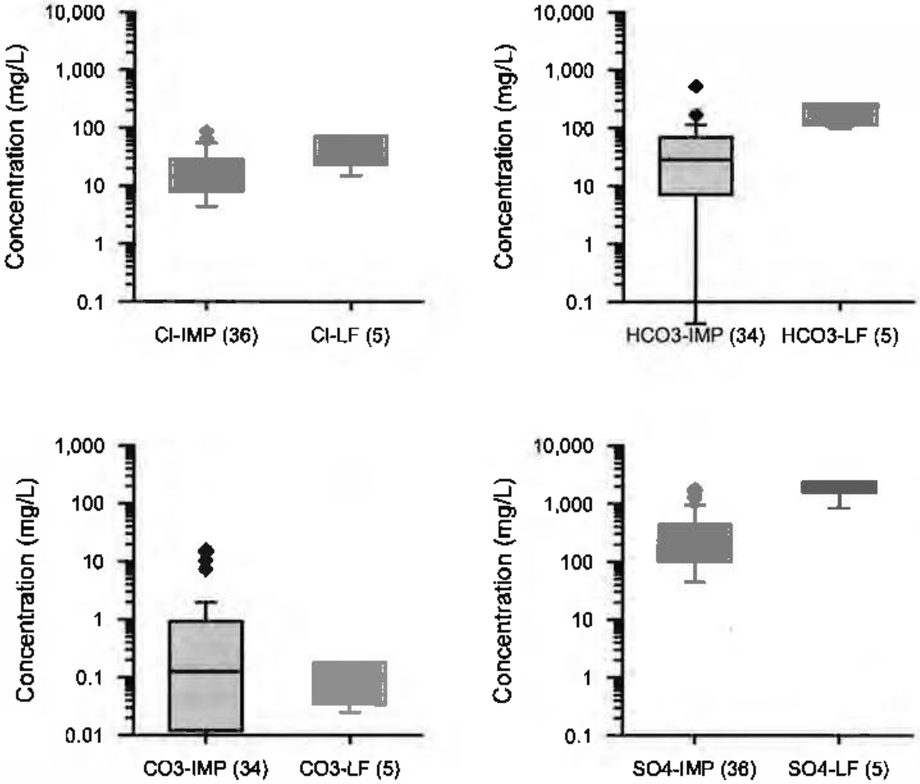

Figure C-1
Comparison of Field Leachate Concentrations: Bituminous Coal Ash, Landfill versus Impoundment (continued)

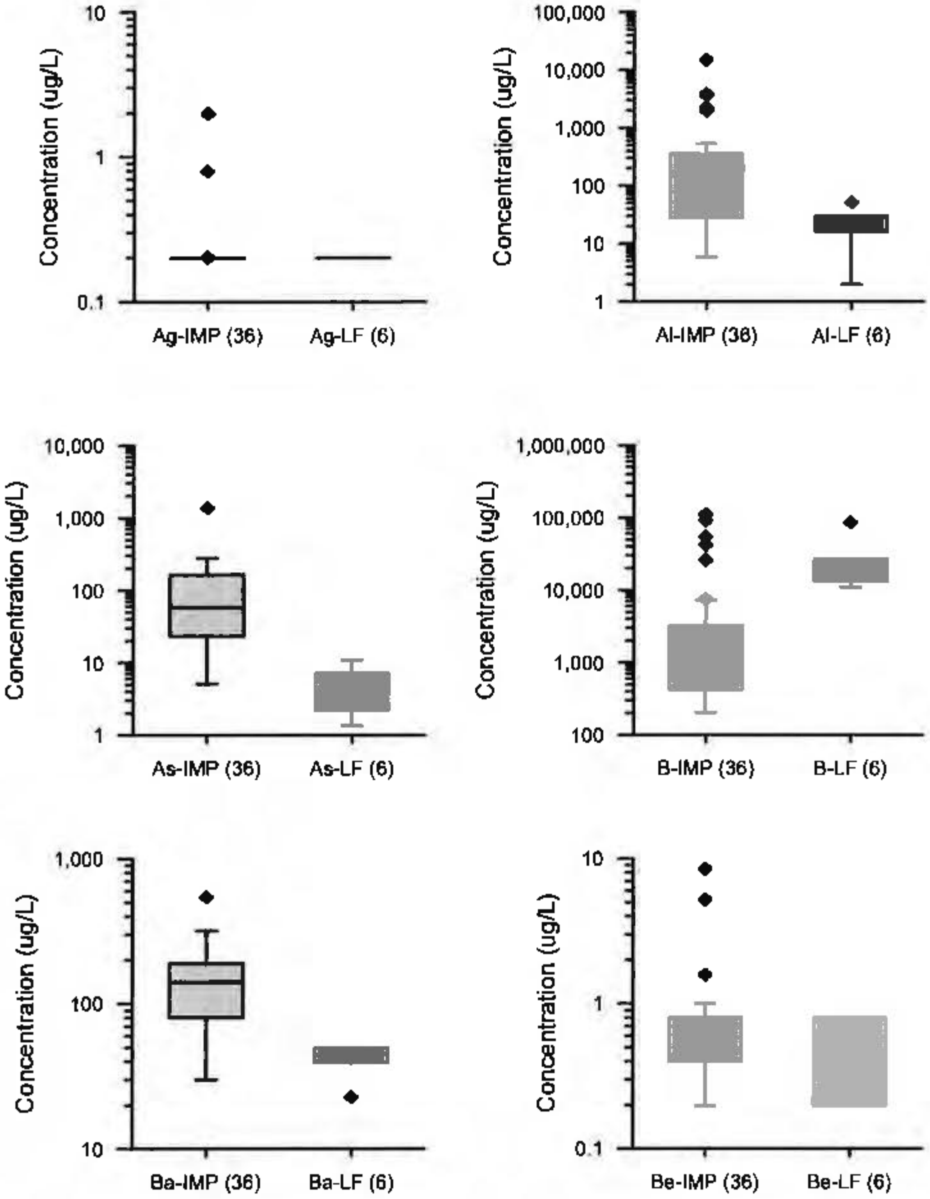

Figure C-1
Comparison of field Leachate Concentrations: Bituminous Coal Ash, Landfill versus Impoundment (continued)

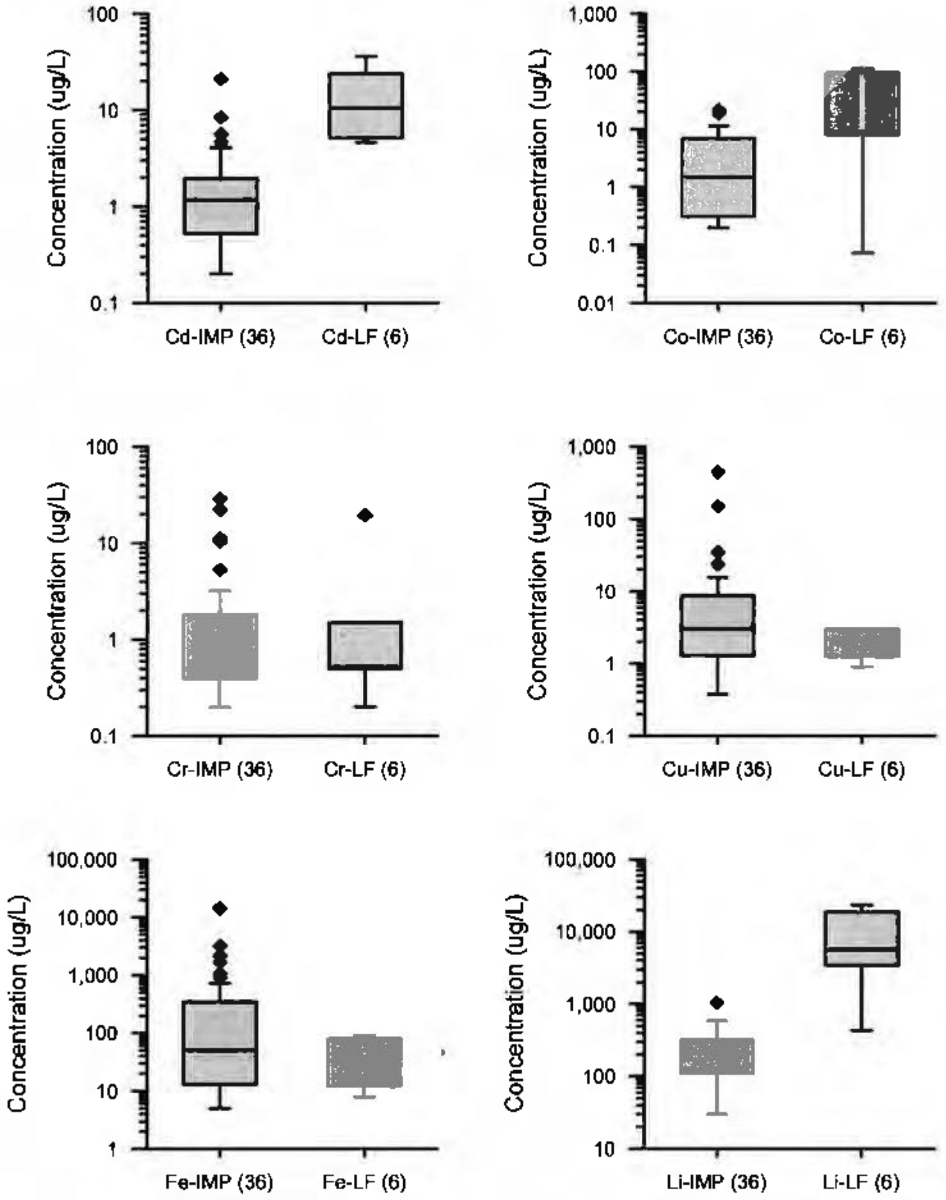

Figure C-1
Comparison of field Leachate Concentrations: Bituminous Coal Ash, Landfill versus Impoundment (continued)

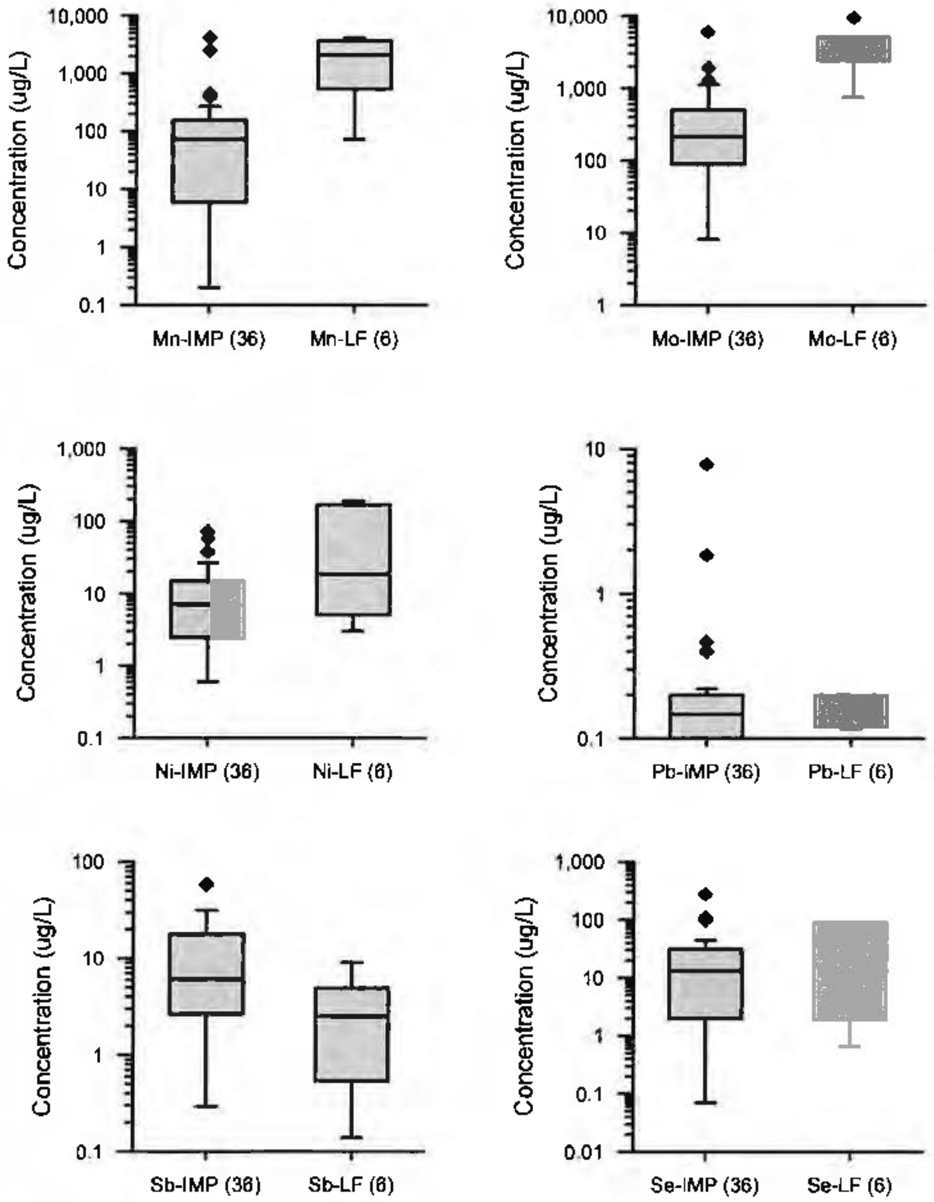

Figure C-1
Comparison of Field Leachate Concentrations: Bituminous Coal Ash, Landfill versus Impoundment (continued)

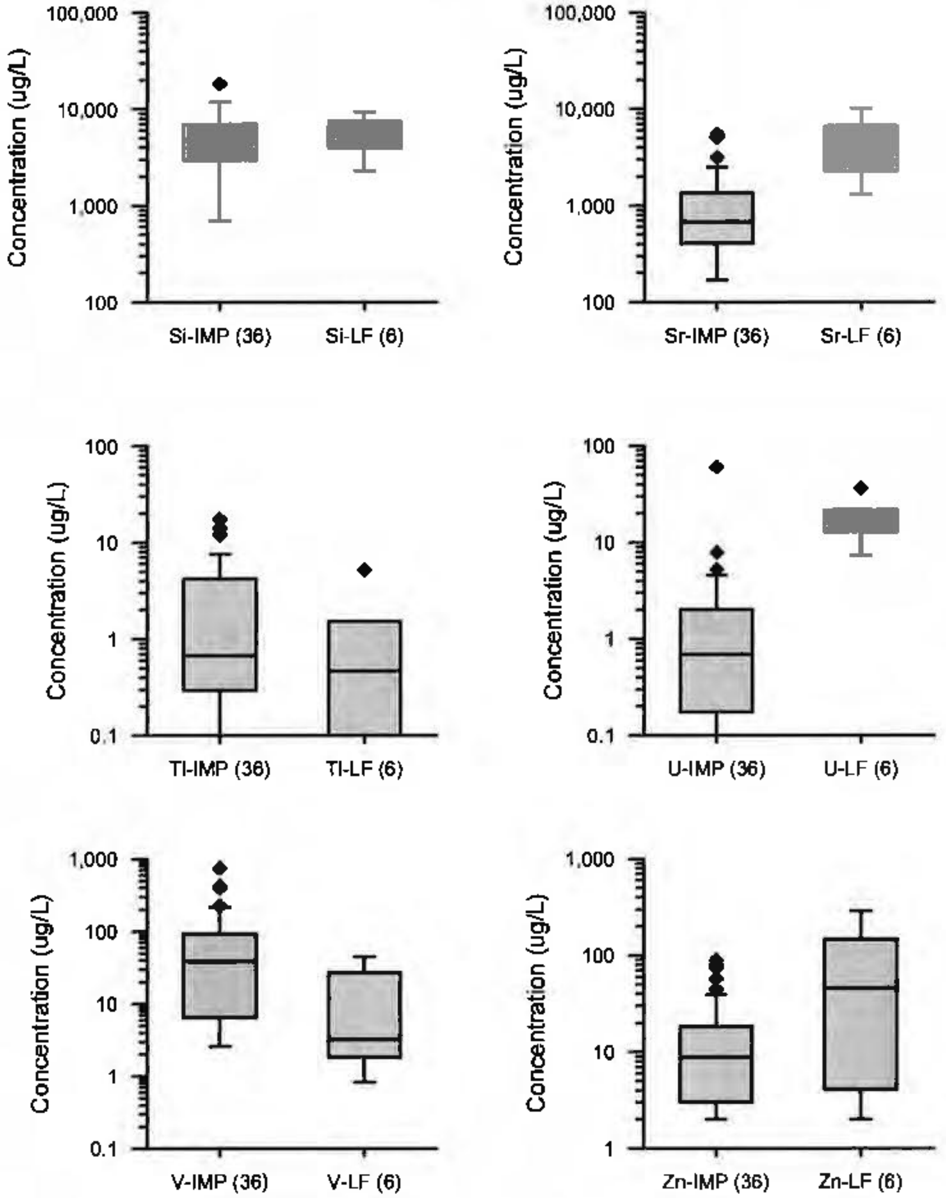

Figure C-1
Comparison of Field Leachate Concentrations: Bituminous Coal Ash, Landfill versus Impoundment (continued)

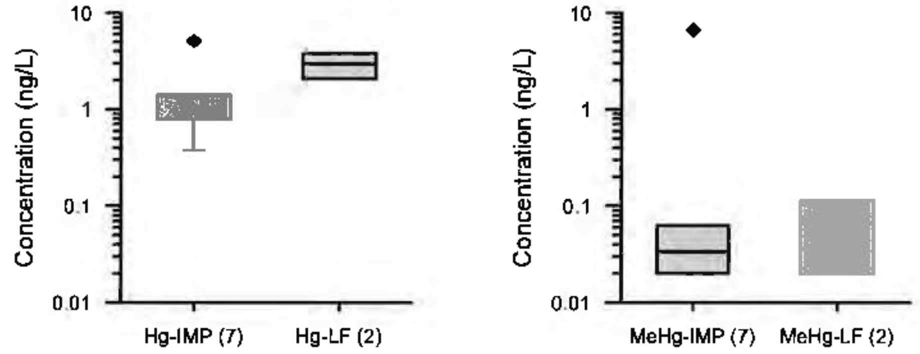

Figure C-1
Comparison of Field Leachate Concentrations: Bituminous Coal Ash, Landfill versus Impoundment (continued)

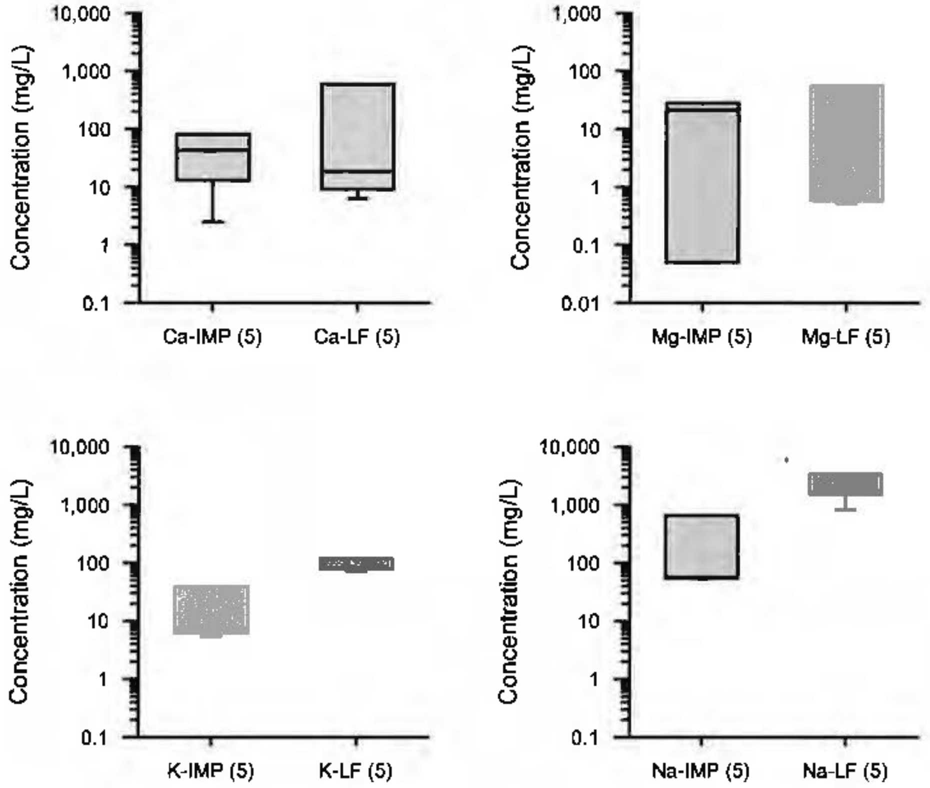

Figure C-2
Comparison of Field Leachate Concentrations: Subbituminous/Lignite Coal Ash, Landfill versus Impoundment

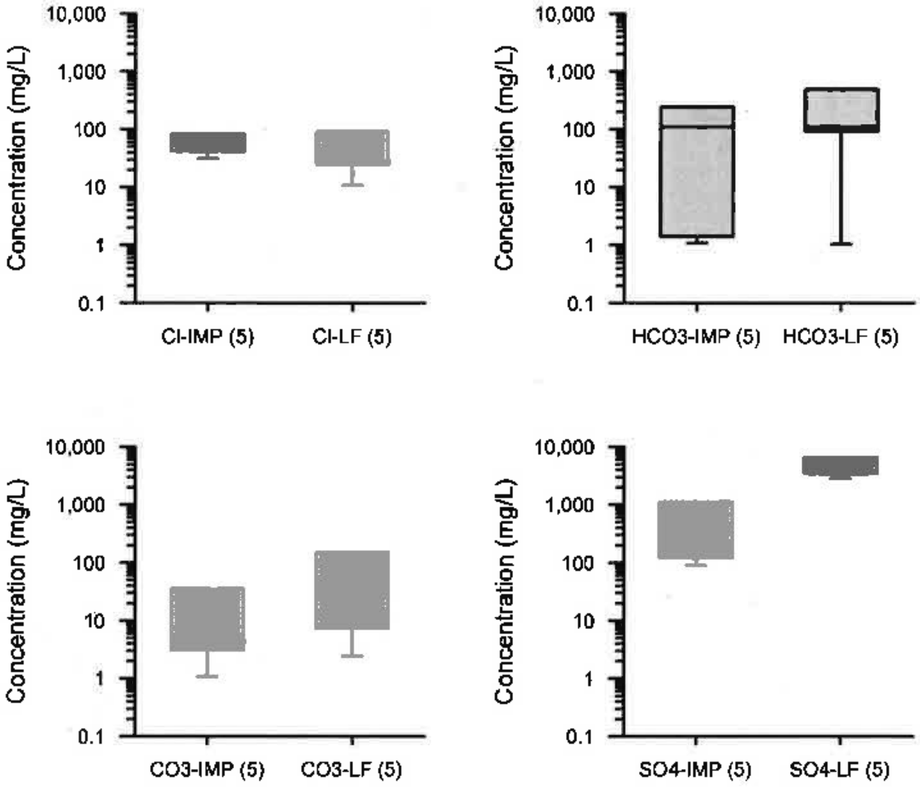

Figure C-2
Comparison of Field Leachate Concentrations: Subbituminous/Lignite Coal Ash, Landfill versus Impoundment (continued)

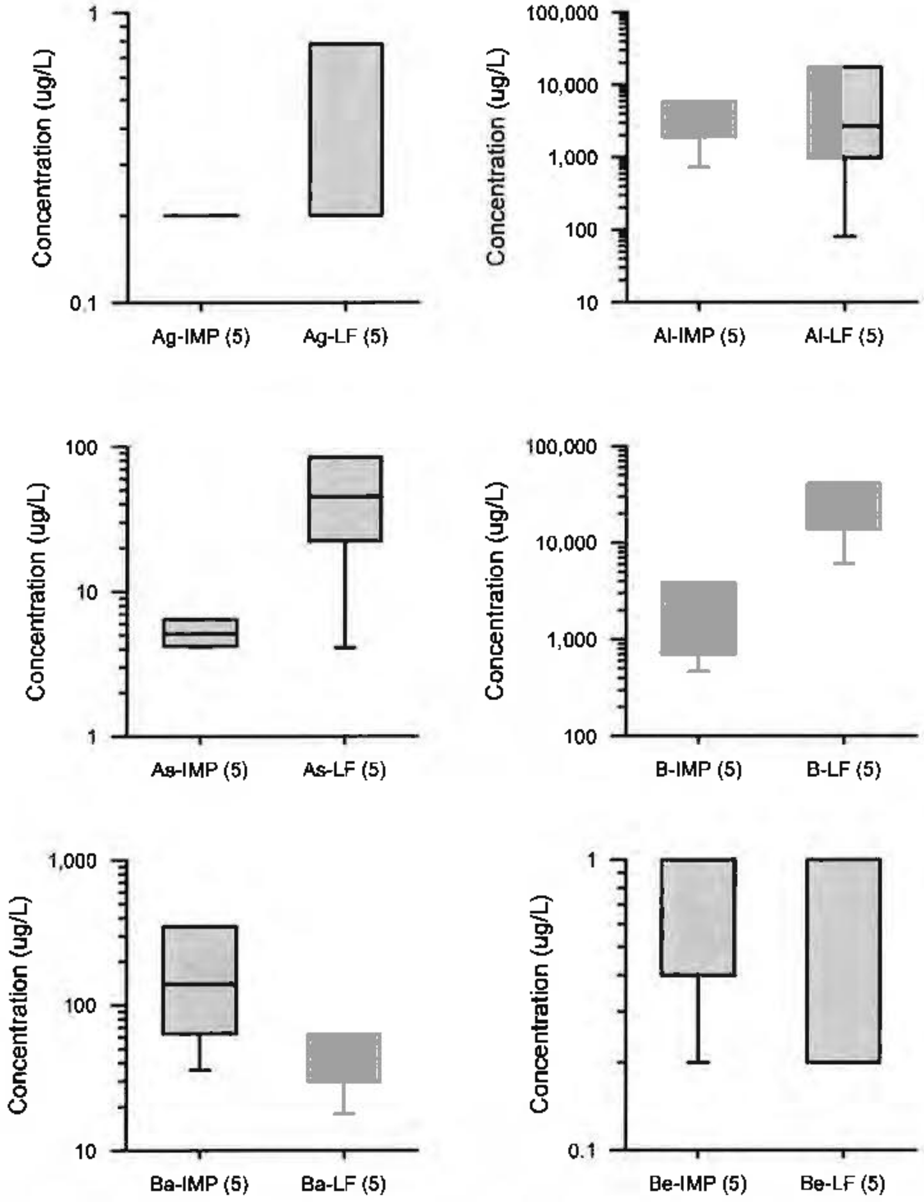

Figure C-2
Comparison of Field Leachate Concentrations: Subbituminous/Lignite Coal Ash, Landfill versus Impoundment (continued)

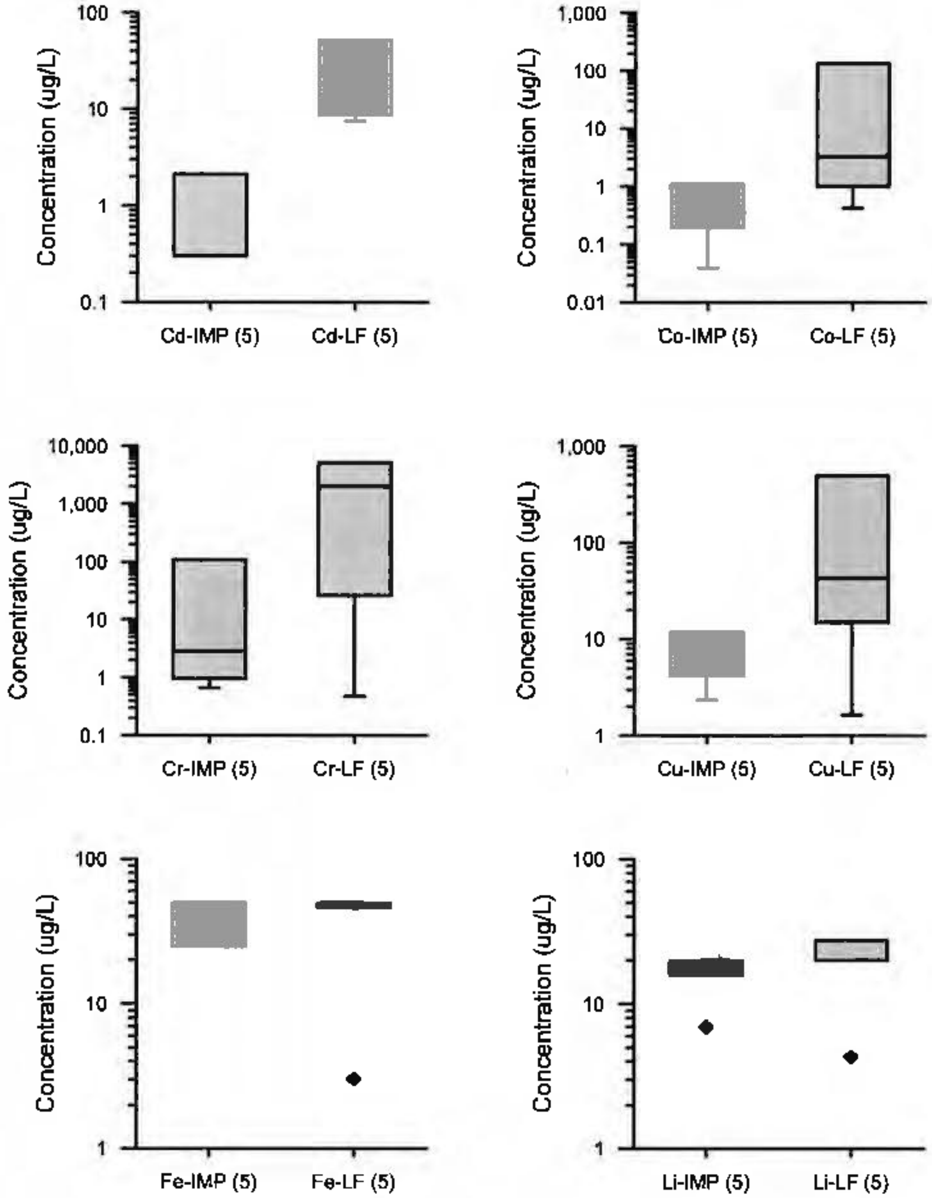

Figure C-2
Comparison of Field Leachate Concentrations: Subbituminous/Lignite Coal Ash, Landfill versus Impoundment (continued)

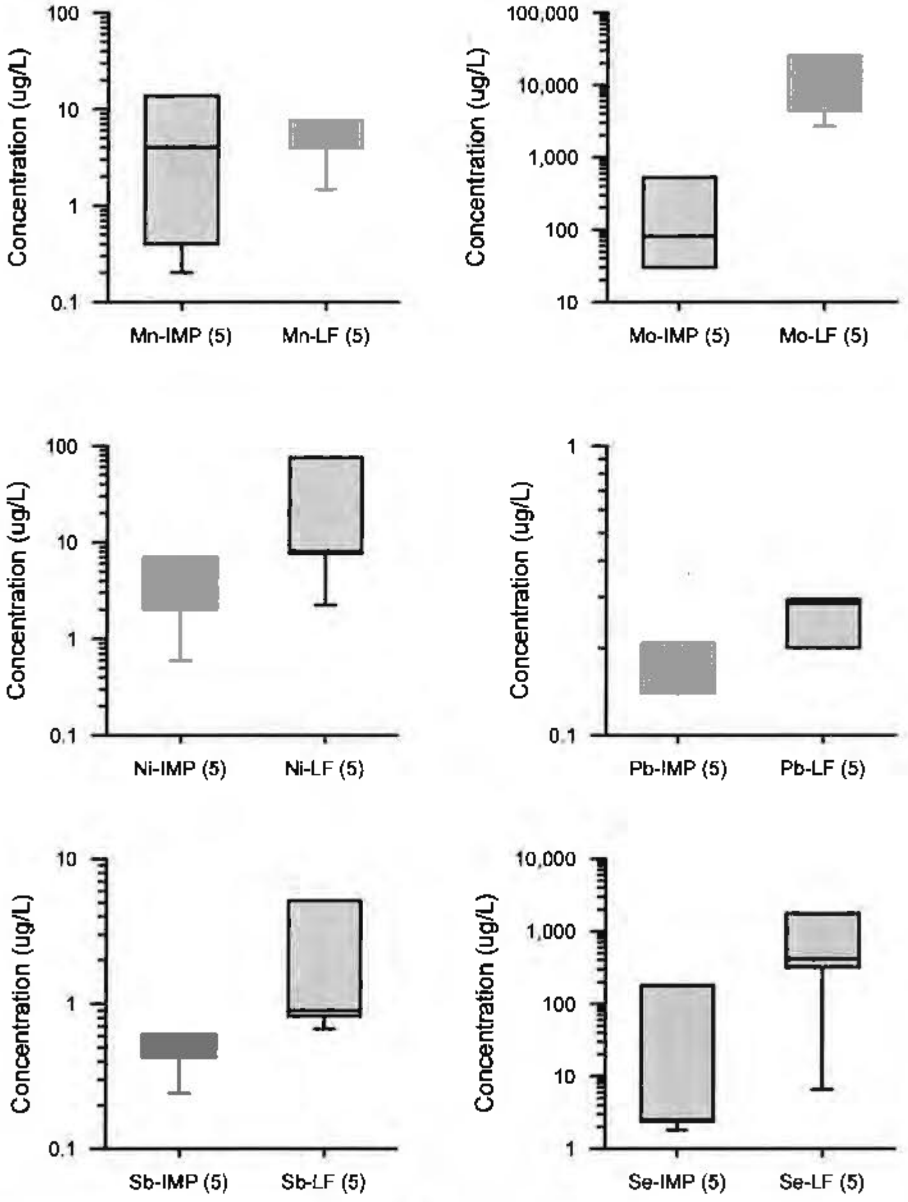

Figure C-2
Comparison of Field Leachate Concentrations: Subbituminous/Lignite Coal Ash, Landfill versus Impoundment (continued)

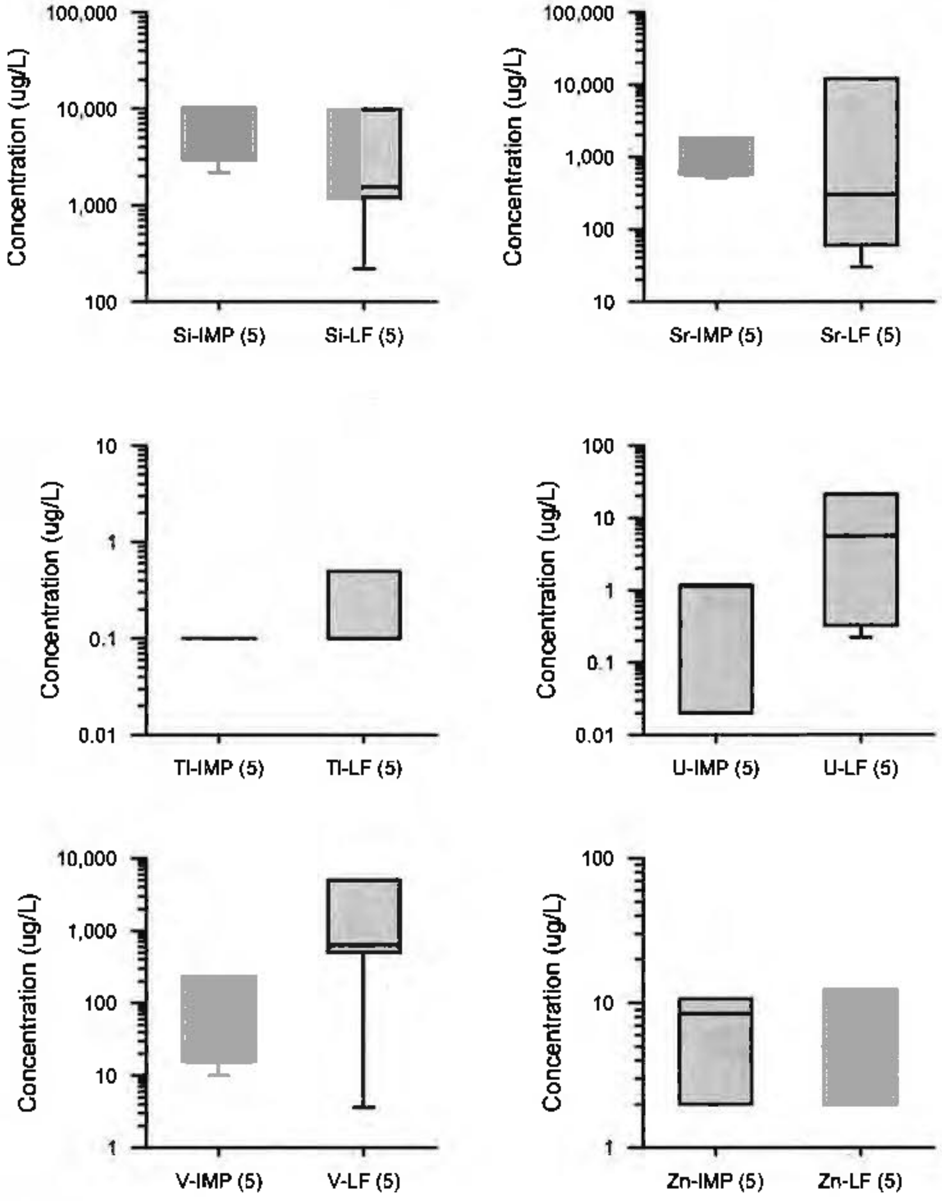

Figure C-2
Comparison of Field Leachate Concentrations: Subbituminous/Lignite Coal Ash, Landfill versus Impoundment (continued)

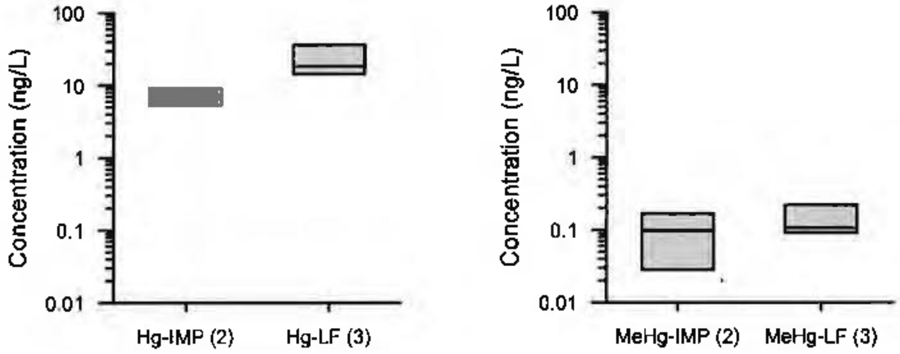

Figure C-2
Comparison of field Leachate Concentrations: Subbituminous/Lignite Coal Ash, Landfill versus Impoundment (continued)

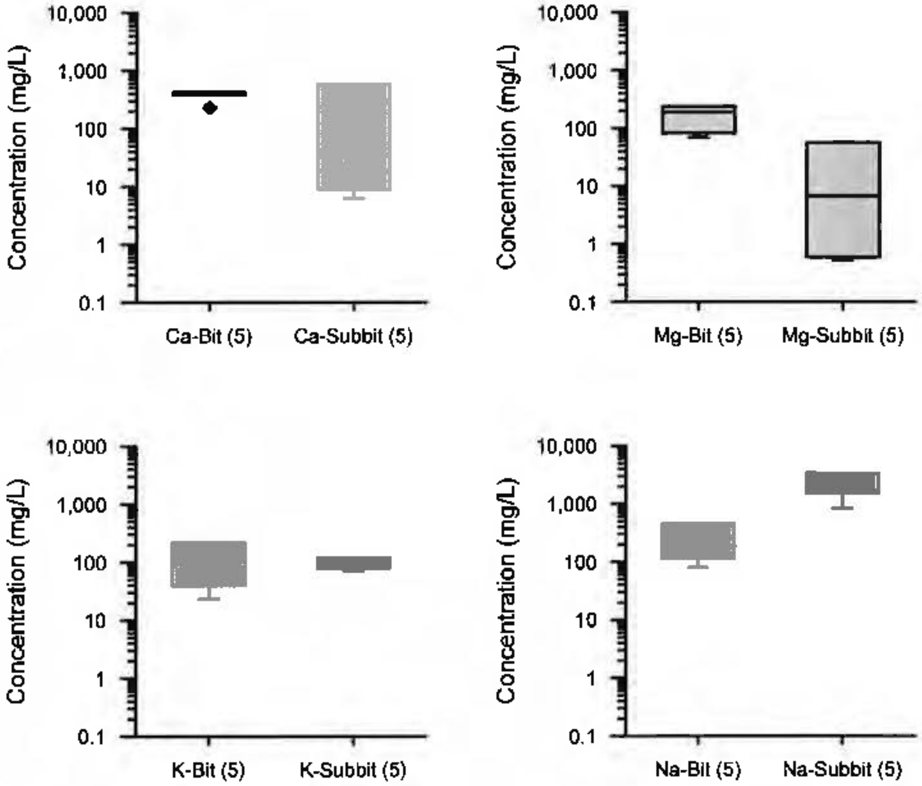

Figure C-3
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Landfills

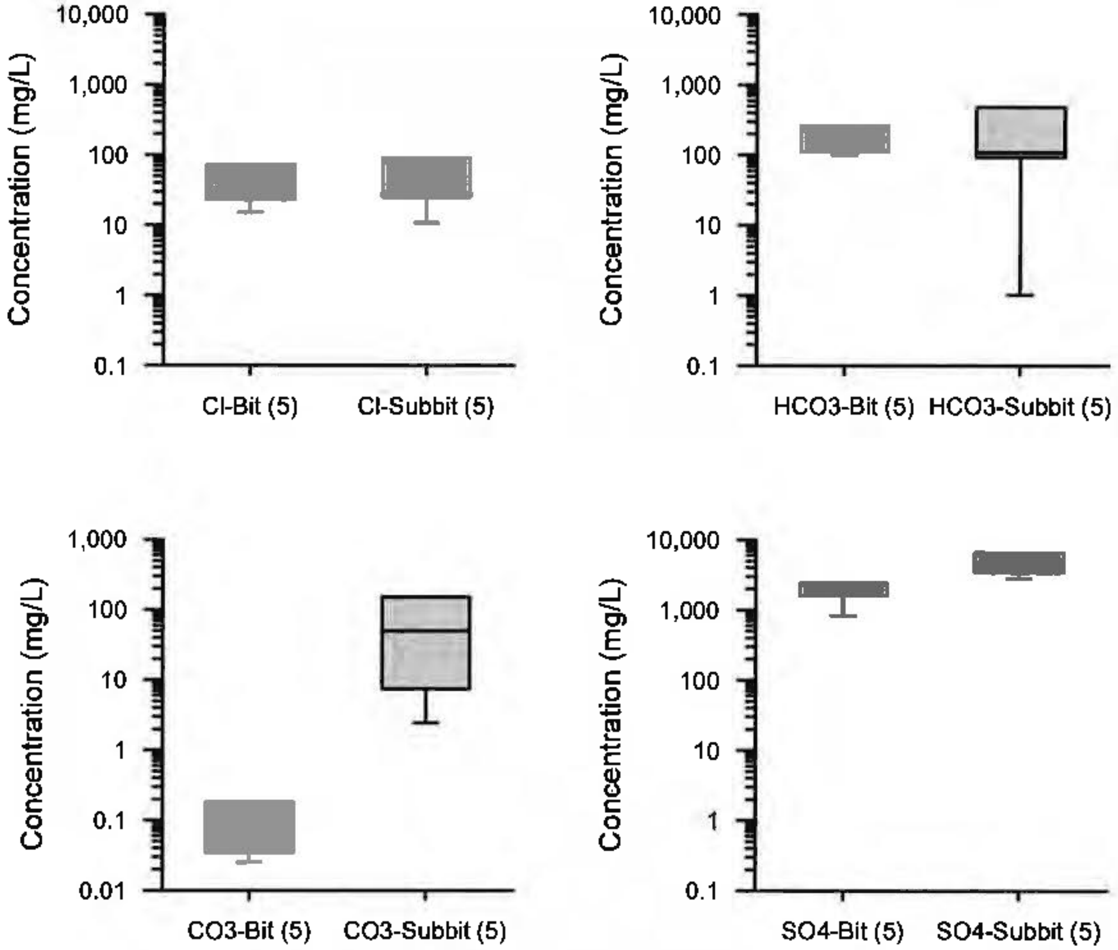

Figure C-3
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Landfills (continued)

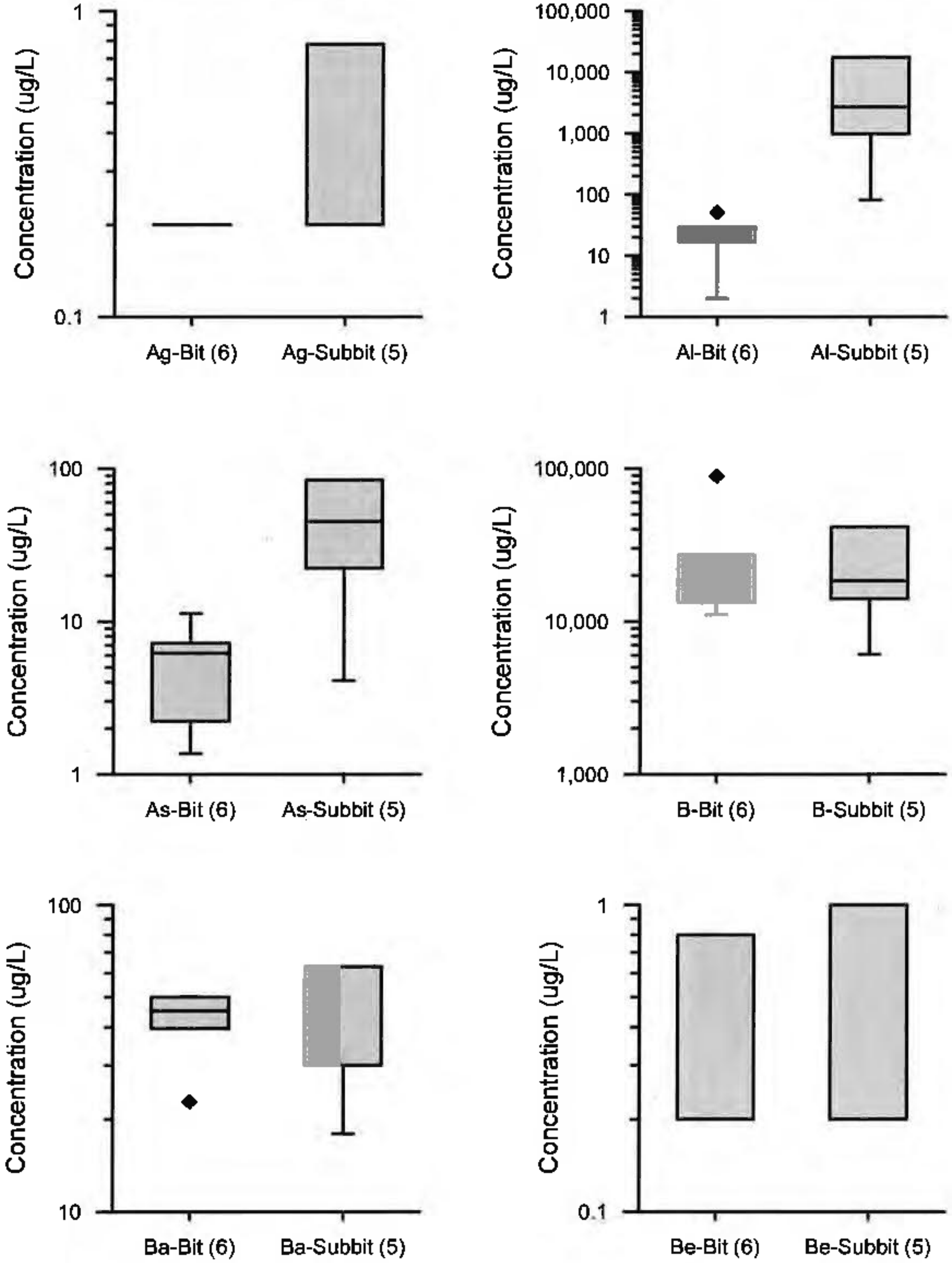

Figure C-3
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Landfills (continued)

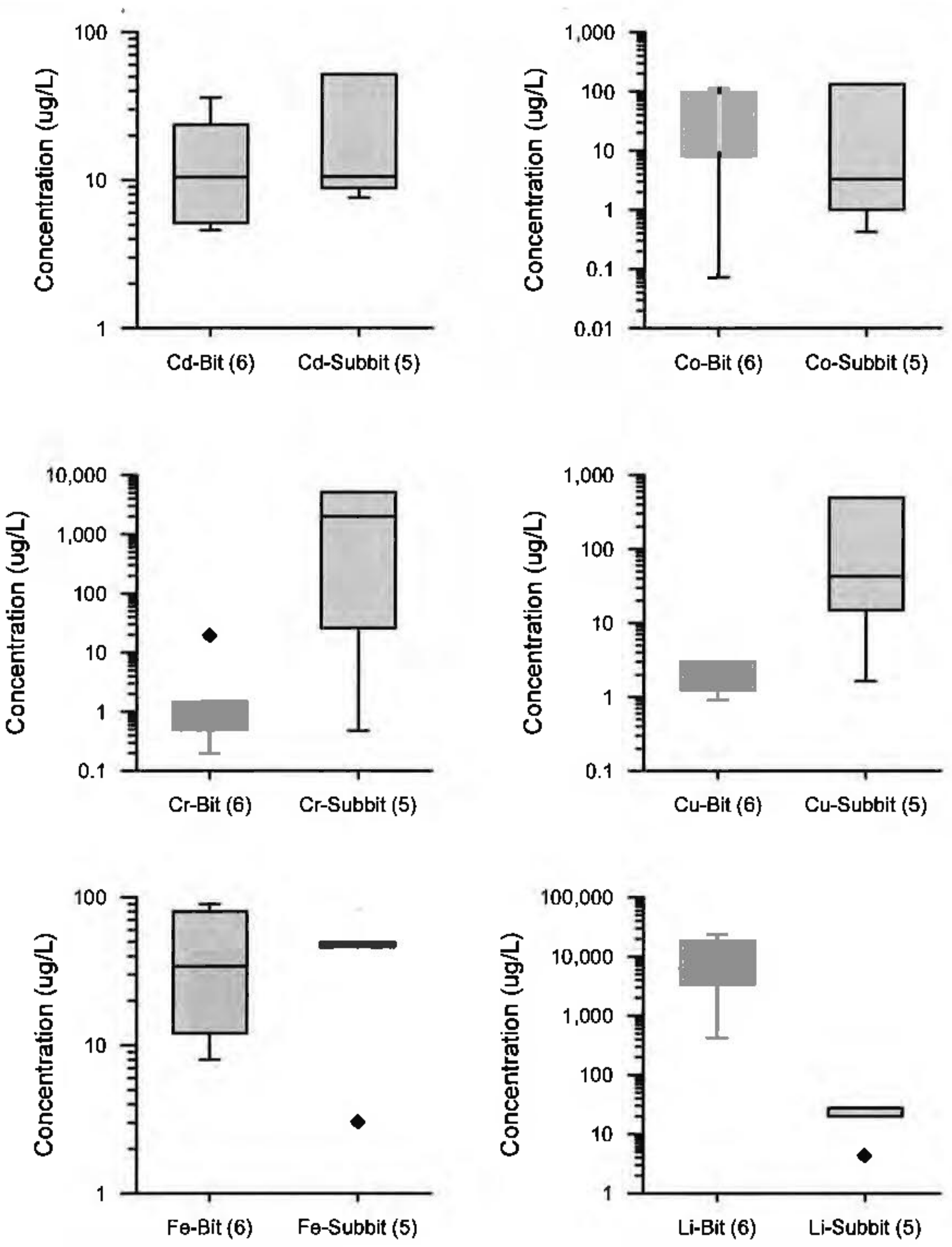

Figure C-3
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Landfills (continued)

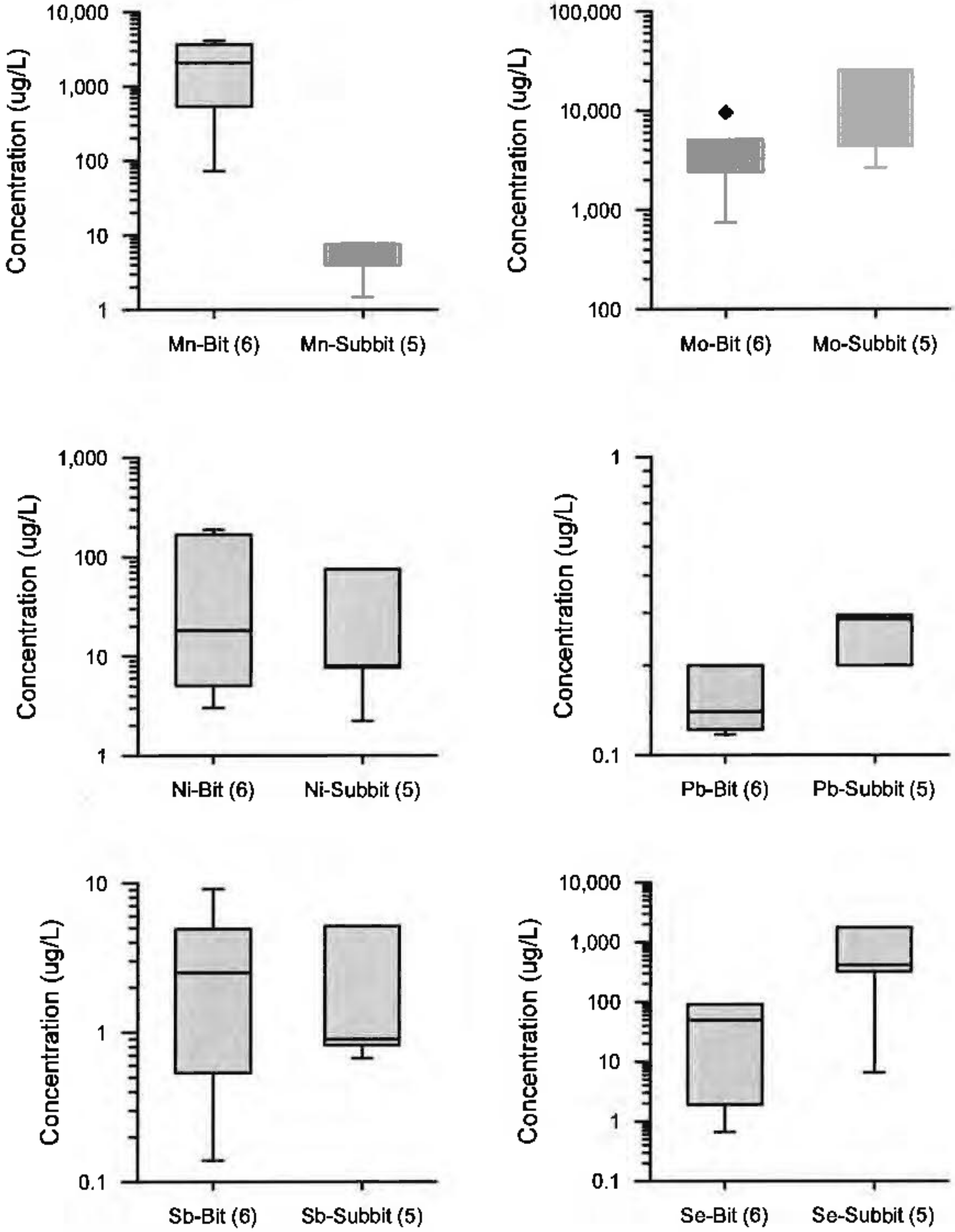

Figure C-3
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Landfills (continued)

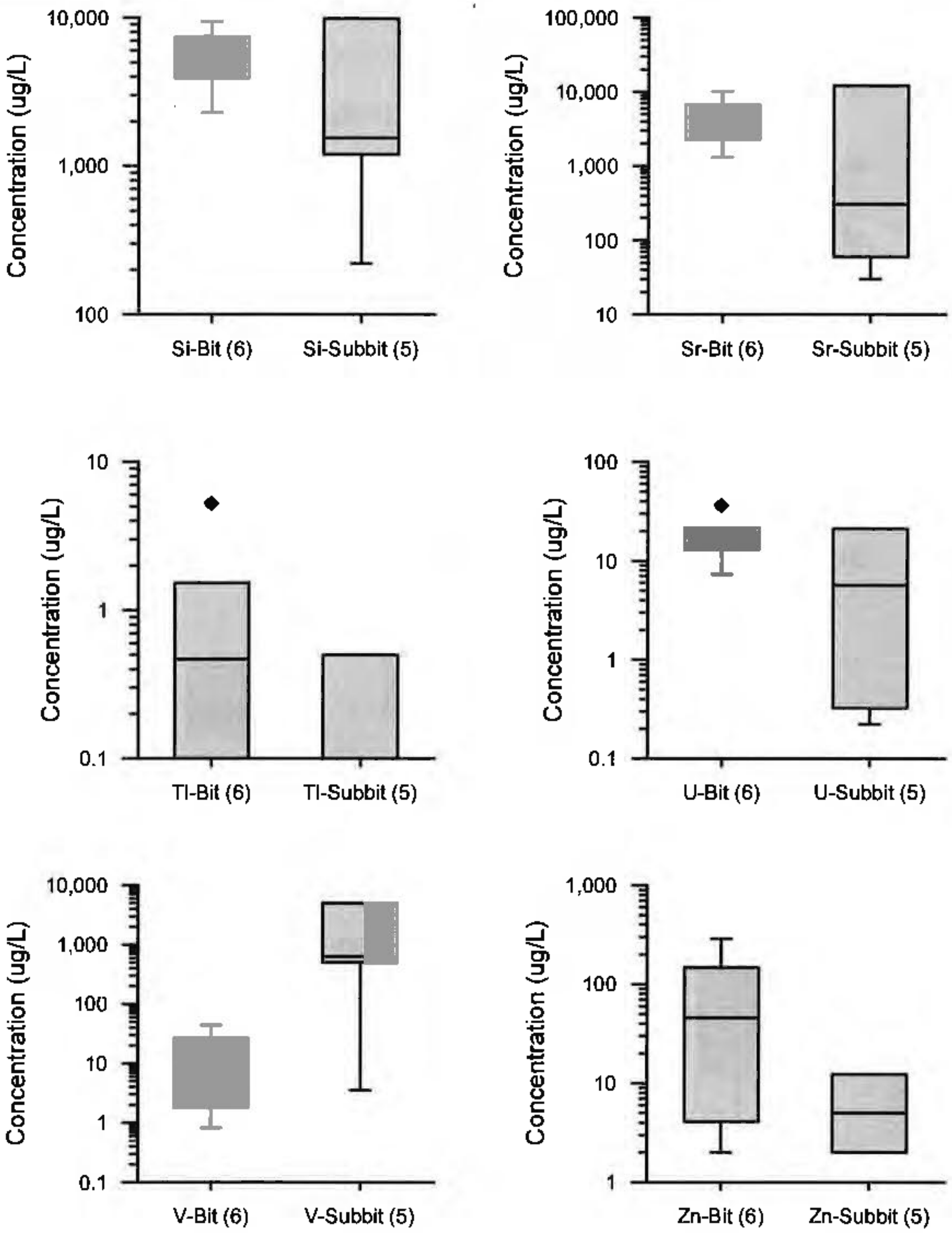

Figure C-3
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Landfills (continued)

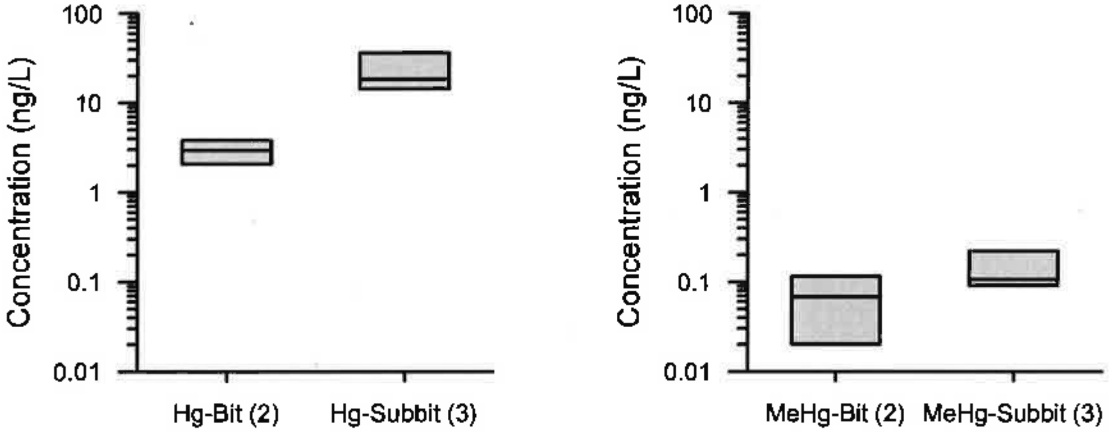

Figure C-3
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Landfills (continued)

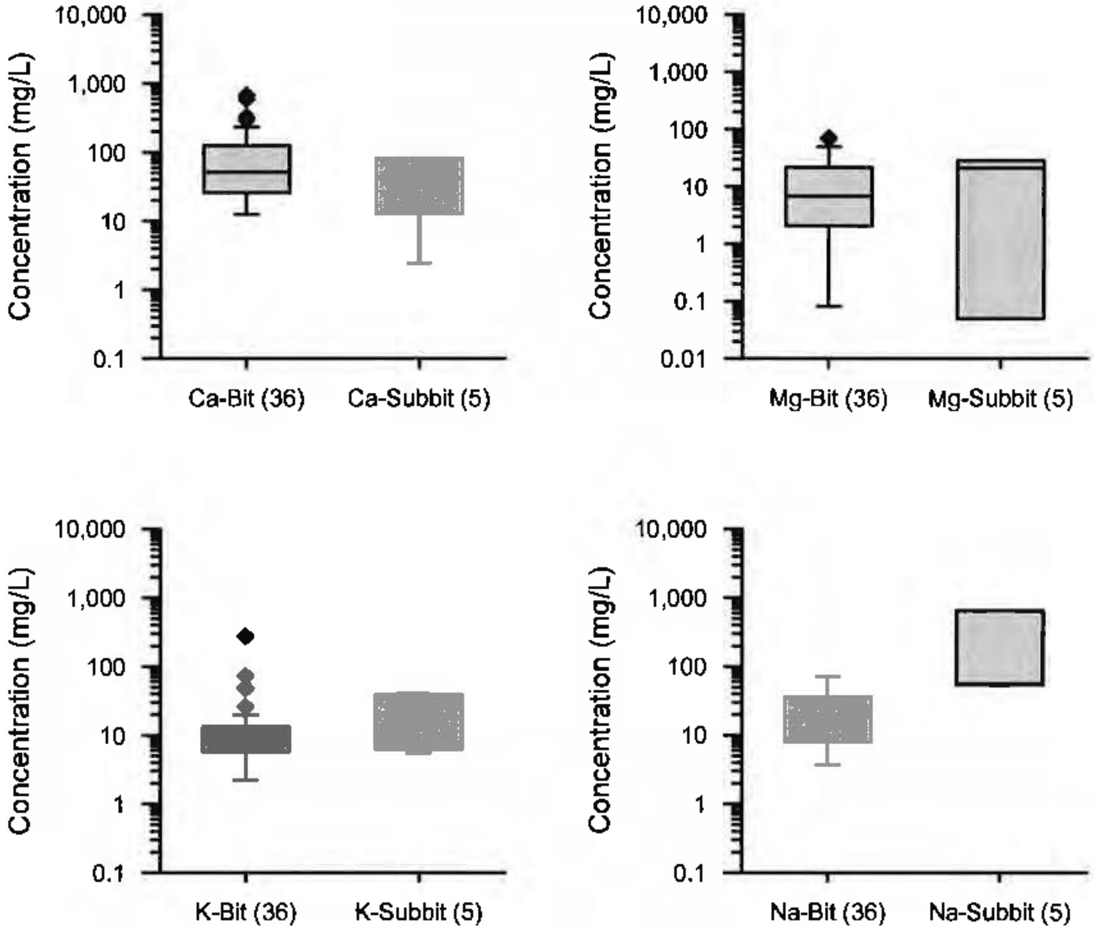

Figure C-4
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Impoundments

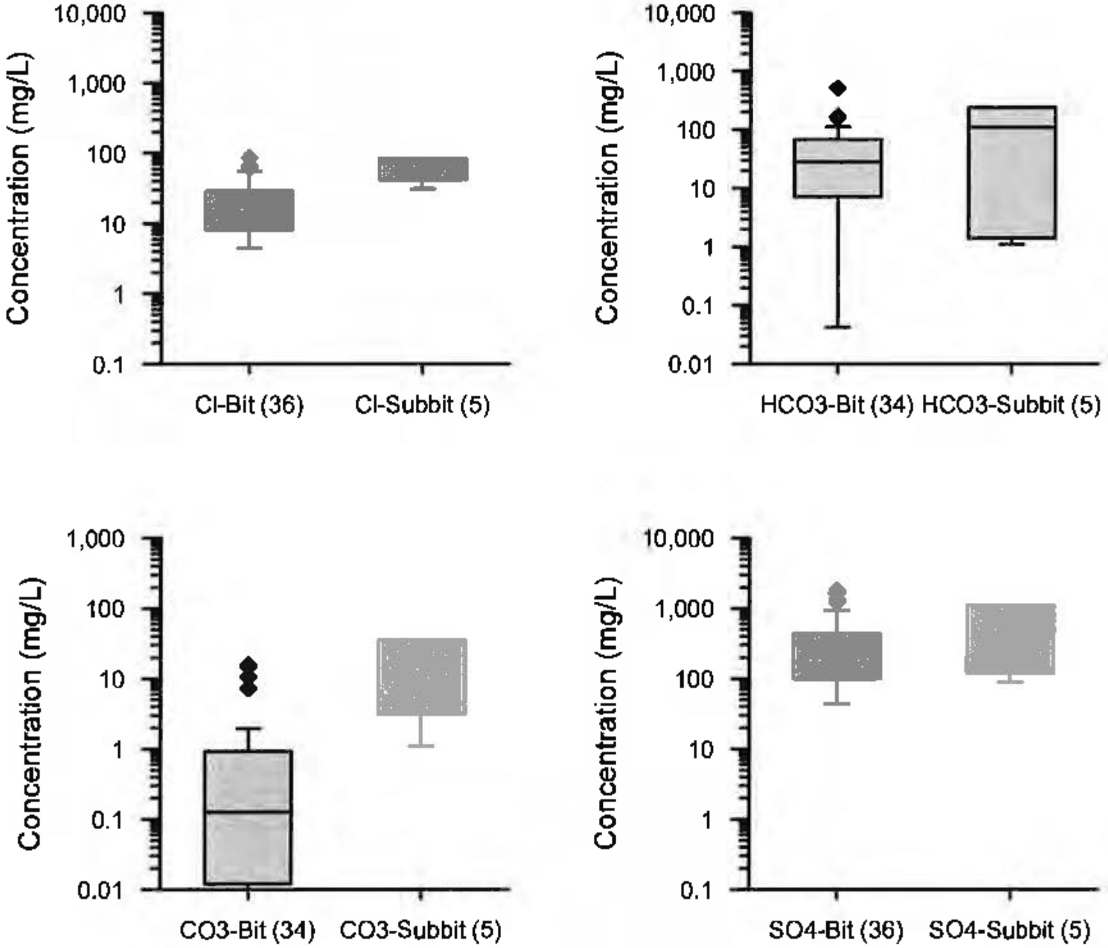

Figure C-4
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Impoundments (continued)

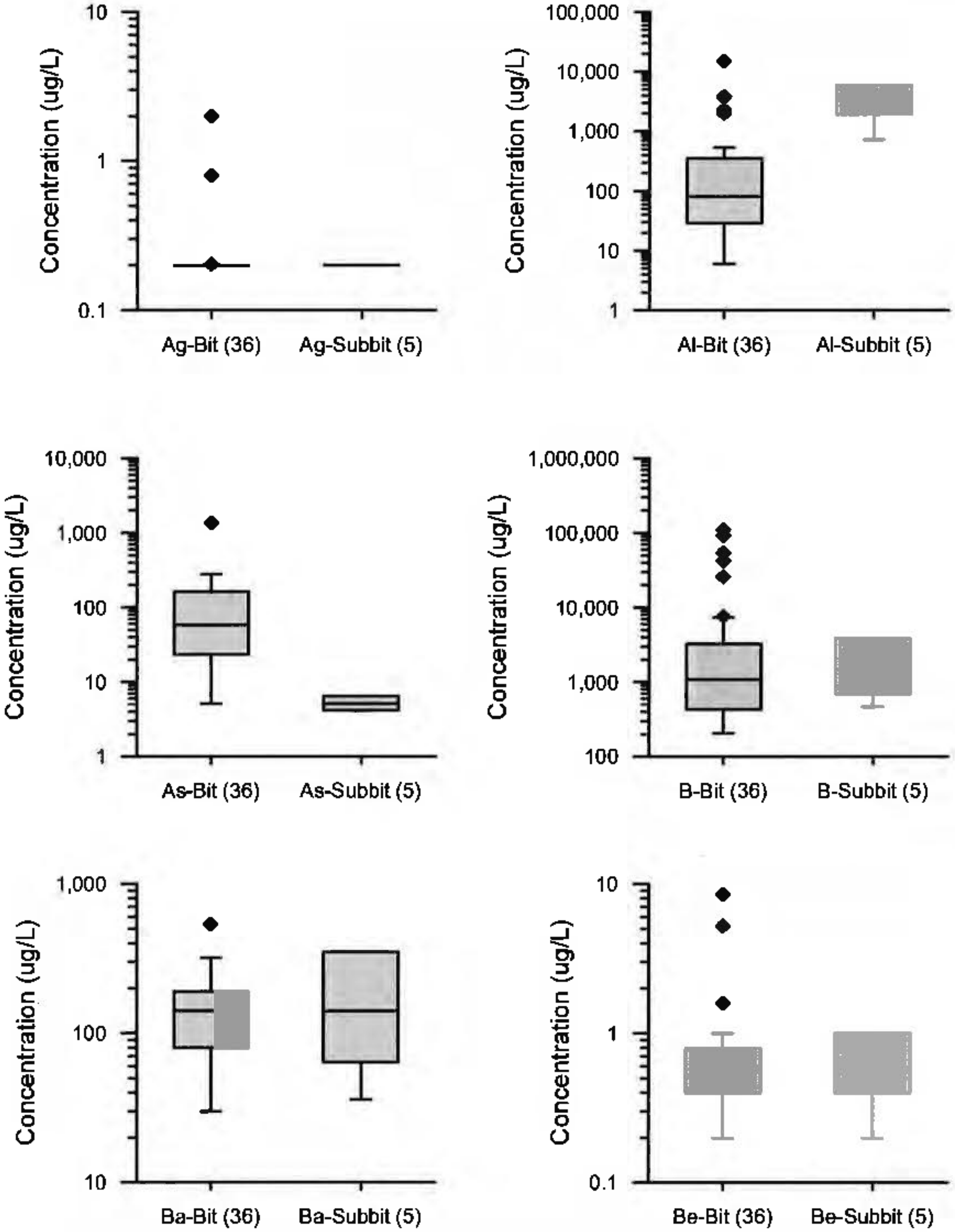

Figure C-4
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Impoundments (continued)

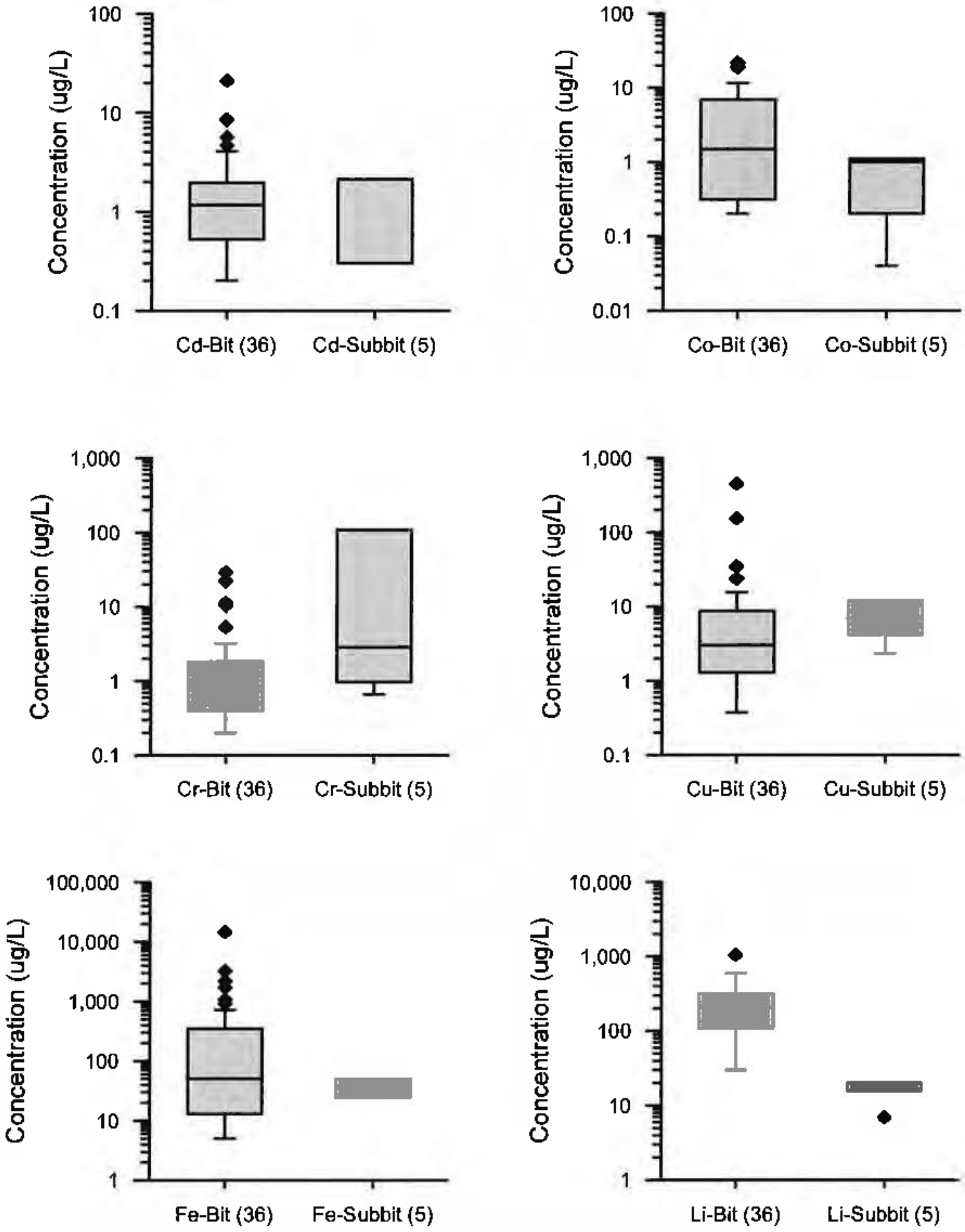

Figure C-4
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Impoundments (continued)

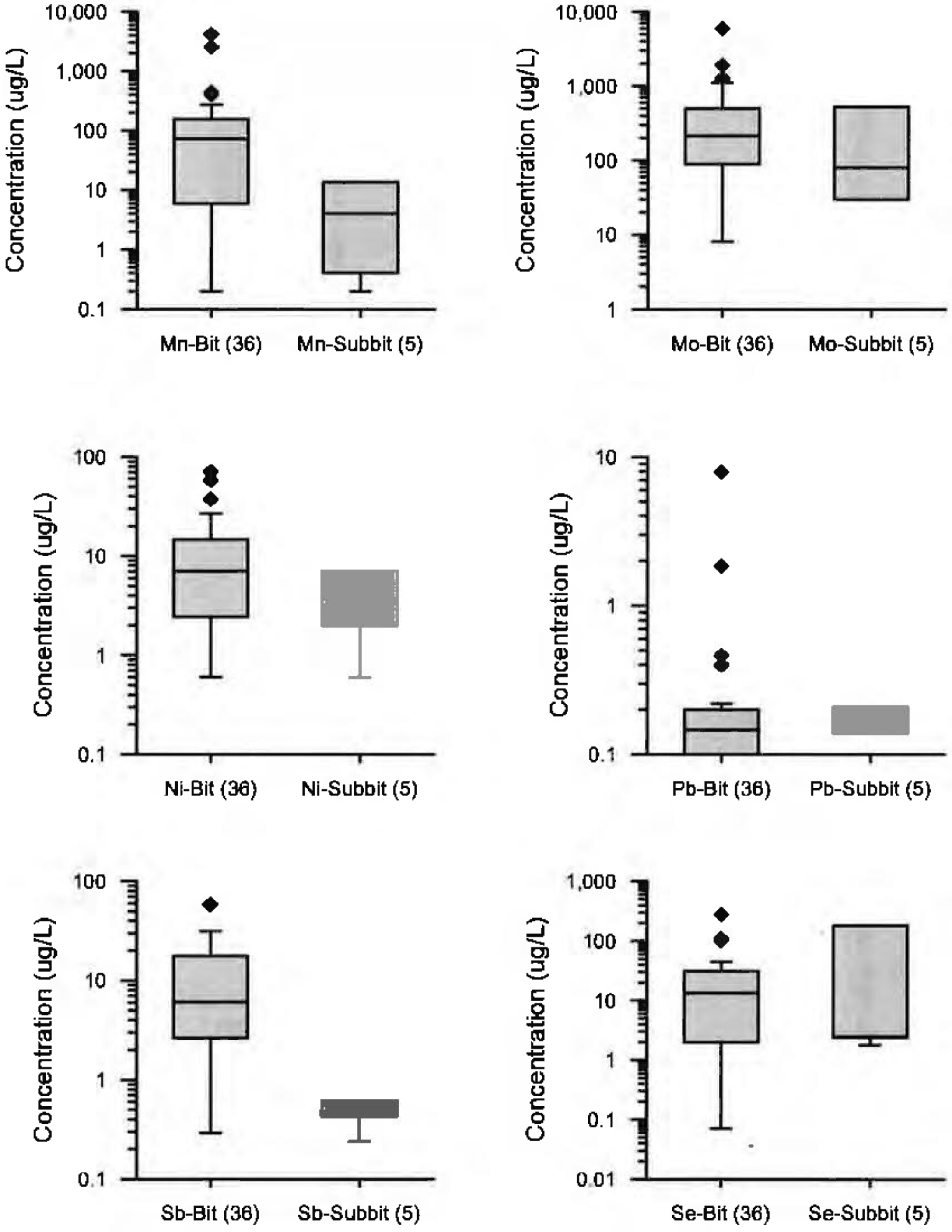

Figure C-4
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Impoundments (continued)

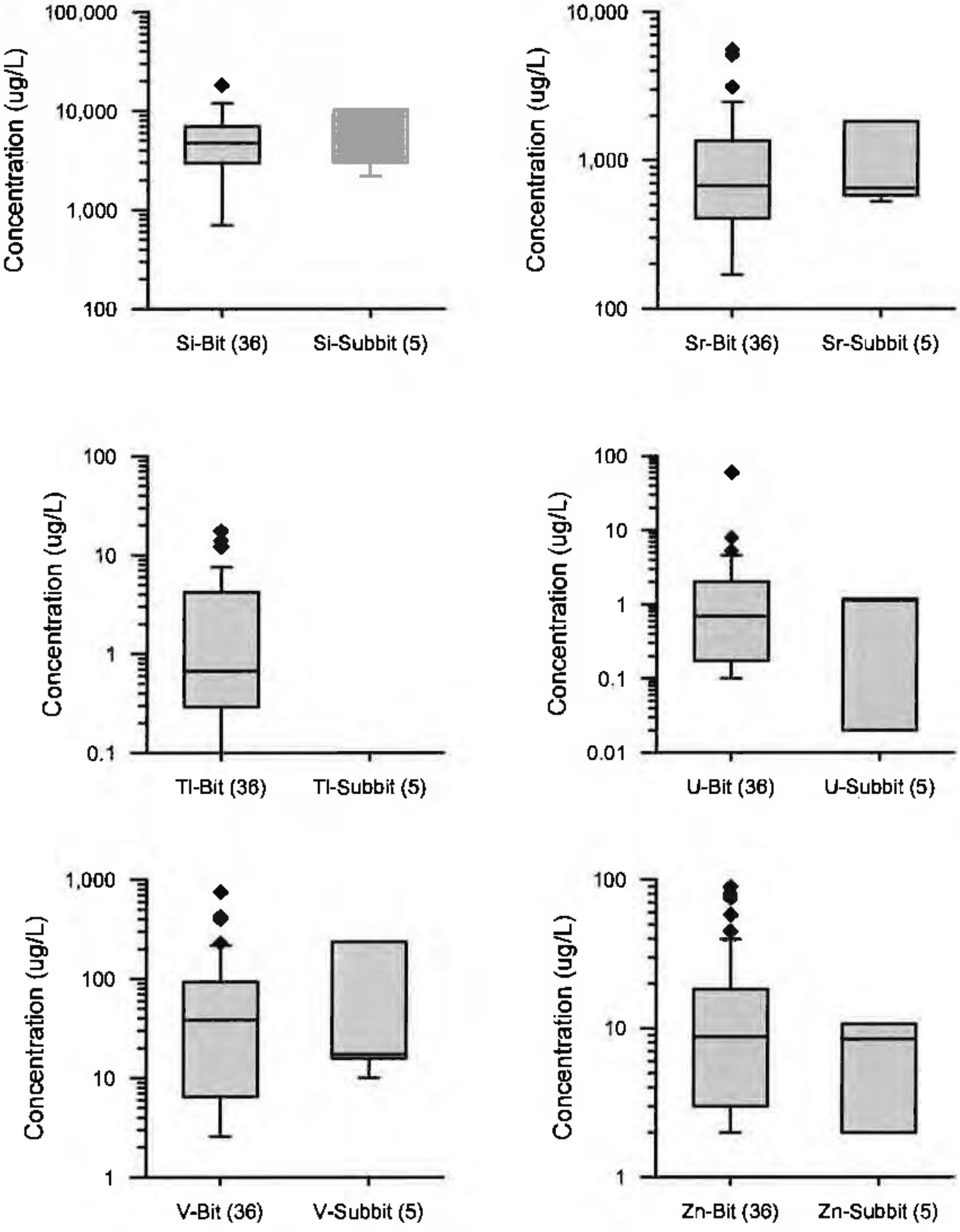

Figure C-4
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Impoundments (continued)

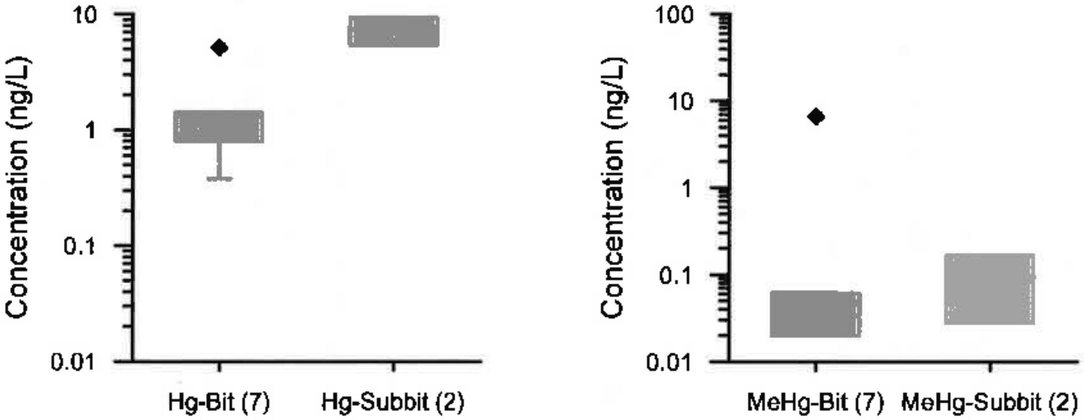

Figure C-4
Comparison of Field Leachate Concentrations: Bituminous vs. Subbituminous/Lignite Coal Ash, Impoundments (continued)

D

EVALUATION OF ARSENIC, SELENIUM, AND CHROMIUM SAMPLE PRESERVATION AND ANALYSIS METHODS

Cryofreezing Overview

Cryofreezing was used as the default sample preservation strategy for the speciation samples in this project for two reasons:

- Recent research has shown that both arsenic and selenium form soluble sulfur species in sulfidic waters, which are decomposed and precipitated under acidic conditions, thereby completely altering the original speciation information. This would have affected all samples that contain detectable concentrations of "other" arsenic or selenium species, although in most cases, these "other" species constituted less than 10 percent of the total concentration of the element, and so the associated error would have been relatively small. However, six samples (five arsenic and one selenium) contained "other" species at fractions > 10 percent of the corresponding total arsenic or selenium concentration. Since it wasn't known in advance how strongly sulfidic the sampled waters would be, and field observations confirmed (via smell) that some samples had significant concentrations of free reduced sulfur compounds, cryofreezing was used instead of acidification to prevent decomposition of soluble arsenic- and selenium-sulfur compounds.
- It is well established that Cr(VI) gets reduced by dissolved organic matter in acidified samples during storage. Since nearly all samples containing elevated chromium concentrations had Cr(VI) as their major species, this could have led to significantly altered chromium speciation results. Again, cryofreezing circumvents the issue of pH change during storage. This was confirmed in a test of preservation methods performed in 2004 (after analytical issues had been observed in 2003); while the cryofrozen split yielded almost exclusively Cr(VI), acidified splits yielded lower Cr(VI) concentrations (see Table D-2) and increasing Cr(III) concentrations over time. This already led to an altered chromium speciation pattern immediately after sample receipt, but yielded a completely reversed speciation result after several weeks of storage. For this reason, Cr(VI) is typically preserved under strongly alkaline conditions, but for the present project, this would have created other analytical issues related to the precipitation of Cr(III) and major trace elements (e.g. iron and manganese), and was thus avoided.

Unfortunately, during the analysis of samples collected in 2003, it was observed that the cryofreezing approach created another, unanticipated problem, during storage. When the cryofrozen samples were thawed prior to analysis, varying degrees of white-yellowish precipitates were observed in many samples, which did not re-dissolve at room temperature (over a time frame of weeks). When speciation analyses of these samples were conducted, a significant gap in the mass balance (= total element concentration – sum of its individual species) of arsenic and/or selenium was observed; chromium was not significantly affected by this issue. It was theorized that these precipitates were calcium sulfate or carbonate, and geochemical model calculations confirmed that the solubility of these minerals was exceeded in many samples.

To test if the precipitates contained the "missing" fractions of arsenic (for which the mass balance discrepancies were worse than for selenium), the precipitates were digested in nitric acid, and the resulting solutions analyzed for arsenic released from the precipitates. Table D-1 shows that for some samples, the "missing" fraction of arsenic was apparently indeed bound to the observed precipitates, but there are more samples than that for which this did not confirm the postulated loss mechanism. Additionally, significant mass balance discrepancies were also observed in samples containing no visible precipitates. Therefore, while this storage artifact was certainly responsible for incomplete arsenic or selenium speciation mass balance in some samples, it was definitely not the only process involved, and possibly not even the major one. Dissolution of the precipitates in nitric acid changes arsenic speciation, so it remains unclear if any one species of arsenic was selectively or preferentially removed from solution during the formation of the precipitates.

Formation of these precipitates was only observed in samples collected in 2003, because those samples were stored for a long period (up to 6 months) prior to analysis. By comparison, samples collected in 2004 and 2005 were typically analyzed for their arsenic and selenium speciation within four weeks after collection, and the sum of species in these samples was closer to the total concentration than in the 2003 samples. Consequently, it seems likely that the formation of precipitates resulted from excessively long cryofrozen storage, and can be avoided by keeping storage time to one month or less. Attempts to "recreate" the precipitates were unsuccessful (on a time scale of weeks), so no further attempts were made to resolve the issue and correct the speciation mass balance for samples with precipitates.

Table D-1
Arsenic Speciation Mass Balance, Including Losses to Precipitates Formed During Cryofrozen Storage, for Leachate Samples Collected In 2003

Sample ID	Lab ID	Total As	As(III)	As(V)	other As species	precipitated As	mass balance without precipitated As [%]	mass balance including precipitated As [%]
001	1	20.4	< 0.3	9.5	2.1	7.04	57	91
002	2	48.4	< 6	47	< 6	1.10	98	100
003	3	84	< 6	69	< 6	7.50	82	91
004	4	18.6	8.4	5.2	< 0.3	0.59	73	76
005	5	3.0	< 0.2	1.3	< 0.2	0.08(a)	45	47
006	6	12.2	< 0.3	0.9(a)	< 0.3	<0.05	8	8
007	7	20.1	< 2	< 2	< 2	0.07(a)	0	0
008	8	16.9	0.7(a)	< 0.5	< 0.3	0.07(a)	4	5
009	9	28.9	< 6	< 10	< 6	0.09(a)	0	0
010	10	22.3	1.5(a)	10	< 0.6	0.46	52	54
011	11	4.8	< 0.2	0.6	< 0.2	0.26	12	17
012	12	238	97.0	66	< 0.6	38.1	69	85
013	13	21.6	3.7	< 0.5	< 0.3	11.8	17	72
013D	13A	22	1.9	< 0.5	< 0.3	NA	9	9
014	14	163	1.9	86	0.9(a)	25.1	54	70
015	15	23.8	< 0.6	24	< 0.6	1.72	99	106
016	16	68.6	< 0.6	25	< 0.6	23.4	36	70
SX-1	core 3	72.0	0.9	46.9	< 0.1	1.16	66	68
017	17	4.11	0.88	<0.08	0.1	0.26	23	30
018	18	23.1	0.42	5.22	< 0.06	17.8	24	101
019	19	5.11	0.57	<0.08	< 0.06	0.36	11	18
020	20	4.19	1.00	0.53	0.1	0.14(a)	40	43
HN-1	core 1	59.8	< 0.1	33.6	0.2	5.65	57	66
HN-2	core 2	20.6	< 0.1	6.9	0.1	1.64	34	42
021	21	194	2.1	208	< 0.3	2.38	108	110
022	22	11.1	12.5	0.49	< 0.06	0.11(a)	118	119
023	23	218	0.8(a)	189	< 0.3	12.4	87	93
024	24	11.2	0.4(a)	<0.2	< 0.2	1.47	3	16
025	25	6.47	1.35	<0.08	< 0.06	1.04	21	37
026	26	10.8	11.2	0.4(a)	< 0.2	0.11(a)	107	108
027	27	39.1	13.2	4.8	1.3	2.31	49	55
028	28	30.0	2.4	1.7	0.2	0.17(a)	14	15
029	29	48.9	1.7	8.9	0.3	4.01	22	31
030	30	42.5	3.5	29.5	0.4	0.58	79	80
031	31	221	201	23.6	0.7	3.65	102	103
032	32	25.4	17.5	16.9	0.1	0.43	136	137

(a) = sample concentration less than 5 times blank
Concentrations in µg/L

Due to the large heterogeneity of the collected sample set, additional issues related to speciation preservation were observed in individual samples. Some samples showed obvious loss of total arsenic, selenium, and/or chromium upon acidification, which was verified by analyzing total arsenic, total selenium, and total chromium in the cryofrozen speciation samples (and finding significantly higher concentrations). For those samples, the formation of a brownish flocculate was usually observed in the acidified splits, which is probably due to precipitation of humic acids (which are soluble under the original alkaline conditions present in most samples, but insoluble at acidic pH). Evidently, the precipitates removed a fraction of total arsenic, selenium, or chromium from solution, which would have led to a speciation mass balance > 100 percent (barring other analytical issues). In such cases, the corresponding total element concentration measured in the cryofrozen split was used instead of the one in the acidified sample. By contrast, there were also a number of samples in which the formation of brownish precipitates was observed in the non-acidified splits taken for major anion and cation analysis. This reflects the precipitation of iron (oxy)hydroxide minerals caused by oxidation of high Fe(II) concentrations present in reducing waters. This problem was avoided by acidification, unless the process was so rapid that it began as the sample was being pumped and filtered.

In conclusion, the preservation for arsenic and selenium speciation by acidification does not appear suitable for the whole collected sample set, and must certainly be avoided for chromium speciation. Cryofreezing appears to be suitable in principle, but the sample storage time must be minimized to avoid irreversible formation of precipitates. Finally, it appears that the collected sample set is too heterogeneous for any one procedure that will preserve arsenic, selenium, and chromium speciation in all samples reliably; therefore, it might be necessary to collect multiple splits in parallel that are preserved differently.

Evaluation of Preservation Arsenic, Chromium, and Selenium Speciation by Preservation Method

The field team returned to the location of sample 002 and collected replicate samples for analysis of preservatives and differences associated with analytical laboratories. Five preservation techniques were used: no preservation, hydrochloric acid (HCl) in opaque bottles, hydrochloric acid in foil-wrapped (dark) bottles, ethylenediaminetetraacetic acid (EDTA), and nitric acid (HNO_3). Sample 002 is geochemically characterized by alkaline pH (>10), ORP of > 200, low dissolved oxygen (0.2%), low iron (<50 µg/L), and high sulfate (> 6,000 mg/L) concentration.

Results varied by analyte, preservation method, and laboratory (Table D-2). Chromium was most strongly effected. Concentrations of Cr(VI) in the acid-preserved samples were less than one-half of the concentration determined in the cryofrozen and unpreserved samples. This analysis clearly suggests that acid-preservation is not an appropriate technique for Cr(IV) in this geochemical environment.

Selenium concentrations were least affected by preservation technique. The poorest result was for the cryofrozen sample (sample 002), in which the sum of species was 76 percent of the total selenium concentration. This sample was collected in 2003 and subject to the issues described above associated with long hold times. The only apparent laboratory related relationship was for Se(IV); which was below detection limits in all samples other than the cryofrozen sample analyzed by laboratory 1, and detected at concentrations ranging from 76 to 94 µg/L by laboratory 2.

Table D-2
Arsenic, Selenium, and Chromium Speciation Using Different Preservatives

	As (III)	**As (V)**	**As (other)**	**As species**	**Total Arsenic**	**% Recovery**
Field blank	<5	0.02	NA	NA	0.24	NA
Unpreserved, Lab 1	<5	27.1	6.4	33.5	58.1	58
Unpreserved, Lab 2	4.1	63	NA	67	73	92
Cryofrozen, Lab 1	<6	47	<6	47	48.4	97
0.5% HCl preserved, Lab 1	<5	30.8	9.7	40.5	54.7	74
0.5% HCl preserved, Lab 2	4.9	95	NA	100	82	122
0.5% HCl+ dark preserved, Lab 1	<5	32.2	4.6	36.8	54.9	67
0.5% HCl+ dark preserved, Lab 2	NA	NA	NA	NA	NA	NA
EDTA preserved, Lab 2	4.0	72	NA	76	71	107
0.5% HNO_3 preserved, Lab 1	<5	5.1	2.4	7.5	51.7	15
0.5% HNO_3 preserved, Lab 2	3.7	65	NA	69	82	84
	Cr (III)	**Cr(VI)**	**Cr (other)**	**Cr species**	**Total Chromium**	**% Recovery**
Field blank	NA	<0.1	NA	NA	0.11	NA
Unpreserved, Lab 1	NA	4138	NA	NA	5204	NA
Unpreserved, Lab 2	NA	NA	NA	NA	NA	NA
Cryofrozen, Lab 1	340	5090	NA	5430	5100	106
0.5% HCl preserved, Lab 1	NA	2161	NA	NA	5217	NA
0.5% HCl preserved, Lab 2	NA	NA	NA	NA	NA	NA
0.5% HCl+ dark preserved, Lab 1	NA	1314	NA	NA	5242	NA
0.5% HCl+ dark preserved, Lab 2	NA	NA	NA	NA	NA	NA
EDTA preserved, Lab 2	NA	NA	NA	NA	NA	NA
0.5% HNO_3 preserved, Lab 1	NA	1760	NA	NA	5161	NA
0.5% HNO_3 preserved, Lab 2	NA	NA	NA	NA	NA	NA
	Se(IV)	**Se(VI)**	**Se (Other)**	**Se species**	**Total Selenium**	**% Recovery**
Field blank	<0.05	<0.05	NA	<0.05	0.14	--
Unpreserved, Lab 1	<25	1432	16	1448	1312	110
Unpreserved, Lab 2	94	1270	NA	1364	1400	97
Cryofrozen, Lab 1	19	1300	NA	1319	1730	76
0.5% HCl preserved, Lab 1	<25	1348	27	1375	1426	96
0.5% HCl preserved, Lab 2	91	1423	NA	1514	1500	101
0.5% HCl+ dark preserved, Lab 1	<25	1349	14	1363	1424	96
0.5% HCl+ dark preserved, Lab 2	NA	NA	NA	NA	NA	NA
EDTA preserved, Lab 2	87	1478	NA	1565	1400	112
0.5% HNO_3 preserved, Lab 1	<25	1307	NA	1307	1392	94
0.5% HNO_3 preserved, Lab 2	76	1416	NA	1492	1400	107

Samples collected 4/6/04 except Cryofrozen sample collected 8/5/03
Lab 2 did not analyze chromium
NA=not analyzed

Arsenic concentrations were most variable. First, there was a significant difference by laboratory. Laboratory 1 returned total arsenic concentrations between 52 and 58 mg/L (excluding the cryofrozen sample, which was collected on a different date), while laboratory 2 returned total arsenic concentrations between 71 and 82 mg/L. Laboratory 2 also achieved greater species recovery (84 to 122%) than laboratory 1 (15 to 97 percent). For laboratory 2, all preservation methods proved acceptable for preservation of arsenic species. For laboratory 1, only the cryofrozen sample yielded better than 80 percent species recovery. Significantly, all preservation methods identified As(V) as the species with highest concentration.

This test was performed on samples from a geochemical environment where the oxidized species would be expected in leachate samples, and results cannot be extrapolated to other environments, particularly those where the reduced species may be expected. However, the results show that several different preservation methods are capable of identifying the predominant species of arsenic and selenium in water samples from a high pH, high ORP, low oxygen, low iron, high sulfate environment. However, only cryofreezing adequately preserved chromium species.

Comparison of Cryofrozen and Hydrochloric Acid-Preserved Replicate Samples

Splits of 32 field leachate samples[6] were preserved in the field with HCl and forwarded to a separate laboratory (laboratory 2) for analysis of arsenic and selenium species. Analyses were performed as described in Section 2.

Arsenic

For arsenic, the cryofrozen sample sets[7] typically had lower total concentration than the acid-preserved samples (Figure D-1); however, since the total concentration analyses by both labs were performed on acid-preserved samples, this difference is laboratory related, rather than preservative-related. The percentage difference in total concentration was greatest when values were lower than 10 µg/L; the average difference for samples with concentration greater than 10 µg/L was 27 percent. The difference may be due to a correction applied by laboratory 2 to account for chloride interference.

The sum of arsenic species was compared to the independently measured total arsenic to determine the species recovery. For both sets of samples, the species recovery was typically closer to 100 percent when the total concentration was greater than 10 µg/L. In most cases, the cryofrozen sample had a higher species recovery, and was closer to 100 percent species recovery, than the acid-preserved sample (Figure D-1).

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[6] The split sample comparison included one sample (085) that was taken at one of the field sites for another study, and is not otherwise included in this evaluation. The acid-preserved splits of samples 084 and 085 were not analyzed for selenium species.

[7] The cryofrozen sample sets included acid-preserved samples for total analysis and frozen samples for species analysis.

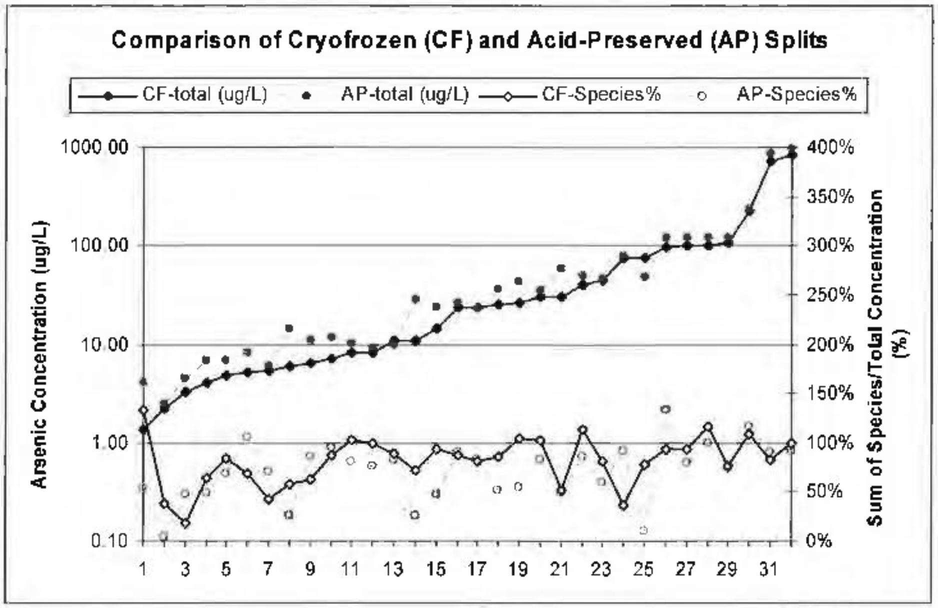

Figure D-1
Comparison of Total Arsenic Concentration and of Percent Species Recovery for Cryofrozen and Acid-Preserved Sample Splits

The dominant species in each sample split was determined based on the following criteria:

- For species recovery greater than 80 percent, a species was identified as dominant if its concentration was 60 percent or more of the sum of species.
- If species recovery was greater than 80 percent, and no species concentration was greater than 60 percent of the sum of species, then the sample was listed as "neutral".
- For species recovery less than 80 percent, a species was identified as dominant if its concentration was greater than 50 percent of the total concentration.[8]
- Samples with less than 80 percent species recovery in which no species concentration was greater than 50 percent of the total concentration were not tabulated.

Based on this approach, 27 of the 32 cryofrozen samples, and 22 of the 32 acid-preserved samples can be classified as dominated by As(III), dominated by As(V), or neutral (Table D-3). In 17 of the 20 common splits (where the dominant species could be determined in both samples), the two preservation techniques yielded similar results. In the three splits with different results, As(V) was dominant in the cryofrozen sample and As(III) in the acid-preserved sample. Two of these three samples had total arsenic concentration lower than 5 µg/L; the other was sample 106, which had an arsenic concentration of 110 µg/L.

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[8] If the sum of species is 80 percent, and the species concentration is 50 percent of the total concentration, then that species accounts for at least 62.5 percent of the sum of species.

Table D-3
Dominant Arsenic Species in Split Samples

Cryofrozen								Acid-Preserved					
Split	**% As(III)**	**% As(V)**	**% other**	**% recov.**	**DS**	**Total As**		**Split**	**% As(III)**	**% As(V)**	**% recov.**	**DS**	**Total As**
T112	50%	70%	14%	133%	V	1.36		W112	54%	0%	54%	(III)	4.04
T101	0%	10%	28%	38%		2.23		W101	0%	0%	4%		2.50
T92	0%	15%	3%	18%		3.34		W92	0%	47%	47%		4.52
T108	9%	56%	0%	65%	(V)	4.09		W108	0%	48%	48%		6.91
T99	2%	78%	4%	84%	V	4.80		W99	69%	0%	69%	(III)	6.79
T126	0%	69%	0%	69%	(V)	5.20		W126	0%	106%	106%	V	8.32
T49	0%	43%	0%	43%		5.40		W49	20%	51%	71%	(V)	5.94
T111	0%	58%	0%	58%	(V)	5.94		W111	0%	27%	27%		14.32
T127	0%	63%	0%	63%	(V)	6.42		W127	0%	86%	86%	V	10.77
T102	0%	88%	0%	88%	V	7.24		W102	0%	94%	94%	V	11.74
T116	12%	90%	1%	103%	V	8.24		W116	10%	71%	81%	V	10.26
T115	37%	63%	0%	100%	V	8.32		W115	0%	77%	77%	(V)	9.08
T91	0%	88%	1%	89%	V	10.76		W91	0%	83%	83%	V	9.98
T121	12%	54%	5%	72%	(V)	11.00		W121	0%	26%	26%		28.36
T128	71%	20%	3%	94%	III	14.27		W128	44%	4%	48%		24.00
T114	0%	87%	0%	87%	V	23.53		W114	9%	81%	90%	V	26.50
T42	0%	81%	0%	81%	V	23.70		W42	8%	75%	83%	V	23.26
T122	30%	32%	24%	86%	neutral	25.54		W122	44%	8%	52%		36.28
T120	27%	43%	35%	104%	neutral	26.79		W120	44%	12%	56%		43.46
T119	0%	101%	1%	102%	V	30.20		W119	3%	79%	82%	V	34.74
T107	3%	49%	0%	52%		30.64		W107	2%	47%	48%		60.00
T118	2%	112%	0%	114%	V	40.78		W118	18%	67%	85%	V	48.94
T97	0%	81%	0%	81%	V	44.89		W97	0%	60%	60%	(V)	46.96
T43	0%	37%	0%	37%		75.20		W43	59%	32%	92%	neutral	77.76
T98	1%	77%	0%	79%	(V)	76.85		W98	10%	0%	10%		47.96
T57	0%	94%	0%	94%	V	98.60		W57	0%	133%	133%	V	120.00
T69	0%	94%	0%	94%	V	99.50		W69	0%	80%	80%	(V)	120.00
T113	1%	115%	0%	116%	V	101.98		W113	23%	76%	99%	V	120.00
T106	14%	57%	5%	77%	(V)	109.83		W106	71%	2%	73%	(III)	122.32
T105	85%	22%	2%	109%	III	229.95		W105	112%	5%	116%	III	233.00
T84	10%	74%	0%	83%	V	726.90		W84	8%	83%	90%	V	870.00
T85	59%	38%	3%	99%	neutral	829.10		W85	52%	41%	93%	neutral	950.00

DS indicates the dominant species in the sample, ( ) indicates that total species recovery was less than 80%, but one species was greater than 50%
Shading indicates samples where the dominant species could be determined in both splits.

Sample 106 was recirculated FGD system water, presenting a highly alkaline (pH near 12) and more concentrated matrix that may have confounded the analyses. Other complicating factors with sample 106 included high dissolved oxygen (95%) yet low ORP (18 mV), and low dissolved iron (4.6 μg/L).

Selenium

For selenium, the cryofrozen sample sets[9] typically had lower total concentration than the acid-preserved samples (Figure D-2). This difference, which, like arsenic, is laboratory related, was greatest when total concentration was lower than 10 μg/L; the average difference for samples with concentration greater than 10 μg/L was 25 percent.

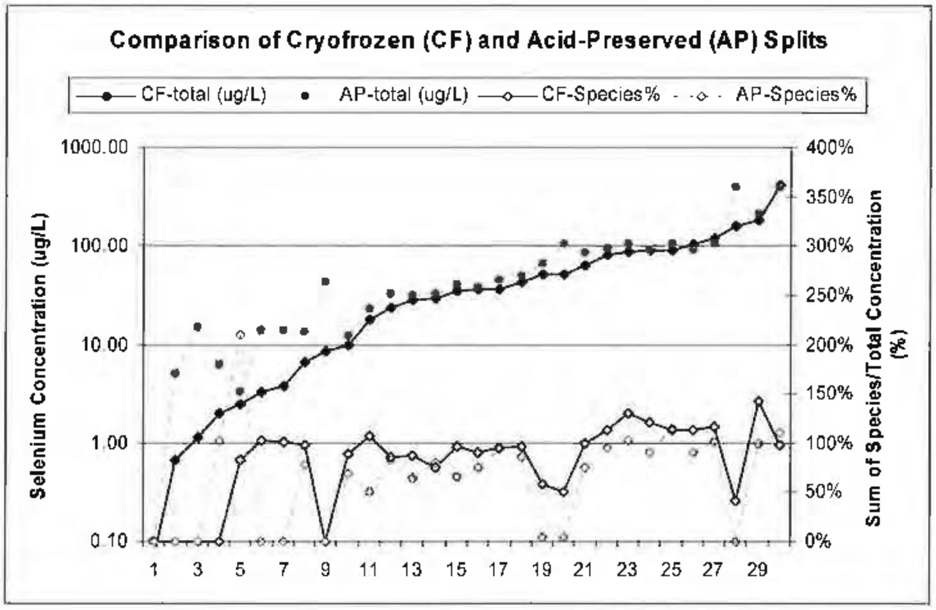

Figure D-2
Comparison of Total Selenium Concentration and of Percent Species Recovery for Cryofrozen and Acid-Preserved Sample Splits

The sum of species for both sets of samples was closer to 100 percent when the total concentration was greater than 10 μg/L. The cryofrozen split typically had higher species recovery than the acid-preserved split; although in some cases, particularly at concentrations near and greater than 100 μg/L, the cryofrozen split recovery was greater than 100 percent and the acid-preserved split recovery was closer to 100 percent. For concentrations greater than 10 μg/L, species recovery correlated well between the two preservation methods (Figure D-2).

The dominant selenium species was determined using the same approach as for arsenic. Based on this approach, 23 of the 30 cryofrozen sample splits, and 20 of the 30 acid-preserved sample splits can be classified as dominated by Se(IV), dominated by Se(VI), or neutral (Table D-4).

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[9] The cryofrozen sample sets included acid-preserved samples for total analysis and frozen samples for species analysis.

Table D-4
Dominant Selenium Species in Split Samples

Cryofrozen								Acid-Preserved					
Split	% Se(IV)	% Se(VI)	% other	% recov.	DS	Total As		Split	% Se(IV)	% Se(VI)	% recov.	DS	Total As
T114	0%	0%	0%	0%		0.07		W114	0%	0%	0%		0.10
T112	0%	0%	0%	0%		0.67		W112	0%	0%	0%		5.00
T122	0%	0%	0%	0%		1.13		W122	0%	0%	0%		15.00
T99	0%	0%	0%	0%		2.04		W99	103%	0%	103%	IV	6.12
T57	83%	0%	0%	83%	IV	2.44		W57	210%	0%	210%	IV	3.23
T120	56%	46%	0%	102%	neutral	3.30		W120	0%	0%	0%		14.00
T121	29%	73%	0%	102%	VI	3.86		W121	0%	0%	0%		14.00
T108	39%	59%	0%	98%	neutral	6.56		W108	38%	39%	77%		13.32
T105	0%	0%	0%	0%		8.47		W105	0%	0%	0%		43.00
T49	83%	6%	0%	89%	IV	10.00		W49	70%	0%	70%	(IV)	12.01
T118	100%	7%	0%	107%	IV	17.62		W118	51%	0%	51%	(IV)	23.00
T43	86%	0%	0%	86%	IV	23.50		W43	83%	0%	83%	IV	32.54
T119	81%	6%	0%	87%	IV	27.95		W119	65%	0%	65%	(IV)	32.00
T113	66%	9%	0%	75%	(IV)	29.27		W113	79%	0%	79%	(IV)	33.00
T116	87%	9%	0%	96%	IV	35.35		W116	66%	0%	66%	(IV)	40.00
T115	82%	8%	0%	90%	IV	36.10		W115	75%	0%	75%	(IV)	37.00
T69	91%	5%	0%	96%	IV	36.40		W69	87%	7%	93%	IV	44.54
T42	92%	5%	0%	96%	IV	42.60		W42	80%	6%	86%	IV	49.94
T98	58%	0%	0%	58%	(IV)	50.74		W98	5%	0%	5%		65.98
T128	34%	13%	3%	51%		50.90		W128	0%	5%	5%		106.36
T106	0%	99%	0%	99%	VI	64.79		W106	3%	73%	76%	(VI)	85.44
T102	7%	106%	0%	113%	VI	80.48		W102	5%	89%	94%	VI	95.40
T126	14%	117%	0%	131%	VI	88.70		W126	14%	88%	102%	VI	104.34
T111	43%	79%	0%	122%	VI	90.54		W111	38%	53%	91%	neutral	91.00
T101	0%	114%	0%	114%	VI	91.00		W101	0%	115%	115%	VI	104.48
T92	1%	113%	0%	113%	VI	103.36		W92	0%	90%	90%	VI	90.86
T91	3%	113%	0%	116%	VI	122.22		W91	0%	102%	102%	VI	102.84
T107	0%	10%	32%	42%		159.00		W107	0%	0%	0%		400.00
T127	7%	136%	0%	143%	VI	180.60		W127	5%	95%	100%	VI	210.00
T97	9%	89%	0%	98%	VI	412.50		W97	16%	95%	111%	VI	380.00

DS indicates the dominant species in the sample, ( ) indicates that total species recovery was less than 80%, but one species was greater than 50%
Shading indicates samples where the dominant species could be determined in both splits.

In 18 of the 19 common splits (where the dominant species could be determined in both samples), the two preservation techniques yielded similar results. The only exception was sample 111, which was dominated by Se(VI) in the cryofrozen split and was neutral in the acid split. However, both samples had more Se(VI) than Se(IV). The species breakdown for sample 111 was 43 percent Se(IV) and 79 percent Se(VI) in the cryofrozen sample, and 38 percent Se(IV) and 53 percent Se(VI) in the acid-preserved sample. Sample 111 had neutral pH (7.2), was oxic (280 mV ORP and 59 percent dissolved oxygen), and did not exhibit a sulfur odor; as a result, the acid-preserved sample would not be expected to undergo precipitation of soluble sulfur species.

Summary

In summary, there are conditions under which one of the preservation methods may be more appropriate than the other. However, the split sample data collected during this study indicate that the preservation method does not affect results sufficiently to alter interpretation of the dominant species present in the sample.

E

LABORATORY ANALYTICAL ISSUES PERTAINING TO SPECIATION ANALYSIS

Determination of Total Arsenic, Selenium, and Chromium Concentrations

The determination of total chromium (TCr) by ICP-MS worked very well. Good agreement was obtained between the two isotopes ^{52}Cr and ^{53}Cr, as well as between the two instruments used (ICP-DRC-MS and ICP-DF-MS). Therefore, there is a high degree of confidence in the reported total chromium results, and they are not a reason if the speciation mass balance for chromium did not work out in any sample, which usually only happened in samples with low total chromium concentrations. Unfortunately, the determination of total arsenic and selenium by ICP-MS is more complicated than that of total chromium, and consequently, the quality of these data is somewhat impaired in certain samples, as discussed below. The problems associated with the determination of total arsenic and selenium by ICP-MS stem mostly from molecular interferences that overlap with the mass of the measured arsenic or selenium isotopes, and thus yield artificially-increased results. These interferences are caused either by constituents of the measured water samples or by molecules formed in the argon plasma used in ICP-MS analyses. To illustrate this problem, the method used for total selenium determination in the collected water samples is explained below.

In ICP-MS analyses, it is desirable to use the major isotope of the trace element of interest for its quantification, because it yields the highest signal, which usually translates into the lowest detection limit. Additionally, at least one other isotope of the same element should be measured, and if the concentrations determined in the sample by using two (or more) different isotopes agree well, then there is a high degree of confidence that this result is correct and not impaired by any significant molecular interferences. For selenium, the main isotope is ^{80}Se, but this isotope is impossible to measure by conventional ICP-MS instruments, because the argon plasma generates a large amount of the dimeric ion $^{40}Ar_2^+$, which has the same nominal mass as the ^{80}Se isotope, and the two signals cannot be separated. Although some publications suggest that ICP-DF-MS can resolve the overlap between analyte and interference for this example when it's used in the high resolution mode, the particular ICP-DF-MS instrument used by laboratory 1 did not achieve this separation consistently, and an ICP-DRC-MS instrument was used to address this issue, which was successful. The ICP-DRC-MS approach uses a cell with a reactive gas (here methane, CH_4) to break up the interference (by collision yielding two Ar atoms of mass 40) between the plasma and the mass spectrometer, while the analyte ^{80}Se remains unaffected, and can thus be determined free of the inference. However, in the collected water samples, there are additional interferences that complicate this approach. High bromide concentrations in the samples lead to the formation of the molecule $^{1}H^{79}Br^+$, which also has the nominal mass 80, but cannot be eliminated effectively by the reaction gas methane. Therefore, a second reaction gas (ammonia, NH_3) was added, which undergoes a chemical reaction with HBr, and thus forms reaction products that have masses other than 80, so ^{80}Se can be measured in waters containing bromide.

The minor isotopes used for confirmation of results obtained using the main isotope usually have different interferences than the main isotope, so if the results obtained for different isotopes agree, it is generally accepted that all known interferences have been removed efficiently, as intended during the method development. In the case of selenium, the control isotopes used were ^{78}Se and ^{82}Se, and it turns out that ^{78}Se has an interference from the plasma ($^{40}Ar^{38}Ar^+$), but not from bromide, while ^{82}Se has an interference from bromide ($^{1}H^{81}Br^+$), but not form the plasma, so the control strategy for these two interferences works very well. Unfortunately, due to the fact that the studied waters were often very complex and generally very different from site to site, there were additional interferences in some samples that could not be resolved by the described approach. While some additional interferences were identified, and their influence on the measured total selenium results was compensated for as much as possible (for example, it was found that copper formed ammonia clusters $Cu(NH_3)^+$ in the DRC, which interfered with the measurement of ^{80}Se and ^{82}Se), there remained some samples that either contained interferences that were not identifiable, or where known interferences exceeded the compensation capacity of the developed analytical method. In those cases, the total selenium concentrations determined using the three different selenium isotopes disagreed beyond the normal range of analytical error, and such results were flagged[10] in the results table (Appendix A). For such samples, the lowest total selenium concentration obtained with any selenium isotope was usually reported, because the molecular interferences are by nature positive (i.e. they mimic selenium), so the lowest result should be the least (or not) interfered.

Figure E-1 shows the agreement between the results obtained for the three measured selenium isotopes as a function of the total selenium concentration: With the exception of three samples, the total selenium concentrations determined using each of the three individual isotopes agree within the analytical uncertainty (± 10 percent) for samples containing total selenium greater than 5 µg/L. Generally, the agreement between the three selenium isotopes is good when total selenium concentrations are higher, and gets worse towards lower concentrations, because a certain amount of an interference caused by the sample matrix would have a bigger impact if the actual selenium signal is small, and because the analytical uncertainty itself increases with decreasing concentration. For those three samples with higher total selenium concentrations where the isotope agreement is not good, the reason probably lies in a combination of complex matrix (high salinity and trace element concentrations) and comparably low total selenium concentration (i.e. too low to resolve the interferences by dilution), although the actual reasons for these discrepancies likely vary from sample to sample, and were not explored further in this project. To eliminate this problem in future similar studies, it would be necessary to either add hydride generation (HG) as a sample introduction technique, which selectively volatilizes the selenium into the plasma while most of the other sample constituents stay behind in the liquid phase and are not introduced into the plasma (so they cannot produce interferences), or switch to a different detection technique altogether (e.g. atomic fluorescence spectrometry, AFS). There are also other potential analytical issues associated with HG and AFS, and there is no guarantee that these approaches would have resolved all problems for the present sample set.

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[10] Identified in Table A-2 using flag (b), "isotope ratios do not match"

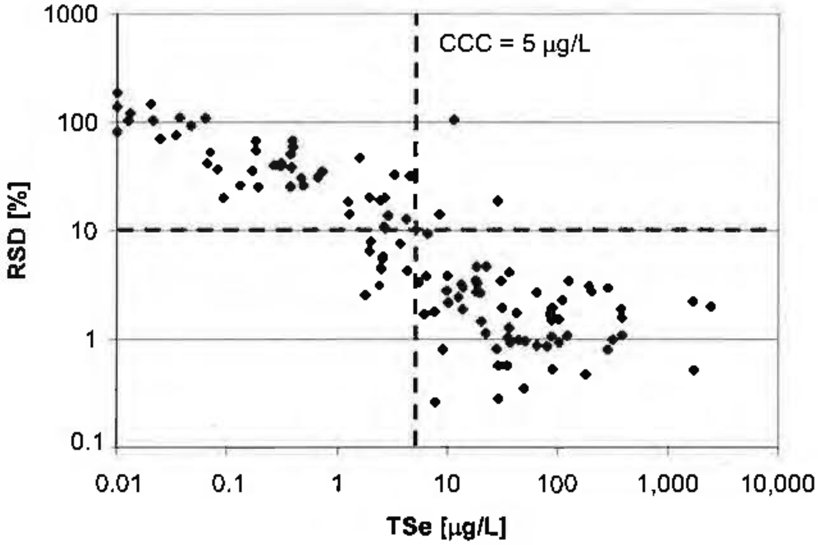

Figure E-1
Agreement Between Total Selenium Concentrations Determined Using the Isotopes ^{78}Se, ^{80}Se and ^{82}Se in All Collected Water Samples (expressed as percent relative standard deviation between the three individual results)

Besides interferences that affect individual selenium isotopes during the ICP-MS measurement, there are also matrix effects that affect all selenium isotopes at once, which relate to processes such as the sample introduction into the ICP-MS and the ionization of selenium in the plasma. The sample flow rate in ICP-MS measurements of bulk samples is regulated by the (constant) rotation speed and tubing diameter of a peristaltic pump, but the uptake of the sample into the plasma depends on its nebulization in the spray chamber; this process is assumed to be constant, and the fraction of the pumped sample nebulized is typically around 3 percent (so 97 percent of the sample goes to waste and is not measured). Parameters like the sample's viscosity or salinity can alter the nebulization process, and thus lead to higher or lower nebulization efficiency, thereby affecting the selenium signal obtained, which is proportional to the total amount of sample introduced into the plasma. To recognize and correct for such interferences, one or more internal standards (IS) are used, which are other trace elements spiked to the samples at a known concentration before analysis. The idea behind this is that a change in the sample introduction efficiency would affect the IS to the same degree as the analytes, and could thereby be compensated for mathematically.

The only condition that the IS needs to fulfill to be used for this correction approach is that it cannot be present in the samples in a measurable/significant concentration (so that the IS signal should always be constant if there were no sample uptake variations); for this reason, "exotic" elements like platinum group metals are commonly used for this purpose. In this project, rhodium was routinely used as the primary IS for total selenium measurements, and indium was used as a secondary IS to identify if there were problems associated with the rhodium measurement in any given sample. Several other commonly used IS elements were tried as well, but yielded less satisfactory results, usually because they occurred in the analyzed water samples in significant concentrations. The same was true to a lesser degree for indium, so it was not always usable as an IS, whereas rhodium generally fulfilled the absence condition. However, two additional problems were encountered related to the IS approach, which have not been reported in the literature before, and therefore were unanticipated and had to be recognized and dealt with during this project.

First, it was observed that certain matrix elements present in the studied waters produced interferences in the DRC process that mimicked one of the IS elements (for example, the strontium isotope ^{86}Sr forms an ammonia cluster $Sr(NH_3)^+$ in the DRC, which has the same nominal mass as the only rhodium isotope ^{103}Rh). This increases the apparent IS signal and suggests increased sample introduction efficiency for the particular sample, and since the analyte signal is normalized to the IS signal, leads to artificially decreased total selenium concentrations. This interference was recognized by the fact that the secondary IS was not elevated, and compensated for as much as possible by varying instrument parameter like the DRC gas flow rates and Rpa and Rpq (two DRC settings), but could not be eliminated altogether without compromising the efficiency with which the DRC removes the main interferences on the analytes (as discussed above). No alternate IS was found that fulfilled the absence condition and was not affected by this phenomenon, so more research is needed in this respect to find a way to compensate for this problem. One way to address the issue is the method of standard addition, where an interfered sample is measured repeatedly with varying amounts of the analyte added prior to analysis, but this procedure is impractical in routine operation, because every sample would need to be analyzed multiple times.

Secondly, it was noticed that the signal for either IS element increased unspecifically when high concentrations of a matrix element with similar or higher mass were present in the sample, e.g. barium (mass 137) increasing the IS signal for rhodium (mass 103) and indium (mass 115). This effect is the opposite of a well-known process in mass spectrometry called "space-charge effect", and could thus be referred to as "inverse space-charge effect". It was beyond the scope of this project to investigate the reasons for this observation, and the effect could not be eliminated by changing instrumental parameters, although it was moderated by increasing the acceleration voltage for the ions through the DRC. Like the previous interference, this issue causes an artificially-increased IS signal and thus leads to reduced total selenium concentrations. Contrary to interferences that lead to decreased sample introduction efficiency (and thereby to elevated apparent total selenium concentrations), these two effects would result in a positive speciation mass balance discrepancy (i.e. recovery > 100 percent), so since most samples showed a negative deviation in their selenium speciation mass balance, these two types of interferences did apparently not affect many of the measured samples; they may, however, explain why the sum of selenium species in some samples was significantly > 100 percent.

The second type of interference that is commonly compensated for by using internal standards relates to the ionization efficiency of the analyte in the plasma. This is a particular problem for selenium and arsenic, which have very high first ionization energies, and are ionized incompletely (25-50 percent) in the ICP. Major constituents of the matrix can alter the properties of the plasma, and thereby change the degree of ionization for these elements (and consequently their signal intensity); typical examples include major cations like sodium, which are easily ionized and thereby decrease the "energy" of the plasma, leading to reduced arsenic and selenium ionization, and organic carbon, which appears to enhance the ionization of arsenic and selenium by unknown mechanisms. Again, the IS could be used to compensate for these effects, but only if it shows a similar response to such interferences as the analytes of interest. This "similarity condition" is much harder to fulfill than the absence condition, and it's nearly impossible to fulfill them both perfectly for a large and inhomogeneous sample set, such as the present one. Of all tested IS elements, rhodium yielded that best results, but it has a significantly lower ionization energy than both arsenic and selenium, so that the analyte signals may have been suppressed in some samples without an effect on the IS. Again the result would be an artificially reduced total selenium or total arsenic concentration.

The preceding discussion makes it clear that the determination of total selenium in such complex samples as the studied waters is complicated, and that not all interferences can be compensated for, leading to possibly "wrong" total selenium concentrations, which in turn would impact the selenium speciation mass balance. This is probably one of the main reasons of why this mass balance did not work well in samples with low total selenium and high concentrations of certain matrix elements. Besides the mentioned HG sample introduction, an elegant way to eliminate many of the discussed interferences would be isotope dilution, which involves spiking a known amount of a particular selenium isotope to the sample prior to analysis. This is, however, expensive, because pure selenium isotopes would need to be obtained, and was consequently not available and could not be developed during this project. Given the (eco) toxicological importance of measuring relatively low total selenium concentrations in complex aqueous samples, this is an area which should be explored in future research, so that a much improved and reliable method for total selenium determinations by ICP-MS becomes available.

All analytical issues discussed above hold true for arsenic as well, but contrary to selenium, arsenic is monoisotopic, and consequently does not offer the possibility of compensating for (or even recognizing) certain interferences by "switching" to another isotope, which suggests that the total arsenic data quality should be poorer than for total selenium (which of course cannot be proven directly). The suggested improvements like HG sample introduction would also remedy many of the raised problems, and even isotope dilution with a long-lived arsenic radionuclide could be used for internal standardization. However, similar to selenium, these aspects were not explored during this project, and the fact that the arsenic speciation mass balance did not work well in some samples can certainly be partially attributed to problems associated with the total arsenic determination.

Determination of Arsenic, Selenium, and Chromium Speciation

The determination of Cr(III) and Cr(VI) by AEC-ICP-MS worked quite well, as supported by the reasonable chromium speciation mass balance. The only issue that was addressed during this project was the relatively high background caused by the presence of inorganic carbon in the used chromatographic eluant: this leads to the formation of $^{40}Ar^{12}C^+$, which interferes with the determination of the main chromium isotope ^{52}Cr, but this background was easily eliminated by using NH_3 as the reaction gas in the DRC.

For arsenic and selenium, the measurement of their speciation in the collected water samples was more complicated, and a number of significant interferences were encountered. These interferences are generally not related to the presence of spectral interferences, as discussed for the total arsenic and total selenium determinations above, because typically the interfering sample constituent is separated chromatographically in time from the analyte species. As an example, bromide in the samples will still produce a signal on mass 82, but this does not interfere with the measurement of Se(IV) or Se(VI), because the bromide signal either elutes before the Se(IV) peak, or–if the interfering peak is too large–Se(IV) at mass 77 can be used for quantification. Rather, besides the preservation/stability issues discussed above for the cryofrozen sample, the main problems encountered are caused by high salinity in some of the collected water samples, and by the presence of major trace elements that are incompatible with the chosen chromatographic conditions, so both are chromatographic issues occurring in the AEC, and not spectroscopic issues arising in the ICP-MS.

The salinity-based interference is caused by the fact that major anions, especially sulfate in the studied waters, are present in very high concentrations (up to 300 mmol/L), whereas the arsenic and selenium species are present in much lower concentrations (up to 9 μmol/L for selenium and 7 μmol/L for As), so the major anions are present in 30,000-fold excess. During the AEC analysis, the major anion competes with the trace element anions for binding sites on the chromatographic column, and if this competition becomes too strong, then the analytes are "flushed" out of the column without interacting properly with the stationary phase, which results in bad peak shapes that makes quantification inaccurate to impossible, and in the change of retention times, which makes identification uncertain or eliminates separation of different species altogether. The best way to eliminate this problem is by diluting the sample prior to analysis, but this approach is limited by the absolute concentration of the analytes in the same, so if the ratio of major anions to analytes is too large, the samples would have to be diluted to the point where the analytes fall below the detection limits to overcome the chromatographic problems.

This issue was encountered for a large number of the studied samples, and was addressed by modifying the AEC separation. Sulfate (instead of hydroxide) was used as the eluant anion, and this increases the tolerance of the separation for elevated sulfate concentrations in the sample (this approach is called "matrix matching"). However, even this remedy is limited by the absolute binding capacity of the column, so if the total amount of matrix anions injected exceeds this capacity, then proper separation of the analytes is no longer possible. Matrix matching yielded a significant improvement for the speciation mass balance of arsenic and selenium in many samples collected in 2004 and 2005, and for those samples where the mass balance still remained poor, there appeared to be a general correlation with the ratio of sample salinity to analyte concentration.

The second chromatographic issue was caused by high iron and especially manganese concentrations in some of the studied waters. Since the AEC separation is conducted under alkaline conditions (even after modification) to prevent the loss of acid-labile arsenic and selenium species, major sample constituents that precipitate under strongly alkaline conditions may cause problems. Although many of the collected samples were alkaline to begin with, the separation conditions were even more alkaline; this pH change during analysis particularly affected those samples that were acidic or circumneutral in the field. Under such conditions, manganese (and iron) can precipitate in the form of (oxy)hydroxide minerals within the AEC, and these precipitates bind the species As(V) and Se(IV) very strongly, which could lead to artificially low results for these two species. This issue was addressed by raising the pH of the eluant by about one unit, and by adding some oxalate into the eluent, which keeps manganese in solution. As for the salinity issue, though, there are limits to this approach, and the problems could not be eliminated in all samples, which is probably the main reason for the very low speciation mass balances encountered in some samples.

As the constitution of real world samples is highly variable and unpredictable, the best way to resolve this problem is by using more sensitive detection principles, because then the problematic samples can be diluted even more. At this point, though, ICP-MS is the most sensitive detection approach, even if certain ICP-MS instruments not available during this project may possibly yield lower detection limits for the AEC-ICP-MS determination of arsenic and selenium species than the used ICP-DRC-MS (in the standard mode for arsenic and selenium speciation). Further increases in detection sensitivity for arsenic and selenium can be achieved by using high-efficiency sample introduction systems, such as HG or membrane desolvation, between the AEC separation and the ICP-MS detection. This, however, is complicated and more expensive for use on a routine basis, and the required equipment was either not available permanently at Trent, or was incompatible with the relatively high chromatographic flow rates (and would thus have necessitated some modifications), so these options were not incorporated into the used methods. It should be noted, though, that AEC-HG-ICP-DRC-MS has been used successfully to measure selenium speciation at ng/L-levels in sea water, so this approach could be used in future studies, because it works in principle for the species As(III)/As(V) and Se(IV)/Se(VI), while its suitability for any other arsenic or selenium species is untested, which constitutes another reason why this technique was not routinely used in this project.

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