Speciation and Attenuation of Arsenic and Selenium at Coal Combustion By-Product Management Facilities

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ABSTRACT

Field leachate samples are being collected from coal combustion product (CCP) management sites from several geographic locations in the United States to provide broad characterization of major and trace constituents in the leachate. In addition, speciation of arsenic, selenium, chromium, and mercury in the leachates is being determined. Through 2003, 35 samples were collected at 14 sites representing a variety of CCP types, management approaches, and source coals. Samples have been collected from leachate wells, leachate collection systems, drive-point piezometers, lysimeters, the ash/water interface at impoundments, impoundment outfalls and inlets, and seeps. Additional sampling at 23 sites has been conducted in 2004 or is planned for 2005.

First-year results suggest distinct differences in the chemical composition of leachate from landfills and impoundments, and from bituminous and subbituminous coals. Concentrations of most constituents were generally higher in landfill leachate than in impoundment leachate. Sulfate, sodium, aluminum, molybdenum, vanadium, cadmium, mercury and selenium concentrations were higher in leachates for ash from subbituminous source coal. Calcium, boron, lithium, strontium, arsenic, antimony, and nickel were higher for ash from bituminous source coal. These variations will be explored in more detail when additional data from the 2004 and 2005 samples become available.

CONTENTS

EXECUTIVE SUMMARY

Introduction

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.

Previous research has indicated that arsenic and selenium are present in laboratory-generated ash leachates. Only limited, mostly site-specific, work has been performed to characterize the concentration and of these constituents in field leachate. Furthermore, little work has been performed to determine the species of arsenic and selenium present in field leachates, which may have a significant effect on their release from the ash and mobility in groundwater.

The objectives of this research are to characterize CCP leachate samples collected in the field, including speciation of arsenic, selenium, chromium, and mercury. The research will provide fundamental data necessary for evaluation of the effects of CCP management methods on leachate quality and of the long-term fate of inorganic constituents at CCP management sites.

Approach

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 these management sites was selected for sampling, based on individual site considerations as well as development of a range of site types representative of the industry.

As of the end of 2003, 35 leachate samples were collected at 14 sites. The 2003 samples included 16 from landfills and 19 from impoundments. Twenty-eight of these samples were from coal ash management sites, and seven were from sites where FGD solids, FGD solids stabilized with fly ash, or spray dryer ash were managed. Half (18) of the samples came from sites that received CCP from bituminous coal, 11 samples were from sites that received CCP derived from subbituminous coal, and six were derived from mixed coals.

Leachate samples were collected from available 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. Speciation samples were not acid-preserved, instead they were cryofrozen in the field by submerging the sample in a bath of liquid nitrogen. Samples were analyzed using state-of-the-art analytical methods, resulting in detection limits of less than a part per billion for most trace constituents and less than a part per trillion for mercury.

First Year Results

Concentration Ranges in CCP Leachate

The pH of the leachate samples was neutral to strongly alkaline. Leachate from landfills and ash derived from subbituminous coal tended to be more alkaline than impoundment/bituminous coal leachate. Dissolved oxygen and ORP were lower in landfill samples than in impoundment sanmples.

The anion chemistry of most samples was dominated by sulfate (median concentration of 1,370 mg/L), while cation chemistry of most samples was dominated by calcium (median 231 mg/L) and/or sodium (median 70 mg/L). Sodium was typically dominant in samples from plants that burned subbituminous or a mixture of subbituminous and bituminous coal, and calcium was typically dominant in samples from plants that burned bituminous or a mixture of bituminous and subbituminous coals.

In most cases, the range of concentrations for minor and trace elements spanned two to three orders of magnitude. Boron had the highest maximum (102,000 µg/L) and median (8,855 µg/L) concentration of the minor and trace elements. Other minor and trace elements with median concentrations greater than 100 µg/L were aluminum, silica, strontium, and molybdenum. Elements with median concentrations less than 1 µg/L included chromium, lead, mercury, silver, and thallium. The *maximum* concentrations of beryllium, silver, and mercury were lower than 5 µg/L.

Total arsenic concentrations ranged from 3 to 238 µg/L, with a median of 24 µg/L. Five samples, from three different sites, had an arsenic concentration greater than 100 µg/L. Conversely, five samples, from three different sites, had arsenic concentration lower than 10 µg/L.

Total selenium concentration exhibited a larger range than arsenic, from 0.3 to 2,360 µg/L, although the median selenium concentration of 15 µg/L was lower than for arsenic. Three samples from two sites had concentrations greater than 1,000 µg/L, and five samples from four additional sites had concentrations greater than 100 µg/L. Fourteen samples had a selenium concentration lower than 10 µg/L. These fourteen samples included all five of the arsenic samples with concentration lower than 10 µg/L, and three of the five arsenic samples with concentration greater than 100 µg/L.

Speciation data for arsenic, selenium, and, to a lesser extent, chromium exhibited discrepancies between the sum of species and total concentrations. One possible factor contributing to this discrepancy was the formation of precipitates in some of the sample bottles during storage. A priority of the 2004/2005 field and laboratory work is determining the causes and developing solutions to resolve the species discrepancy.

Effects of Management Method and Source Coal Type on Leachate Concentrations

Concentrations of all major ions, except chloride, were higher in landfill leachate than in impoundment leachate. There was also a difference in major ion composition by source coal type. Sulfate and sodium concentrations tended to be higher when the source coal was subbituminous, rather than bituminous. Conversely, calcium concentrations were higher when the source coal was bituminous.

Source coal type also affected minor and trace constituent concentrations. Some of the elements that had higher concentration in leachate from subbituminous coals included aluminum, mercury, selenium, and vanadium, while leachate from bituminous coals often had higher concentrations of lithium, strontium, antimony, and nickel.

These observations are based on a relatively limited set of 35 leachate samples collected through 2003. Some of these relationships may become clearer, or may change, after analysis of the full sample set is completed in 2005.

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.

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 done to determine 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, 2000; EPRI, 2004).

Objectives

The objectives of this research are to characterize CCP leachate samples collected in the field, including speciation of arsenic, selenium, chromium, and mercury. The research will provide fundamental data necessary for evaluation of the effects of CCP management methods on leachate quality and of 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.

Individual sites were evaluated based on:

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

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.

Based on these criteria, 37 CCP sites in 16 states were selected for possible sampling. Field sampling was initiated in 2003 and will continue into 2005.

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.

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 material to the desired sampling depth using a slide hammer. 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.

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. 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.

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 devices, 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 were also installed to monitor leachate quality, and differ from leachate wells in that they collect porewater beneath the CCP.[1] 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.

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

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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.

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.[2]

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. Sluice and outfall samples were collected directly from the sluice pipe or outfall structure in a clean plastic container or plastic dip cup sampler. 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.

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.

Fresh CCP Samples

In addition to the leachate samples described above, fresh samples of CCP were collected from most of the source power plants. These samples were collected by utility personnel directly from the ash hopper, or along the FGD process line, in 5-gallon metal or plastic buckets. Results of analysis of these samples will be described in another EPRI report.

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[2] Newall, J., Groundwater Monitoring with the Waterra Inertial Pump, http://www.waterra.com/pages/techpapers/TechA(Groundwater%20Monitoring)/techA1.html

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 freezing, 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. Freezing 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, and then kept frozen on dry ice with minimal air contact until analysis to prevent changes in speciation by oxidation.

Separate water samples were collected for the determination of total mercury (THg), dissolved mercury (DHg), total methylmercury (TMeHg), dissolved methylmercury (DMeHg), and dimethylmercury (DMM). New tubing, filter materials, and sampling containers were used to prevent sample contamination. Samples for DHg and DMeHg were collected using in-line filtration. All samples except the DMM samples were preserved in the field with HCl. 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. All collected samples were double-bagged to prevent contamination, and clean sampling protocols (consistent with EPA method 1631) were followed.

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

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

A Thermo Finnigan Element II double-focusing inductively coupled plasma-mass spectrometer (DF-ICP-MS) in medium resolution mode was used to determine 22 elements of interest (Table 2-1). 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 of different elements, the 500x diluted samples were analyzed for lithium, boron, aluminum, silica, iron, strontium, and molybdenum; the 100x diluted samples for lithium, beryllium, boron, aluminum, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, strontium, molybdenum, silver, cadmium, antimony, barium, thallium, lead, and uranium; and the 20x diluted samples for lithium, beryllium, aluminum, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum, silver, cadmium, antimony, barium, thallium, lead, and uranium. 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.

At least two isotopes for each element (if possible) were measured 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 2-1. Typically, the results obtained for the measured and the control isotope were identical (within the analytical uncertainty); however, some exceptions are explained in the paragraph below. Typical instrumental detection limits (IDLs) are also listed in Table 2-1, calculated as three times the standard deviation of four instrument blanks (1% HNO_3). 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. Per 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 2-1, the results obtained for the measured and the control isotope did not match. For some elements (e.g., silver, zinc, thallium), the analyte concentrations in many samples were only 5 to 10 times the detection limit, so that analytical uncertainty 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%). 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 ~ 4,000). As the ^{58}Fe abundance is only 0.28%, 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%. 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 the correct result.

Table 2-1
Trace Metals by DF-ICP-MS

Element	Measured Isotope	Control Isotope	Isotopes Agree?	Typical IDL [ppb]
Aluminum	^{27}Al	monoisotopic		0.08
Antimony	^{121}Sb	^{123}Sb	Y	0.005
Barium	^{136}Ba	^{137}Ba	Y	0.1
Beryllium	^{9}Be	monoisotopic		0.01
Boron	^{10}B	^{11}B	Y	0.07
Cadmium	^{110}Cd	^{111}Cd, ^{114}Cd	N	0.005
Chromium	^{53}Cr	^{52}Cr	Y	0.01
Cobalt	^{59}Co	monoisotopic		0.001
Copper	^{65}Cu	^{63}Cu	Y	0.01
Iron	^{56}Fe	^{57}Fe	Y	0.05
Lead	^{208}Pb	^{206}Pb, ^{207}Pb	Y	0.005
Lithium	^{7}Li	not available		0.05
Manganese	^{55}Mn	monoisotopic		0.005
Molybdenum	^{98}Mo	^{95}Mo	Y	0.01
Nickel	^{60}Ni	^{58}Ni	Y (except in samples with high Fe concentrations)	0.03-0.05
Silica	^{28}Si	^{30}Si	Y	0.3-0.6
Silver	^{107}Ag	^{109}Ag	Y? (concentrations close to MDL)	0.01
Strontium	^{88}Sr	^{87}Sr	Y (after Rb correction of ^{87}Sr)	0.01
Thallium	^{205}Tl	^{203}Tl	Y? (concentrations close to MDL)	0.005
Uranium	^{238}U	not available	no interferences	0.0005
Vanadium	^{51}V	^{50}V	N	0.005
Zinc	^{66}Zn	^{68}Zn	Y? (concentrations close to MDL)	0.1

Determination of Total Arsenic, Selenium, and Chromium by Dynamic Reaction Cell-ICP-MS (DRC-ICP-MS)

Total arsenic, selenium, and chromium 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 and chromium. Although chromium can be measured reliably by DF-ICP-MS, the results obtained by DRC-ICP-MS were reported for consistency reasons, as the speciation of chromium was also performed on this instrument. The chromium results obtained by DRC-ICP-MS and DF-ICP-MS were in good agreement. Instrument settings and detection limits, calculated as three times the standard deviation of four instrument blanks (1% HNO_3), are reported in Table 2-2.

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. As mentioned before, 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 current 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 (Table 4-1). ^{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.

Table 2-2
Method Parameters for Total As, Se, and Cr Determinations by DRC-ICP-MS

	Arsenic	**Selenium + Chromium**
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 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. Method parameters are listed in Table 2-3. The ICP-MS was used in standard mode as the interfering anions are chromatographically separated in time from the analytes (Figures 2-1 and 2-2). 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.

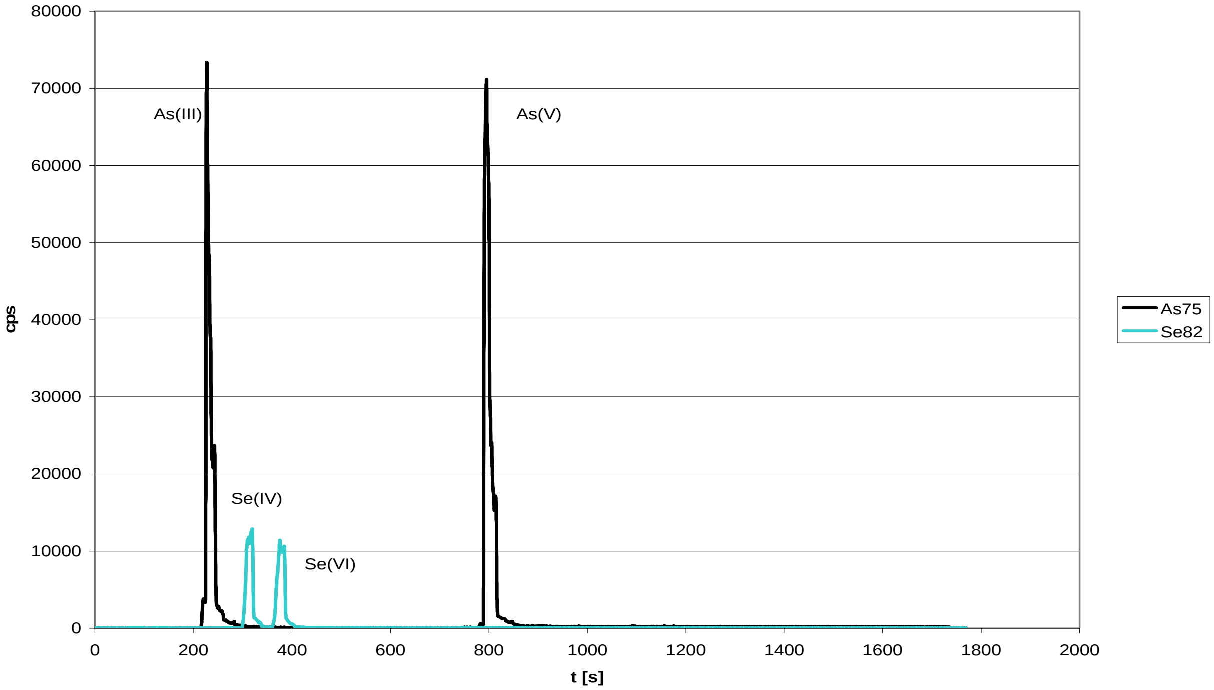

Figure 2-1
Chromatograph Showing 5 ppb each for As(III), As(V), Se(IV), and Se(VI)

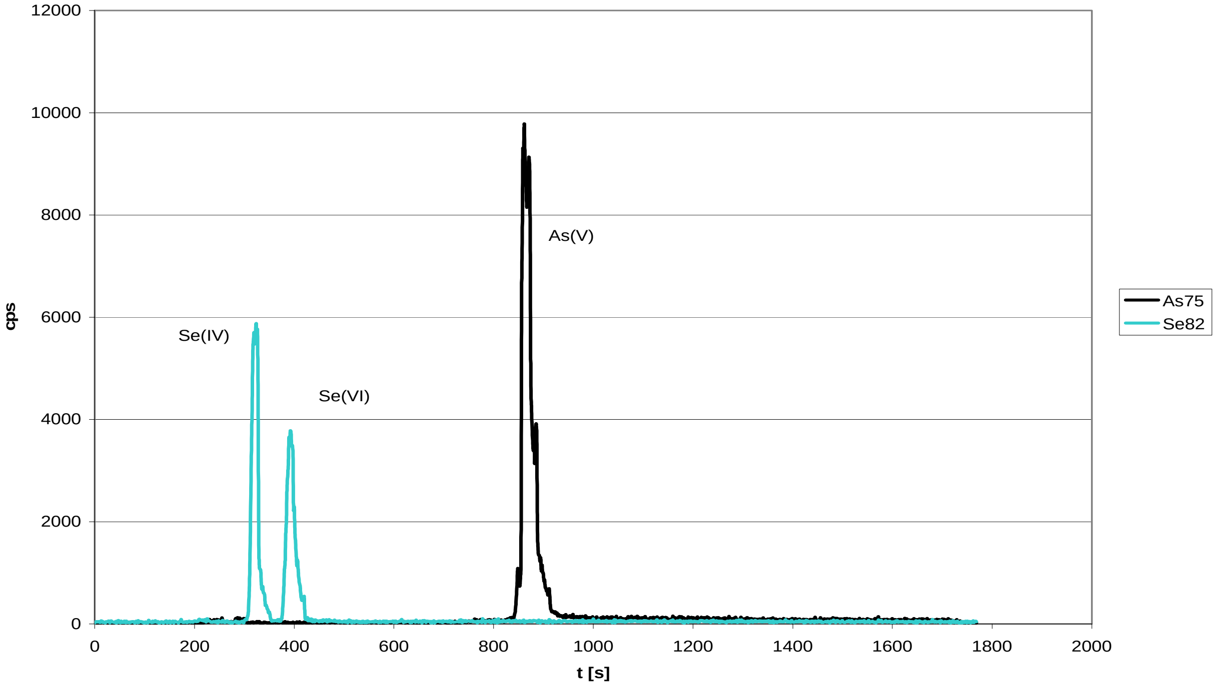

Figure 2-2
Chromatograph Showing Selenium and Arsenic Species for a Real Sample (10x dilution)

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 As+Se 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-chromatography prior to ICP-MS detection (Gürleyük and Wallschläger, 2001) (Figures 2-3 and 2-4). Modifications from the method are listed in Table 2-3.

Table 2-3
Method Parameters for As+Se and Cr Speciation by IC-ASRS-DRC-ICP-MS

	Arsenic + Selenium	**Chromium**
Column	Dionex AS-16 4-mm + AG-16 4-mm	Dionex AS-16 4-mm + AG-16 4-mm
Eluent	0-7 min: 20 mM NaOH 7→17 min 20→100 mM NaOH 17-25 min 100 mM NaOH 25-18 min 20 mM NaOH	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)

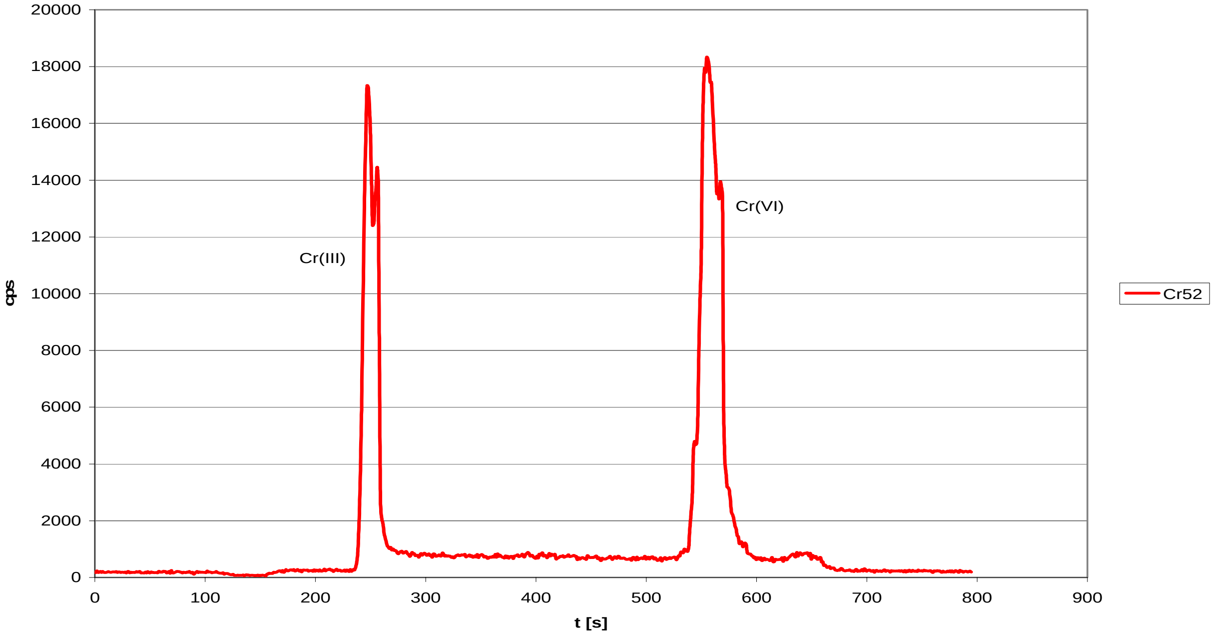

Figure 2-3
Chromatograph Showing 0.5 ppb each for Cr(III) and Cr(VI)

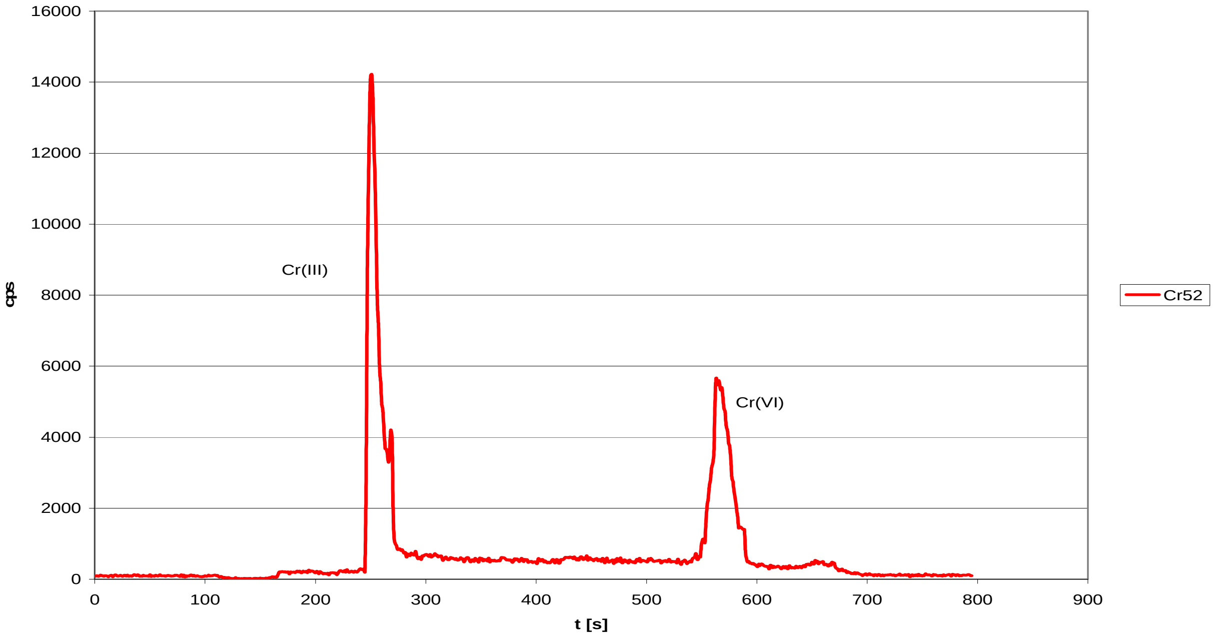

Figure 2-4
Chromatograph for Sample #34 Analyzed at a 2x Dilution

Mercury Speciation Methods

As previously described, 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 thermally desorbed from the adsorbent trap and analyzed by gas chromatography–ICP-MS (GC-ICP-MS) (similar to Lindberg et al., 2004).

Monomethyl mercury was determined by GC-ICP-MS after derivatization to methylethylmercury with sodium tetraethylborate. MeHg was isolated from filtered waters and particulate matter (yielding dissolved and particulate MeHg) by steam distillation as methylmercury chloride (MeHgCl), and determined using isotope dilution with isotopically-enriched MeHg. Total mercury (THg) in filtered waters and filters with particulate matter (yielding dissolved and particulate mercury) was determined by cold vapor-ICP-MS (CV-ICP-MS) also using isotope dilution. Samples for THg analysis were digested with BrCl and pre-reduced with $NH_2OH \bullet HCl$ prior to the CV-ICP-MS measurement (Hintelmann and Ogrinc, 2003).

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 happened 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.

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

Sample Site Attributes

The selected sample sites are concentrated in the eastern United States where coal-fired power plants predominate (Figure 3-1). The sites are nearly evenly split between landfills and impoundments (Table 3-1). Other characteristics of the sample sites include:

- Fly ash is managed at most sites; five sites manage FGD solids or FGD solids stabilized with or codisposed with fly ash, and two sites manage spray dryer ash.
- Seventeen sites received CCP from plants burning bituminous coal, 11 from plants burning subbituminous coal, six received CCP from a mixture of coals, and three received ash from lignite plants.
- Dry bottom pulverizers were the predominant boiler type for the source power plants.
- Electrostatic precipitators (ESPs) were the predominant particulate control device, and most ESPs were cold-side; in addition, four sites received CCP from fabric filters, one from a cyclone collection device, and one listed a wet ESP as the primary control device.
- Low-NOx burners were the primary NOx control. Several plants had recently added or were planning to add selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) devices. At many plants, the NOx control devices varied by unit.
- Fourteen sites received CCP from units using flue gas conditioning to enhance precipitator performance.

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

	FA		FGD/SDA	
	LF	IMP	LF	IMP
2003 Sites (completed)	★	▼	✦	▰
2004 Sites (in progress)	☆	▽	✧	⏢

Figure 3-1
Sample Site Locations by State

Table 3-1
Summary of Sampled Sites

Site Code	Sample IDs	Management Method	CCP Managed	Source Coal		Source Plant				
				Type	Region	Boiler	Particulate Coll.	FGD System	NOx Control	Flue Gas Cond.
AK	10, 11	Landfill	FA Class C	Subbit	PRB+5% pet coke	Wet Bottom Cyclone	ESP - cold side	No	Overfired Air - 2001	No
AL	4, 5	Landfill	FA, BA	mix	Western & S. Illinois	Dry Bottom Pulverizer (3 plants, varies by plant)	ESP - cold side (2 plants), - hot side (1 plant)	No	Low NOx (1 plant)	Yes (2 plants)
AN	2004	Impoundment	FA, BA	Bit	West Virginia	Dry Bottom Pulverizer-Tangential	ESP - cold side	No	Low NOx Burner, SNCR (U1)	Yes (U 3,4,5)
BB1	2004	Landfill	FA, BA	Bit	Southern Appalachian	Dry Bottom Pulverizer-Opposed	ESP - may be a mix	No	Low NOx Burners, Overfire Air, SCR	No
BB2	2004	Landfill	FA, BA	Bit	Southern Appalachian	Dry Bottom Pulverizer-Opposed	ESP - may be a mix	No	Low NOx Burners, Overfire Air, SCR	No
BR1	2004	Landfill	FA	Bit	Kentucky Low-Sulfur	Dry Bottom Pulverizer-Tangential	ESP - cold side	No	other - SCR to be added.	No
BR2	2004	Impoundment	FA, BA	Bit	Kentucky Low-Sulfur	Dry Bottom Pulverizer-Tangential	ESP - cold side	No	other - SCR to be added.	No
CC1	2004	Impoundment	FGD, BA	Lig	North Dakota	Dry Bottom Pulverizer-Tangential	ESP - cold side	Wet Scrubber - Spray Type - Mag Lime	Low NOx Burner - OFA	No
CC2	2004	Landfill	FGD, FA, BA	Lig	North Dakota	Dry Bottom Pulverizer-Tangential	ESP - cold side	Wet Scrubber - Spray Type - Mag Lime	Low NOx Burner - OFA	No
CC3	2004	Landfill	FA	Lig	North Dakota	Dry Bottom Pulverizer-Tangential	ESP - cold side	Wet Scrubber - Spray Type - Mag Lime	Low NOx Burner - OFA	No

Site Code	Sample IDs	Management Method	CCP Managed	Source Coal		Source Plant				
				Type	Region	Boiler	Particulate Coll.	FGD System	NOx Control	Flue Gas Cond.
CL	2004	Impoundment	FA, BA	Bit	Kentucky	Dry Bottom Pulverizer-Tangential	ESP - cold side	No	SCR	No
CS	2004	Landfill	FA, BA	Bit	Southern Illinois - Rend Lake	Pulverizer-Wall	ESP	No	No	No
CV1	27, 28, 29	Impoundment	FA	Bit	Northern Appalachian	Dry Bottom Pulverizer-Tangential / Front, WB Cyclone	ESP - cold side	Wet Scrubber - Mg enhanced lime	Low NOx Burner	No
CV2	30, 31, 32	Landfill	FGD, FA	Bit	Northern Appalachian	Dry Bottom Pulverizer-Tangential	ESP - cold side	Wet Scrubber - Mg enhanced lime	Low NOx Burner	Yes, last couple years
ES	2004	Landfill	FA, FGD, BA	Subbit	Western-Lee Ranch Mine	Dry Bottom Pulverizer-Tangential	FF - reverse air	Wet Scrubber - Spray Type – Limestone	Excess Air	No
HNE	17, 19, 20	Impoundment	FA, BA	Subbit	Western	Dry Bottom Pulverizer-Tangential	ESP - cold side	No	Overfire/Low NOx Burner, 4/03	Yes
HNW	18, Core1, Core2	Impoundment	FA, BA	Bit	Illinois	Dry Bottom Pulverizer-Tangential	ESP - cold side	No	Gas reburn sorbent injection for 1 year	Yes
HO	2004	Landfill	SDA	Subbit	PRB	Dry Bottom Pulverizer-Opposed	FF & Spray Dryer	Dry Injection - spray dryer	Low NOx Burner	not listed
JA1	21, 22, 23, 26	Impoundment	FA	Bit	Central Appalachian	Dry Bottom Pulverizer-Opposed	ESP - cold side	No	Low NOx Burner & SCR since 02	Yes
JA2	24, 25	Landfill	FA	Bit	Central Appalachian	Dry Bottom Pulverizer-Opposed	ESP - cold side	No	Low NOx Burner	No
JS	2004	Impoundment	FA, BA	Bit	SW Virginia	Dry Bottom Pulverizer-Tangential	ESP	No		not listed

Site Code	Sample IDs	Management Method	CCP Managed	Source Coal		Source Plant				
				Type	Region	Boiler	Particulate Coll.	FGD System	NOx Control	Flue Gas Cond.
KI	2004	Impoundment	FA, some BA	Bit	E Tennessee & Kentucky, low sulfur	Dry Bottom Pulverizer-Tangential	Cyclone	No	Low NOx Burners (4 units)	not listed
KW1	2004	Impoundment	FA, BA	mix	Formerly all Bit, 80% Subbit 20% Bit since 2002	Dry Bottom Pulverizer-Tangential (U1),Front (U2)	ESP - cold side	No	Low NOx Burner (U2)	Yes
KW2	2004	Impoundment	FA, BA	mix	Formerly all Bit, 80% Subbit 20% Bit since 2002	Dry Bottom Pulverizer-Tangential	ESP - cold side	No		Yes
L	2004	Impoundment	FA, BA	Bit	Eastern	Dry Bottom Pulverizer-Tangential	ESP - hot side	No	Overfire Air & Low NOx Burner	No
NC	2004	Landfill	FA, BA	Subbit	PRB	Dry Bottom Pulverizer-Opposed	ESP - cold side	No	Overfire Air	No
NO	2004	Landfill	FA, BA	Subbit	PRB	Dry Bottom Pulverizer-Front & Tangential	ESP - cold side	No	Low NOx Burner (3 units)	Yes (U 1,2,3,4)
OC	1	Landfill	FA, BA	mix		Dry Bottom Pulverizer-Front & Tangential	ESP - cold side	No	Low NOx Burner (3 units)	No
PU	2004	Landfill	FA	Subbit		Dry-Bottom Pulverizer-Rear	ESP - cold side	No	Low NOx burner (2 units)	Yes
SC1	6	Landfill	SDA	Subbit	PRB	Dry Bottom Pulverizer-Opposed & Tangential	FF & Spray Dryer	Dry Injection - lime spray dryer	Overfire Air (U1), Low-NOx Burner (U2&3)	not listed

Site Code	Sample IDs	Management Method	CCP Managed	Source Coal		Source Plant				
				Type	Region	Boiler	Particulate Coll.	FGD System	NOx Control	Flue Gas Cond.
SC2	7, 8, 9	Impoundment	FGD	Subbit	PRB	Dry Bottom Pulverizer-Opposed & Tangential	Wet ESP	Wet Scrubber – Dual Alkali	Overfire Air (U1), Low-NOx Burner (U2&3)	not listed
SX1	15, 16	Impoundment	FA, BA	mix	PRB & Illinois	Wet Bottom Cyclone	ESP - cold side	No	Overfire Air	Yes
SX2	Core3	Impoundment	FA	mix	PRB & Illinois	Wet Bottom Cyclone	ESP - cold side	No	Overfire Air	Yes
SY	2004	Landfill	FA	Bit		Dry Bottom Pulverizer-Front	FF - pulse	No	Low NOx Burner	not listed
UV	12, 13, 14	Landfill (sluiced ash from an impoundment)	FA (sluiced)	Bit	Illinois	Dry Bottom Pulverizer-Front & Tangential	ESP - cold side	No	Low NOx Burner (U3)	Yes (U 2,3,4,6)
WL	2004	Landfill	FA	Subbit	PRB	Dry Bottom Pulverizer-Opposed	ESP - hot side	No	Low NOx Burner	No
WS	2, 3	Landfill	FA	Subbit	PRB	Dry Bottom Pulverizer-Tangential & Front	ESP - cold (U.1-2), - hot (U.3), FF - U.3 (2001)	No	Low NOx Burner (U3)	Yes (U 1,2)

As of the end of 2003, 35 leachate samples were collected at 14 sites (Table 3-2), and an additional 68 samples were scheduled for the remaining 23 sites. Low-level mercury samples were collected, or were scheduled to be collected, at 13 sites. The 2003 sample breakdown is as follows:

- 16 landfill samples:
    - 8 leachate collection system samples;
    - 3 lysimeter samples;
    - 5 leachate well samples.
- 19 impoundment samples:
    - 4 ash/water interface samples;
    - 4 drive-point piezometer samples;
    - 3 leachate well samples;
    - 3 samples from pond outfalls;
    - 1 leachate seep;
    - 1 sample of incoming sluice water from the sluice line;
    - 3 porewater samples from ash cores.
- 28 samples were from fly ash or fly ash mixed with bottom ash, 6 samples were from FGD solids or FGD solids stabilized with fly ash, and 1 sample was from spray dryer ash.
- 18 samples of CCP derived from bituminous coal, 11 of CCP derived from subbituminous coal, and 6 derived from mixed coals.
- 30 samples from dry-bottom pulverizer boilers, 5 from wet-bottom cyclone boilers.

Table 3-2
2003 Sample Summary

Site	Sample ID	CCP Sampled[1]	Source	Sampling Point	Method	Hg Sample?
AK	11	FA, BA	Landfill	Lysimeter	Waterra Pump[2]	No
AK	10	FA, BA	Landfill	Leachate Collection System	Bailer[2]	No
AL	4	FA, BA	Landfill	Leachate Collection System	Peristaltic Pump	Yes
AL	5	FA, BA	Landfill	Leachate Well	Waterra Pump[2]	Yes
CV1	27	FGD	Landfill	Leachate Collection System	Dip Sampler[2]	Yes
CV1	28	FGD	Landfill	Leachate Collection System	Dip Sampler[2]	Yes
CV1	29	FGD	Landfill	Leachate Collection System	Dip Sampler[2]	Yes
CV2	30	FA, BA	Impoundment	Outfall	Peristaltic Pump	Yes
CV2	31	FA	Impoundment	Drive Point Piezometer	Peristaltic Pump	Yes
CV2	32	FA	Impoundment	Seep	Dip Sampler[2]	Yes
HNE	20	FA, BA	Impoundment	Outfall	Peristaltic Pump	No
HNE	17	FA, BA	Impoundment	Ash/Water Interface	Peristaltic Pump	No
HNE	19	FA	Impoundment	Sluice Line	Dip Sampler[2]	No
HNW	Core1	FA, BA	Impoundment	Soil Boring	Core Extract	No
HNW	Core2	FA, BA	Impoundment	Soil Boring	Core Extract	No
HNW	18	FA, BA	Impoundment	Leachate Well	Peristaltic Pump	No
JA1	21	FA	Impoundment	Drive Point Piezometer	Peristaltic Pump	Yes
JA1	23	FA	Impoundment	Drive Point Piezometer	Peristaltic Pump	Yes
JA1	22	FA	Impoundment	Ash/Water Interface	Peristaltic Pump	Yes
JA1	26	FA	Impoundment	Outfall	Dip Sampler[2]	Yes
JA2	24	FA	Landfill	Leachate Collection System	Dip Sampler[2]	No
JA2	25	FA	Landfill	Leachate Collection System	Dip Sampler[2]	No
OC	1	FA, BA	Landfill	Leachate Well	Waterra Pump[2]	Yes
SC1	6	SDA	Landfill	Leachate Collection System	Peristaltic Pump	Yes
SC2	7	FGD	Impoundment	Leachate Well	Bladder Pump	Yes
SC2	8	FGD	Impoundment	Leachate Well	Bladder Pump	Yes
SC2	9	FGD	Impoundment	Ash/Water Interface	Peristaltic Pump	Yes
SX1	16	FA, BA	Impoundment	Drive Point Piezometer	Peristaltic Pump	No
SX1	15	FA, BA	Impoundment	Ash/Water Interface	Peristaltic Pump	No
SX2	Core3	FA	Impoundment	Soil Boring	Core Extract	No
UV	13	FA, BA	Landfill	Leachate Well	Peristaltic Pump	No
UV	12	FA, BA	Landfill	Leachate Well	Waterra Pump[2]	No
UV	14	FA, BA	Landfill	Leachate Well	Peristaltic Pump	No
WS	2	FA	Landfill	Lysimeter	Bladder Pump	Yes
WS	3	FA	Landfill	Lysimeter	Bladder Pump	Yes

1. FA—fly ash, BA—bottom ash, FGD—FGD solids, SDA—spray dryer ash
2. Sample was discharged to a flask; then extracted from the flask through the filter and to a sample bottle using a peristaltic pump.

4

2003 RESULTS

Summary of All Data

Analytical data were entered in a database and reviewed for outliers; anomalous values were checked and corrected, if appropriate, by the Trent University laboratory. Carbonate and bicarbonate concentrations were calculated from total inorganic carbon (TIC) and pH based on the Henderson Hasselbach equation:

$$pH = pKa + \log[CO_3]/[HCO_3], \text{ where } pKa = 10.33$$

All of the data for sites sampled in 2003 are statistically summarized in Table 4-1.

Major Constituents

Major constituent concentrations were converted to milliequivalents and plotted on ternary plots (Figure 4-1), which show the relative percentage of each constituent. The ternary plots show several distinct groupings of samples:

- Cation chemistry of most samples is dominated by calcium and/or sodium. Only sample 9 had a relatively high percentage of magnesium. Sample 9 was sampled at the ash/water interface of an FGD pond, and is from the only plant that listed a wet ESP and dual alkali wet scrubber as emission control devices. However, two leachate well samples from the same site (samples 7 and 8) had relatively low percentages of magnesium. Sample 9 had relatively high absolute concentrations of several other elements, and the concentrations of sulfate, magnesium, selenium, and mercury in this sample were higher than any other 2003 samples.
- Samples 27, 28, and 29 are fly ash samples, and the absolute concentrations of potassium (> 400 mg/L) in these samples were higher than in any other samples. Magnesium concentrations were low in these samples, and in the FGD solids leachate samples from this plant (samples 30, 31, and 32), even though the FGD system at this plant used magnesium-enhanced lime as the FGD sorbent.
- Samples 1, 2, 3, 4, 7, 10, and 16 had relatively high percentages of sodium and potassium. The only similarity between these samples is that they are from plants that burn subbituminous or a mixture of subbituminous and bituminous coal. However, several samples from plants burning subbituminous coal did not fall into this grouping.
- Samples 6, 12, 13, 14, 15, 18, 30, and 31 had relatively high percentages of calcium. All except sample 6 were from plants burning bituminous or a mixture of bituminous and subbituminous coals. Sample 6 is from the only sampled plant with a spray dryer system.
- Anion chemistry for most samples is dominated by sulfate.
- Samples 27, 28, and 29 had a significant percentage of chloride, and the highest absolute concentrations of chloride (> 900 mg/L) in the 2003 samples. These samples are from a landfill that received FGD solids stabilized with fly ash derived from bituminous coal and with 2% to 3% lime.

- Samples 17, 18, 19, and 20 are from different sites associated with the same power plant. Sample 18, which has a relatively high percentage of carbonates, is from an inactive site, and the plant had a considerably different configuration when that site was active. The relatively high percentage of chloride and carbonates in these samples may reflect their relatively low absolute sulfate concentrations (< 400 mg/L).
- Sample 11 is dominated by carbonates, and has relatively low absolute concentrations of boron (0.26 mg/L) and sulfate (93 mg/L). This sample was collected from a lysimeter beneath the liner of a landfill. At the time of sample collection, it was thought that this lysimeter was above the water table, and any liquid in the lysimeter would be leachate. However, sample 10, which was collected from the leachate collection system at the same site, has higher absolute boron (10.7 mg/L) and sulfate (3,830 mg/L) concentrations, and distinctly different major constituent chemistry ratios. These differences suggest that sample 11 is not representative of CCP leachate; therefore, this sample is not included in the discussions that follow.

Minor and Trace Elements

Boron had the highest maximum, mean, and median concentration of the minor and trace elements (Table 4-1). Other minor and trace elements with median concentrations greater than 100 µg/L were aluminum, silica, strontium, and molybdenum; although the aluminum result is a function of the detection limit (150 µg/L). Elements with median concentrations less than 1 µg/L included chromium, lead, mercury, silver, and thallium. The *maximum* concentrations of beryllium, silver, and mercury were lower than 5 µg/L.

Total arsenic concentrations ranged from 3 to 238 µg/L, with a median of 24 µg/L. Five samples, from three different sites, had an arsenic concentration greater than 100 µg/L. In all five cases, the leachate was from sluiced fly ash[3] that was a by-product of bituminous coal. Conversely, five samples, from three different sites, had arsenic concentration lower than 10 µg/L. There was no correlation between low arsenic concentration and management method or coal type.

Total selenium concentration exhibited a much larger range than arsenic, from 0.3 to 2,360 µg/L, although the median selenium concentration of 15 µg/L was lower than for arsenic. Three samples from two sites had concentrations greater than 1,000 µg/L, and five samples from four additional sites had concentrations greater than 100 µg/L. These samples represented both FGD solids and fly ash leachate, from landfills and impoundments. The source coal for six of these eight samples was subbituminous, one was a mixture of bituminous and subbituminous, and only one was derived from bituminous coal. Fourteen samples had a selenium concentration lower than 10 µg/L. These fourteen samples included all five of the arsenic samples with concentration lower than 10 µg/L, and three of the five arsenic samples with concentration greater than 100 µg/L. Again, there was no correlation between low selenium concentration and management method or coal type.

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[3] Two of these samples are from a site characterized as a landfill; however, the fly ash in the landfill was excavated from an impoundment.

Table 4-1
Statistical Summary of 2003 Samples

Parameter	Unit	Count[1]	Minimum	Mean	Median	Maximum	Extreme[2]	% BDL
Major Constituents								
Bicarbonate (calc)	mg/L	31	1.0	105	60	584	18	0%
Calcium	mg/L	31	9.1	299	231	730	29	0%
Carbonate (calc)	mg/L	31	<0.1	10	0.69	152	3	23%
Chloride	mg/L	31	6.5	181	33	1,260	28	0%
Magnesium	mg/L	31	0.53	97	23	1,990	9	0%
Potassium	mg/L	31	0.95	96	24	581	28	0%
Sodium	mg/L	31	17	471	79	3,410	2	0%
Sulfate	mg/L	31	91	1,785	1,370	10,400	9	0%
Carbon, total inorganic	mg/L	31	0.95	23	12	115	18	0%
Carbon, total organic	mg/L	27	0.51	11.8	6.2	55	2	0%
Minor and Trace Elements								
Aluminum	µg/L	34	<150	2,316	<150	36,400	16	56%
Antimony	µg/L	34	<0.25	6.8	1.2	74	23	9%
Arsenic (III)	µg/L	27	<0.25	5.5	<2.5	39	12	52%
Arsenic (total)	µg/L	34	3.0	54	24	238	12	0%
Arsenic (V)	µg/L	27	<0.1	1.6	<0.2	13	2	63%
Barium	µg/L	34	27	99	68	298	15	0%
Beryllium	µg/L	34	0.1	1.4	1.5	1.9	16	9%
Boron	µg/L	34	456	20,293	8,855	102,000	12	0%
Cadmium	µg/L	34	0.17	8.6	1.7	75	16	0%
Chromium (total)	µg/L	34	<0.45	184	0.51	3,150	2	47%
Chromium (VI)	µg/L	27	<0.05	221	0.90	3,220	2	33%
Cobalt	µg/L	34	<0.02	14	8.9	116	2	3%
Copper	µg/L	34	1.6	31	15	401	2	0%
Iron	µg/L	34	2.0	440	16	9,600	13	3%
Lead	µg/L	34	0.066	0.73	0.34	4.5	16	0%
Lithium	µg/L	34	3.6	1,593	88	21,300	24	0%
Manganese	µg/L	34	1.0	485	59	4,230	25	6%
Mercury (dimethyl)	ng/L	18	<0.005	0.013	<0.005	0.055	1	61%
Mercury (monomethyl, diss.)	ng/L	18	<0.02	0.59	0.079	6.7	31	22%
Mercury (monomethyl, part.)	ng/L	18	<0.02	0.037	0.024	0.11	30	39%
Mercury (total, dissolved)	ng/L	18	0.38	6.8	2.0	28	9	0%
Mercury (total, particulate)	ng/L	18	<1.0	57	25	254	2	17%
Molybdenum	µg/L	34	29	3,516	473	34,000	16	0%
Nickel	µg/L	34	0.33	35	6.4	380	7	0%
Selenium (IV)	µg/L	27	<0.1	14	1.7	237	23	33%
Selenium (total)	µg/L	34	0.30	217	15	2,360	9	0%
Selenium (VI)	µg/L	27	<0.25	125	1.8	1,180	9	30%
Silica	µg/L	34	180	4,499	3,960	13,600	16	0%
Silver	µg/L	34	<0.25	0.35	<0.25	1.69	core 1	62%
Strontium	µg/L	34	19	3,271	1,275	17,400	7	0%
Thallium	µg/L	34	<0.1	1.7	<0.5	15	32	59%
Uranium	µg/L	34	<0.002	4.8	1.2	61	23	3%
Vanadium	µg/L	34	0.50	254	26	3,950	10	0%
Zinc	µg/L	34	1.9	19	10	124	24	0%
Field Parameters								
Dissolved Oxygen	%	31	0.10	9.0	4.5	39	1 / 22	0%
Electrical Cond.	mS/cm	31	0.61	3.9	2.9	13	21 / 9	0%
ORP	mV	31	-260	9.6	49	184	31 / 5	0%
pH	SU	31	6.2	8.6	8.5	12	7 / 16	0%
Temperature	°C	31	14	21	20	36	32 / 19	0%

1. Statistics exclude sample 11, duplicates, and QC samples.
2. Indicates the sample with the highest value. Low / high samples are indicated for field parameters.

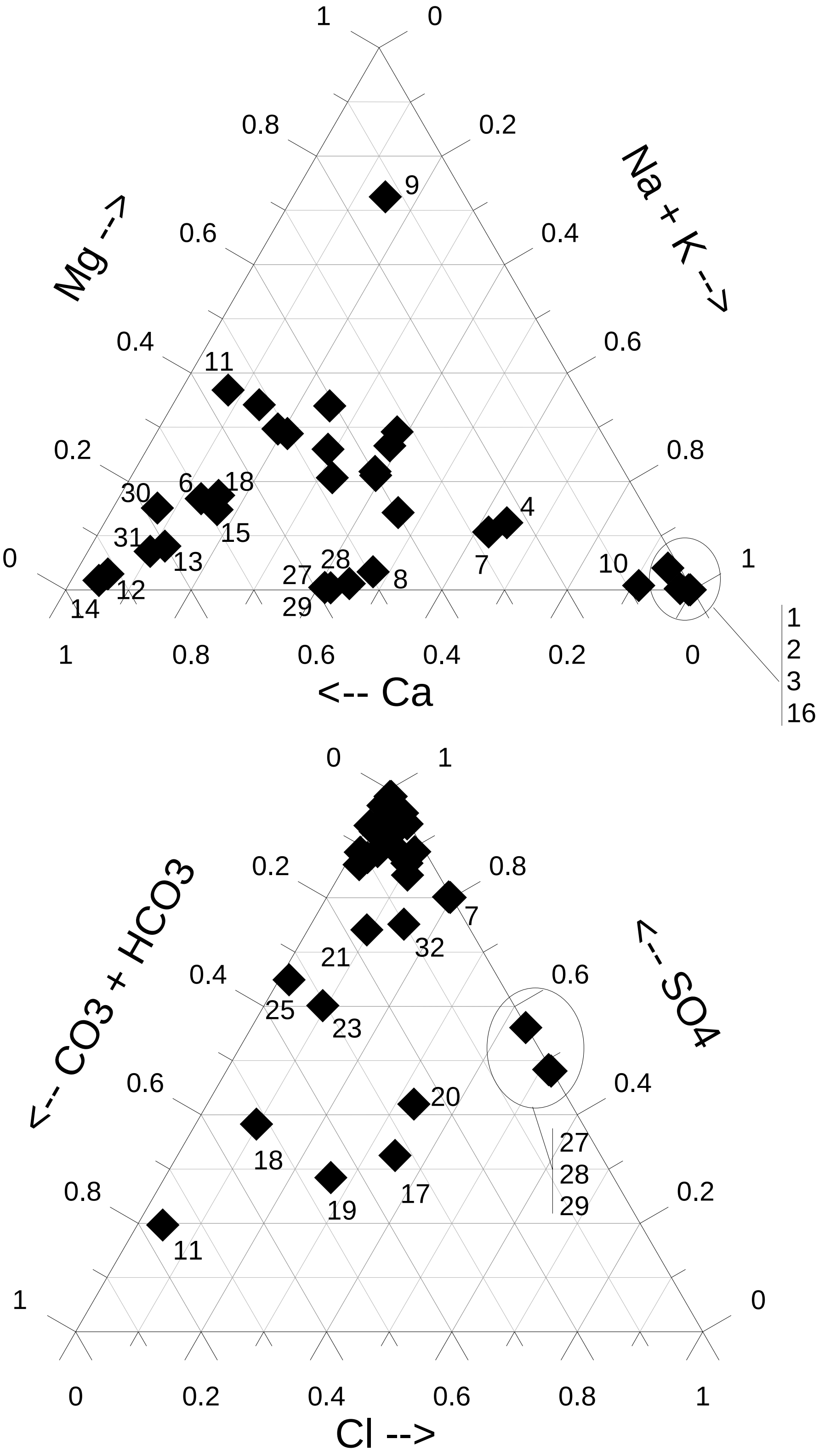

Figure 4-1
Ternary Plot Showing Relative Percentages of Major Constituents in the 2003 Samples

Speciation data for arsenic, selenium, and chromium are still being developed due to discrepancies in the sum of species and total concentrations. Some of the 2003 sites were resampled in 2004 to evaluate possible influence of preservatives and holding times on the samples, particularly for arsenic and selenium. The efforts to resolve these discrepancies are discussed in Appendix A.

Comparison of Ash Leachate Concentrations to Site Attributes

Leachate concentrations for sites managing only ash were compared using box-whisker plots (Figure 4-2), which graphically show the distribution of concentrations for a given group of data. Non-detect values were plotted at their detection limit.

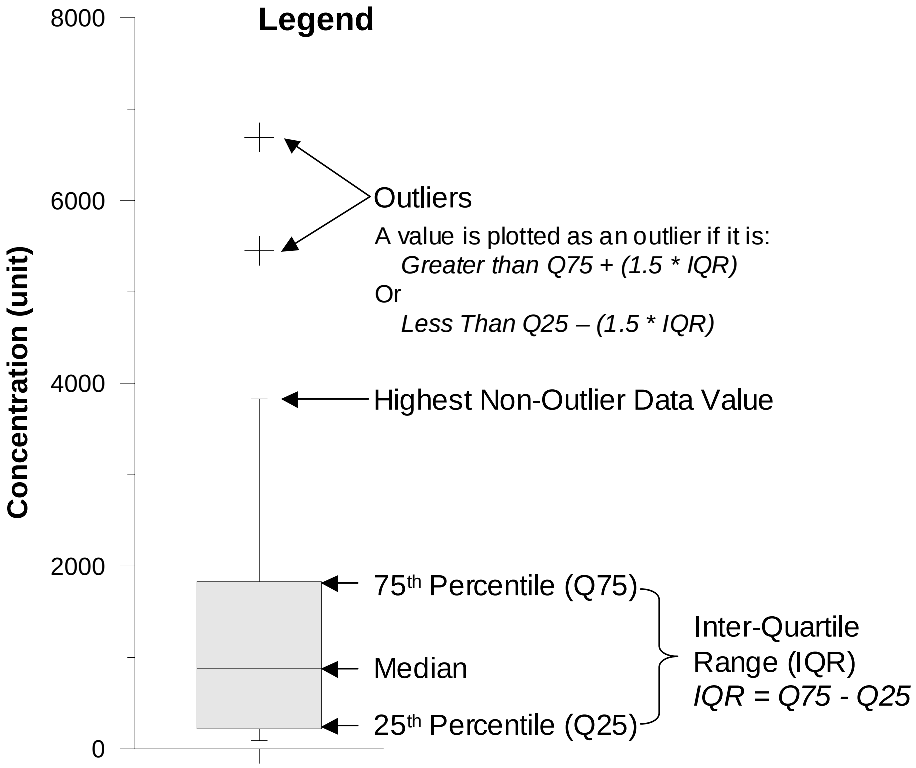

Figure 4-2
Legend for Box-Whisker Plots

Because there are only six samples of leachate from FGD solids, which came from two sites, and because FGD leachate is expected to be considerably different from fly ash leachate, these samples were not grouped with the fly ash samples in this comparison. The single spray dryer ash sample was similarly not grouped with the fly ash samples.

Major Constituents

As previously stated in the summary for all data, the 2003 ash leachate samples were dominated by sulfate, calcium, and sodium (Figure 4-3). Concentrations of all major ions, except chloride, were higher in landfill leachate than in impoundment leachate (Figure 4-4). This relationship likely reflects washing of the ash particles that occurs during sluicing.

There was also a difference in major ion composition by source coal type (Figure 4-5). Sulfate, sodium, and potassium concentrations tended to be higher when the source coal was subbituminous, rather than bituminous. Conversely, calcium concentrations were higher when the source coal was bituminous.

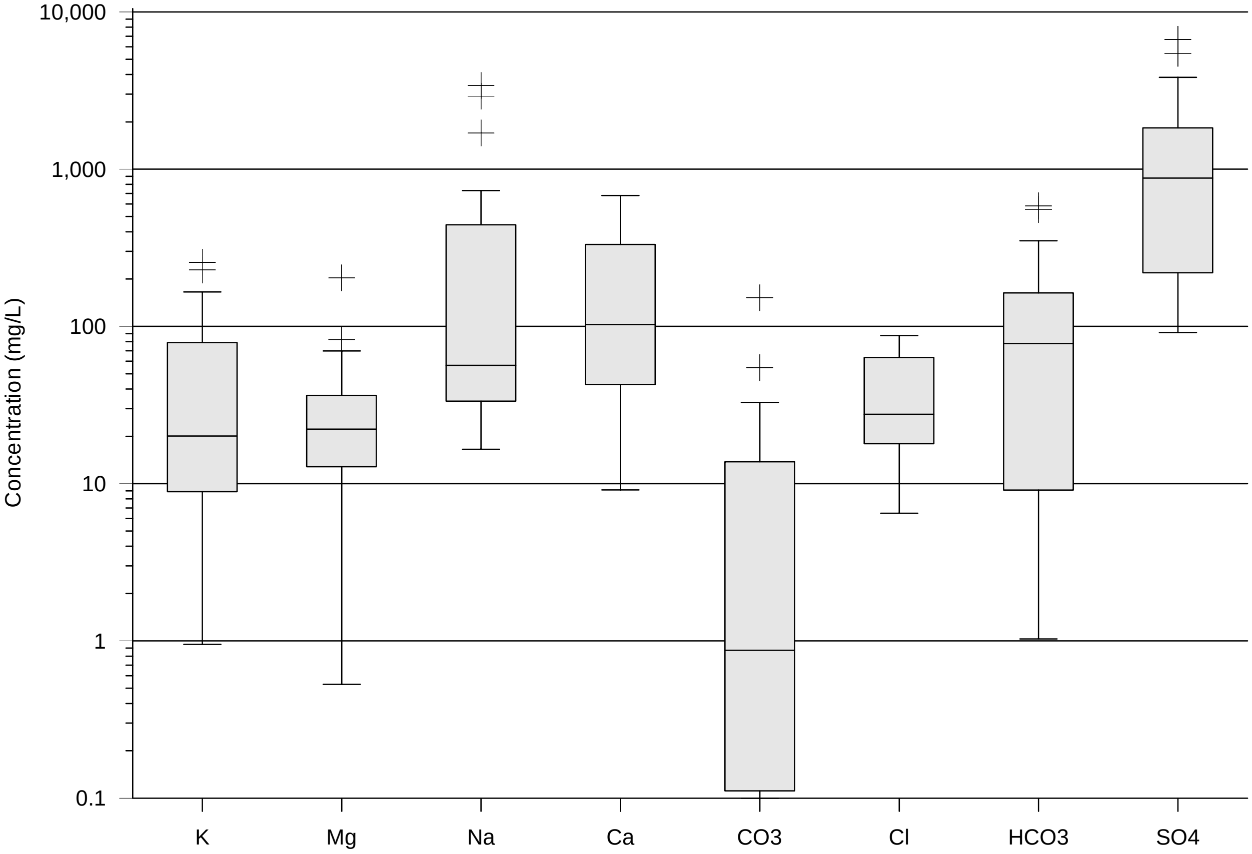

Figure 4-3
Box-Whisker Plot Showing Major Constituent Concentrations for All Coal Ash Samples.

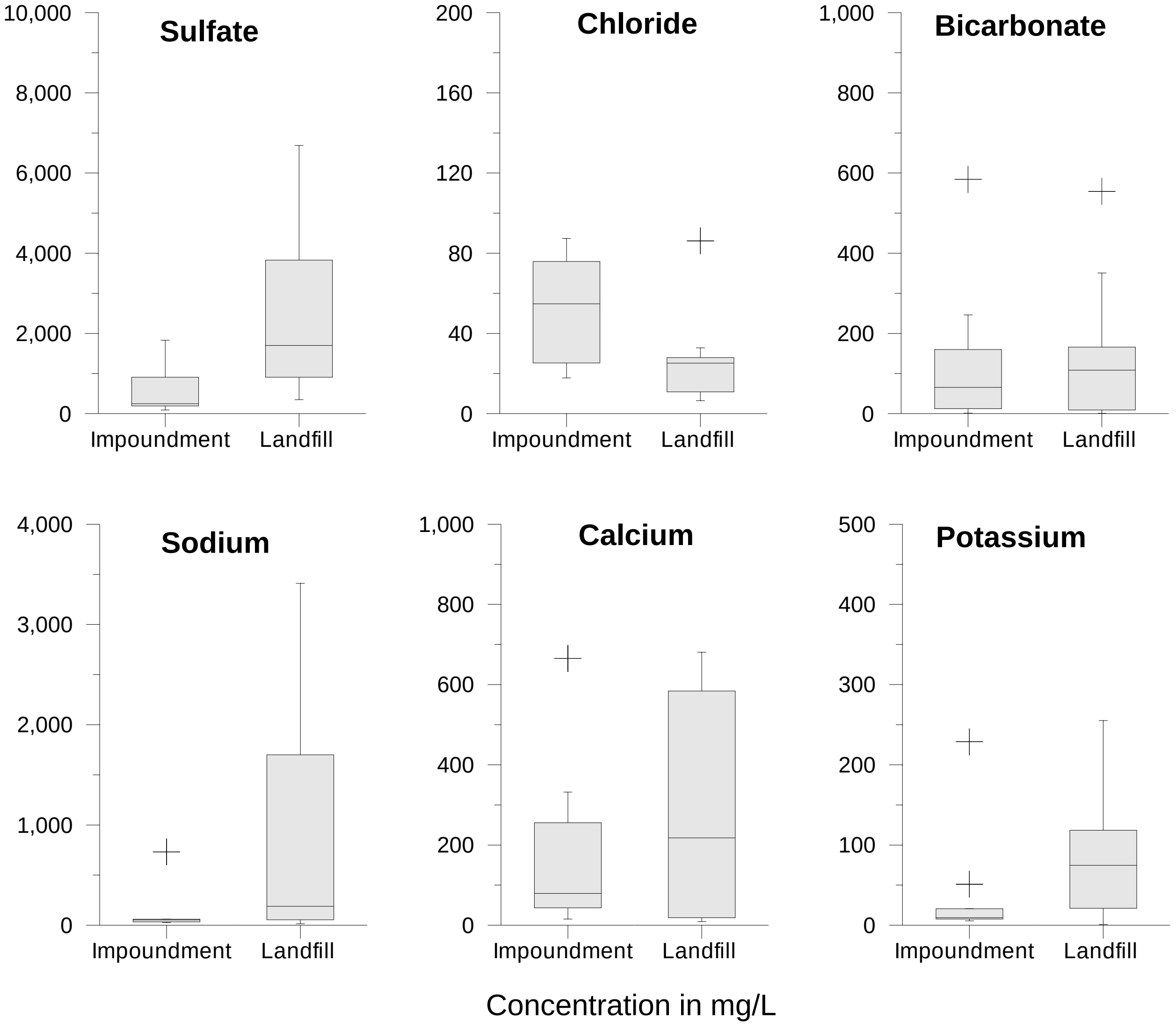

Figure 4-4
Box-Whisker Plot Comparing Major Constituent Concentrations in Coal Ash Landfill and Impoundment Leachate

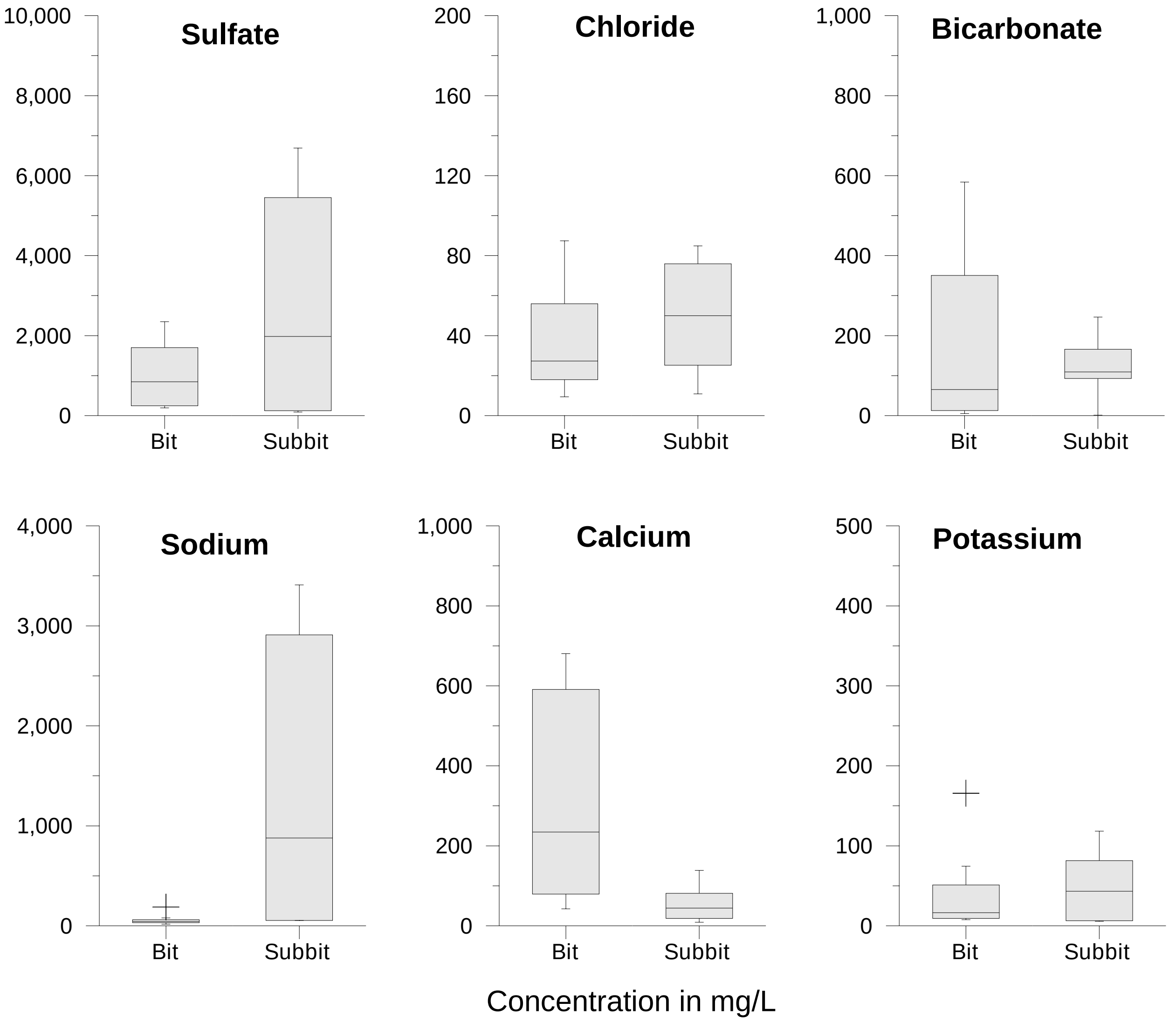

Figure 4-5
Box-Whisker Plot Comparing Major Constituent Concentrations in Coal Ash Leachate Derived from Bituminous and Subbituminous Coal

Minor and Trace Elements

The interquartile range for most trace elements spanned almost an order of magnitude, and the range from the highest to the lowest values spanned two to three orders of magnitude in most cases (Figure 4-6). Twelve elements were selected for further comparison, due to their concentration in CCP leachate or regulatory significance.

Similar to the major constituents, most of the plotted minor and trace elements (aluminum, boron, lithium, molybdenum, strontium, vanadium, cadmium, mercury, and selenium) had higher concentrations in landfill leachate samples than in impoundment samples; antimony had higher concentration in impoundment leachate samples, and there was little difference for arsenic and nickel (Figure 4-7). Again, this difference may reflect washing of ash as it is sluiced to the impoundments.

Source coal type also affects minor and trace constituent concentrations. Coal ash from subbituminous coals had higher concentration ranges for aluminum, molybdenum, vanadium, cadmium, mercury, and selenium, while ash from bituminous coals yielded higher leachate concentrations for boron, lithium, strontium, arsenic, antimony, and nickel (Figure 4-8).

These comparisons highlight how CCP management methods and source coal type can influence leachate chemistry, although there are likely interrelationships between these broad categories. The current data set is not sufficiently large to explore these interrelationships; therefore, this analysis will be completed after the 2004/2005 sample results are available.

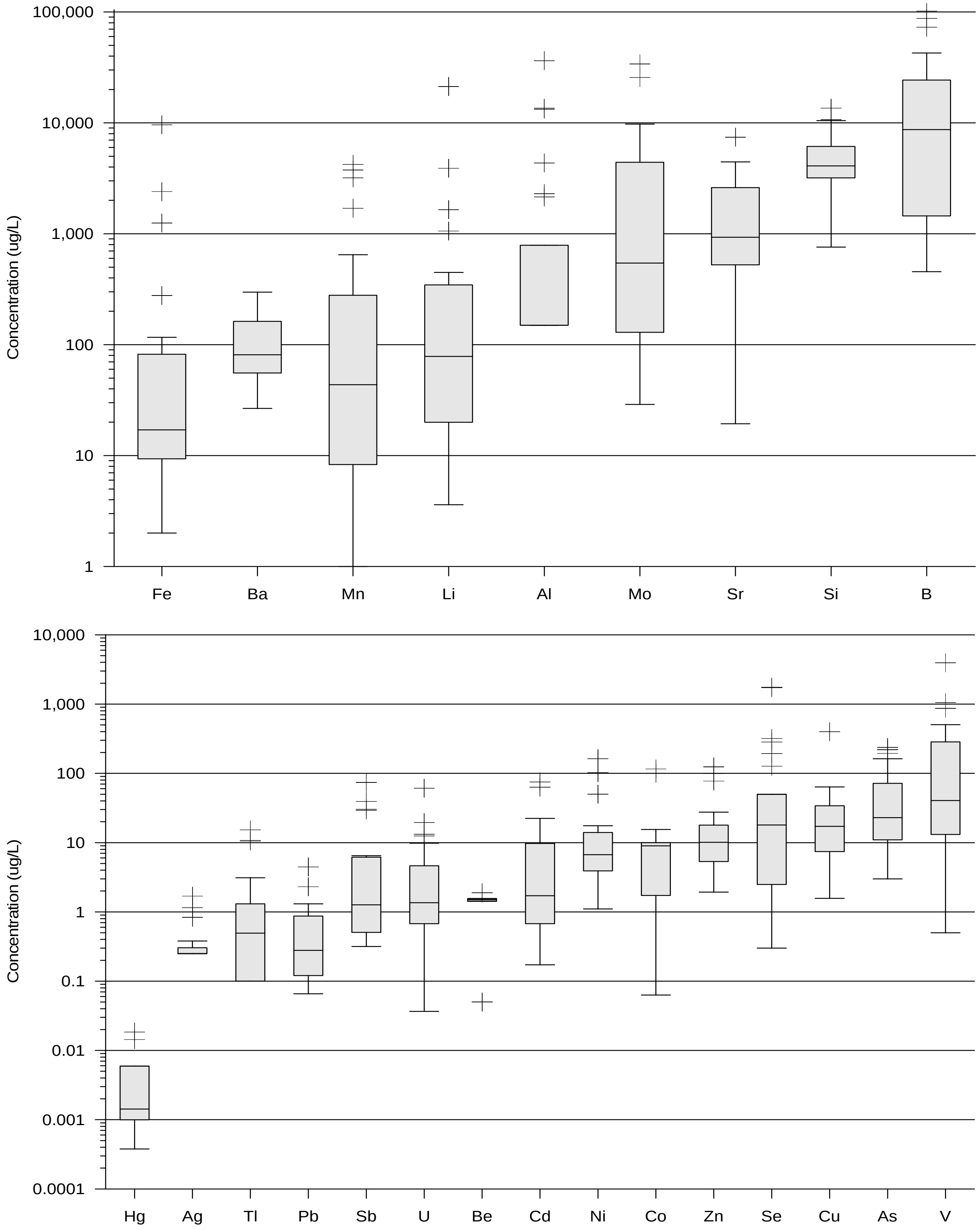

Figure 4-6
Box-Whisker Plot Showing Ranges of Minor and Trace Elements in Coal Ash Leachate

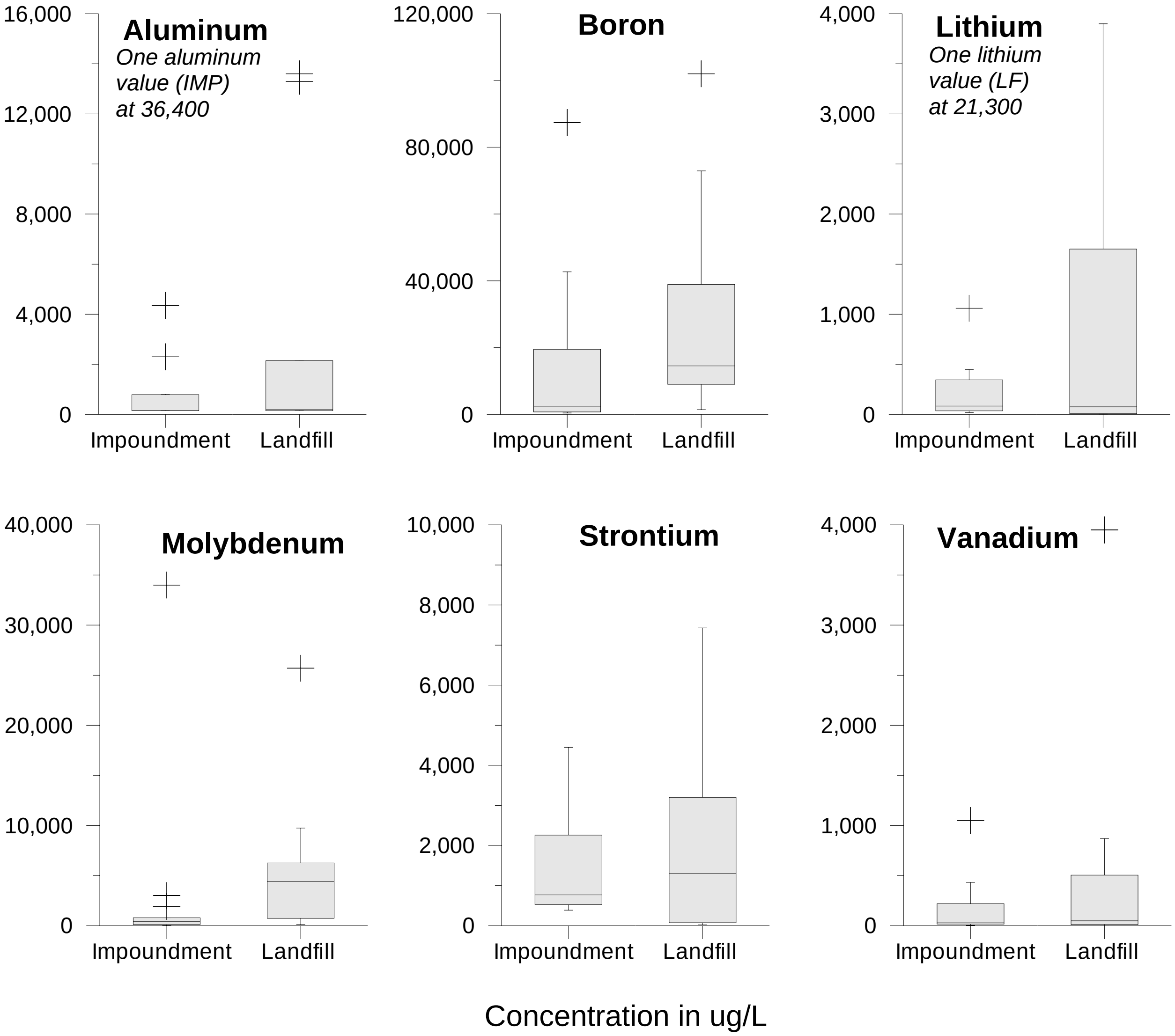

Figure 4-7a
Box-Whisker Plot Comparing Minor/Trace Element Concentrations in Coal Ash Landfill and Impoundment Leachate

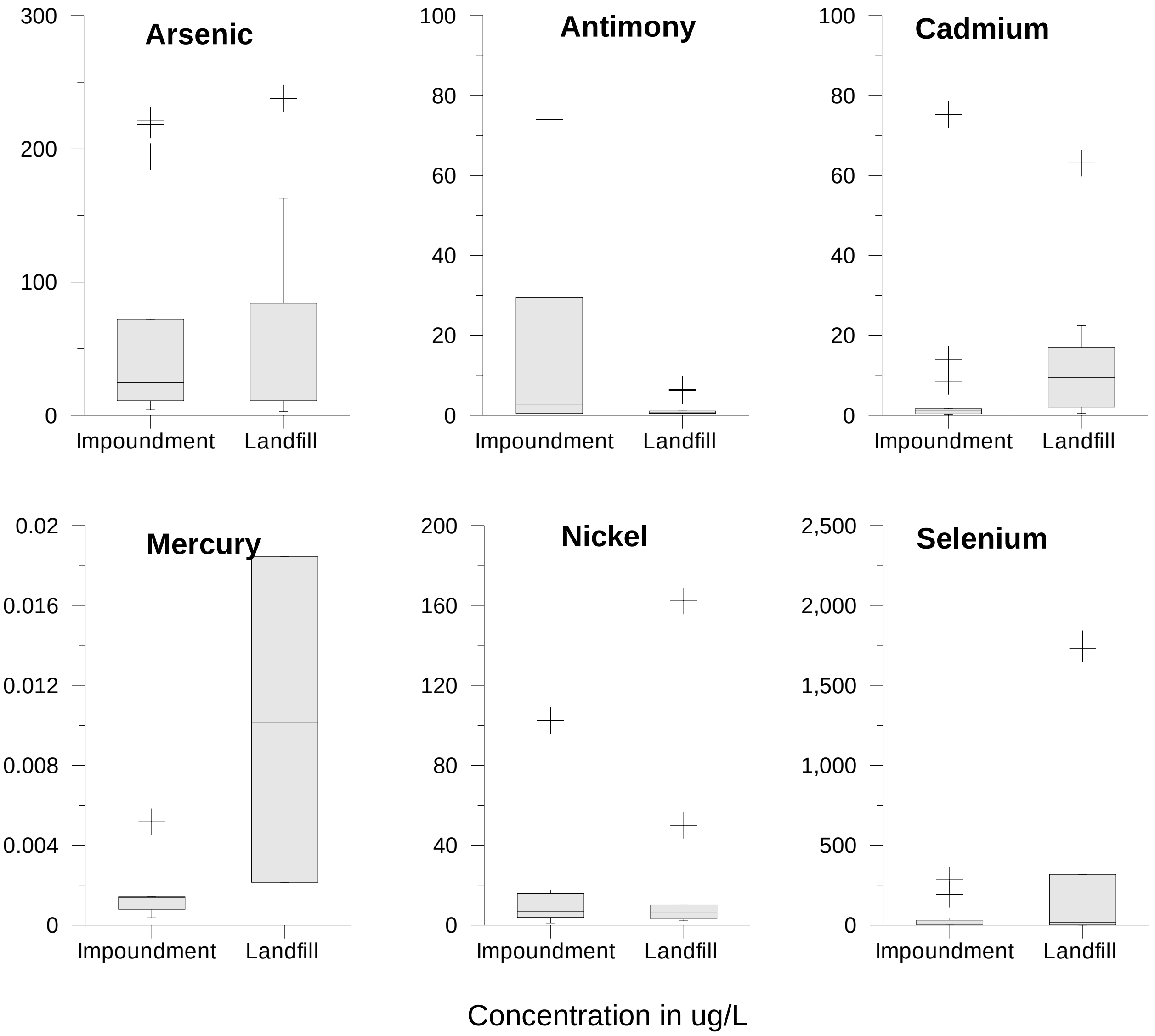

Figure 4-7b
Box-Whisker Plot Comparing Minor/Trace Element Concentrations in Coal Ash Landfill and Impoundment Leachate

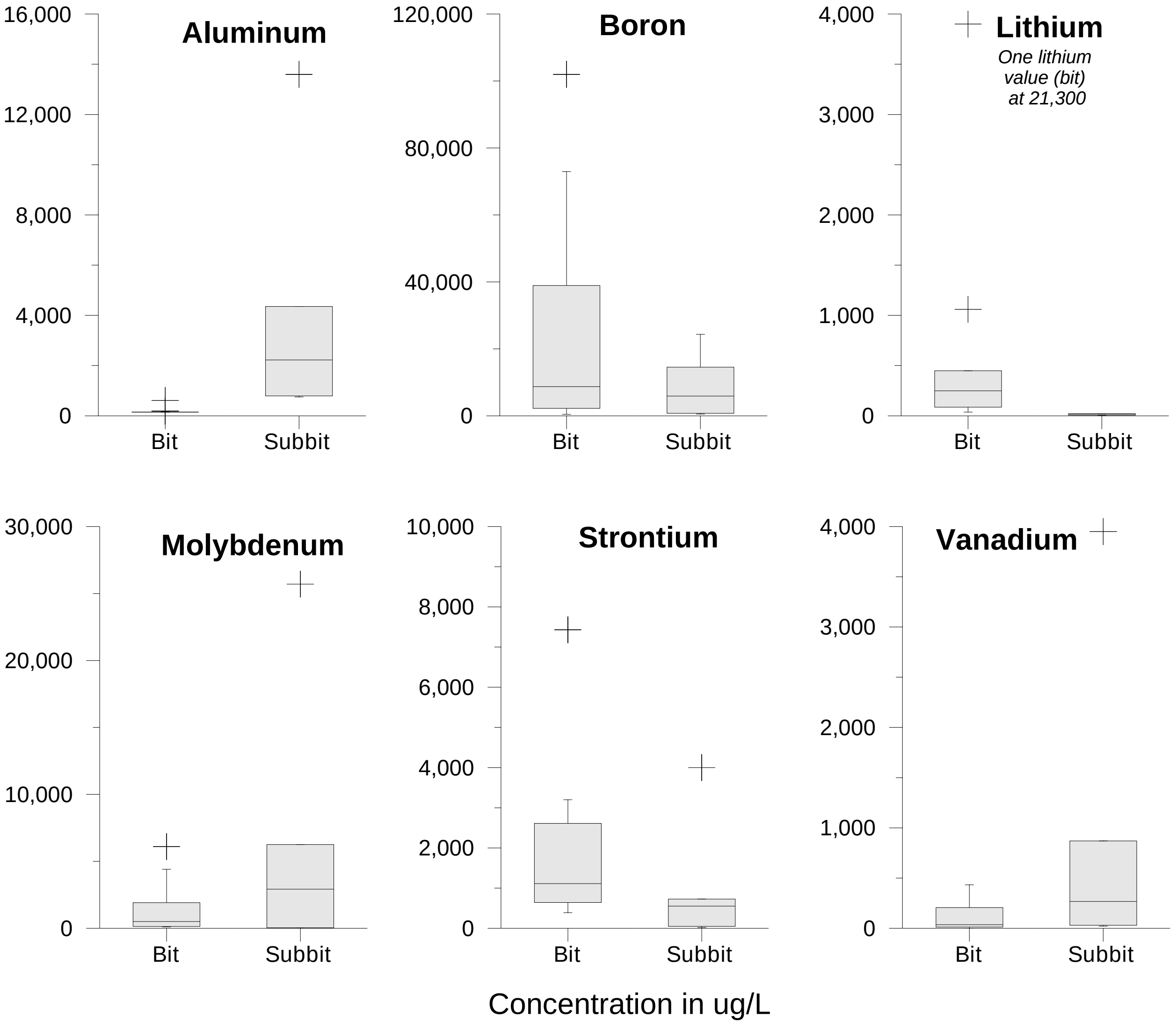

Figure 4-8a
Box-Whisker Plot Comparing Minor/Trace Element Concentrations in Coal Ash Leachate Derived from Bituminous and Subbituminous Coal

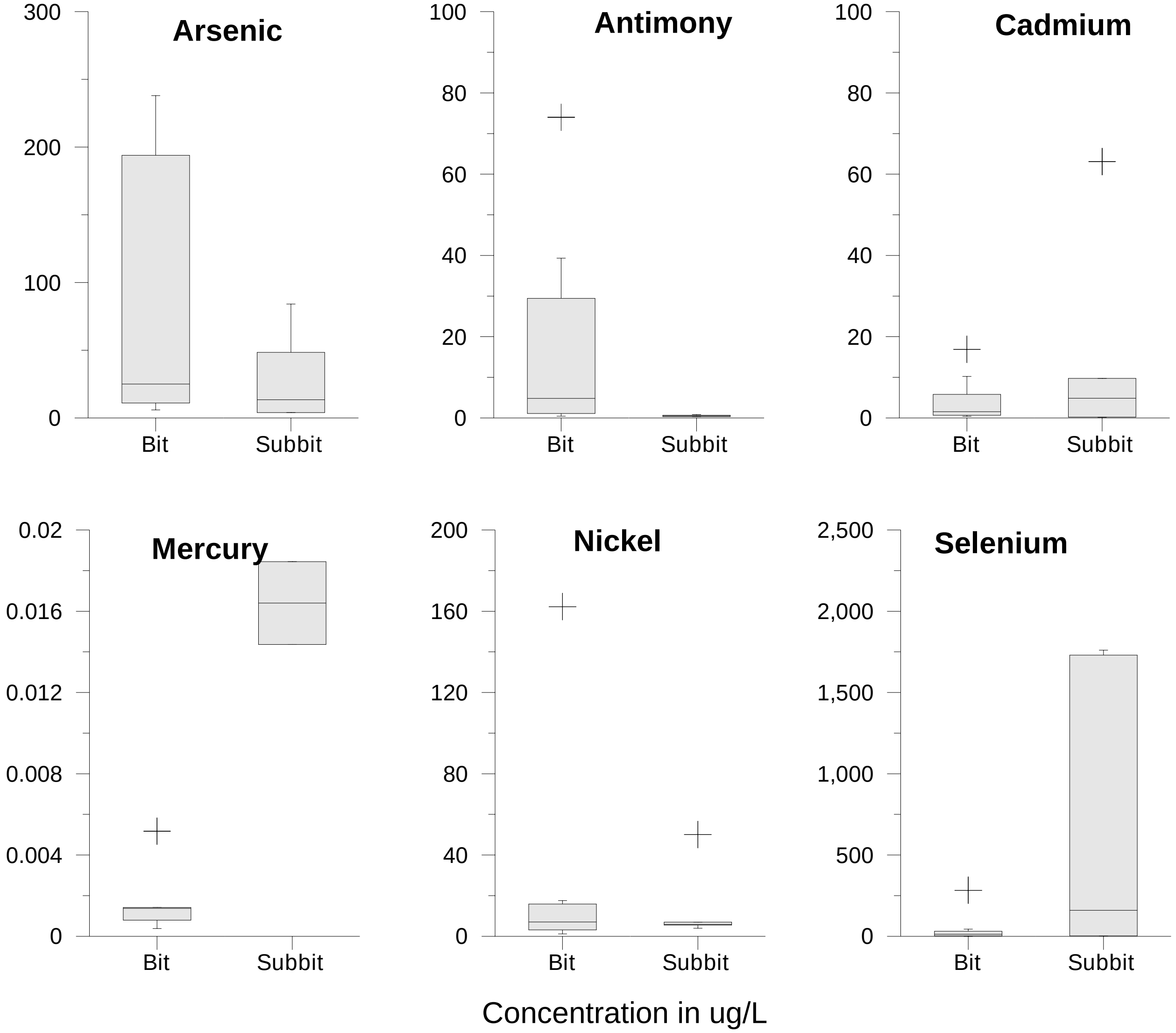

Figure 4-8b
Box-Whisker Plot Comparing Minor/Trace Element Concentrations in Coal Ash Leachate Derived from Bituminous and Subbituminous Coal

Field Parameters

The pH of the leachate samples was neutral to strongly alkaline. Leachate from landfills (Figure 4-9) and ash derived from subbituminous coal (Figure 4-10) tended to be more alkaline than impoundment/bituminous coal leachate. Dissolved oxygen and ORP were lower in landfills than in impoundments. Reflecting major ion concentrations, specific conductance tends to be higher in landfill leachate than in impoundment leachate, and for ash leachate from subbituminous coal rather than bituminous coal. TOC and TIC concentrations were higher in leachate from landfills than in impoundments. Results for these two parameters were mixed when comparing source coals.

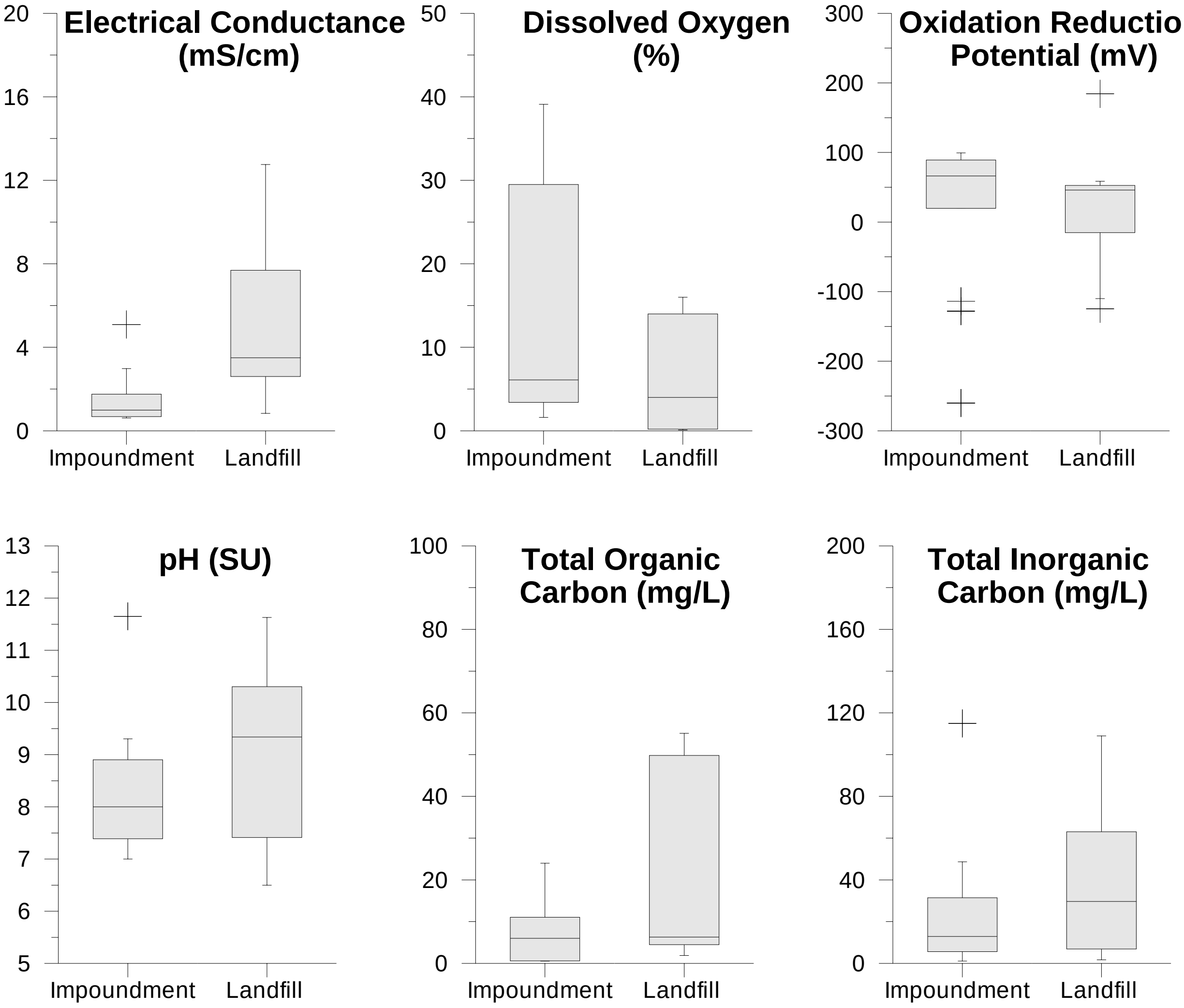

Figure 4-9
Box-Whisker Plot Comparing Field Parameters in Coal Ash Landfill and Impoundment Leachate

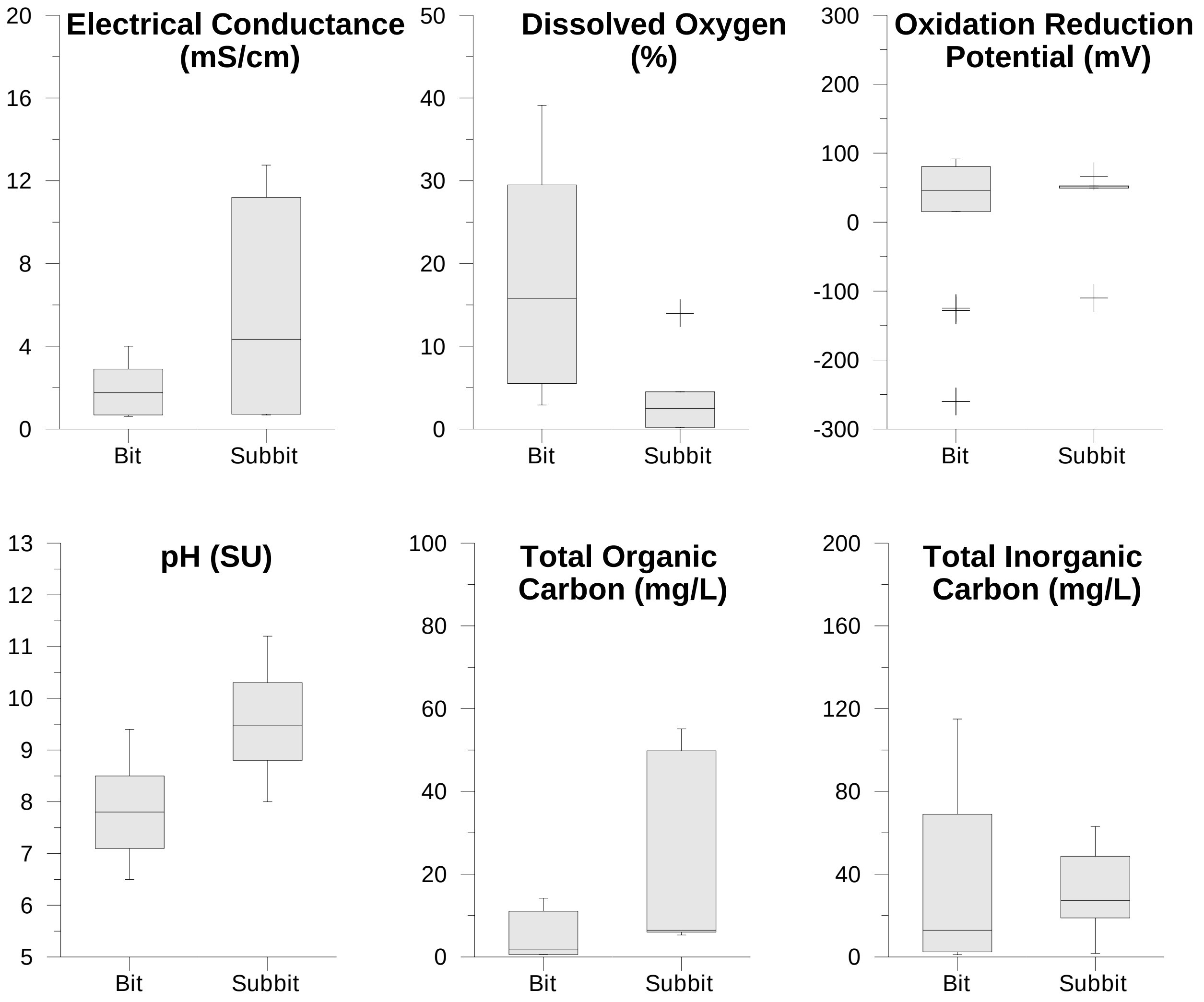

Figure 4-10
Box-Whisker Plot Comparing Field Parameters in Coal Ash Leachate Derived from Bituminous and Subbituminous Coal

Leachate Variability as a Function of Sample Point

Leachate samples were collected from a variety of sample points such as wells at landfills and impoundments, leachate collection systems at landfills, and the ash/water interface at impoundments. Potential differences between sample points were reviewed by comparing the range of total dissolved solids concentrations and sum of trace elements for samples collected at each point (Figures 4-11 and 4-12).

Total dissolved solids (TDS) values were calculated by summing the concentrations of all constituents analyzed. Median TDS concentrations were highest in samples from lysimeters, leachate collection systems, and leachate wells, and lowest in samples from pond outfalls, sluice lines, and the ash/water interface (Figure 4-11). Minor and trace element concentrations, primarily driven by boron, were highest in leachate well, lysimeter, and soil boring[4] samples, and lowest in outfall, seep, and sluice line samples (Figure 4-12). In both cases, there is a tendency for concentrations in leachate porewater to be higher than for leachate pond water.

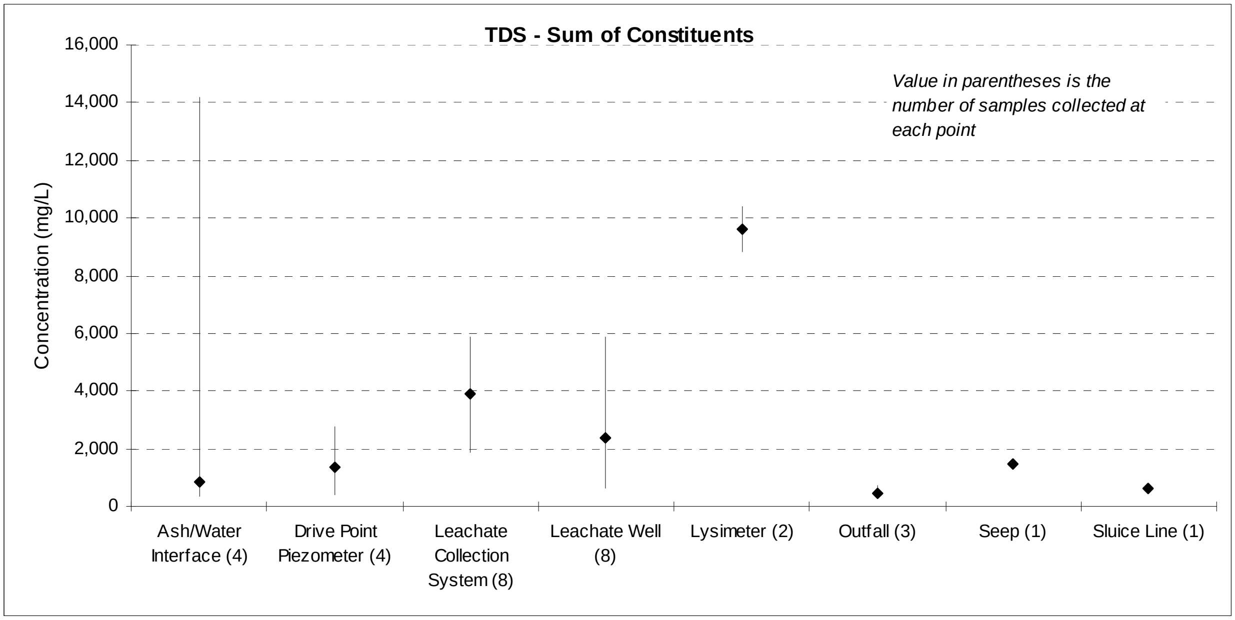

Figure 4-11
Range and Median of Total Dissolved Solids Concentrations by Sample Collection Point

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[4] Major constituent concentrations were not determined for core samples; therefore TDS concentrations could not be calculated.

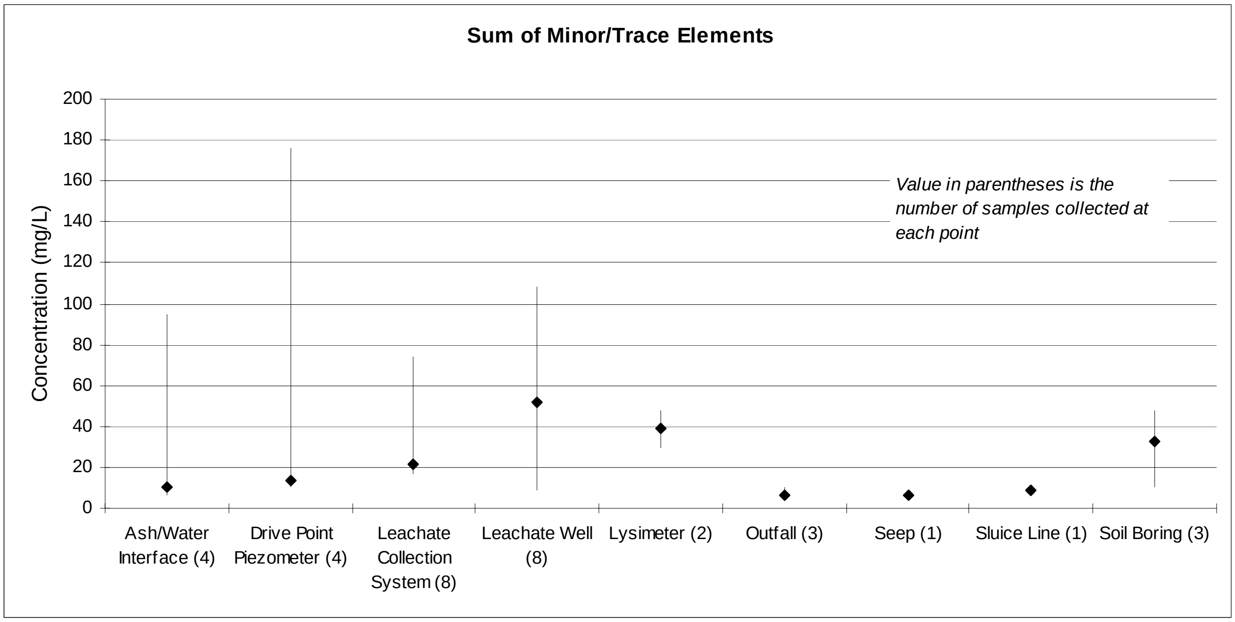

Figure 4-12
Range and Median of Sum of Minor/Trace Elements by Sample Collection Point

As follow-up to these observations, different sampling points within the same site were compared to determine whether or not there was a difference between pond water and porewater concentrations. Four sites had both porewater and pond water samples (CV2, JA1, SC2, and SX1). In three of the four cases, the porewater sample returned a higher TDS value, and a higher sum of minor/trace constituents value than the pond water samples (Table 4-2). This observation suggests that additional leaching may occur as pond water equilibrates with the sediments in an impoundment.

Table 4-2
Comparison of Pond Water and Porewater Leachate Samples

	Pond Water Samples			Porewater Samples	
Site	Seep	Outfall	Ash/Water Interface	Drive Point Piezometer	Leachate Well
Total Dissolved Solids					
CV2	1,454	733		2,754	
JA1		359	362	379/595	
SC2			14,200		3,775/5,875
SX1			1,268	2,164	
Sum of Minor/Trace Elements					
CV2	6.4	10		17	
JA1		6.1	6.6	10/11	
SC2			95		54/85
SX1			14	176	

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A

Appendix

Discrepancies in the Mass Balance of Arsenic, Selenium and Chromium Species

If the speciation method is capable of determining all present species of a given element, then the sum of the independently determined species should equal the total dissolved concentration of this element. However, in practice, this "species mass balance" does not always add up, and there are a number of possible reasons for deviation from this ideal behavior, including (but not limited to):

- The measured total dissolved element concentration is systematically high or low.
- One or more measured concentration of the individual determined species is systematically high or low.
- There are species present in significant amounts that cannot be determined by the speciation method.
- There are significant losses of individual species during preservation or storage (we know from experience that this is not the case for the total element concentration).

The species mass balance was not satisfactory for many of the samples collected in 2003. Three potential causes for this discrepancy have been identified and are discussed next.

Irreversible Formation of Precipitates in the Speciation Samples

In many of the 2003 samples, formation of significant amounts of a white-yellow precipitate was observed when the samples were thawed in a glovebox prior to analysis. It is important to understand that the cryofreezing preservation procedure was chosen to avoid potential speciation changes associated with the commonly used sample acidification preservation approach. Research conducted by Trent University demonstrates unequivocally that, in reducing waters containing free sulfide, acidification destroys reduced thio-species of arsenic and selenium, and either removes them from solution or converts them into oxy-species. This issue would be potentially problematic for a significant fraction of the 2003 samples. Sulfide is not measured for this project; however, several samples clearly smelled of sulfide during collection, and many fall into the Eh-pH range where sulfate reduction occurs. However, for the samples where reducing conditions were not encountered (which is the majority of the collected samples), acid preservation should yield the "correct" speciation results, and eliminate the formation of precipitates.

The precipitates did not re-dissolve when the sample was kept at room temperature for several days; therefore, this precipitation process appears to be irreversible. Also, since the samples were stored and thawed in the absence of air, sample oxidation can be excluded as a reason for the precipitation. Based on geochemical modeling using the known major element composition of the samples, it was assumed that the precipitates consist mostly of calcium minerals, particularly calcite ($CaCO_3$) and gypsum ($CaSO_4$). Researchers at Trent University attempted to re-create the formation of these precipitates by making model solutions mimicking several of the collected samples (in terms of major anions and cations), and subjecting these model solutions to freezing and thawing under various conditions, but precipitates were not observed. This leads to the conclusion that the formation of these precipitates was predominantly caused by the relatively long storage times for the 2003 speciation samples prior to analysis, which resulted from problems with the IC and ICP-MS equipment required for the speciation analyses. This theory is supported by the fact that no precipitates have been observed in any speciation samples collected in 2004, which were typically analyzed for speciation within two weeks after collection.

Since the sum of the measured species in many samples is significantly lower than the independently determined total dissolved element concentration, it was assumed that a fraction of the species was lost from solution by co-precipitation with these minerals. However, it is significant to note that similar discrepancies were also observed when no visible precipitate was formed, both in cryofrozen speciation samples and in the corresponding acid-preserved samples (from which the total dissolved element concentrations were determined) when these were analyzed for speciation.

To resolve this question, it will be necessary to isolate the precipitates, and determine if they contain significant amounts of the respective trace element(s). This will be investigated in the future; however it has not been attempted yet, because it involves chemical digestion methods that will likely alter the speciation of any trace elements bound to the precipitates (if that is indeed the case). Before attempting this task, all other potential explanations (see below) will be fully explored. Each collected speciation sample also has a parallel cryofrozen sample that has not yet been used for any purpose, so if a significant fraction of some trace element species is bound to the precipitates, this research avenue can be pursued by identifying the precipitates mineralogically, devising leaching/dissolution procedures that release the bound metal(loid) species from them without destroying their chemical identity (if that is possible), and then analyzing the parallel speciation samples using the new methods.

Presence of Species that Cannot be Analyzed Using Current Methods

Based on commonly accepted geochemical models, only two inorganic species for each of the three speciation elements are expected in the leachate samples: arsenite [As(III)] and arsenate [As(III)], selenite [Se(IV)] and selenate [Se(VI)], and trivalent chromium [Cr(III)] and chromate [Cr(VI)]. The only other species routinely analyzed for are the organometallic compounds mono- and dimethylarsenate, but due to the low biological activity expected in the types of waters studied here, it is unlikely that these would constitute a significant fraction of the total arsenic present. Therefore, the IC-ICP-MS methods should be capable of measuring all relevant dissolved arsenic, selenium, and chromium species in the collected samples. In support of this assumption, there was no evidence of any additional species for these elements in the 2003 samples (an unknown species would be detected because the ICP-MS will yield the same relative signal for any form of a trace element eluting from the IC column; however, its signal would appear at a different retention time than the known species).

The preceding discussion is limited to dissolved trace element species that can pass through the IC column. Therefore, there are two other possible explanations for the observed discrepancies: a fraction of the trace elements in the speciation samples is present either in a different physical state (since the samples were filtered in the field, geochemists would call this state “colloidal”), or in the form of a dissolved chemical species that does not pass through the IC column. The latter hypothesis could be tested by measuring the dissolved trace element concentrations in the speciation samples after they have been thawed in the glovebox, which will be performed. The presence of colloids is currently under investigation using ultrafiltration as a means of characterizing the size distribution of the trace elements in the samples; at this point, those studies are being hampered by blank issues and unspecific retention behavior on the ultrafiltration membranes.

Systematic Analytical Bias

The Trent University laboratory routinely performs matrix spike experiments as part of their QC protocol, and can demonstrate that there are no significant losses for any of the individual determined species by the fact that matrix spike recoveries are typically quantitative within the margin of analytical error. By contrast, a number of analytical interferences were observed that led to increased total element concentrations, particularly for arsenic and selenium, in some samples. However, all of these issues have been corrected in the data set reported here. Therefore, there is no reason to believe that this potential concern is a major factor in the observed species mass balance discrepancies.

Interpretation of the Reported Speciation Patterns

It is clear at this point that the speciation results reported here do not adequately characterize arsenic, selenium, and chromium speciation in the collected water samples: either the analytical methods “missed” one or more important species per element, or some fraction of the dissolved species has been “lost” during storage. In the first case, a major task becomes to prove this theory, and identify the “missing” trace element species, so that a better and complete understanding of biogeochemical cycling and potential management options for elevated arsenic, selenium, or chromium concentrations in particular settings can be obtained. However, this would mean that the reported concentrations for the “known” species are correct, even though they don’t add up to the total trace element concentration.

In the second case, the reported species concentrations would be wrong, and it is unclear whether they would even have any qualitative meaning. This depends on whether both species of one element are removed from solution by the precipitation process to the same extent, or whether one species is removed preferentially (or exclusively). If the chemical identity of the precipitates were known, one could speculate on the relative removal rates for each metal(loid) species, but in the absence of that knowledge, it is impossible to say if the reported “remaining” speciation patterns in the thawed speciation samples are even somewhat representative of the native geochemical conditions. A preliminary geochemical analysis of the reported speciation data shows that in many samples, the measured speciation patterns do not correspond to thermodynamic equilibrium predictions based on pH and Eh; however, this is not unusual, and has been observed in many studies where no species mass balance issues were reported.

Chromium

The main reason that the chromium speciation results appear incomplete is that Cr(III) has not yet been determined for the 2003 samples, because the derivatization capability was not available at the time. This will be remedied by re-analysis, but is relatively meaningless until the species mass balance issue has been resolved, at least for samples without precipitate formation (for the

2004 samples, where no precipitates have been observed, Cr(III) and Cr(VI) have generally had good species mass balance). Total chromium concentrations agree very well between the two isotopes ^{52}Cr and ^{53}Cr, as well as between the two different ICP-MS instruments that were used, so there is a high degree of confidence in the reported total chromium results. For many samples, Cr(VI) and total chromium agree quite well, and so the assumption that any reported discrepancy is caused by the presence of significant amounts of Cr(III) appears justified. It is especially noteworthy that in all cases where total chromium exceeds 5 µg/L, there is a very strong correlation between Cr(VI) and total chromium (Figure A-1). This is not surprising, because Cr(VI) is very soluble under the hydrogeochemical conditions encountered in the collected samples, while Cr(III) should be almost insoluble.

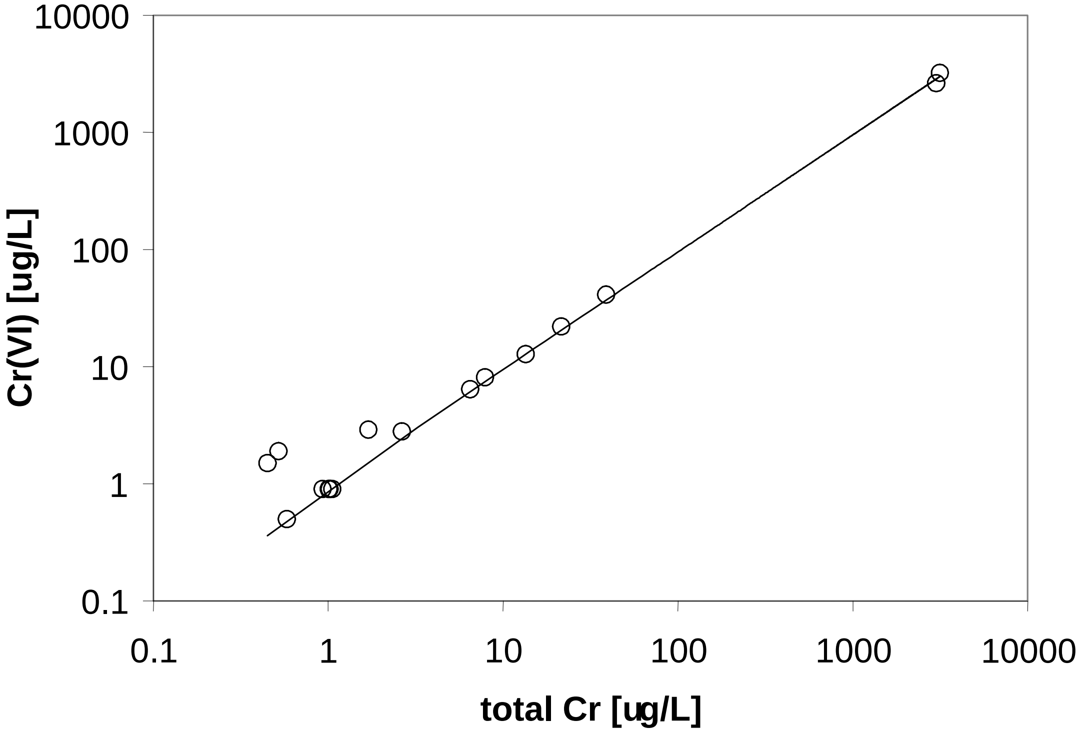

Figure A-1
Total Chromium vs Cr(VI) Concentrations in 2003 Samples

Selenium

Selenium speciation patterns show Se(VI) as the predominant species in 14 out of 22 samples in which at least one of the two selenium species was present above the detection limit. This is in sharp contrast to the speciation predicted for these samples based on their Eh-pH characteristics, which favors Se(IV) and (insoluble) Se^0. Since Se(IV) is generally the more surface-reactive of the two selenium species, this finding supports the hypothesis that a significant fraction of Se(IV) was lost to the precipitates. The species recovery for Se was 36 ± 36 % (average ± standard deviation).

Arsenic

Arsenic speciation patterns show As(III) as the predominant species in 13 of the 17 samples in which at least one of the two arsenic species was present above the detection limit. This is in contrast to the speciation predicted for these samples based on their Eh-pH characteristics, which favors As(V) in most samples, although As(III) is predicted to dominate in certain samples. Since As(V) is generally the more surface-reactive of the two As species, this finding supports the hypothesis that a significant fraction of As(V) was lost to the precipitates. The species recovery for arsenic was 14 ± 19 % (average ± standard deviation).