State of Wisconsin
Department of Administration
Division of Energy

Environmental Research Program

Final Report

September 2005

Characterization of Mercury in Coal Combustion Products Generated in Wisconsin

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This report in whole is the property of the State of Wisconsin, Department of Administration, Division of Energy, and was funded through the FOCUS ON ENERGY program.

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This document describes research sponsored by EPRI and Wisconsin Focus on Energy
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EXECUTIVE SUMMARY

Mercury in coal combustion products (CCPs) produced in Wisconsin was evaluated by collecting solid ash samples from power plants and field leachate samples from CCP landfills. The samples were analyzed for total mercury concentration, volatilization, and speciation of dissolved mercury. The overall results suggest that mercury is stable with respect to leaching and volatilization in the fly ash currently produced.

Field sampling found that concentrations of dissolved mercury are very low in leachate at CCP landfills in Wisconsin, usually less than 50 ng/L. The dissolved mercury concentrations were all well below the Wisconsin Preventative Action Limit for groundwater (200 ng/L). Concentrations of the more toxic organic mercury species, methyl mercury, were less than 1 ng/L in all ten field leachate samples in which it was analyzed. Given these extremely low concentrations, and the low mobility of mercury in groundwater, there is little threat of impacts to groundwater from mercury at existing CCP sites in Wisconsin.

Field and laboratory flux testing was performed to evaluate the potential for volatilization of mercury from the fly ash to the atmosphere in the landfill environment. Factors controlled in the laboratory studies included light, temperature, and moisture. Results indicated that fresh fly ash (collected from the hoppers) generally sorbs mercury from the ambient air. Field tests were carried out continuously over a one week period to allow for a wide range in natural environmental conditions. The field study confirmed the laboratory results, indicating little net gain or loss of mercury from CCPs due to exchange with the atmosphere over the one week period.

Changes in emissions controls that may impact the release behavior of mercury are enhanced mercury capture using activated carbon injection (ACI), and ammonia addition for NOx control. Testing of ash from an ACI demonstration project at a Wisconsin power plant indicated that while the total mercury concentration in the fly ash will increase, leaching and volatilization are still very low. Ammonia-based NOx controls have the limited potential to increase mercury leaching and mobility due to complexation, but only at very high ammonia levels (>1,000 mg/L) and in a narrow pH range between 8 and 9.

ACKNOWLEDGEMENTS

EPRI and the authors would like to acknowledge Dairyland Power Cooperative, We Energies, and Wisconsin Public Service Corporation for their assistance and cooperation, which made this work possible.

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INTRODUCTION

Background

Coal Combustion Products

Coal combustion products (CCPs) refer to the residues resulting from the burning of coal for generation of electricity. The four primary CCPs are fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) solids. Fly ash, bottom ash, and boiler slag are derived from the inorganic mineral matter in the coal, along with small amounts of unburned carbon. FGD solids are the reaction products of sulfur dioxide scrubbers. Scrubber systems using lime or limestone as the sorbent generate solids consisting primarily of calcium sulfate, with small amounts of unused sorbent and fly ash carryover.

U.S. electric utilities generate about 120 million tons of CCPs annually (ACAA, 2003). Fly ash accounts for the largest proportion, about 70 million tons. FGD solids account for about 30 million tons, and bottom ash and boiler slag account for the remainder. Nationally, about 35 to 40 percent of the CCPs are utilized in a variety of applications, primarily related to construction, and the remaining 60 to 65 percent are stored or disposed of in landfills and impoundments. The utilization rate has increased steadily over the last several years.

In Wisconsin, coal-fired power plants account for about 7,500 megawatts (MW) of generating capacity, or 80 percent of the electrical generation in Wisconsin. These plants collectively produce over 1.5 million tons of fly ash, bottom ash, and boiler slag annually. Currently, no operating power plants in Wisconsin have FGD systems, although the use of FGD systems will increase over the next decade, both nationally and within Wisconsin. Wisconsin utilities are among the leaders in CCP utilization, currently using over 60 percent of the ash generated each year. CCPs that are not beneficially reused are managed in landfills; there are currently no ash impoundments in Wisconsin.

Mercury in Coal Combustion Products

Mercury is present in coal and is released during combustion at coal-fired power plants. The total amount of mercury in the fuel coal going into power plants in the United States is 75 tons per year, of which 45 tons, or 60 percent, is emitted from stacks to the atmosphere (EPRI, 2000). The emitted mercury is estimated to be 56 percent elemental mercury (Hg^0), 42 percent ionic mercury (HgII), and 2 percent particulate mercury. Based on these emissions, the amount of mercury retained in coal ash and/or FGD solids is estimated to be about 30 tons per year. Actual amounts at individual plants are variable, depending on coal type and chemistry, control technologies, and furnace configurations.

On March 15, 2005, USEPA issued the Clean Air Mercury Rule to permanently cap and reduce mercury emissions from coal fired power plants. Reducing air emissions will increase mercury concentration in CCPs. The impact that this may have on the potential release of mercury to groundwater and surface water from CCPs is not completely known. An additional concern is the possibility for captured mercury to be reemitted from the CCP to the atmosphere, which would negate the beneficial effect of enhanced capture from the flue gas.

Mercury concentrations are relatively low in CCPs, generally less than 1 mg/kg (EPRI, 2003; Gustin and Ladwig, 2004). While existing data suggest that mercury release via leaching from currently produced CCPs is also low, most of the leachate data were generated using methods with detection limits of 0.2 µg/L or higher; field data using clean sampling methods are extremely limited. There is also very little data on mercury speciation in leachate and groundwater. Mercury concentrations in CCPs are expected to increase as a result of the USEPA regulatory decision to reduce mercury air emissions from power plants, highlighting the need to address data gaps on the fate of mercury captured in CCPs.

Other Constituents

While this project was focused on mercury, concentrations of a wide range of other inorganic constituents were also analyzed in the field leachate samples. Arsenic and selenium are of particular interest within the utility industry. The data reported herein included concentrations of all inorganic constituents measured, as well as speciation of arsenic and selenium. In addition, the research considered leaching behavior of metals determined by sequential leaching, and field and laboratory studies of the attenuation of arsenic and selenium at a CCP landfill site in Wisconsin.

Objectives

The purpose of this project was to evaluate mercury in CCPs generated at Wisconsin power plants. The project included collection of leachate samples and analyses for low levels of the various mercury species, including methyl and dimethyl mercury; laboratory batch and sequential leaching; and volatilization to the atmosphere under laboratory and field conditions. The ash samples tested included fly ash from an activated carbon injection demonstration for enhanced mercury control. These data will serve as a baseline for mercury releases from existing sites in Wisconsin, and can be used to evaluate the potential for mercury releases from CCP management facilities at power plants that employ enhanced mercury capture technologies in the future.

Specific objectives for this project:

- Characterize overall chemistry of CCP leachate generated at field sites in Wisconsin
- Identify the concentration and species of mercury present in the field CCP leachate
- Evaluate the potential for release of mercury to groundwater and air
- Evaluate the mobility of mercury in groundwater
- Measure the speciation of arsenic and selenium in CCP leachate, and species-specific mobility in groundwater

2
APPROACH

Overview

The study consisted of three primary elements:

- Field leachate sampling and analysis
- Laboratory analysis of solid ash samples
- Mercury volatilization testing

Each element is briefly described next. Detailed descriptions of sampling and analysis methods are included in Appendix A.

Field Leachate Sampling and Analysis

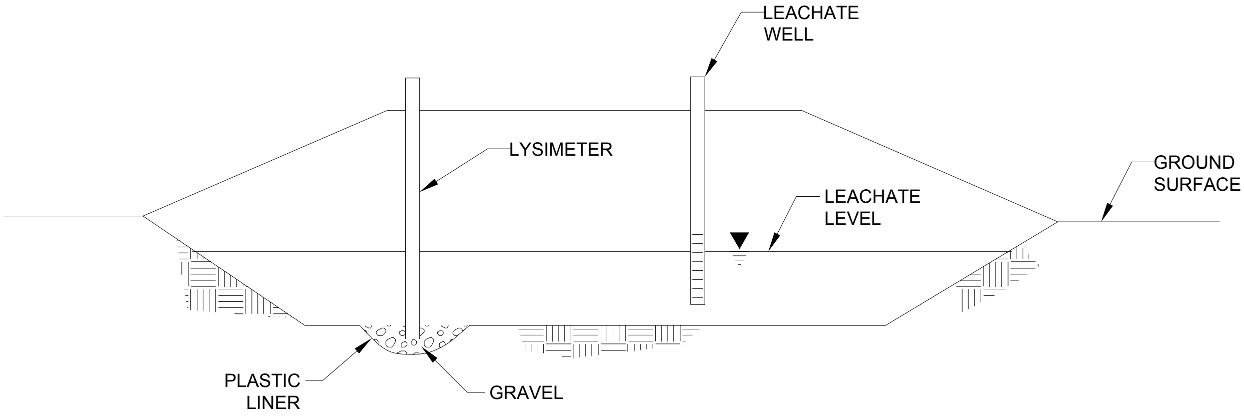
Field leachate samples were collected from six CCP management sites and analyzed for mercury species and other constituents. Results are presented in Sections 3 and 4. In all cases, the management unit was a landfill and the CCP was dry-disposed. Fly ash at Sites A through E was collected by an electrostatic precipitator, and fly ash at Site F was collected using a fabric filter (Table 2-1). The only power plant that changed coal type (bituminous, subbituminous) during the active life of the management site was Plant A. A mixture of source coals is listed for Site C because it receives ash from multiple power plants, some of which also burn blends of bituminous and subbituminous coal. Furthermore, at the time of sampling, the source power plants were burning the same coal as during the active life of the management units.

Table 2-1
Description of Field Leachate Sites

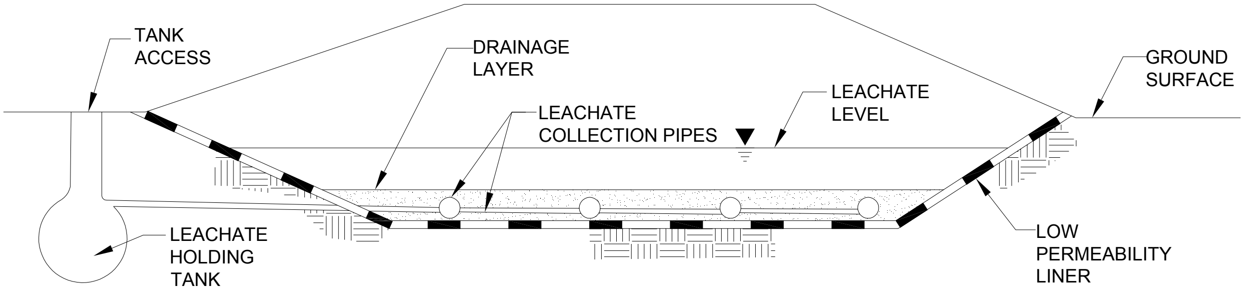
Site	CCP Type***	Source Coal	Leachate Sample IDs*	Leachate Sample Point**
A	FA, BA	Mixture	01	Well
B	FA	Subbituminous	02, 03	Lysimeter
C	FA, BA	Mixture	04, 05, 88, 89	Well, LCS
D	FA	Subbituminous	85, 87	LCS
E	FA, BA	Bituminous	91	LCS
F	FA	Bituminous	92	LCS

* does not include replicates and QC samples
** LCS = leachate collection system
*** FA = fly ash; BA = bottom ash

Leachate samples were collected from wells screened in CCP, lysimeters, and leachate collection systems (Figure 2-1), using low-flow methods whenever possible, and following low-level mercury sampling protocols. The goal was to obtain undiluted samples representative of CCP leachate.



CONSTRUCTION OF LEACHATE WELL AND LYSIMETER



TYPICAL CONSTRUCTION OF LEACHATE COLLECTION SYSTEM

Figure 2-1
Schematic diagram of landfill leachate sampling points

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.

Laboratory Analysis of Solid Ash Samples

Total, recoverable, and leachable mercury concentrations were measured on all of the fresh fly ash samples in the laboratory volatilization study (Sections 3 and 5). These tests respectively determine:

- Total: the total mass of individual elements, in solid form (mg/kg), within the fresh fly ash samples;
- Recoverable: the mass of elements, in solid form (mg/kg), that can be removed from the fly ash sample by a specific, typically aggressive, leaching solution. This is an approximation of the mass that is available to eventually be removed by leaching.
- Leachable: the dissolved concentration (mg/L) of elements removed from the fly ash sample by a specific leaching solution that is typically less aggressive than that used in the recoverable test.

Sequential leaching was performed on one fresh fly ash sample collected from the hopper at Plant B. This analysis was performed to evaluate the associations of inorganic constituents that may affect their leachability; results are discussed in Section 4. Sequential leaching is designed to progressively release different phases within the ash, from the most easily leached phases to the most recalcitrant. The actual amount of a constituent leached is generally dictated by the form it is in, and the conditions under which leaching occurs, particularly pH and redox.

In addition, studies were performed on three fly ash samples to determine the potential for increased Hg concentrations in leachate due to complexation with ammonia (Table 2-2). Results are discussed in Section 3. This testing was performed to determine if ammonia deposition on ash by new NOx control technologies (selective catalytic reduction and selective non-catalytic reduction) may affect future mercury leaching.

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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.

Table 2-2
Fly Ash Samples Used for Complexation with Ammonia Testing

Sample ID	Description
Unit B	subbituminous
Unit C1	blended bituminous/subbituminous
Unit C2	blended bituminous/subbituminous

Mercury Volatilization

Seven fresh fly ash samples were collected from hoppers at five plants that burn bituminous, subbituminous, or blended bituminous/subbituminous coal for analysis of mercury volatilization (Table 2-3). These tests provided data on the release and deposition of mercury associated with fresh fly ash.

Table 2-3
Fly Ash Samples Used in Laboratory Hg Volatilization Tests

Sample ID	Plant	Description	Sample Type
B10A	C	blended bituminous/subbituminous	fly ash
B2A	H	bituminous	fly ash
B3A	F	bituminous	fly ash
S2A-1	G	subbituminous	fly ash
S2A-2	G	subbituminous	fly ash + ACI*
S2A-3	G	subbituminous	fly ash + ACI*
S4A	B	subbituminous	fly ash

* ACI = Activated Carbon Injection
Samples S2A-1,2,3 , B2A,and B3A were also reported in Air & Waste Manage. Assoc.54:320-330,2004

In addition, in-situ Hg fluxes were measured in the field from three different types of substrate (Table 2-4; Figures 2-2 and 2-3) at the Site C fly ash landfill. These tests provide data on the mercury flux at an active fly ash landfill in Wisconsin. All of the volatilization results are presented in Section 5.

Table 2-4
Field Hg Flux Measurement Site Descriptions

Substrate Type	No. of Sampling Locations	No. of Measurement Per Location	Site Description
Fly ash	15	25 (1 location) 33 (1 location) 4 (2 locations) 3 (11 locations)	uncovered fly ash (Figure 2-2)
Vegetated fly ash	20	32 (1 location) 3 (19 locations)	top soil over ash with grass vegetation (Figure 2-3)
Background soil	20	56 (1 location) 2 (2 locations) 3 (17 locations)	natural grass land

Figure 2-2
Mercury volatilization field measurements on barren ash

Figure 2-3
Mercury volatilization field measurements on vegetated ash

3

MERCURY IN CCPS AND IN CCP LEACHATE

Total Composition

The range of Hg total composition values for ash derived from different coal types may vary by several orders of magnitude (EPRI, 2001a). Hg total composition in ash samples is influenced by factors such as the Hg content of the source coal (Figure 3-1), unburned carbon content of the ash, particle size of the ash, and the surface area and morphology of the ash (EPRI, 2001a). The latter three factors are a function of the power plant boiler configuration and emission control devices. Emission control systems also influence total composition in the ash because some technologies, such as a fabric filter with a wet FGD system, remove a higher percentage of mercury from the flue gas than technologies such as a hot-side electrostatic precipitator (Table 3-1). These differences in removal efficiency are reflected in Hg total composition, which tends to be higher in ash from fabric filters (baghouse) and lower in ash collected by electrostatic precipitators (ESPs) (Figure 3-2).

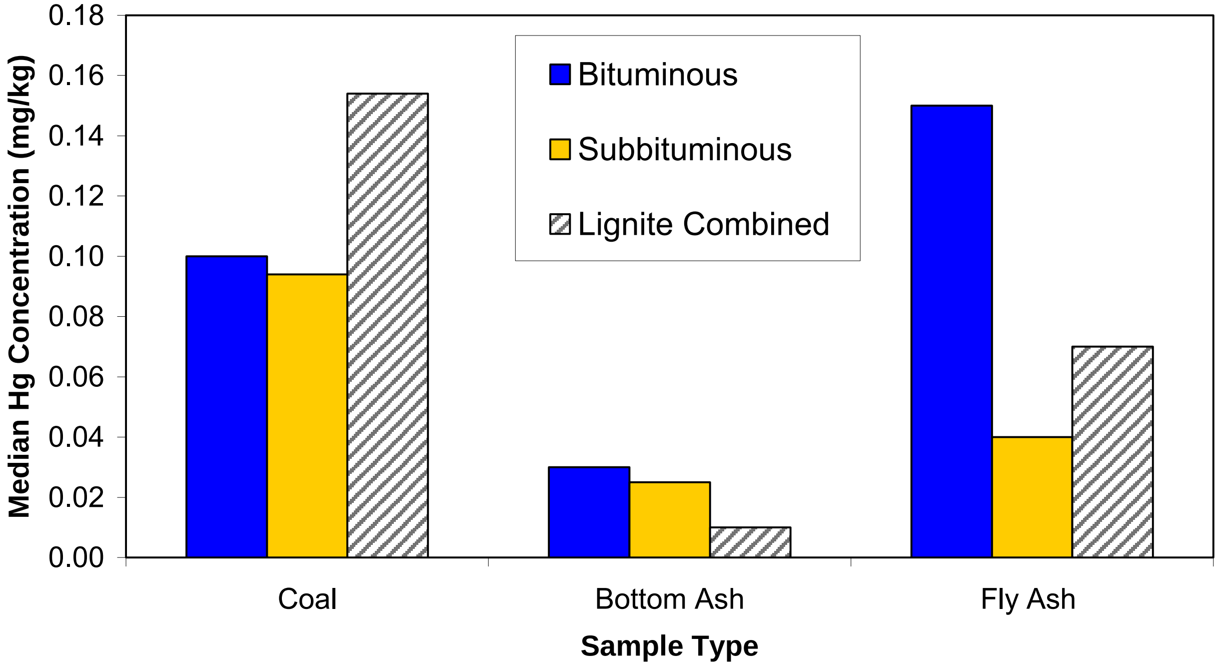

Figure 3-1
Median Hg concentrations in coal, bottom ash, and fly ash by coal type (EPRI, 2001a)

Table 3-1
Mercury Removal Efficiencies of Selected Control Technologies

Air Pollution Control Class	Average Percent Removal Efficiency	Minimum Percent Removal Efficiency	Maximum Percent Removal Efficiency	Average Percent Elemental Hg*	Average Percent Particulates
ESPc	27	0	55	47 (12-85)	1.5
ESPc/FGDw	49	24	70	89 (81-98)	0.4
ESPh	4	0	27	66 (34-91)	1.3
ESPh/FGDw	26	4	65	93 (80-99)	0.65
FBC/FF	86	66	99	23 (3-33)	2
FF	58	40	85	64 (45-84)	0.6
FF/FGDw	88	79	96	96 (81-98)	5
SD/ESP	18	5	25	96 (91-98)	0.4
SD/FF	38	0	99	83 (64-99)	0.5

ESP=electrostatic precipitator, c=cold side, h=hot side; FGD=flue gas desulfurization, w=wet system, d=dry system; FBC=fluidized bed combustion unit; FF=fabric filter; SD=spray dryer.

*In flue gas downstream of the pollution control device; values in parentheses are the range for the control class; see EPRI (2000) for more information on sample collection and locations.

Source: EPRI, 2000.

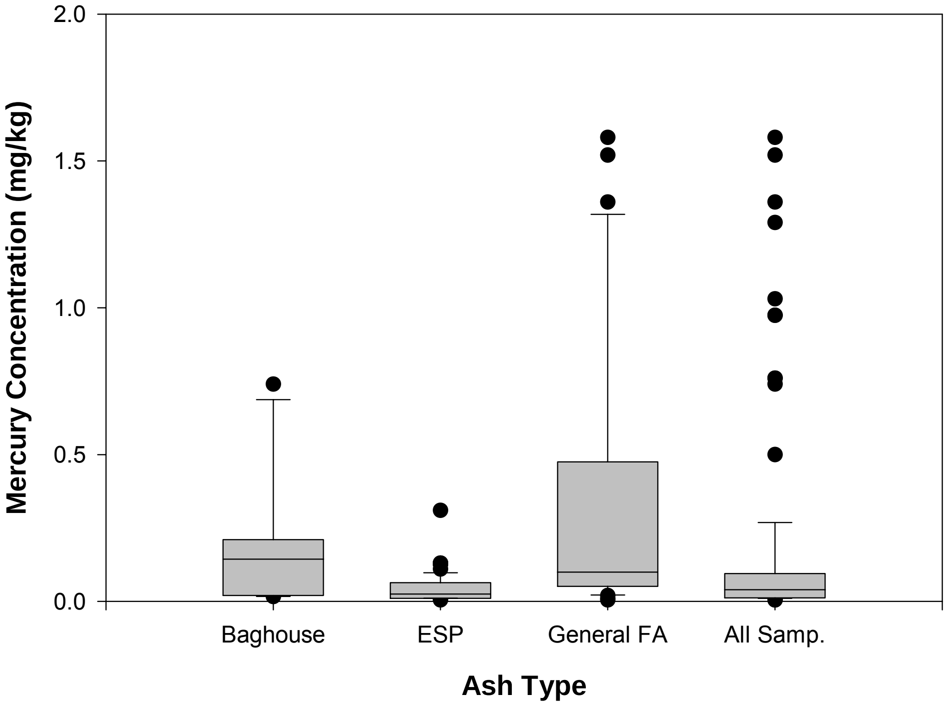

Figure 3-2
Box plot comparing Hg total composition in subbituminous ash samples (source: EPRI, 2001a)

Total Hg concentration in fresh fly ash generated at Wisconsin power plants was determined on samples collected for the volatilization study (Section 5). Excluding the ACI samples[2], total concentrations ranged from 30 to 563 µg/kg (Table 3-2). The Wisconsin values are within the range of Hg concentrations reported for fly ash samples (0.2 to 2,100 µg/kg) throughout the United States by EPRI (2001a). There was no differentiation between bituminous and subbituminous ash samples in this limited data set. Excluding the anomalous result in sample B3A, recoverable concentrations are 25 to 67 percent of the total concentration.

Table 3-2
Total Composition Data for Fresh Fly Ash Samples

Sample	Plant	Description	Hg concentration (µg/kg)	
			Total	Recoverable
B10A	C	blended bituminous/subbituminous	30	14
B2A	H	bituminous	563	133
B3A	F	bituminous	47	72
S2A-1	G	subbituminous	247	92
S2A-2	G	Subbituminous (with ACI)	2300	596
S2A-3	G	subbituminous (with ACI)	1040	439
S4A	B	subbituminous	60	40

Results also presented in Table 5-1

Laboratory Leachate Concentrations

SPLP leach testing was performed on the fly ash samples for which total and recoverable Hg were measured. Mercury concentrations in all of the lab leachates were very low. The highest concentrations were only 2.9 ng/L[3] and 6.9 ng/L (Table 3-3). These concentrations occurred in the two ACI samples, which also had the highest total and recoverable Hg concentration (Table 3-2). All other samples had Hg concentrations lower than 1 ng/L.

Samples B10A, B3A, and S4A were obtained from the hoppers at the power plants that supplied CCP to field leachate Sites C, F, and B, respectively. In all three cases, the field leachate dissolved Hg concentrations (see Table 3-4) were higher than the leach test concentrations. Based on this limited sample set, it appears that the SPLP method may under represent Hg concentration in CCP leachate, although both lab and field concentrations are low.

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[2] No power plants in Wisconsin currently use this technology.

[3] ng/L indicates *nanograms* per liter; 1 ng/L is one part per trillion, or 0.001 ug/L.

Table 3-3
Laboratory Leach Test Results for Hg

Sample ID	Plant	Description	Sample Type	Hg (ng/L)
B10A	C	blended bituminous/subbituminous	fly ash	<0.05
B2A	H	Bituminous	fly ash	<0.05
B3A	F	Bituminous	fly ash	<0.05
S2A-1	G	Subbituminous	fly ash	0.7
S2A-2	G	Subbituminous	fly ash + ACI*	2.9
S2A-3	G	Subbituminous	fly ash + ACI*	6.9
S4A	B	Subbituminous	fly ash	0.9

Leach Method: SW-846 1312 (SPLP)

Field Leachate Concentrations

Data Summary

Dissolved Mercury

Dissolved mercury (Hg_d) concentrations were low, ranging from 2 to 61 ng/L (Table 3-4). The highest concentration (sample 88) of the ten field leachate samples was from Site C, where three other samples had concentrations lower than 10 ng/L. Sample 88 is a resample of sample 04; these samples were collected from the same leachate collection system manhole during separate trips (June 2003 and September 2004, respectively). Sample 88 had a slightly lower pH (8.6) in 2004 compared to sample 04 in 2003 (9.3); partially reducing conditions, as indicated by relatively low Eh, dissolved oxygen, and relatively high concentration of Se(IV); and less Ca and more CO_3 than the 2003 sample (see Tables 4-1, 4-2, and 4-4). The two samples from this location also had considerably different concentrations for many minor and trace elements, both for geochemically reactive constituents, such as manganese, and less reactive constituents, such as lithium (see Table 4-3). This is an active site that receives varying percentages of ash from subbituminous and bituminous coals, and the observed differences in Hg_d concentrations between samples 04 and 88 may reflect differences in the characteristics of the ash most recently added at the time of sampling, or differences in geochemical conditions.

Table 3-4
Hg Speciation Results

Sample ID	Type	Site	CCP	Coal Type[+]	Dissolved (ng/L) DMM	Dissolved (ng/L) $MeHg_d$	Dissolved (ng/L) Hg_d	Particulate (ng/L) $MeHg_p$	Particulate (ng/L) Hg_p
01	Leachate	A	FA, BA	Mix	0.055	*	*	0.03	*
02	Leachate	B	FA	Sub	0.005	0.11	14.4	0.03	254
03	Leachate	B	FA	Sub	< 0.005	0.09	18.4	< 0.02	26
04	Leachate	C	FA, BA	Mix	0.010	0.26	5.9	0.04	< 1
05	Leachate	C	FA, BA	Mix	< 0.005	0.12	2.1	0.09	44
85	Leachate	D	FA	Sub	**	0.22	29.5	0.03	23
86	Duplicate 85	D	FA	Sub	**	0.20	32.2	0.03	10
87	Leachate	D	FA	Sub	**	0.22	36.5	0.05	16
88	Leachate	C	FA, BA	Mix	**	0.76	60.6	< 0.02	11
89	Leachate	C	FA, BA	Mix	**	0.03	5.7	< 0.02	13
91	Leachate	E	FA, BA	Bit	**	< 0.02	2.1	< 0.02	3
92	Leachate	F	FA	Bit	**	0.12	3.8	< 0.02	52
83	field blank				*	0.03	1.9	< 0.02	15
84	equipment blank				**	0.06	0.9	< 0.02	6
90	equipment blank				**	< 0.02	1.5	< 0.02	3

* no result, sample broken
** no result, sample failed QC criteria
[+] Bit = bituminous; Sub = subbituminous; Mix = mixture of bituminous and subbituminous

A key indicator of geochemical conditions is pH, which influences both leaching and sorption. There was not a linear correlation between pH and dissolved Hg concentration (Figure 3-3). The highest Hg concentration (sample 88) occurred at a pH of 8.6. This result is of interest because leach testing of fly ash at multiple pH values, reported later in this section, often yielded the highest Hg concentrations in the pH range of 8 to 9, and sample 88 is the only field leachate with a pH in this range. However, more research in this area is needed before any definitive conclusions can be drawn.

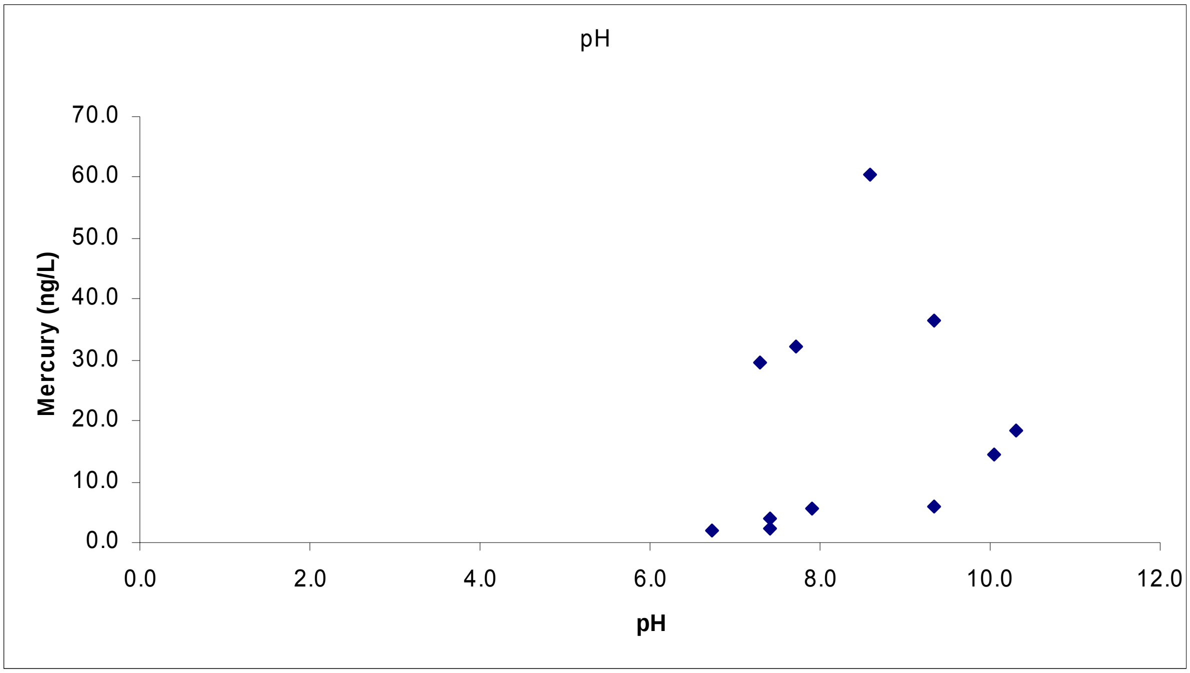

Figure 3-3
Relationship between Hg in field leachate and pH

Other constituents that potentially affect mercury leaching are alkalinity, organic carbon, and ions such as SO_4, Cl, Fe, and Mn (Table 3-5). No relationship is apparent in the field leachate data for SO_4, Cl, or Fe (Figure 3-4). However, there does appear to be a relationship with alkalinity (expressed as total inorganic carbon), organic carbon (expressed as total organic carbon), and Mn:

- Hg concentrations are lower than 10 ng/L when Mn concentrations are greater than 50 µg/L. The effect of manganese on Hg concentrations at these sites is unclear. Mercury is strongly sorbed to manganese oxides, and it is possible that the elevated Mn concentrations are indicative of abundant manganese oxides at these CCP sites.

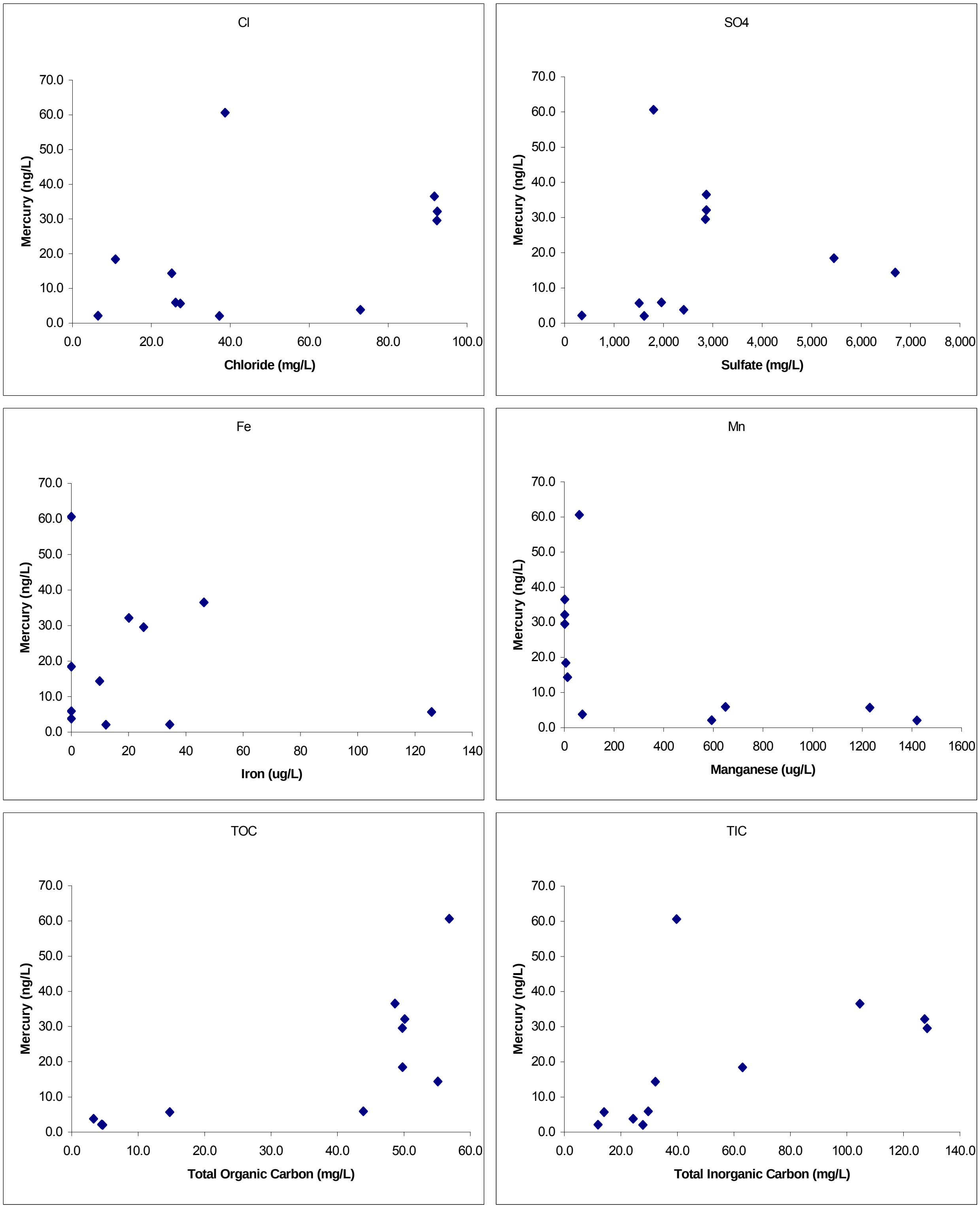

Figure 3-4
Hg concentration in leachate as a function of other water quality parameters

Table 3-5
Influence of Water Quality Parameters on Hg in CCP Management Settings (EPRI, 2003)

Parameter	Ponds	Landfills
Calcium	Can decrease gill uptake of Hg by fish, less important factor for Hg methylation	Little influence on Hg methylation
Chloride	Forms Hg complexes that keep Hg in solution; both charged and uncharged complexes can be formed; charged complexes may be less available for methylation	Same role in porewater as in pond
Dissolved Organic Carbon	Forms Hg complexes that keep Hg in solution; reduces photodemethylation and photoreduction of Hg(II); provides energy source for bacteria	Forms Hg complexes that keep Hg in porewater; provides energy source for bacteria
Dissolved Oxygen	Methylation occurs at oxic-anoxic (O/A) interface that may occur in water column or sediment; influences demethylation process and rate	Same role as in pond
Nitrogen	Needed to support primary producers (algae, plants) that provide source of organic matter for heterotrophic bacteria (e.g. sulfate reducers), which generate reducing conditions	May support bacteria
Organic Carbon Content	Provides substrate for sulfate-reducing bacteria (SRB); decomposition promotes anoxic conditions in water or sediment.	Same role as in pond
pH	Influences methylation rate, faster under acidic conditions; alkaline conditions favor greater reduction to Hg(0) and evasion	Influences methylation rate and redox conditions
Phosphorus	Needed to support primary producers (algae, plants) that provide source of organic matter for heterotrophic bacteria (e.g. sulfate reducers), which generate reducing conditions; influences extent of biodilution if P is limiting nutrient	May support bacteria
Sulfate	Necessary for some SRB that can methylate Hg; <10 mg/L may be optimum for some SRB species, but not others; at high sulfate concentrations, methylation can occur as seen at mine sites, estuaries, and coastal waters and in lab experiments.	Same role as in pond
Sulfide	Can form complexes with Hg and solid-phases; dissolved neutral HgS species can be methylated, but possible inhibitor of methylation at high sulfide concentrations	Same role as in pond
Moisture Content	Likely to be adequate in pond sediment, consisting of ash or sludge	Needed to support SRB, could be limiting in landfill
Suspended Solids	Provide surfaces for Hg sorption, which can then settle and be buried below active methylation zone (O/A interface)	Hg in leachate will sorb to ash/sludge particles

- Hg concentrations in leachate are highest when total organic carbon is 50 mg/L or greater. Organic carbon forms complexes with Hg, keeping more mercury in solution (Ravichandran et al., 1999).
- There appears to be a positive, increasing correlation between Hg concentration in leachate and total inorganic carbon.

Consistent with results of a broad sampling of field leachates at CCP management sites in the United States (EPRI, 2005), Hg concentrations were higher in leachate from the two sites that received ash from subbituminous coal (greater than 10 ng/L) than in leachate from the two sites that received ash from bituminous coal (less than 5 ng/L).

Monomethyl and Dimethyl Mercury

Bacteria have the ability to convert inorganic mercury to methyl mercury ($MeHg_d$) and dimethyl mercury (DMM), which are more toxic than inorganic mercury. Such reactions should be limited in a landfill CCP environment due to the low amount of moisture, which is necessary for anaerobic bacterial activity (EPRI, 2003). Specifically, sulfate reducing bacteria have been identified as important to the methylation process. The high sulfate, low iron, and relatively high Eh results from the field leachate samples suggest that sulfate-reducing conditions were not encountered within the CCP environments sampled for this analysis.

DMM results were lower than 0.06 ng/L in the samples that passed QC (samples 01 through 05). Samples 84 through 92 reported higher DMM concentrations than samples 01 through 05; however, the second highest concentration was from equipment blank sample 84 (0.81 ng/L). As a result, DMM samples 84 through 92, which were collected on a single trip, failed to meet QC criteria, and were not reported here.

$MeHg_d$ concentrations ranged from 0.03 to 0.76 ng/L, with a median concentration of 0.16 ng/L. The highest and lowest concentrations were both collected from Site C. $MeHg_d$ concentrations displayed a tendency to increase with Hg_d concentrations (Figure 3-5). There is some indication that the correlation is different for bituminous and subbituminous coal ash types, but the dataset is too small for definitive conclusions. The $MeHg_d$ concentrations were between 1 and 6 percent of Hg_d concentration in three of the four samples from Site C and in the sample from Site F, while the remaining samples has less than 1 percent $MeHg_d$.

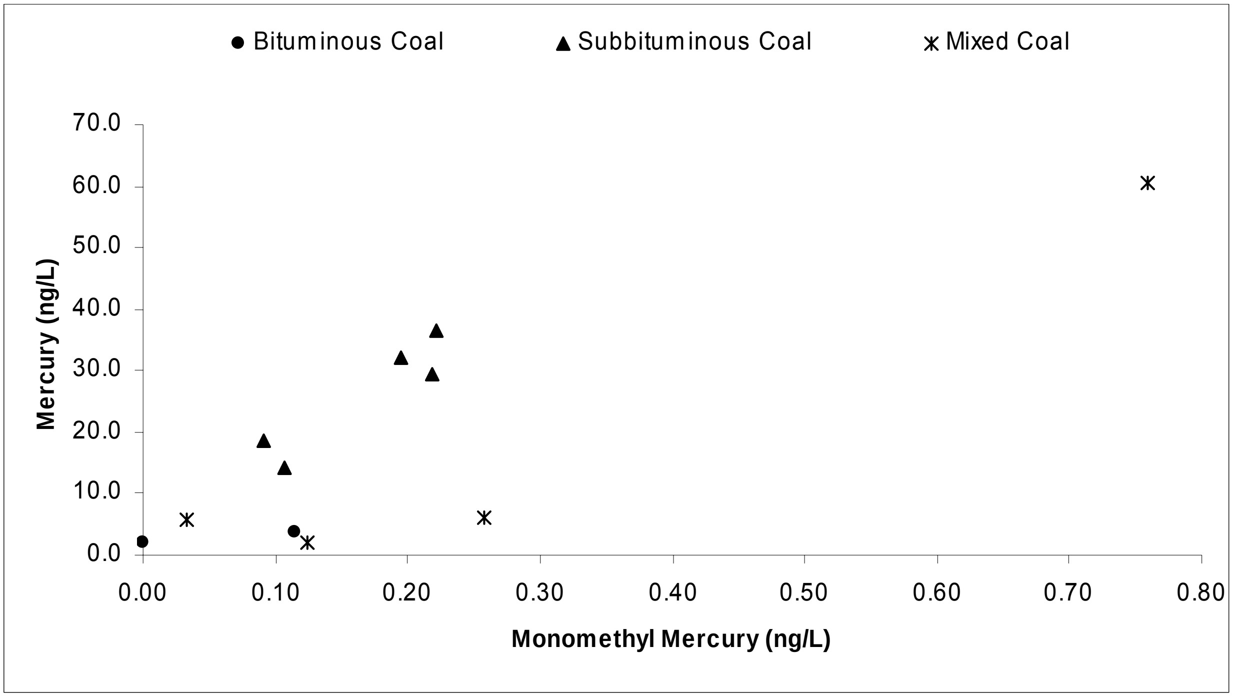

Figure 3-5
Relationship between Hg_d and $MeHg_d$ concentrations by source coal type

Particulate Mercury

Particulate mercury (Hg_p) is a measure of the mercury on colloids in the water, which accumulate on the filter during sampling. As such, the Hg_p 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.

The Hg_p concentrations in the Wisconsin field leachate samples were low, ranging from <1 to 254 ng/L (Table 3-4). The highest concentration (sample 02) was obtained from a lysimeter at Site B, where subbituminous fly ash was managed. A second lysimeter at the same site had a particulate concentration of 26 ng/L. The Hg_d concentration associated with these two samples did not exhibit the variability of the particulate concentrations, although other trace constituents had considerable variability (see Table 4-3). There was no relationship between Hg_p and Hg_d concentration, nor was there a relationship between Hg_p concentration and pH (Figures 3-6 and 3-7).

The particulate concentrations of monomethyl mercury ($MeHg_d$) were only a small fraction (<1 percent) of the Hg_p concentration at all sites except one sample from Site C (>4 percent). Nearly half were non-detect and the highest value was 0.09 ng/L. These results indicate that colloidal transport is not a significant transport mechanism for the organic form of Hg.

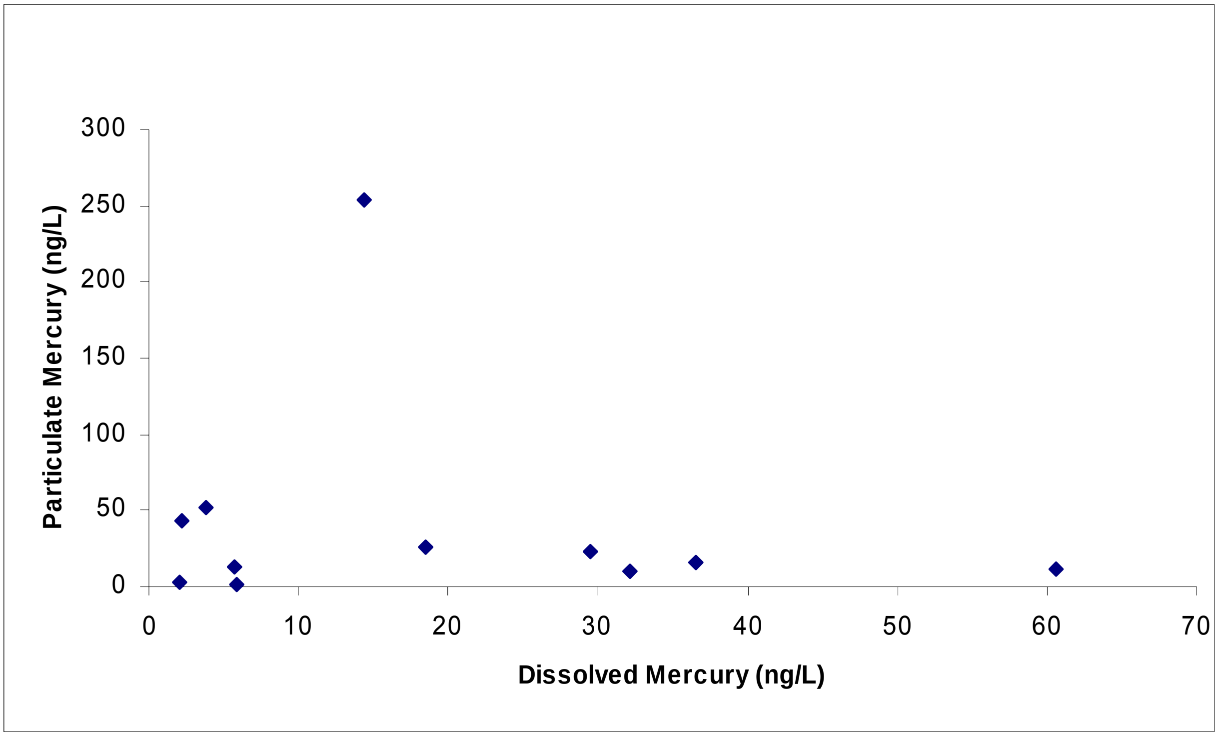

Figure 3-6
Comparison of dissolved and particulate Hg concentrations

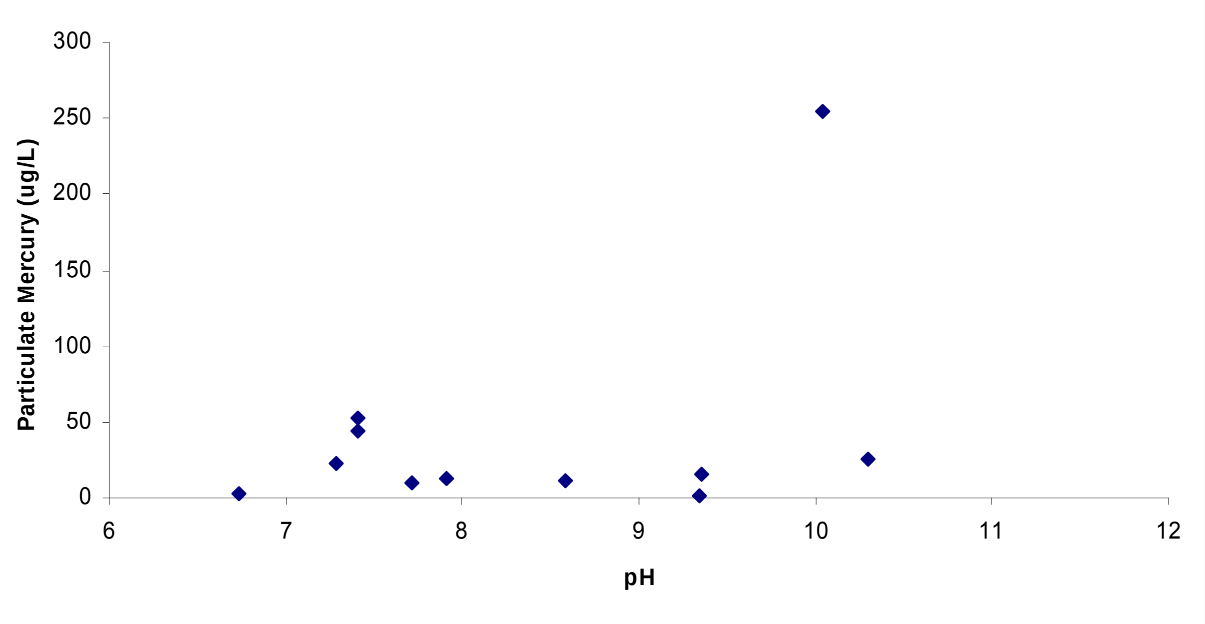

Figure 3-7
Relationship of Hg_p and pH

Complexation with Ammonia

Introduction

Ammonia-based systems, such as selective catalytic and non-catalytic reduction (SCR and SNCR), are increasingly being used to control nitrogen oxides (NO_x) at coal-fired power plants. Application of SCR and SNCR controls is expected to increase significantly over the next five to ten years.

The ammonia in SCR and SNCR systems can influence mercury in fly ash in two ways. First, recent research suggests that the SCR/SNCR systems may also oxidize Hg, particularly at plants burning eastern bituminous coals. Since oxidized mercury is more readily captured from the flue gas than elemental Hg, the use of SCR/SNCR may lead to higher concentrations collected in the air emissions control systems (EPRI, 1999).

Second, unreacted ammonia, referred to as ammonia slip, can deposit on the fly ash. This ammonia is present in a highly soluble form (EPRI, 2001b). When water contacts the fly ash, the ammonia will partition to the gas or water phase. Above pH 9.3, most of the ammonia partitions to the gas phase. Below this pH, most will partition to the water phase. At low to moderate pH, ammonia concentrations in leachate may range from tens to hundreds of ppm (EPRI, 1999 and 2001b). Ammonia in solution is known to form aqueous complexes with metals, including Hg, thereby increasing their solubility (EPRI, in preparation; Wang et al., 2005).

Laboratory studies were performed on three fly ash samples to determine the potential for increased Hg concentrations in leachate due to complexation with ammonia. Batch leaching tests were used, with controlled spikes of ammonia. For each sample, tests were performed at the natural pH of the fly ash, as well as two other pH levels. All three samples had natural pH levels greater than 11.

Mercury Leaching as a Function of pH and Ammonia Concentration

The fly ash from Unit B leached very low levels of mercury under all pH and ammonia conditions (Figure 3-8). Hg concentration in field leachate from this site was 14.4 and 18.4 ng/L (Site B, Table 3-4). The highest Hg concentration in the ammonia leach test was 10.5 ng/L, at the lowest pH and highest ammonia addition (Table 3-6). Under natural pH conditions, the highest Hg leach test concentration was 5 ng/L. This sample was very alkaline and it was difficult to adjust the pH downward. The results suggest that ammonia addition will have little or no impact on mercury leaching from this ash.

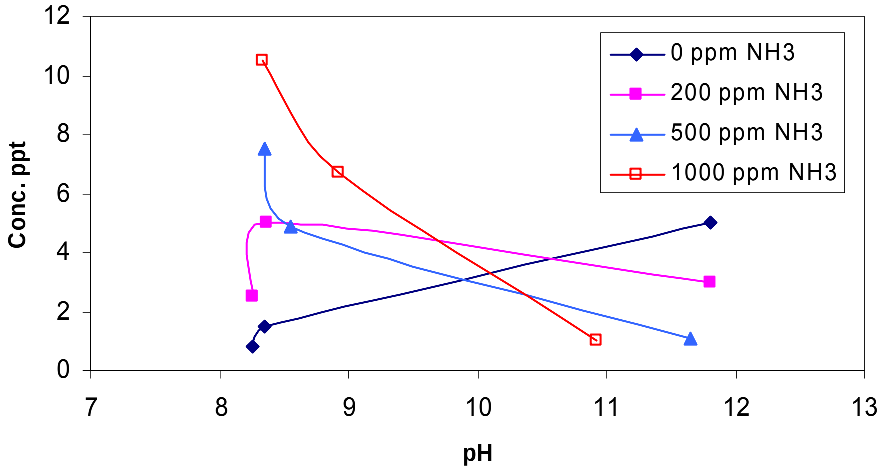

Figure 3-8
Plot of Hg leaching as a function of pH and ammonia concentration for the Unit B sample

Table 3-6
Hg Leaching as a Function of pH and Ammonia Concentration

Ammonia Concentration (mg/L)	**Unit B**		**Unit C1**		**Unit C2**	
	pH	**Hg (ng/L)**	**pH**	**Hg (ng/L)**	**pH**	**Hg (ng/L)**
0	11.80	5.0	11.48	12.5	11.83	8.6
	8.35	1.5	8.90	6.5	9.02	7.7
	8.25	0.8	8.20	10.0	3.75	1.2
200	11.80	3.0	11.50	7.5	11.7	8.8
	8.36	5.0	8.75	26.7	8.80	10.8
	8.26	2.5	8.13	28.5	3.70	1.2
500	11.65	1.1	11.38	1.0	11.55	15.8
	8.55	4.9	8.73	80.6	8.60	12.5
	8.35	7.5	8.12	15	3.70	2.4
1000	10.93	1.0	10.60	2.9	10.74	14.4
	8.93	6.7	8.60	464	8.40	19.1
	8.33	10.5	8.10	120	3.60	2.2

The fly ash from Unit C1 exhibited a larger Hg concentration range in the batch leaching tests than the Unit B sample, 1.0 to 464 ng/L (Table 3-6). Similarly, field leachate from the landfill receiving ash from this unit had a large range and the highest concentration of the field leachate samples, 2.1 to 60.6 ng/L (Table 3-4). The lowest ammonia leach test concentrations were observed under alkaline conditions, ranging from 1.0 to 12.5 ng/L, and concentrations decreased with increasing ammonia levels at this pH. At pH of about 8.6, Hg concentrations were generally higher and consistently increased with increasing ammonia addition. The highest Hg concentrations were observed at pH 8.6 and high ammonia addition (>500 mg/L). For ammonia concentration less than 500 mg/L, the magnitude of the increase is significantly lower (Figure 3-9). At pH near 8, the ammonia effect was only observed at the highest ammonia concentration and Hg concentrations were less than 150 ng/L.

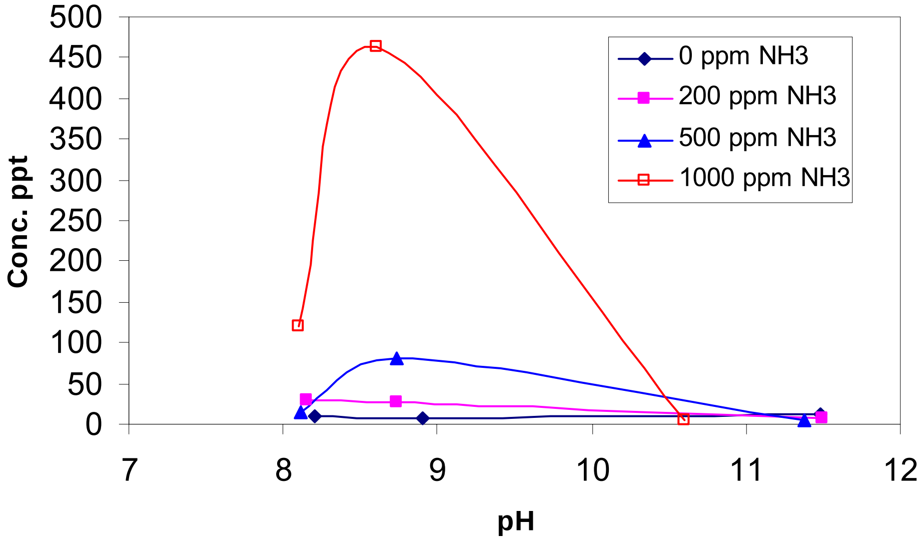

Figure 3-9
Plot of Hg leaching as a function of pH and ammonia concentration for the Unit C1 sample

The fly ash from Unit C2 yielded relatively low Hg concentrations under all ammonia leach test conditions. Field leachate for this site had Hg concentrations ranging from 2.1 to 60.6 ng/L. The maximum observed ammonia leach test concentration was 19.1 ng/L, for pH 8.4 and ammonia addition of 1,000 mg/L. At very low pH levels (<4), Hg concentrations were very low for all ammonia additions (<3 ng/L). In general, Hg concentrations increased with increasing ammonia additions, with the greatest impact at pH levels near 8.5 to 9.0, but the magnitude of the effect was small (Figure 3-10).

At pH values of 10 to 11, mercury leaching was low for all ammonia addition concentrations. In fact, Hg concentrations tended to decrease with increasing ammonia addition at these very alkaline pH levels. In all cases, the effect of ammonia on mercury leaching was greatest in the pH range of about 8.5 to 9.0. Under field conditions over the long-term, the pH of the ash leachate is likely to eventually decrease to the 8.5 range as alkalinity is depleted. However, the ammonia is highly soluble and will rapidly leach from the ash, and it is unlikely that significant amounts of ammonia will be present over the long term. The results suggest that use of ammonia-based NO_x controls at these plants will not significantly affect mercury leaching from the fly ash, as long as the ash is not blended with another material that would lower the pH.

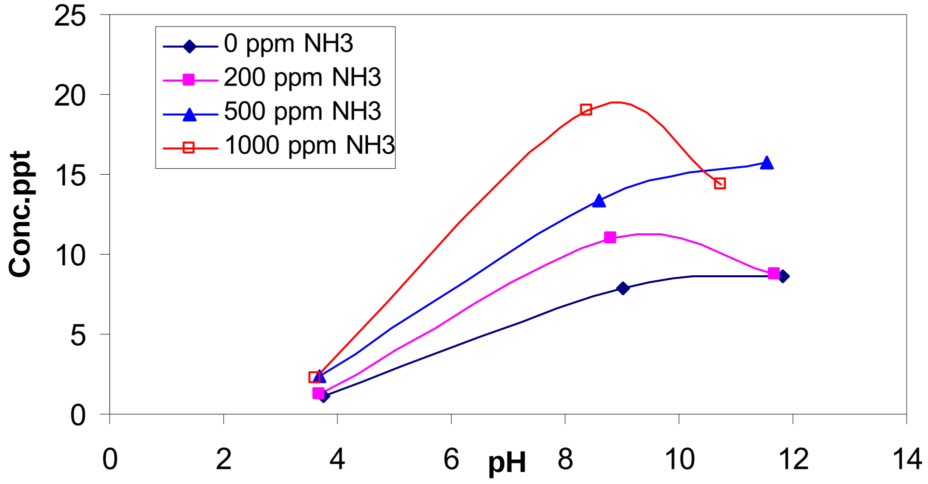

Figure 3-10
Plot of Hg leaching as a function of pH and ammonia concentration for the Unit C2 sample

Key Points

- Total mercury concentrations in fly ash samples collected for this study ranged from 30 to 563 µg/kg, and were comparable to concentrations reported for fly ash throughout the United States. Concentrations in fly ash samples with activated carbon for mercury control were 1,040 to 2,300 µg/kg.
- Concentrations of mercury in field leachate samples were low, ranging from 2 to 61 ng/L, with a median concentration of 14 ng/L. Concentrations in leachate from subbituminous ash were higher than in leachate from bituminous ash, although the sample set is small.
- Concentrations of organic mercury species in Wisconsin coal ash leachates were very low, less than 1 ng/L in all samples. In most samples, concentrations of organic mercury species were less than 1 percent of inorganic mercury species.
- Ammonia in ash leachate associated with NOx controls is not expected to significantly increase mercury leaching. Significantly increased leaching due to ammonia complexation with mercury occurred only at very high ammonia concentrations (>1,000 mg/L) in a limited interval between pH 8 and 9.

4

OTHER CONSTITUENTS IN CCPS AND IN CCP LEACHATE

Introduction

The focus of this effort was Hg; however, the field sampling effort afforded an opportunity to analyze for other constituents that may be found in coal ash leachate in Wisconsin. Of particular interest to the utility industry are concentrations and speciation of key trace constituents such as arsenic and selenium. A sequential leaching study of a fresh ash sample collected from a one of the power plants was performed to obtain additional insights into the leaching process.

Field Leachate

Field Parameters

The leachate samples had pH ranging from neutral to alkaline (Table 4-1). Relatively low dissolved oxygen and Eh readings suggest that samples from Sites A, B, and C were less oxic than samples from Sites D, E, and F. The less oxic samples were obtained from a leachate well and lysimeter, while the more oxic samples were obtained from leachate collection systems.

Major Constituents

The constituent with highest concentration in the leachate samples was SO_4, which ranged from 350 to 6,690 mg/L, and had a median concentration of 2,185 mg/L (Table 4-2). Na had the next highest concentration (93 to 3,410 mg/L, median of 754 mg/L). Total carbonate concentrations (HCO_3 + CO_3) were usually above 100 mg/L (35 to 653 mg/L, median of 157 mg/L). All other major constituents were typically less than 100 mg/L.

Ternary plots of the major constituents were prepared to characterize the major ion chemistry of the field leachate samples (Figure 4-1). Anion composition was completely dominated by SO_4 for all ash types, as is typical for ash leachate. Cation composition was dominated by Na and K for the leachates of ash derived from subbituminous coal. Ca and Mg were present in higher percentages for leachates derived from bituminous coal ash, while mixed bituminous/subbituminous ashes were intermediate in nature.

Table 4-1
Field Measurements of Indicator Parameters

Sample ID	Type	Site	CCP	Coal Type⁺	Temp (° C)	EC (mS/cm)	DO (*)	pH (SU)	Eh (mV)
01	Leachate	A	FA, BA	Mixture	20.2	3.5	0.1	11.6	-15
02	Leachate	B	FA	Subbituminous	21.5	12.8	0.2	10.0	49
03	Leachate	B	FA	Subbituminous	15.4	11.2	0.2	10.3	53
04	Leachate	C	FA, BA	Mixture	14.9	3.8	0.2	9.3	59
05	Leachate	C	FA, BA	Mixture	21.3	0.8	0.2	7.4	184
85	Leachate	D	FA	Subbituminous	16.1	7.3	67.0	7.3	204
86	duplicate 85	D	FA	Subbituminous	16.5	7.4	61.1	7.7	204
87	Leachate	D	FA	Subbituminous	17.4	7.3	69.4	9.4	185
88	Leachate	C	FA, BA	Mixture	12.9	4.3	27.5	8.6	24
89	Leachate	C	FA, BA	Mixture	15.1	3.5	37.0	7.9	85
91	Leachate	E	FA, BA	Bituminous	16.9	3.4	86.1	6.7	193
92	Leachate	F	FA	Bituminous	15.8	4.9	94.7	7.4	203
83	field blank				12.4	0.0	84.0	6.2	213
84	equipment blank				13.7	0.0	73.3	5.4	245
90	equipment blank				13.4	0.0	81.1	5.9	222

* Dissolved oxygen for samples 1-5 was measured in mg/L; samples 83-92 in percent of saturation

Table 4-2
Major Constituent Concentrations

Sample ID	Type	Site	CCP	Coal Type[+]	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO_4 (mg/L)	TOC (mg/L)	TIC (mg/L)	HCO_3* (mg/L)	CO_3* (mg/L)
01	Leachate	A	FA, BA	Mix	9.84	86.2	255	0.78	443	909	13.9	6.9	1.7	32.9
02	Leachate	B	FA	Sub	18.7	25.2	81.6	0.59	3,410	6,690	55.1	32.2	108.2	54.6
03	Leachate	B	FA	Sub	9.12	10.9	78.9	0.53	2,910	5,450	49.8	63.1	166.0	152.3
04	Leachate	C	FA, BA	Mix	218	26.2	21.2	69.8	672	1,960	43.9	29.7	137.0	13.8
05	Leachate	C	FA, BA	Mix	70.5	6.48	0.95	15.3	92.6	350	4.5	11.9	60.4	0.1
85	Leachate	D	FA	Sub	8.72	92.4	74.2	9.17	1,560	2,850	49.8	128	652.3	0.6
86	duplicate 85	D	FA	Sub	10.7	92.5	76.8	10.3	1,560	2,870	50.1	128	646.8	1.5
87	Leachate	D	FA	Sub	6.32	91.7	72.6	6.67	1,560	2,870	48.7	105	481.5	49.6
88	Leachate	C	FA, BA	Mix	52.1	38.7	31.5	43.5	837	1,800	56.8	39.7	198.2	3.5
89	Leachate	C	FA, BA	Mix	73.5	27.3	5.53	16.1	651	1,510	14.7	14.1	71.2	0.3
91	Leachate	E	FA, BA	Bit	392	37.2	23.4	188	117	1,610	4.6	27.8	141.4	< 0.1
92	Leachate	F	FA	Bit	431	73.0	219	69.0	455	2,410	3.3	24.3	123.5	0.1
83	field blank				< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.3	0.2	1.1	<0.1
84	equip. blank				< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.3	0.2	1.2	<0.1
90	equip. blank				0.2	< 0.1	< 0.1	< 0.1	1.3	< 0.1	0.4	0.3	1.4	< 0.1

* HCO_3 and CO_3 calculated from TIC and pH based on the Henderson Hasselbach equation

[+] Bit = bituminous; Sub = subbituminous; Mix = mixture of bituminous and subbituminous

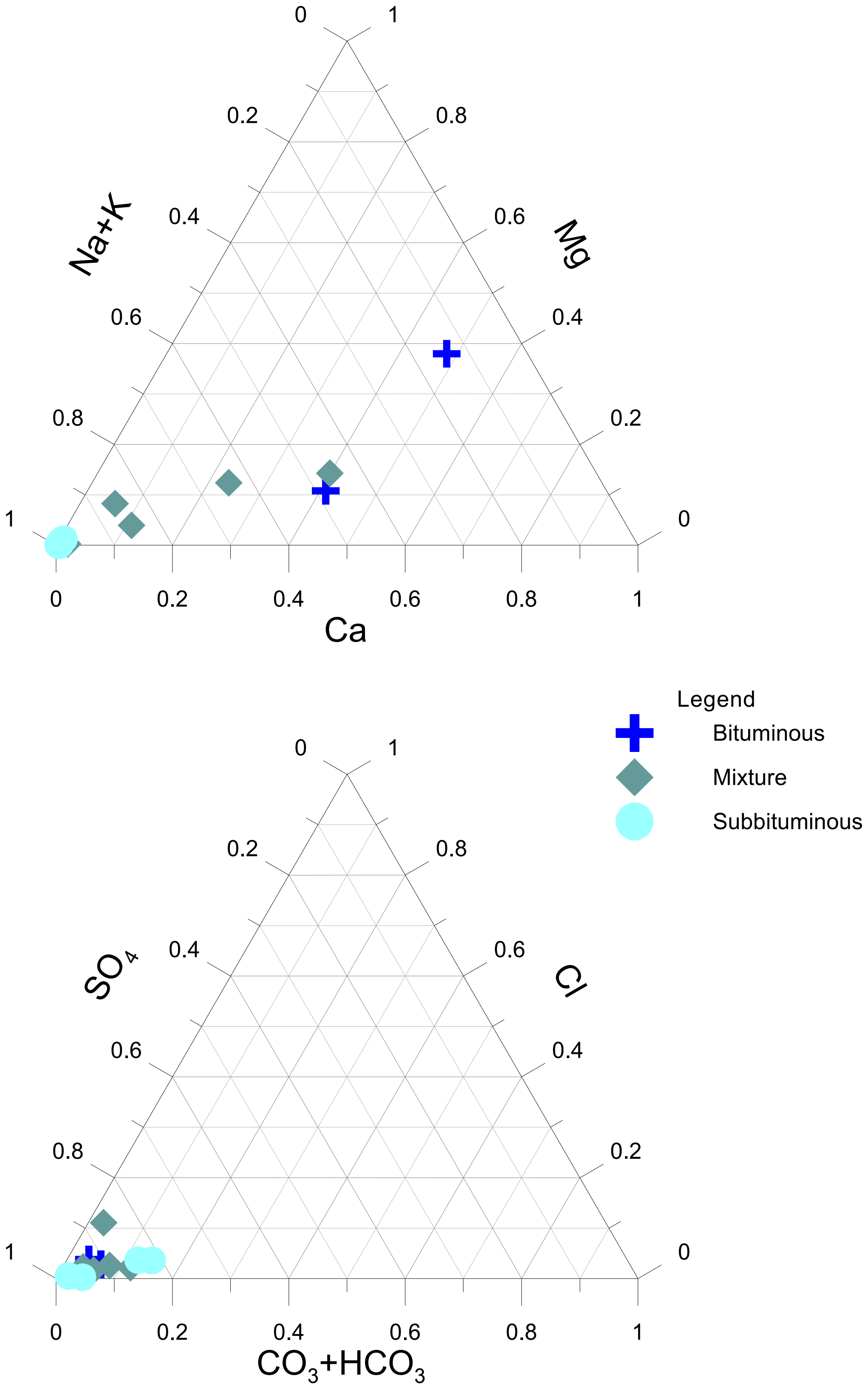

Figure 4-1
Ternary plots showing percentages of major constituents in CCP leachate

Minor and Trace Elements

Ag and Tl were not detected in any leachate samples (Table 4-3). Be was only detected in one of the ten leachate samples, and that concentration (0.14 µg/L) was only slightly higher than the detection limit of 0.10 µg/L. All other analyzed constituents were detected in more than half of the samples.

B had the highest maximum and median concentration of the trace and minor constituents (89,500 and 5,950 µg/L, respectively; Figure 4-2). Mo and Si concentrations were greater than 1,000 µg/L in most samples. Al concentrations were greater than 1,000 µg/L in leachate samples for ash derived from subbituminous coal, and below detection limits in the two samples for ash derived from bituminous coal. Similarly, Cr concentrations were greater than 1,000 µg/L in leachate samples for ash derived from subbituminous coal, and low in the two samples for ash derived from bituminous coal

The effect of source coal on leachate composition has previously been described, most recently in a broad field study where 81 leachate samples were collected at 33 CCP sites across the United States (EPRI, 2005). In addition to Al, that study included results showing that landfills receiving subbituminous coal ash yielded higher leachate concentrations of As, Cr, Cu, Hg, Se, and V, while landfills receiving bituminous coal ash yielded higher concentrations of Co, Li, Mn, Ni, Sb, Sr, Tl, U, and Zn. The Wisconsin samples were mostly consistent with these findings, having higher concentrations of As, Cr, Cu, Se, and V in leachate from subbituminous coal ash than in leachate from bituminous coal, and higher concentrations of Li and Sr in leachate from bituminous coal ash.

Speciation results for As, Se, and Cr show that the oxidized form is typically predominant in the Wisconsin leachate samples (Table 4-4). The exceptions were sample 01 (Site A), which had more reduced than oxidized As, and sample 88 (site C), which had more reduced than oxidized Se. Sample 01 had negative Eh and low dissolved oxygen, indicative of reducing conditions. Sample 88 had relatively low dissolved oxygen and Eh (Table 4-1), which suggests that redox conditions at the time of this sample were less oxidizing than for the other samples collected at Site C.

SPLP Leaching

SPLP leach tests were performed on seven fresh fly ash samples obtained at five Wisconsin power plants (Table 4-5). These data cannot be quantitatively compared to the field leachate data because of differences in the age of the ash (weathered versus fresh) and possible variations in the coal sources and firing conditions that may affect ash concentrations and leachability. Qualitative comparison for three of these power plants (B, C, and F)[4] indicated that the SPLP results based on fresh ash samples were consistently very poor indicators of field leachate concentrations for soluble constituents (sodium, chloride, and sulfate), yielding significantly lower concentrations. Results were mixed with respect to trace constituents.

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[4] Leachate samples were not available for the other two plants.

Table 4-3
Minor and Trace Element Concentrations

Sample ID	Type	Site	CCP	Coal Type[+]	Ag (µg/L)	Al (µg/L)	As (µg/L)	B (µg/L)	Ba (µg/L)	Be (µg/L)	Cd (µg/L)	Co (µg/L)
01	Leachate	A	FA, BA	Mix	<0.25	13,300	20	1,550	63	<0.10	22	8.7
02	Leachate	B	FA	Sub	<0.25	2,150	48	14,500	37	<0.10	9.7	116
03	Leachate	B	FA	Sub	<0.25	13,600	84	24,300	27	<0.10	9.5	16
04	Leachate	C	FA, BA	Mix	<0.25	<150	19	9,000	114	<0.10	2.1	9.6
05	Leachate	C	FA, BA	Mix	<0.25	<150	3.0	1,450	57	<0.10	2.1	9.1
85	Leachate	D	FA	Sub	<0.25	1,700	28	5,650	20	<0.10	15	3.3
86	Duplicate 85	D	FA	Sub	<0.25	1,700	27	5,950	16	<0.10	13	3.3
87	Leachate	D	FA	Sub	<0.25	4,300	34	6,080	18	0.14	13	3.3
88	Leachate	C	FA, BA	Mix	<0.25	<150	52*	11,700	34	<0.10	7.7	0.88
89	Leachate	C	FA, BA	Mix	<0.25	<150	4.8	2,590	66	<0.10	6.1	0.29
91	Leachate	E	FA, BA	Bit	<0.25	<150	2.2	89,500	23	<0.10	4.6	9.2
92	Leachate	F	FA	Bit	<0.25	<150	7.2	23,800	48	<0.10	36	0.072
83	field blank				<0.25	<150	<0.10	1.1	<1	<0.10	<0.10	<0.10
84	equip. blank				<0.25	<150	<0.10	0.68	<1	<0.10	<0.10	<0.10
90	equip. blank				<0.25	<150	0.20	0.80	<1	<0.10	<0.10	<0.10

* Sample shows precipitate upon acidification

[+] Bit = bituminous; Sub = subbituminous; Mix = mixture of bituminous and subbituminous

Table 4-3 (continued)
Minor and Trace Element Concentrations

Sample ID	Type	Site	CCP	Coal Type[+]	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Li (µg/L)	Mn (µg/L)	Mo (µg/L)	Ni (µg/L)	Pb (µg/L)
01	Leachate	A	FA, BA	Mix	<0.5	13	13	1,650	6.9	9,750	2.2	0.17
02	Leachate	B	FA	Sub	3,150	401	9.9	6.0	13	5,750	50	0.19
03	Leachate	B	FA	Sub	3,000	52	<10	3.6	6.2	6,250	5.5	0.16
04	Leachate	C	FA, BA	Mix	7.9	9.9	<10	21	649	1,250	10	0.09
05	Leachate	C	FA, BA	Mix	0.45	9.9	34	5.3	594	451	4.5	0.09
85	Leachate	D	FA	Sub	2,140	30	25	4.7	1.5	4,510	6.8	0.07
86	duplicate 85	D	FA	Sub	2,140	30	20	4.7	1.4	4,450	6.9	0.21
87	Leachate	D	FA	Sub	2,190	43	46	4.4	1.5	4,480	7.7	0.29
88	Leachate	C	FA, BA	Mix	2.3	1.7	<10	63	60	2,580	8.9	0.29
89	Leachate	C	FA, BA	Mix	<0.5	1.5	126	<0.9	1,230	2,070	1.8	0.17
91	Leachate	E	FA, BA	Bit	1.2	2.8	12	431	1,420	751	31	0.12
92	Leachate	F	FA	Bit	18	1.6	<10	6,950	72	9,630	3.0	0.12
83	field blank				<0.5	1.4	<10	<0.05	<1	<1	0.057	0.09
84	equip. blank				<0.5	2.5	<10	<0.05	<1	<1	0.081	0.06
90	equip. blank				<0.5	1.6	<10	<0.05	<1	<1	0.18	0.04

[+] Bit = bituminous; Sub = subbituminous; Mix = mixture of bituminous and subbituminous

Table 4-3 (continued)
Minor and Trace Element Concentrations

Sample ID	Type	Site	CCP	Coal Type[+]	Sb (µg/L)	Se (µg/L)	Si (µg/L)	Sr (µg/L)	Tl (µg/L)	U (µg/L)	V (µg/L)	Zn (µg/L)
01	Leachate	A	FA, BA	Mix	0.76	127	4,400	799	<0.10	0.063	285	3.5
02	Leachate	B	FA	Sub	0.66	1,730	4,100	51	<0.50	0.23	869	2.0
03	Leachate	B	FA	Sub	0.51	1,760	820	19	<0.50	9.8	504	1.9
04	Leachate	C	FA, BA	Mix	0.41	50	4,600	951	<0.10	1.4	49	2.0
05	Leachate	C	FA, BA	Mix	0.41	7.6	5,800	74	<0.10	1.4	12	6.4
85	Leachate	D	FA	Sub	0.78	382	1,400	311	<0.10	5.5	473	<2.0
86	duplicate 85	D	FA	Sub	0.76	377	1,340	293	<0.10	5.4	477	<2.0
87	Leachate	D	FA	Sub	0.90	347	1,540	303	<0.10	5.7	500	<2.0
88	Leachate	C	FA, BA	Mix	0.68	6.5*	4,620	1,700	<0.10	1.9	159	<2.0
89	Leachate	C	FA, BA	Mix	0.18	2.0	4,410	93	<0.10	0.19	3.8	<2.0
91	Leachate	E	FA, BA	Bit	0.14	91	6,750	1,320	<0.10	37	0.83	86
92	Leachate	F	FA	Bit	4.4	80	3,940	10,300	<0.10	7.4	44	<2.0
83	field blank				<0.10	<0.10	<50	0.31	<0.10	<0.002	0.13	3.3
84	equip. blank				<0.10	<0.10	<50	0.11	<0.10	<0.002	0.15	4.3
90	equip. blank				<0.10	<0.10	<50	0.72	<0.10	<0.002	0.10	4.7

* Sample shows precipitate upon acidification

[+] Bit = bituminous; Sub = subbituminous; Mix = mixture of bituminous and subbituminous

Table 4-4
As, Se, and Cr Species Analysis

Sample ID	Type	Site	CCP	Coal Type[+]	As (µg/L)				Se (µg/L)				Cr (µg/L)		
					total	III	V	other	total	IV	VI	other	total	III	VI
01	Leachate	A	FA, BA	Mix	20	11	4.5	NA	127	4.1	73	NA	<0.50	NA	2.2
02	Leachate	B	FA	Sub	48	NR	NR	NA	1,730	4.1	1,120	NA	3,150	NA	3,220
03	Leachate	B	FA	Sub	84	NR	NR	NA	1,760	NR	NR	NA	3,000	NA	2,630
02R[#]	Leachate	B	FA	Sub	55	<5.0	31	9.7	1,426	<25	1,348	27	5,204	NA	4,138
04	Leachate	C	FA, BA	Mix	19	NR	NR	NA	50	NR	NR	NA	7.9	NA	8.1
05	Leachate	C	FA, BA	Mix	3.0	NR	NR	NA	7.6	NR	NR	NA	0.45	NA	1.5
85	Leachate	D	FA	Sub	28	<0.20	28	<0.20	382	37	363	<0.50	2,140	119	2,050
86	duplicate 85	D	FA	Sub	27	<0.20	28	<0.20	377	38	367	<0.50	2,140	136	2,030
87	Leachate	D	FA	Sub	34	<0.20	36	<0.20	347	38	366	<0.50	2,190	44.9	2,230
88	Leachate	C	FA, BA	Mix	52*	0.70	60	0.30	6.5*	29	<0.5	<0.50	2.3	NR	NR
89	Leachate	C	FA, BA	Mix	4.8	<0.20	3.8	<0.20	2.0	NR	NR	NR	<0.50	NA	NA
91	Leachate	E	FA, BA	Bit	2.2	NR	NR	NR	91	<1.0	104	<1.0	1.2	NR	NR
92	Leachate	F	FA	Bit	7.2	<0.20	6.3	<0.10	80	5.3	86	<0.25	18	NA	NA
83	field blank				<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.50	NA	NA
84	equip. blank				<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.50	NA	NA
90	equip. blank				0.20	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.50	NA	NA

NA = not analyzed
NR = species results not reported if less than 60 percent of total concentration
* Sample showed precipitate upon acidification
[+] Bit = bituminous; Sub = subbituminous; Mix = mixture of bituminous and subbituminous
[#] Sample 02R is a resample with splits preserved using different preservatives. Listed results are for preservatives with best species recovery (HCL for As and Se, and no preservative for Cr).

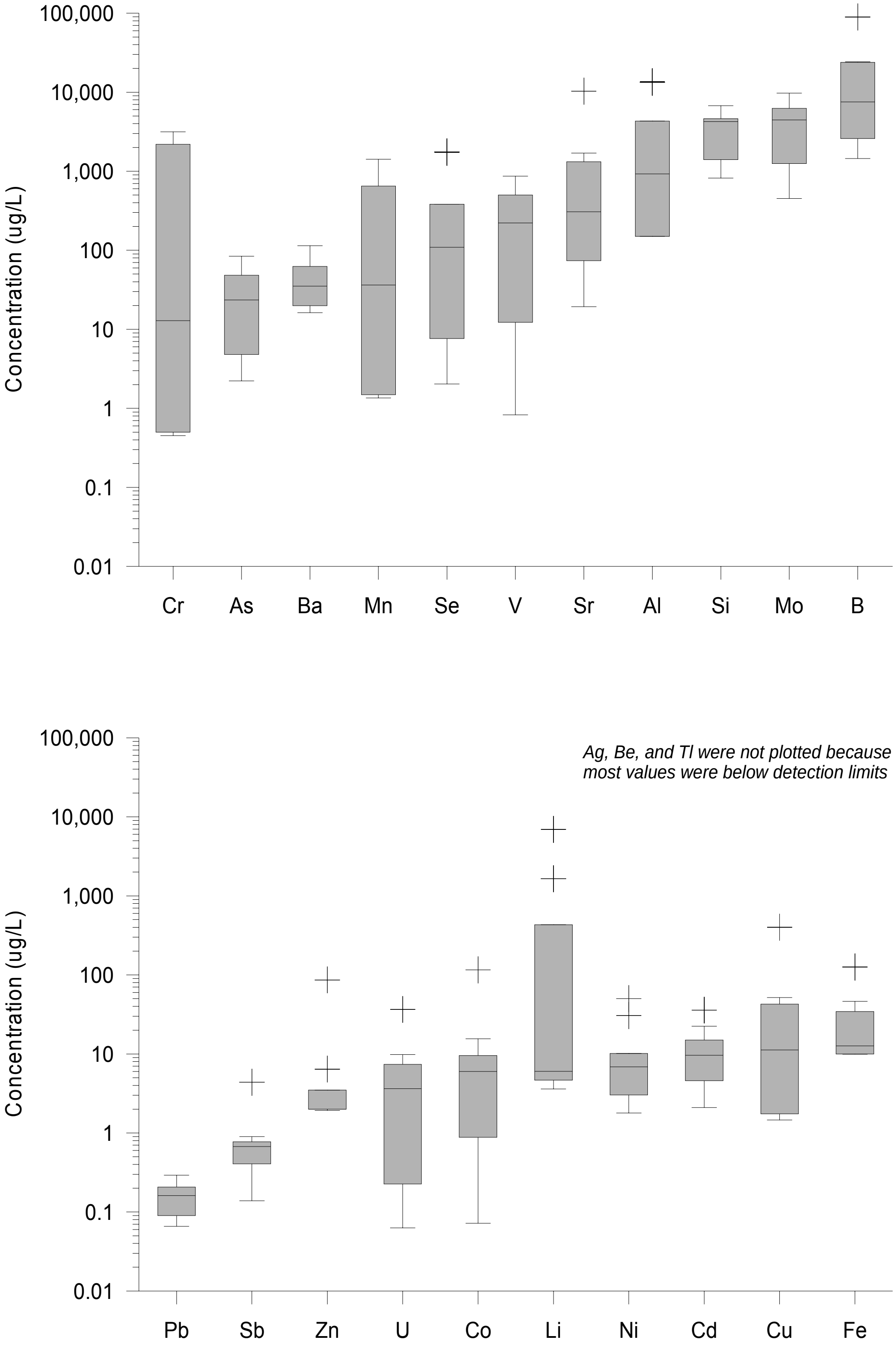

Figure 4-2
Box-whisker plots showing concentration ranges for minor and trace constituents, sorted by median concentrations

Table 4-5
Laboratory CCP Leach Test Results Using SPLP (SW-846 1312) Method

Sample	Plant	Description	Sample Type	Na (mg/L)	Ca (mg/L)	Cl (mg/L)	SO_4 (mg/L)	Mg (mg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Se (µg/L)
B10A	C	blended bit/subbit	fly ash	235.0	119.3	2.1	28.3	<0.10	16.1	<1.0	<1.0	<1.0	3.1
B2A	H	bituminous	fly ash	214.0	100.0	338.0	3030.0	12.2	562.0	1.9	29.0	21.0	180.1
B3A	F	bituminous	fly ash	0.9	33.7	0.1	94.0	3.4	30.0	2.8	12.0	2.3	65.4
S2A-1	G	subbituminous	fly ash	10.8	156.1	<0.01	55.0	0.3	11.0	<1.0	20.0	<1.0	2.1
S2A-2	G	subbituminous	fly ash + ACI*	8.1	211.0	NA	NA	0.2	17.0	<1.0	25.0	<1.0	1.6
S2A-3	G	subbituminous	fly ash + ACI*	1.4	230.5	2.9	66.0	0.2	26.0	<1.0	20.0	4.5	97.3
S4A	B	subbituminous	fly ash	203.5	13.5	0.3	19.4	<0.10	56.8	3.8	4.1	1.6	13.9

* ACI = Activated Carbon injection
NA = not analyzed

Sequential Leaching

Introduction

Sequential leaching was performed on one fresh fly ash sample collected from the hopper at Plant B. This analysis was performed to further evaluate the associations of inorganic constituents that may affect their leachability. Sequential leaching is a detailed set of extractions designed to progressively release different phases within the ash, from the most easily leached phases to most recalcitrant. The actual amount of a constituent leached is generally dictated by the form it is in and the conditions under which leaching occurs, particularly pH and redox.

Results

The concentrations of metals in the digestate solutions determined by ICP-OES analysis are shown in Table 4-6. The results of the sequential extraction are shown in Table 4-7 and Figures 4-3 through 4-5.

The sequential chemical extraction procedure (SCEP) selected for use in this study was designed to separate metal and metalloid elements associated with the following fractions: (1) water soluble, (2) exchangeable, (3) carbonate, (4) manganese oxides, (5) amorphous iron oxides, (6) crystalline iron oxides, and (7) organic and sulfides. In general, the mobility of elements associated with these fractions decreases with each successive extraction step. It should be noted that the metal concentrations for Step 7 (of the SCEP) are minimum values, as the total volume of the extractant solution varied, depending upon the extent of evaporation. A total volume of 50 mL was used in the calculation, although the true volume was slightly higher due to incomplete evaporation of hydrogen peroxide added before the final extractant solution. The values shown for Step 7 (organics and sulfide fraction) should be accurate to within 10%.

The Plant B fly ash is derived from subbituminous coal and is highly alkaline. Cations with highest recoverable concentrations were Ca, Mg, Fe, and Al, all present at concentrations greater than 10,000 mg/kg (Table 4-6). The next highest group (1,000 to 10,000 mg/kg) included Si, Ti, Sr, Ba, K, and Na, followed by B and Cu with concentrations from 100 to 1000 mg/kg. All other constituents were present at less than 100 mg/kg.

The first two steps of the sequential extraction—water extractable and exchangeable fractions—represent the most easily leached forms. Figure 4-3 shows the percentages of the major cations (Ca, Mg, K, and Na) extracted during each leaching step. The water soluble and exchangeable fractions comprise less than 10 percent of the total extractable concentrations of these constituents. However, because of their high concentrations, even a small percentage can result in high concentrations in leachate. The field leachate corresponding to this ash sample had relatively low calcium and magnesium concentrations, and relatively high potassium and sodium concentrations (Site B, Table 4-2). Part of the reason for low calcium and magnesium concentrations may be the high pH of the field leachate (Table 4-1), resulting in additional precipitation reactions. The highest percentage extractions for these constituents were in step 3 (acid soluble), and steps 5 and 6, which indicate associations with amorphous and crystalline iron and aluminum.

Figure 4-4 shows minor elements. Most noteworthy in this group is boron, which is frequently found in ash leachate and is not significantly affected by pH. About 40 percent of the B was associated with the exchangeable fraction. Boron concentrations in the Site B field leachate were relatively high, greater than 10 mg/L (Table 4-3). Aluminum was primarily associated with the amorphous iron and aluminum phase. However, Al is strongly affected by pH, with increasing solubility at both low and high pH. The concentrations in the field leachate (>1,000 µg/L) reflect the higher solubility of Al at high pH.

Figure 4-5 shows selected trace elements. Most noteworthy in this group are Se, Mo, and Cr. These three constituents have high percentages associated with the water soluble and exchangeable fractions. They are all present in the field leachates at concentrations greater than 1 mg/L (Table 4-3).

Table 4-6
Total Recoverable Concentrations for the Plant B Sample (mg/kg on dry weight basis)

Al	As	B	Ba	Be	Ca
67,389	14	396	4,665	<0.01	153,714
Co	**Cr**	**Cu**	**Fe**	**K**	**Mg**
16	36.	109	37,643	1,208	23,649
Mn	**Mo**	**Na**	**Ni**	**Pb**	**Se**
80	2.5	4,047	30	23	<0.01
Si	**Sr**	**Ti**	**V**	**Zn**	
1,006	3,761	1,916	114	83	

Digestate solutions were also analyzed for Cd, Sb, Ag, Sn, and Tl; however, all values were less than ICP-OES LOD.

Table 4-7
Concentrations in Each Extraction Step (mg/kg on dry weight basis)

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn
STEP 1	3120	BDL	20	308	BDL	8430	BDL	BDL	1.75	<0.005	13	49	BDL	BDL
STEP 2	4	2.22	218	48	BDL	3223	BDL	BDL	9.59	7.63	5	30	1286	BDL
STEP 3	8641	0.78	76	505	BDL	28767	0.58	5.61	4.09	19.62	1472	41	11257	23.22
STEP 4	2378	BDL	7	479	0.15	2214	BDL	BDL	0.72	7.71	1677	43	433	5.29
STEP 5	40013	11.29	69	38	BDL	63671	BDL	1.75	26.61	24.73	23781	920	7267	12.26
STEP 6	7262	4.58	13	1015	BDL	55	BDL	5.85	3.62	10.57	4440	619	948	9.85
STEP 7	937	0.86	5	593	BDL	5035	BDL	0.78	BDL	3.60	492	133	171	5.52
Total Extractable	**62354**	**19.72**	**409**	**2985**	**0.15**	**111393**	**0.58**	**13.98**	**46.39**	**73.84**	**31878**	**1836**	**21362**	**56.14**

	Mo	Na	Ni	Pb	Se	Si	Sb	Ag	Sn	Sr	Tl	Ti	V	Zn
STEP 1	1.46	271	BDL	<0.002	0.68	22	BDL	0.45	BDL	420	BDL	BDL	BDL	BDL
STEP 2	1.38	86	1.07	<0.002	4.94	242	0.50	2.25	BDL	313	BDL	BDL	3.36	1.14
STEP 3	BDL	576	17.68	<0.002	BDL	9930	BDL	BDL	BDL	135	BDL	123	1.85	15.17
STEP 4	BDL	156	1.02	0.58	BDL	1913	BDL	BDL	BDL	39	BDL	5	22.70	7.14
STEP 5	BDL	3151	7.14	19.27	BDL	32548	BDL	BDL	BDL	892	BDL	231	18.72	18.61
STEP 6	BDL	1655	4.67	4.79	BDL	5569	2.19	BDL	BDL	14	BDL	BDL	6.92	11.22
STEP 7	BDL	260	0.92	5.55	0.84	1463	BDL	6.35	BDL	120	BDL	302	2.84	4.38
Total Extractable	**2.84**	**6154**	**32.51**	**30.19**	**6.45**	**51687**	**2.69**	**9.05**	BDL	**1934**	BDL	**661**	**56.39**	**57.66**

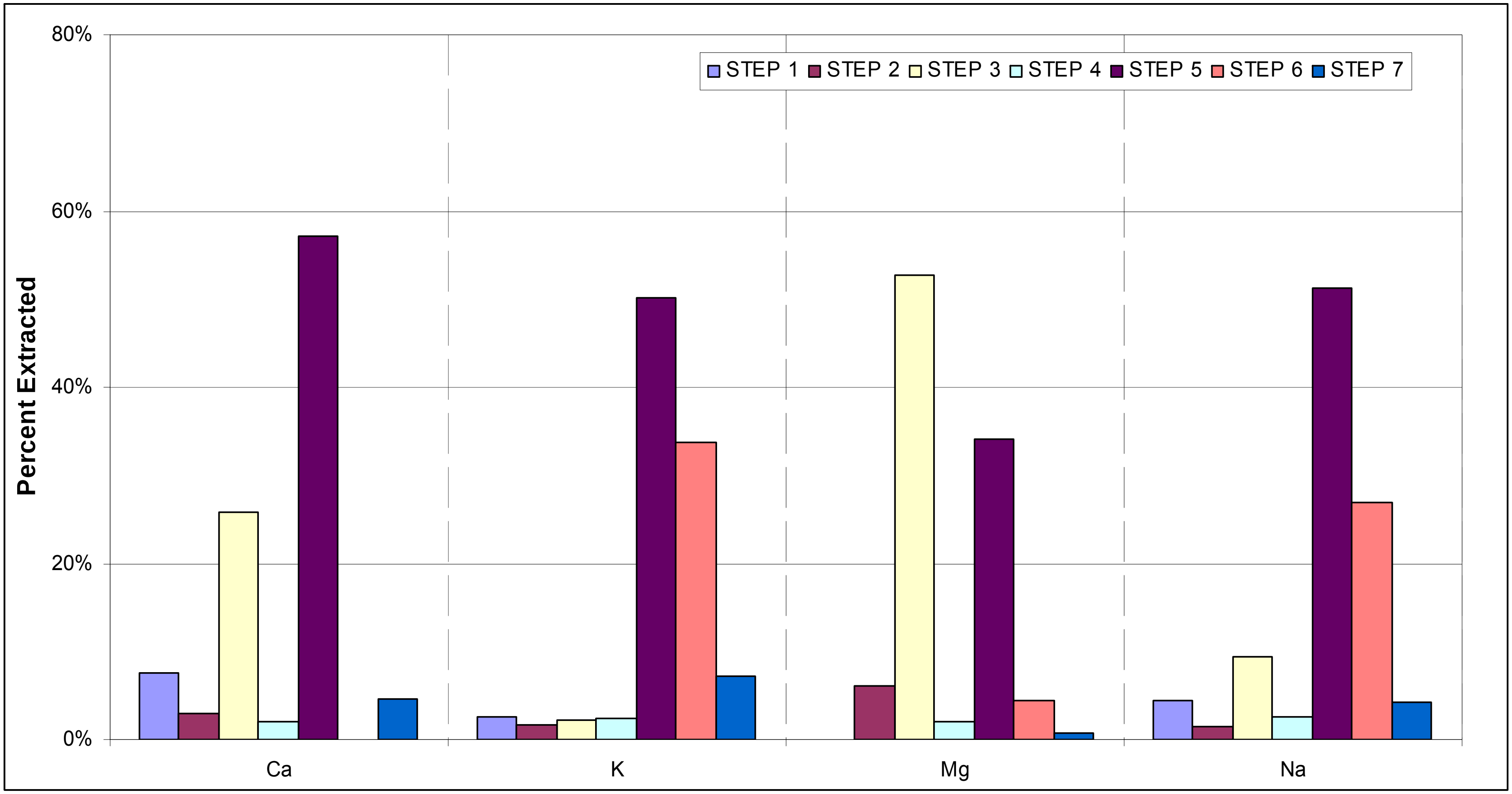

Figure 4-3
Percentages of major elements extracted in each step

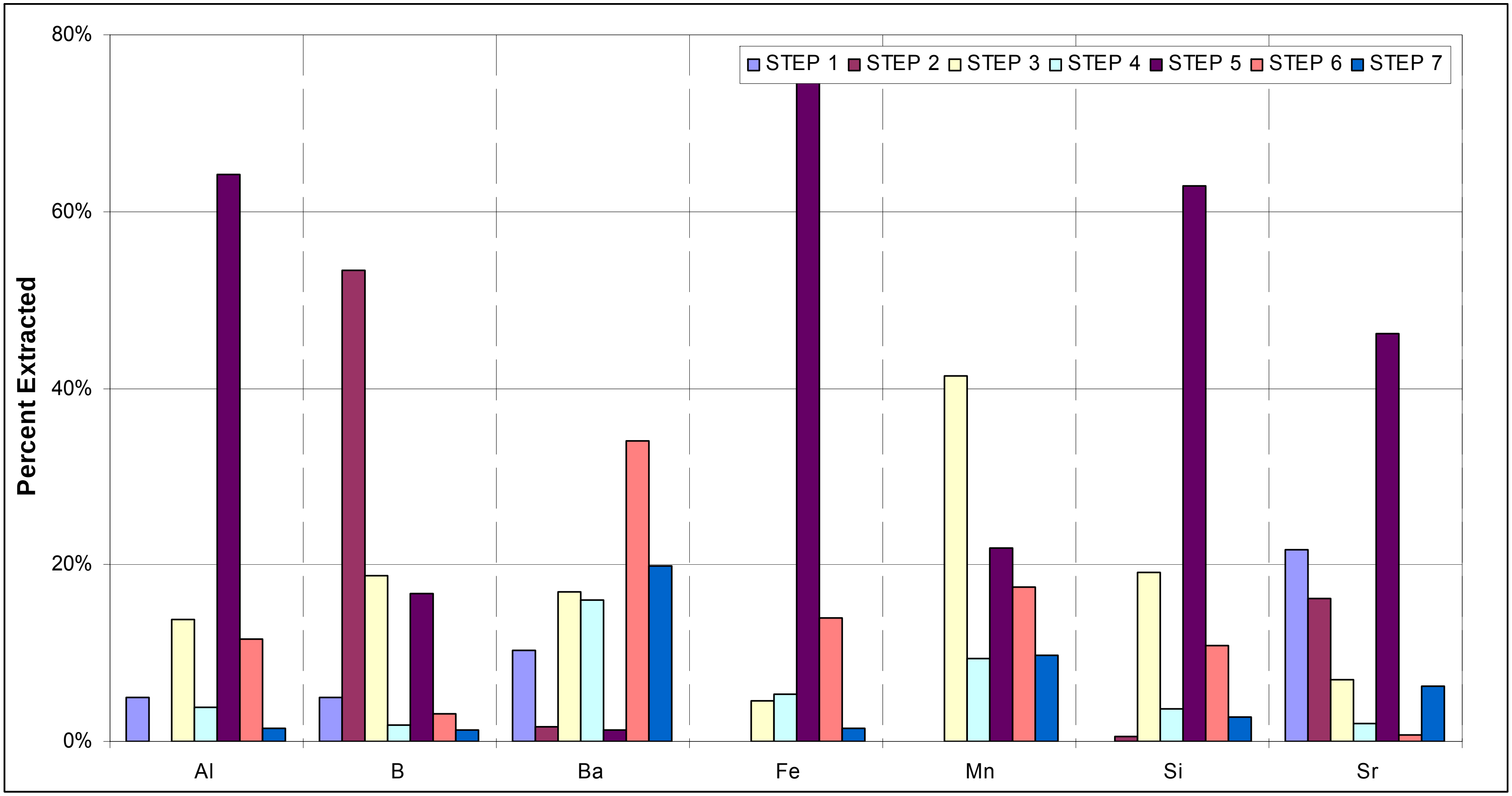

Figure 4-4
Percentages of minor elements extracted in each step

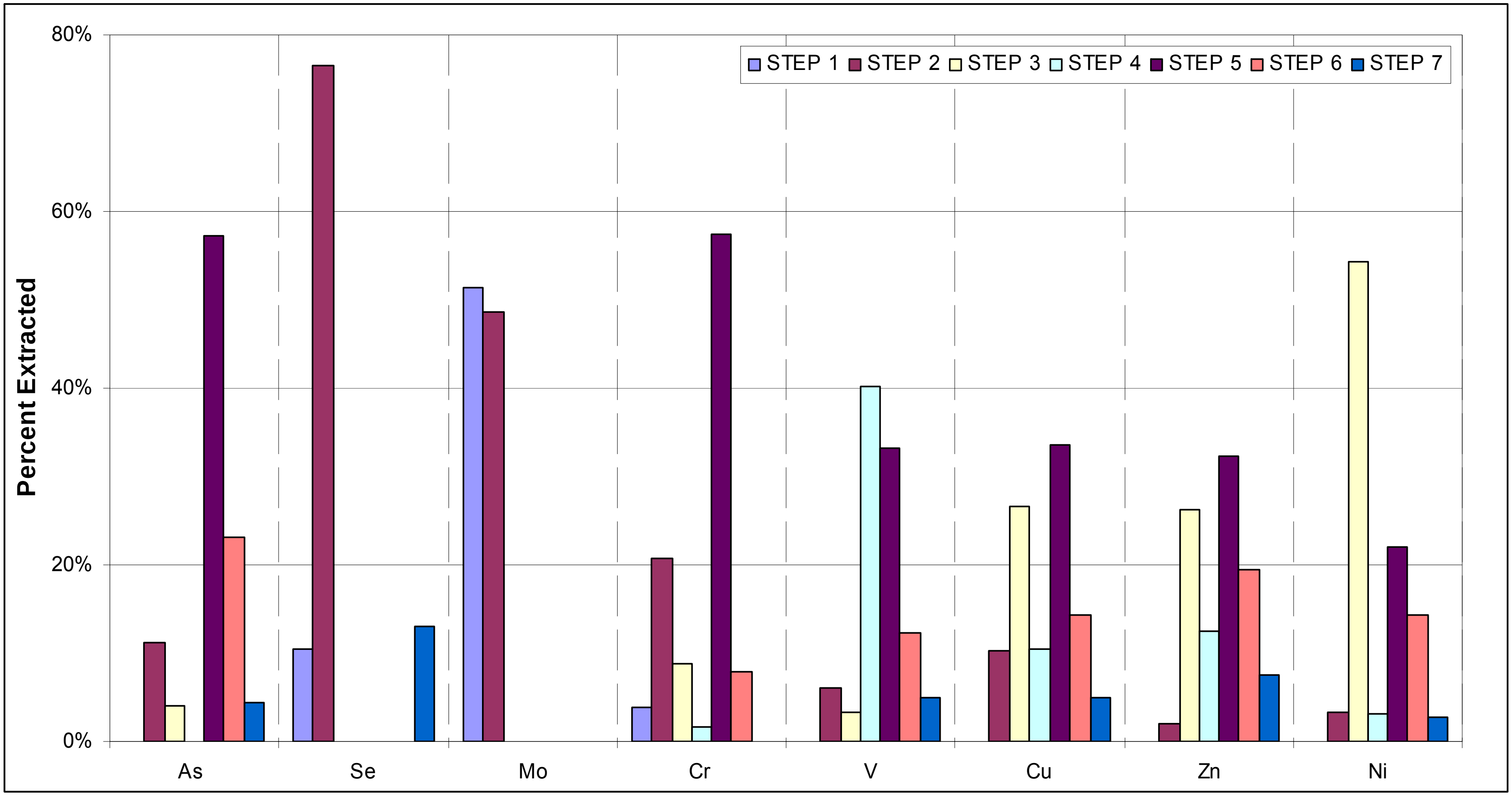

Figure 4-5
Percentages of selected trace elements extracted in each step

Key Points

- Field leachate sampled at CCP management units in Wisconsin was dominated by SO_4 and Na when the source coal was subbituminous, and by SO4, Ca, and Mg when the source coal was bituminous.
- The trace element with highest concentration was B (up to 89,500 µg/L). Other minor and trace constituents with concentrations greater than 1,000 µg/L included Al, Cr, Mo, and Se.
- Three elements, Ag, Be, and Tl, were either not detected or were only detected at a concentration near the method detection limit.
- Sequential leaching tests demonstrated that B, Se, Mo, and Cr had high percentages associated with the water soluble and exchangeable fractions

5

MERCURY VOLATILIZATION FROM FLY ASH GENERATED IN WISCONSIN

The potential for mercury release to air from fly ash was evaluated in the laboratory and in the field. Seven samples were collected from five coal-fired power plants located in Wisconsin. Two of the samples were collected after activated carbon injection (ACI) into the flue gas to enhance mercury capture. Laboratory investigation of mercury exchange between air and the fly ash samples was performed in a controlled experimental setting using a single-pass gas exchange system.

To verify the laboratory results, in-situ mercury emissions were measured at a CCP landfill using a dynamic field chamber. Previous work based on more than 25 CCP samples in the laboratory, and two field sites, has suggested that the mercury captured in fly ash derived from bituminous and subbituminous coal sources is relatively stable (EPRI, 2002; Gustin and Ladwig, 2004).

Laboratory Study

Total Hg concentrations ranged from 30 to 563 µg/kg for the five conventional fly ashes, and from 1040 to 2,300 µg/kg for the two fly ashes with enhanced mercury capture (ACI) (Table 5-1). The total Hg concentrations in the two fly ashes (S2A-2, 3) with ACI were about five to ten times higher than the baseline fly ash (S2A-1) from the plant, reflecting the improved mercury capture from the flue gas. Recoverable concentrations ranged from about 25 to 67 percent of the total concentrations, excluding sample B3A.

Table 5-1
Laboratory Hg Flux Measurement Data

	Hg concentration (µg/kg)		25^{o}C , dark		25^{o}C, light		45^{o}C, dark	
	Total	Recoverable	Flux Rate (ng $m^{-2}hr^{-1}$)	sd	Flux Rate (ng $m^{-2}hr^{-1}$)	sd	Flux Rate (ng $m^{-2}hr^{-1}$)	sd
B10A	30	14	-54.4	3.5	-27.1	6.5	-16.4	3.5
B2A	563	133	-19.4	5.8	-30.9	9.5	-20.7	19.8
B3A	47	72	-9.1	9.9	-18.2	3.6	-18.4	4.5
S2A-1	247	92	-9.9	4.8	-3.6	5.7	-0.6	7.7
S2A-2	2300	596	-13.9	9.7	-6.9	30.4	-6.0	8.7
S2A-3	1040	439	-25.3	9.3	-15.3	7.3	-20.5	0.7
S4A	60	40	-4.1	6.7	16.5	17.1	16.5	2.5

All seven fly ash samples exhibited negative Hg flux (i.e., mercury deposition) of atmospheric mercury at 25°C in the dark. Positive Hg flux (emission of mercury) was observed only for one subbituminous-derived fly ash sample (S4A) during light exposure and in the dark at 45°C. However, the emission level was very low. Deposition to ash in the dark at 25°C exposure was significantly ($p<0.1$) greater than that occurring during the light or dark at 45°C. This was expected, since incident light and increased temperature enhances mercury emission (or reduces deposition), a finding consistent with previous studies (Gustin and Ladwig, 2004).

Field Study

In situ Hg fluxes were measured under highly variable weather conditions from bright sunny days to cold rainy days. This led to a wide range in relative humidity (22%–88 %), solar irradiance (0–738 W m^{-2}), and temperature: (7.6–35.9ºC) (Table 5-2). Fluxes from three types of substrate were measured.

Table 5-3 compares mean Hg fluxes (daytime and nighttime) from the three substrates. During the day, vegetated topsoil over fly ash emitted mercury at a lower rate (0.7 ng m^{-2} hr^{-1}) than barren fly ash and background soil (1.6 and 1.0 ng m^{-2} hr^{-1}, respectively). At night, vegetated topsoil over fly ash acted as a mercury sink (-0.8 ng m^{-2} hr^{-1}). Barren fly ash from the same landfill was a source of atmospheric mercury during day and night (1.6 and 0.2 ng m^{-2} hr^{-1}) but the flux rate was very low and comparable with surrounding background soil (1.0 ng m^{-2} hr^{-1} during the day and 0.0 ng m^{-2} hr^{-1} at night).

Table 5-2
Summary of Hg Fluxes Measured from a CCP Landfill

Sample-ID	Type	Surface (% barren, %dead organic, %grass)	Recoverable Hg (µg/kg)	Flux (ng $m^2 hr^{-1}$)		Temperature,°C			Humidity (%)	Solar Light (W m^{-2})
				Average	sd	Chamber	Soil	Air		
CA1	Fly ash	100, 0, 0	76	0.6	0.3	17.9	16.6	12.3	56	480
CA2	Fly ash	100, 0, 0	59	1.8	0.3	27.1	18.7	14.9	50	587
CA3	Fly ash	100, 0, 0	79	1.8	0.1	31.1	28.8	17.2	45	680
WC1	Fly ash	100, 0, 0	99	1.7	0.4	14.9	12.1	11.5	59	460
WC2	Fly ash	100, 0, 0	61	1.5	0.3	21.8	16.7	15.2	49	591
WC3	Fly ash	100, 0, 0	83	1.4	0.1	29.1	19.3	18.0	43	676
WD1	Fly ash	100, 0, 0	127	1.8	0.3	33.6	26.2	24.5	30	670
WD2	Fly ash	100, 0, 0	63	1.7	0.2	28.5	22.1	24.6	29	640
WD3	Fly ash	100, 0, 0	52	0.2	0.5	11.9	15.3	14.6	63	99
WF1	Fly ash	100, 0, 0	41	5.4	7.3	32.6	26.6	24.9	31	694
WF2	Fly ash	100, 0, 0	42	1.5	0.3	36.4	30.0	26.9	28	612
WF3-FK	Fly ash	100, 0, 0	39	0.2	0.3	12.7	13.5	18.0	65	1
WG-WI1	Fly ash	100, 0, 0	70	0.8	0.3	22.5	15.6	15.8	71	485
WI2	Fly ash	100, 0, 0	<10	0.8	0.2	27.3	18.3	22.4	53	652
WI3	Fly ash	100, 0, 0	185	0.3	0.1	23.4	44.5	26.6	42	688

Table 5-2 (continued)
Summary of Hg Fluxes Measured from a CCP Landfill

Sample-ID	Type	Surface (% barren, %dead organic, %grass)	Recoverable Hg (µg/kg)	Flux (ng m^{2}hr^{-1})		Temperature,^{o}C			Humidity (%)	Solar Light (W m^{-2})
				Average	sd	Chamber	Soil	Air		
FA1	vegetated fly ash	20, 50, 30	24	1.0	0.5	19.5	14.5	16.6	39	219
FA2	vegetated fly ash	0, 0, 100	21	0.7	0.1	20.3	13.9	15.6	40	192
FA3	vegetated fly ash	0, 0, 100	17	1.3	0.1	20.5	14.7	15.4	37	173
FB2	vegetated fly ash	0, 50, 50	13	1.6	4.1	25.9	10.2	27.6	22	167
FB3	vegetated fly ash	0, 50, 50	15	0.8	0.3	25.3	11.7	22.6	29	344
FB4	vegetated fly ash	0, 50, 50	13	0.5	0.6	21.6	15.5	20.2	33	236
FF1	vegetated fly ash	0, 50, 50	19	0.7	0.3	13.0	9.8	11.6	67	80
FF2	vegetated fly ash	0, 50, 50	<10	0.3	0.5	20.4	7.3	14.1	57	458
FF3A	vegetated fly ash	0, 80, 20	15	1.5	0.5	29.7	7.7	17.3	48	615
FF3B	vegetated fly ash	0, 80, 20	15	1.3	0.3	39.0	10.2	21.2	39	382
FG1	vegetated fly ash	0, 80, 20	21	0.6	0.1	29.0	17.4	26.6	33	377
FG2A	vegetated fly ash	0, 80, 20	19	0.3	0.1	28.0	25.4	24.8	39	350
FG2B	vegetated fly ash	0, 80, 20	19	0.0	0.3	21.5	21.3	19.0	55	49
FG3A	vegetated fly ash	0, 80, 20	19	-2.3	0.5	15.5	16.6	15.0	63	8
FG3B	vegetated fly ash	0, 80, 20	19	-0.9	0.0	13.2	16.0	11.2	78	0
FG3C	vegetated fly ash	0, 80, 20	19	-1.0	0.1	12.5	15.2	10.9	79	0
FH	vegetated fly ash	100, 0, 0	19	-0.8	0.2	10.5	13.1	7.6	88	0
WA1	vegetated fly ash	0, 0, 100	19	5.7	7.2	14.4	12.7	15.0	43	308
WA2	vegetated fly ash	0, 0, 100	22	0.4	0.1	14.7	12.8	14.5	38	222
WA3	vegetated fly ash	0, 0, 100	19	0.8	0.3	16.7	12.6	14.0	38	204

Table 5-2 (continued)
Summary of Hg Fluxes Measured from a CCP Landfill

Sample-ID	Type	Surface (% barren, %dead organic, %grass)	Recoverable Hg (µg/kg)	Flux (ng $m^{2}hr^{-1}$)		Temperature,^{o}C			Humidity (%)	Solar Light (W m^{-2})
				Average	sd	Chamber	Soil	Air		
SA1	Soil	80, 20, 0	20	1.7	0.4	39.2	27.6	20.2	37	621
SA2	Soil	80, 20, 0	21	-0.3	0.6	35.4	14.6	28.6	23	533
SB1	Soil	0, 50, 50	15	1.7	0.6	33.6	14.7	26.3	51	640
SB2	Soil	0, 50, 50	<10	3.1	0.7	34.5	28.2	29.6	39	738
SB3	Soil	0, 50, 50	<10	0.7	0.2	39.1	22.5	32.4	30	738
SB 4	Soil	0, 50, 50	<10	0.6	0.2	35.7	17.5	34.2	27	619
SB 5	Soil	0, 50, 50	11	-0.3	0.1	34.2	19.3	35.9	24	364
FI1	Soil	40, 30, 30	<10	0.6	0.3	26.6	18.5	21.0	56	629
FI2	Soil	40, 30, 30	28	1.5	0.1	25.6	35.6	25.4	46	683
WJ1	Soil	35, 20, 45	<10	1.0	0.6	42.0	17.1	33.2	24	522
WJ2	Soil	25, 50, 25	<10	0.1	0.1	34.5	19.6	30.1	27	369
WK1	Soil	0, 50, 50	<10	0.8	0.2	22.8	14.9	24.2	54	688
WK2	Soil	0, 50, 50	<10	0.5	0.2	30.5	16.8	25.9	45	708
S41	Soil	30, 40, 40	11	0.6	0.1	19.1	19.7	28.7	34	89
S42	Soil	40, 50, 10	17	0.8	0.1	29.3	20.6	31.7	29	182
S6	Soil	50, 25, 25	<10	0.0	0.3	17.7	16.1	18.0	77	0
S7A	Soil	10, 45, 45	<10	-0.1	0.1	18.1	13.0	19.8	70	95
S7B	Soil	0, 50, 50	<10	0.0	0.2	18.0	11.0	21.5	65	58
S8A	Soil	100, 0, 0	13	0.2	0.1	46.1	25.6	29.1	40	394
S8B	Soil	100, 0, 0	<10	0.0	0.1	32.3	20.1	28.3	40	415

Table 5-3
Field Study: Comparison of Mean Hg Fluxes (Daytime and Nighttime) for Three Field Substrates

Sample Type	Sample Period	Flux (ng m^{-2} hr^{-1})	Chamber T (°C)	Soil T (°C)	Air T (°C)	Humidity (%)	Light (W m^{-2})	Substrate Hg (µg/kg)
Barren fly ash	day	1.6	26.6	22.7	19.6	45	609	81
	night	0.2	12.3	14.4	16.3	64	50	
Vegetated fly ash	day	0.7	20.6	13.9	17.0	48	219	18
	night	-0.8	10.5	13.1	7.6	88	0	
Soil	day	1.0	32.0	21.7	28.5	36	531	15
	night	0.0	17.7	16.1	18.0	77	0	

Conclusions

Most samples of fly ash in the laboratory study were sinks for atmospheric mercury during the study period. That is, atmospheric mercury deposited onto the fly ash, although the fluxes were very low. This finding is consistent with previous results on fresh fly ash (Gustin and Ladwig, 2004). It is hypothesized that the mercury captured from the flue gas is relatively stable with respect to atmospheric exchange. On exposure to the atmosphere, ambient mercury in the air can undergo deposition or emission, depending on the atmospheric Hg concentration.

Fly ash samples obtained after ACI had Hg concentrations from five to ten times higher than fly ash without ACI. However, the mercury was still stable on the fly ash, exhibiting negative flux.

In situ Hg fluxes measured at the field site were very low, consistent with the laboratory data, and comparable to surrounding soils. If the mean Hg flux data from the three different sites is applied to the individual substrate landfill area, mercury emissions from barren fly ash and vegetated fly ash would be at similar magnitude to that from surrounding background soil at the landfill (Table 5-4).

Table 5-4
Comparison of Scaling of Hg Flux Using In-Situ Data from Three Landfill Substrates

Sample Type	Area (m^2)	Mean Flux (ng m^{-2} hr^{-1})	Total Annual Flux (g $year^{-1}$)
Barren fly ash	30,592	0.9	0.2
Vegetated fly ash	37,096	-0.1	0.0
Soil	67,688	0.5	0.3

Mean flux is the average daytime and nighttime flux listed in Table 5-3

6

MOBILITY OF MERCURY AND OTHER CONSTITUENTS IN GROUNDWATER

Mercury Mobility in Groundwater

The partition coefficient, or distribution coefficient, (K_d) is a commonly cited measure of the mobility of inorganic constituents in groundwater. Constituents that are non-reactive and essentially migrate with groundwater, such as chloride, have a K_d value of zero. Values greater than zero indicate that the constituent sorbs to the aquifer matrix or precipitates, which retards the migration of the constituent relative to groundwater flow. Constituents with K_d values greater than 5 L/kg are considered to have low mobility in groundwater, and constituents with K_d values greater than 50 L/kg are relatively immobile (vanLoon and Duffy, 2000).

It is not possible to apply a single K_d value to most inorganic constituents because speciation, soil type, mineral content, pH, and redox conditions all influence the value. USEPA commissioned a comprehensive review of partitioning coefficients reported in the literature, which were then used in multimedia modeling performed in support of the Hazardous Waste Identification Rule.[5] Field measurements reported in that review suggest that mercury has a higher affinity for sorption in the soil/water system than many other regulated inorganic constituents:

$$\mathrm{Pb} > \mathrm{Cr(III)} > \mathrm{Hg} > \mathrm{As} > \mathrm{Zn} = \mathrm{Ni} > \mathrm{Cd} > \mathrm{Cu} > \mathrm{Ag} > \mathrm{Co}$$

Partition coefficients for elemental mercury reported in the literature range from 160 to 630,000 L/kg, with a median of 6,300 L/kg; partition coefficients for $MeHg_d$ range from 20 to 63,000 L/kg, with a median of 630 L/kg (HydroGeoLogic, 1999). These values suggest that mercury is not mobile in groundwater. The values cited above are based on tests of mercury sorption for actual soil/water systems with system-specific pH values; therefore, the pH dependency of mercury sorption is not represented. Mercury sorption, like that of many metals, decreases as pH decreases.

USEPA used the MINTEQA2 geochemical model to estimate partition coefficients for mercury under a range of pH conditions (USEPA, 2001). The USEPA estimate had the following limitations:

- Mercury was assumed to be in its most mobile oxidation state (II)
- The model only considered sorption to iron oxides and solid organic matter (i.e., not clays or carbonates),
- Volatilization and complexation with other metals was not considered.

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[5] This report was prepared by HydroGeoLogic, 1999. A final report is not available, and the draft report is available on the internet: http://www.epa.gov/epaoswer/hazwaste/id/hwirwste/pdf/risk/reports/s0524.pdf

As a result, the USEPA approach likely underestimated the K_d values for Hg. The following is an excerpt from USEPA (2001):

> MINTEQ-estimated K_d values for mercury (II) range from 0.04 to 200 L/kg. These model-predicted estimates are less than the measured range of 322 to 5,280 L/kg reported by Battelle (1989). This difference may reflect the limited thermodynamic database with respect to mercury and/or that only the divalent oxidation state is considered in the simulation. Allison (1993) reviewed the model results in comparison to the measured values reported by Battelle (1989) and found reasonable agreement between the two sets of data, given the uncertainty associated with laboratory measurements and model precision.

The USEPA (2001) study produced K_d values for mercury that varied from 22 to 200 L/kg in the pH range of most groundwater (6.5 to 8.0) (Figure 6-1). The pH range for the leachates tested in Wisconsin (6.7 to 11.4; Table 4-1) is similar to, or more alkaline than, groundwater; therefore, CCP leachate will not lower the pH of groundwater and cause increased mercury mobility.

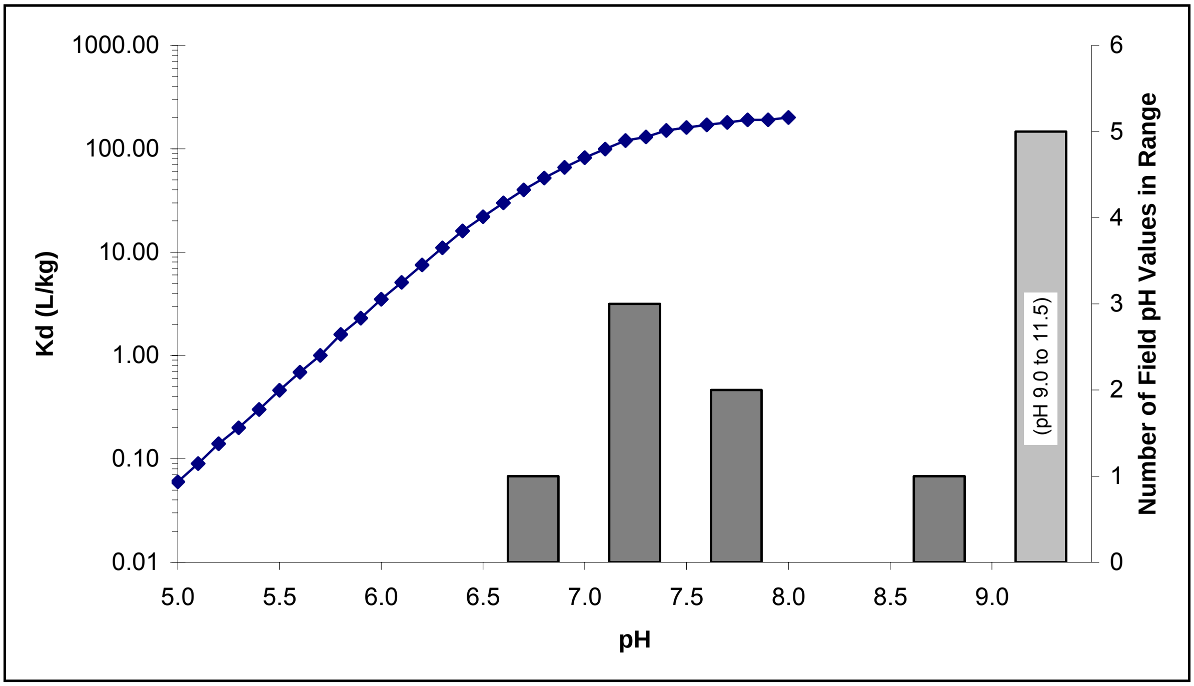

Figure 6-1
Mercury K_d as a function of pH compared to the range of pH values observed in field samples of CCP leachate.

For a sand aquifer with a bulk density of 1.85 kg/L and a porosity of 0.30, the K_d values computed by USEPA (2001), within the pH range of natural groundwater, result in a range of retardation factors between 137 and 1,234. At the low end of this range of retardation values, mercury in groundwater will migrate approximately 2 feet in the time it takes for chloride, a non-reactive (conservative) constituent to migrate 300 feet (Figure 6-2). These results quantitatively demonstrate that mercury has low mobility in groundwater.

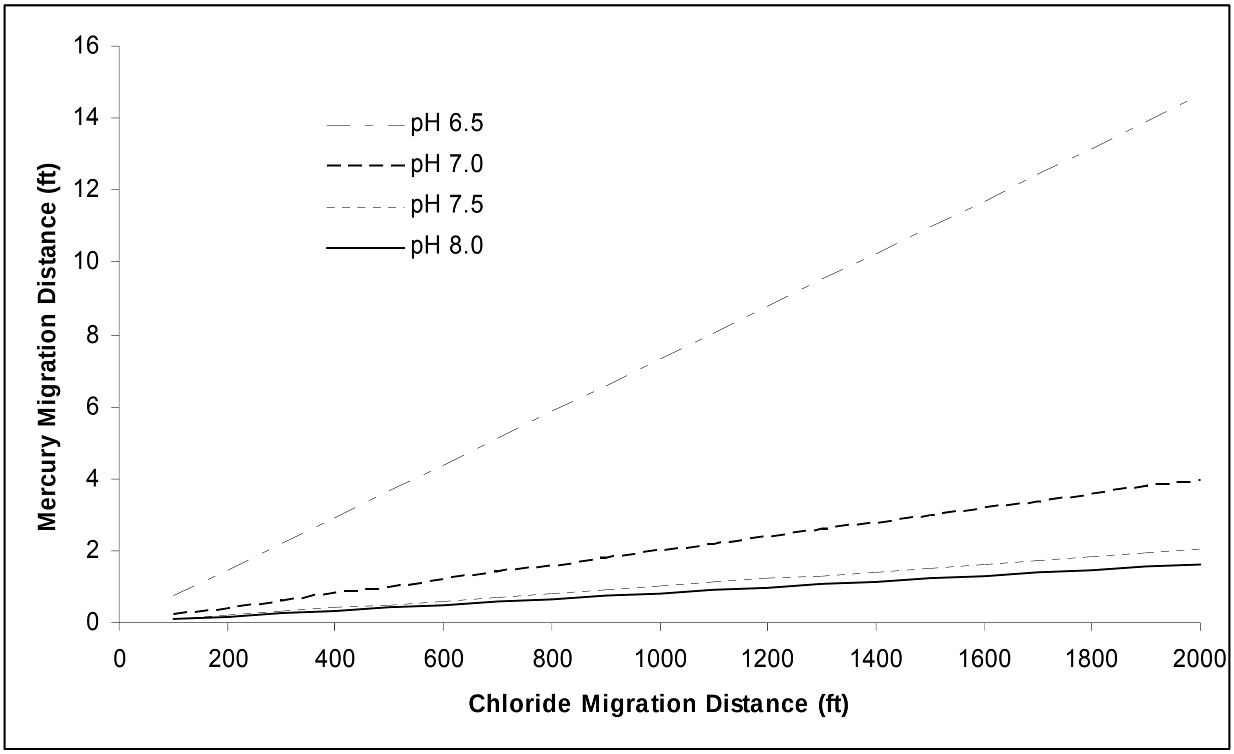

Figure 6-2
Nomograph showing the distance of mercury migration in groundwater relative to a non-reactive constituent (chloride), and as a function of pH

Arsenic Mobility in Groundwater

Six soil samples were collected from Site B and evaluated for arsenic and selenium sorption (Table 6-1). Adsorption data for As(V) and As(III) on the six soils were measured and fitted with Freundlich and Langmuir isotherm models. As(V) and As(III) isotherms were plotted, and modeling fits were determined. Values of K_f ($mg^{1-N}\ m^N\ kg^{-1}$) ranged between 28 and 48 for As(V) sorption, and between 5 and 17 for As(III), which are lower that those observed for clayey soils in the east and southeast U.S. Sorption of As(V) is consistently higher than that observed for As(III). The overall As sorption behavior is illustrated in Figure 6-3, with As(V) and As(III) isotherms for the lowest and the highest sorption observed for the six site soils shown, as well as the effect of nonlinearity on the concentration-specific K_d^* values that would be used to estimate site-specific transport. Linearized K_d values ranged from 30 to 150 L/kg for As(V) and 5 to 30 L/kg for As(III).

Table 6-1
Selected Properties of As and Se Sorption Sample Soils

Soil (depth)	pH*$_{H2O}$	pH*$_{CaCl2}$	Sand %	Silt %	Clay %	CEC (cmol/kg)	DC* - Fe (mg/kg)	DC* - Al (mg/kg)	Ox† - Fe (mg/kg)	Ox† - Al (mg/kg)	DCB - Fe 15 sec (mg/kg)	Base Saturation %	Organic Matter %	Bray P1-PO$_4$ (ppm)
MW1 (17-19)	8.1	7.3	93	4	3	3	4540	610	570	456	69	100	0.3	22
MW1 (33-35)	7.7	6.9	95	4	1	1.4	3781	198	145	78	15	100	0.3	5
MW2 (17-19)	7.5	6.2	95	4	1	1.4	3312	382	261	253	28	100	0.4	11
MW2 (25-27)	6.8	6.3	97	2	1	1.4	3143	175	217	95	12	97	0.4	4
MW3 (17-19)	7.7	6.8	95	4	1	1.7	2718	389	299	384	23	100	0.2	15
MW3 (23-25)	8.0	6.8	95	4	1	1.4	2964	105	241	105	8	100	0.5	4

* dithionite carbonate extractable; † oxalate extractable

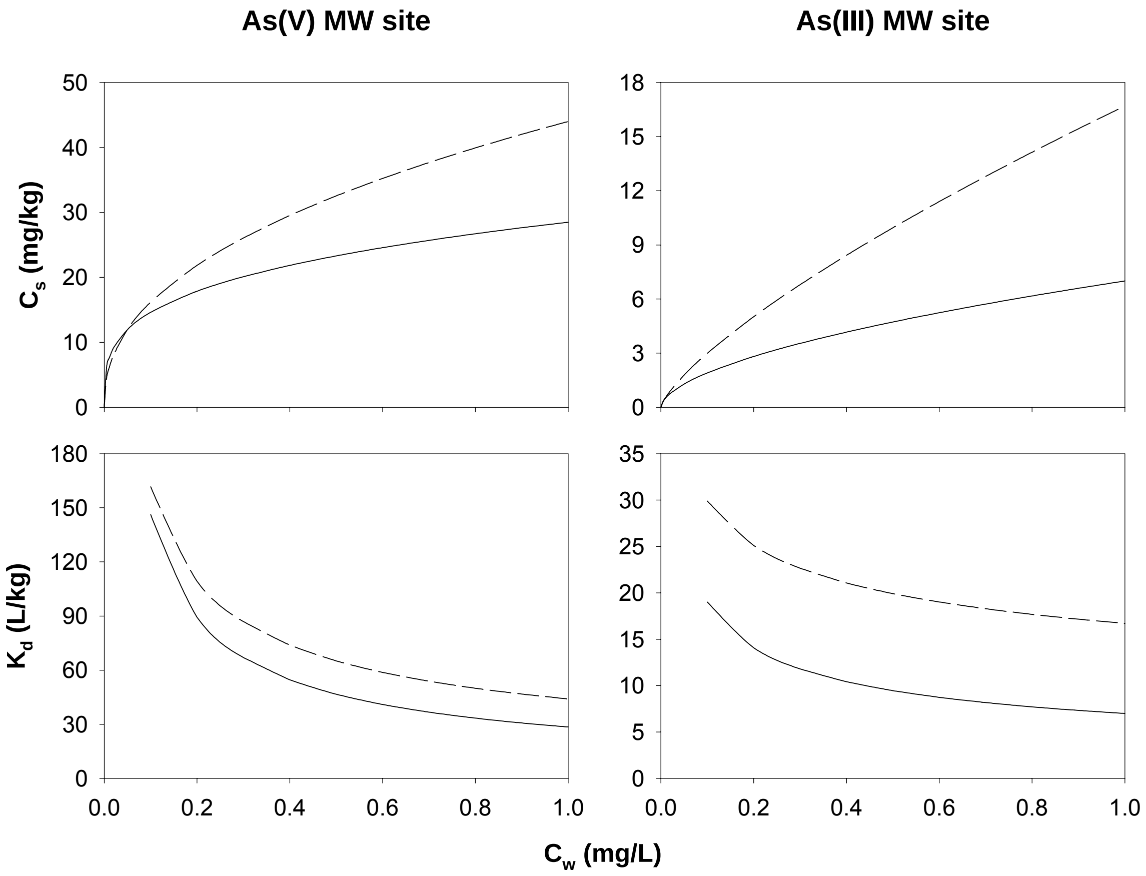

Figure 6-3
As(V) and As(III) sorption for Site B using MW3 23-25 soil (solid line) and MW1 17-19 soil (dashed line). Upper plots are isotherms; lower plots show concentration-specific K_d*

Selenium Mobility in Groundwater

Adsorption data for Se(IV) and Se(VI) on the six soils were measured and fit with Freundlich isotherm model. Se(IV) and Se(VI) isotherms were plotted and modeling fits were determined. K_f adsorption coefficients (mg^{1-N} L^N kg^{-1}) ranged between 8.16 and 15.8 for Se(IV), and between 1.96 and 3.12 for Se(VI), which are lower that those observed for clayey soils in the east and southeast U.S. Adsorption of Se(IV) is consistently higher than that observed for Se(VI). The overall Se adsorption behavior at Site B is illustrated in Figure 6-4, with Se(IV) and Se(VI) isotherms for the lowest and highest adsorption observed for the six site soils shown as well as the effect of nonlinearity on the concentration-specific K_d^* values that would be used to estimate site-specific transport. Linearized K_d values ranged from 10 to 80 L/kg for Se(IV) and 2 to 8 L/kg for Se(VI).

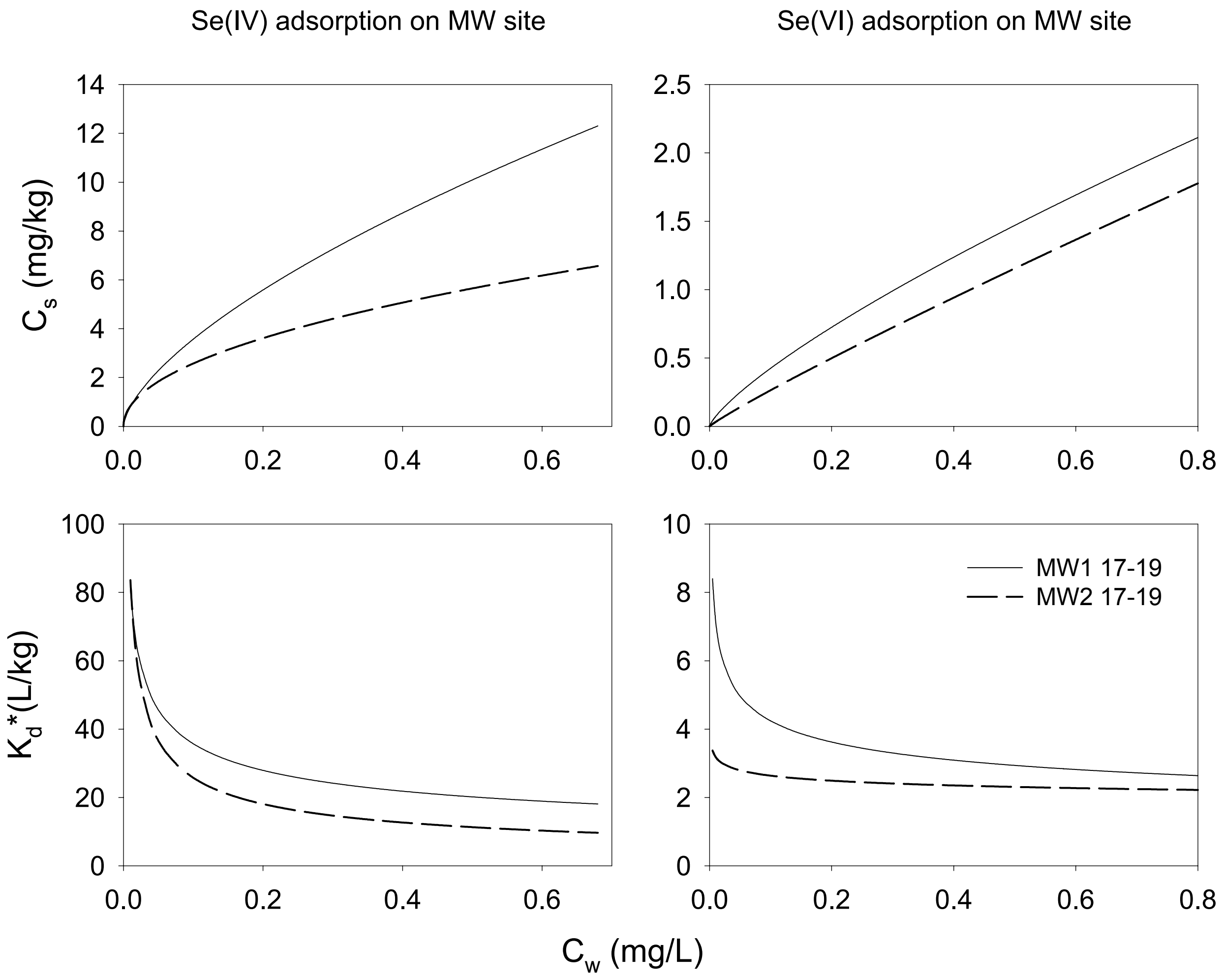

Figure 6-4
Se(IV) and Se(VI) sorption for Site B using soils from MW1 17-19 (solid line) and MW2 17-19 (dashed line). Upper plots are isotherms; lower plots show concentration-specific K_d*

7

CONCLUSIONS

Mercury in Leachate from Wisconsin CCP Management Units

Results of this study indicate that mercury is present in low concentrations in fly ash generated at Wisconsin utility sites. The mercury is relatively stable in the fly ash, with low potential for significant release to the environment. Use of activated carbon injection to enhance mercury capture will increase total mercury concentrations, but does not appear to significantly increase the potential for leaching and volatilization. The use of ammonia-based NOx controls is not expected to increase mercury leaching unless very high ammonia concentrations in leachate occur.

The following specific conclusions from this investigation build upon work performed by EPRI and others.

- Laboratory and field investigations indicate that there is little net gain or loss of mercury from fly ash due to exchange with the atmosphere. In the laboratory, fresh fly ash generally adsorbed mercury. Samples with activated carbon injection actually increased adsorption of mercury.
- Total mercury concentrations (30 to 563 µg/kg) in fly ash samples in this study are comparable to concentrations reported for fly ash throughout the United States. Concentrations in fly ash samples with activated carbon for mercury control were 1,040 to 2,300 µg/kg.
- Concentrations of mercury in field leachate samples are low. For reference, the highest leachate concentration measured in this study, 61 ng/L, is a factor of three lower than the Wisconsin Preventative Action Limit (PAL) of 200 ng/L and a factor of 30 lower than the Enforcement Standard (ES) of 2,000 ng/L.
- Concentrations of organic mercury species in Wisconsin coal ash leachates were very low, less than 1 ng/L in all samples. In most samples, organic mercury species concentrations were less than 1 percent of inorganic mercury species.
- Ammonia in ash leachate associated with NOx controls is not expected to significantly increase mercury leaching. Significantly increased leaching due to ammonia complexation with mercury occurred only at very high ammonia concentrations (>1,000 mg/L) in a limited interval between pH 8 and 9.
- Mercury has low mobility at the highly alkaline pH observed in the leachate samples and the neutral to alkaline pH range expected in Wisconsin groundwater. It is most mobile in groundwater under acidic pH conditions.

- Given the low concentrations of mercury in field leachate, and its low mobility in groundwater, an exceedance of a Wisconsin groundwater quality standard is extremely unlikely.

Other Constituents in CCP Leachate

- Field leachate sampled at CCP management units in Wisconsin was dominated by SO_4 and Na when the source coal was subbituminous, and by SO_4, Ca, and Mg when the source coal was bituminous.
- The trace element with highest concentration was B (up to 89,500 µg/L). Other minor and trace constituents with concentrations greater than 1,000 µg/L included Al, Cr, Mo, and Se.
- Three elements, Ag, Be, and Tl, were either not detected or were only detected at a concentration near the method detection limit.
- Sequential leaching tests demonstrated that B, Se, Mo, and Cr had high percentages associated with the water soluble and exchangeable fractions, which are more easily leached than other fractions.

Arsenic, Selenium, and Chromium in CCP Leachate

As, Se, and Cr are parameters of interest at CCP management sites because they are often present in the CCP and its leachate, and because they are important parameters from a regulatory perspective.

- Cr had the highest concentration of these three elements, ranging from <0.50 to 5,204 µg/L. Se concentrations ranged from 2.0 to 1,760 µg/L. As concentrations were relatively low, with a range of 2.2 to 84 µg/L.
- Concentrations of all three constituents were significantly higher in CCP leachate from subbituminous coal ash than from bituminous coal ash.
- In most cases, the oxidized species of As, Se, and Cr had higher concentration in the leachate than the reduced species. For As, the oxidized species is less mobile in groundwater than the reduced species, while the oxidized species of Se and Cr are more mobile than the reduced species; however, other factors such as pH and geologic media also have important roles in determining the mobility of these three elements.

8
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A Methods

Field Leachate

Site Selection

Field leachate samples were collected from six CCP management sites and analyzed for mercury species and other constituents (Sections 3 and 4). In all cases, the management unit was a landfill and the CCP was dry-disposed. Fly ash at Sites A through E was collected by an electrostatic precipitator, and fly ash at Site F was collected using a fabric filter (Table A-1).

Table A-1
Description of Field Leachate Sites

Site	CCP Type***	Source Coal	Leachate Sample IDs*	Leachate Sample Point**
A	FA, BA	Mixture	01	Well
B	FA	Subbituminous	02, 03	Lysimeter
C	FA, BA	Mixture	04, 05, 88, 89	Well, LCS
D	FA	Subbituminous	85, 87	LCS
E	FA, BA	Bituminous	91	LCS
F	FA	Bituminous	92	LCS

* does not include replicates and QC samples
** LCS = leachate collection system
*** FA = fly ash; BA = bottom ash

Sample Collection

Leachate Samples

Leachate samples were collected from wells screened in CCP, lysimeters, and leachate collection systems. 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. New FEP or Teflon™ tubing was used for each sample.

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.[6] 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 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.[7]

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 Teflon™ bladder pump connected to Teflon™ tubing was used to withdraw the sample.

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.

Solid Samples

Fresh samples of CCP were collected from the source power plants. These samples were collected by utility personnel directly from the ash hopper in 5-gallon metal or plastic buckets.

Sample Preservation

Leachate samples were filtered in the field and then split for the individual analyses. A 0.45 µm filter was used for all leachate samples, and a quartz fiber filter (0.8 µm) was always put in front of the actual filtration membrane to reduce filter clogging by capturing larger particles.

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 acidification changes the speciation of As in certain types of water samples (particularly those containing free sulfide). Freezing is not commonly used and there may be nuances to this method that have not been explored. However, since the hydrochemistry of the sampled waters was generally not known prior to sample collection for this project, the freezing approach was employed throughout as a precaution. Samples for As, Se, and Cr speciation were immediately

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[6] 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.

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

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 dissolved mercury (Hg_d), dissolved methyl mercury ($MeHg_d$), and dimethyl mercury (DMM). New tubing, filter materials, and sampling containers were used to prevent sample contamination. Samples for Hg_d and $MeHg_d$ were collected using in-line filtration of a defined sample volume (40 mL for Hg_d and 250 mL for $MeHg_d$) 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_p) and particulate methyl mercury ($MeHg_p$). 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. 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.

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.

Laboratory Analysis

Mercury Speciation Methods

DMM: 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 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 A-1 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).

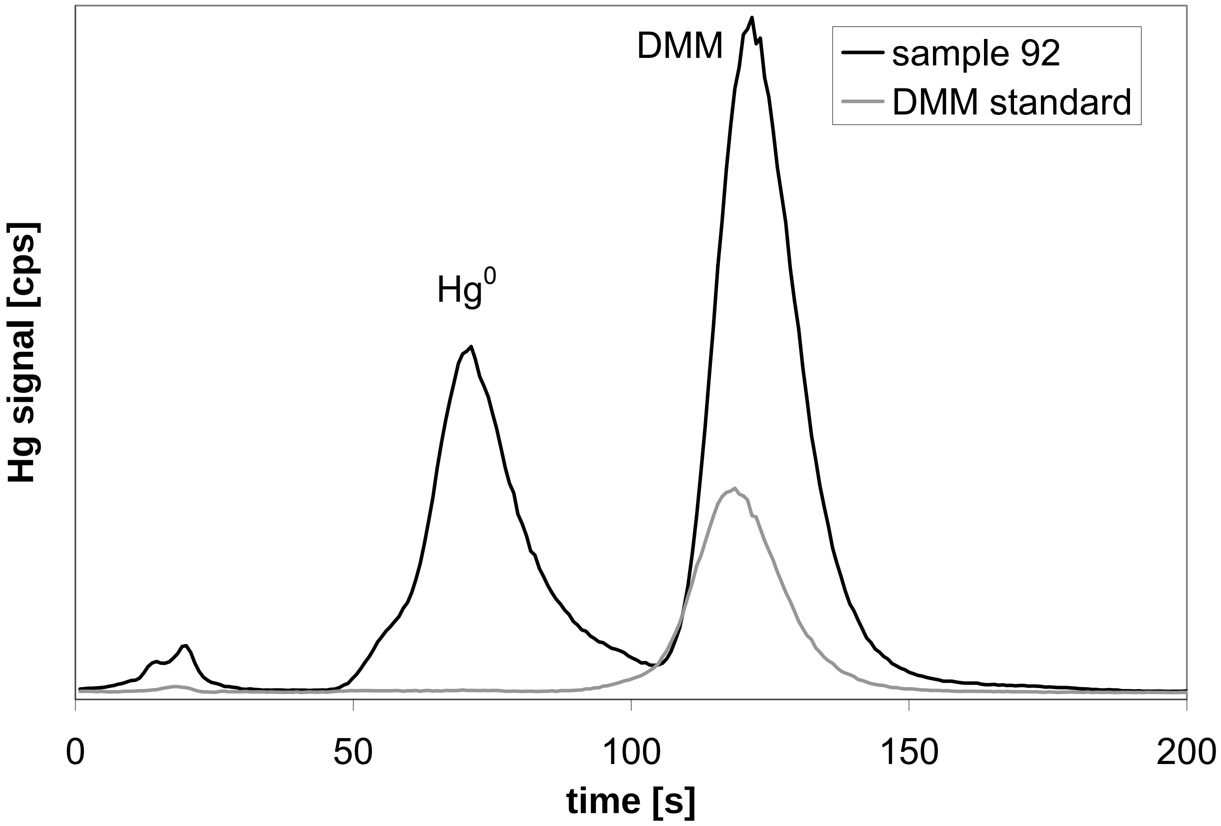

Figure A-1
GC-ICP-MS chromatogram for the determination of DMM

MeHg: Monomethyl mercury 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 A-2) 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 and Hg_d determinations (see below), because it effectively corrects for variable procedural recoveries encountered when normal external calibration methods are used (Hintelmann & Ogrinc, 2003). Figure A-2 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.

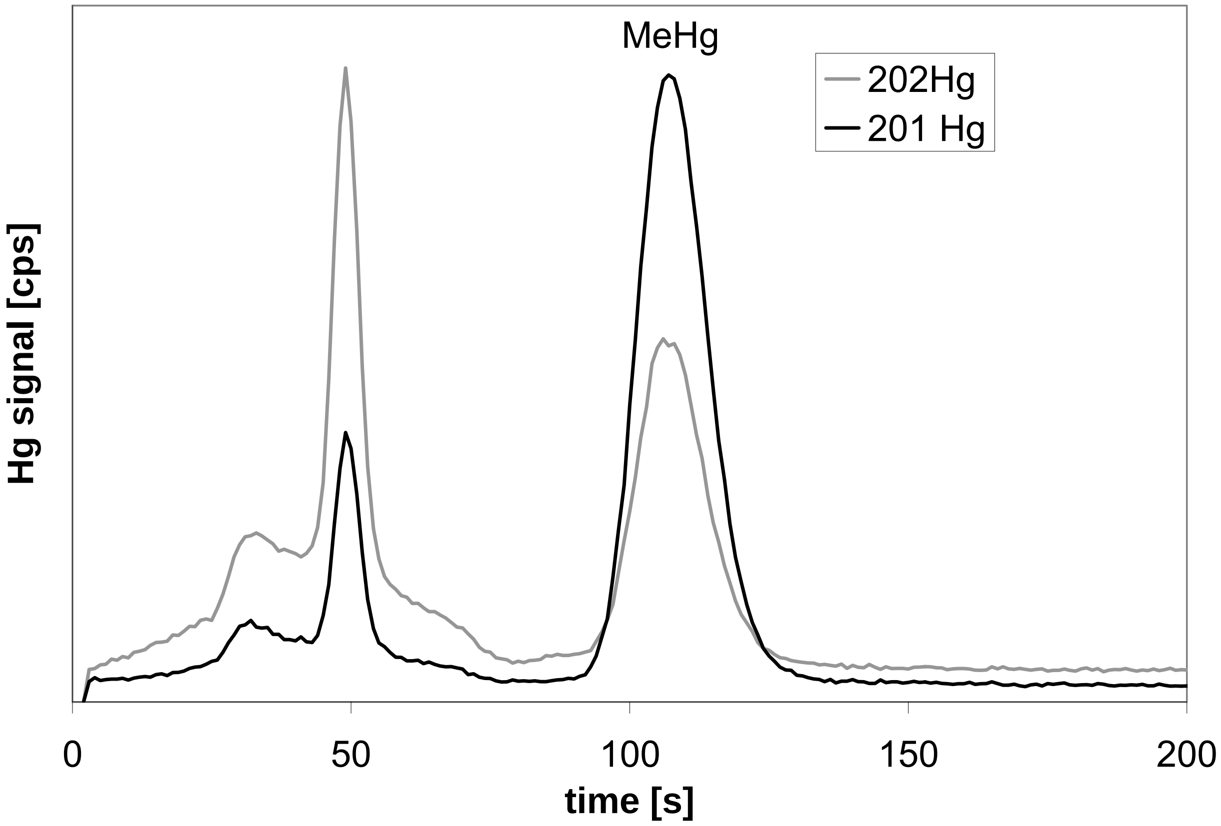

Figure A-2
GC-ICP-MS chromatogram for the determination of MeHg by isotope dilution

<u>Hg:</u> Mercury 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 an analog isotope dilution approach with ^{201}Hg for quantification. Samples for Hg_d 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 A-2 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_d and Hg_p are typically larger than many of the analyzed samples; however, since blanks are fairly constant, they can be subtracted.

Table A-2
Mercury Speciation Methods

Parameter	Analyzed sample volume (mL)	Typical detection limit (ng/L)	Typical analytical blank (ng/L)
DMM	105	0.005	none
$MeHg_d$	50	0.02	0.02
$MeHg_p$	250	0.01	0.01
Hg_d	n/a	0.2	1
Hg_p	40	1	5

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 A-3). 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 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.

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 A-3. 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 A-3, 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. 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.

Table A-3
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

For some of the elements listed in Table A-3, 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%). 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 Fe 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 Cd, 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.

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

Dissolved As, Se, and Cr 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 As, and a methane/ammonia mixture for Se and Cr. Although Cr can be measured reliably by DF-ICP-MS, the results obtained by DRC-ICP-MS were reported for consistency reasons, as the speciation of Cr was also performed on this instrument. The Cr 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 A-4.

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 Se. 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. ^{53}Cr was measured as a control isotope for ^{52}Cr, and the two Cr 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 A-4
Method Parameters for Total As, Se, and Cr 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 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 A-3 and A-4). Method parameters are listed in Table A-5. 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.

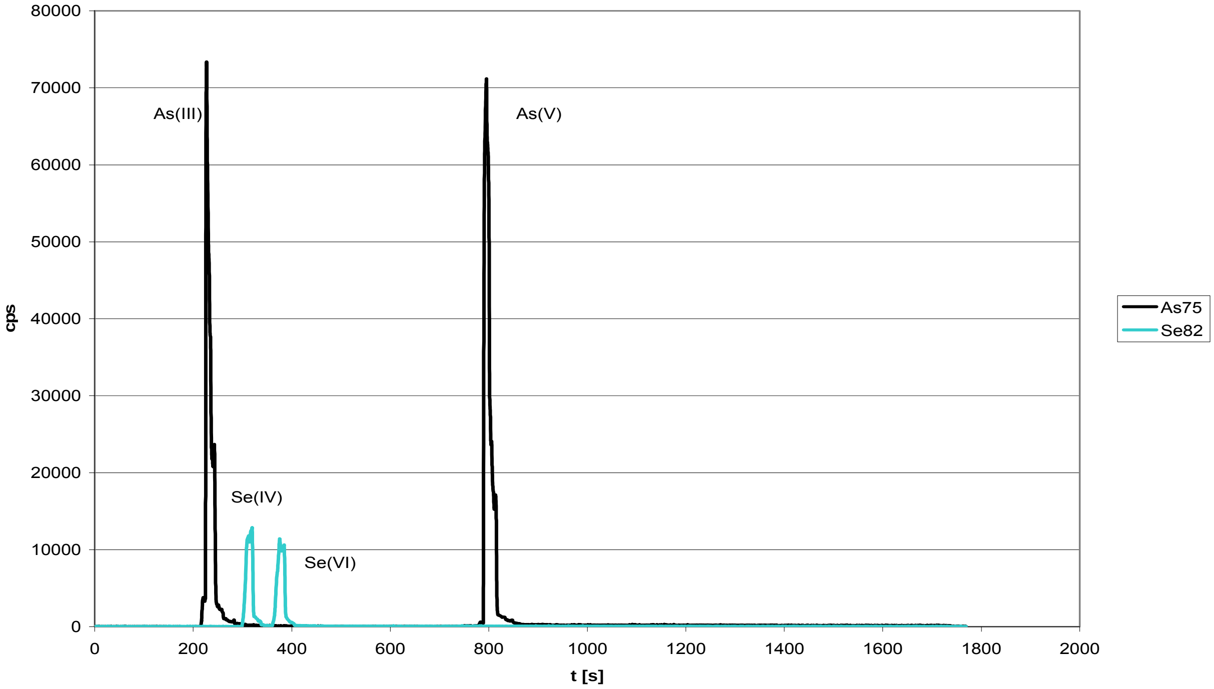

Figure A-3
Chromatogram showing 5 ppb each for As(III), As(V), Se(IV), and Se(VI)

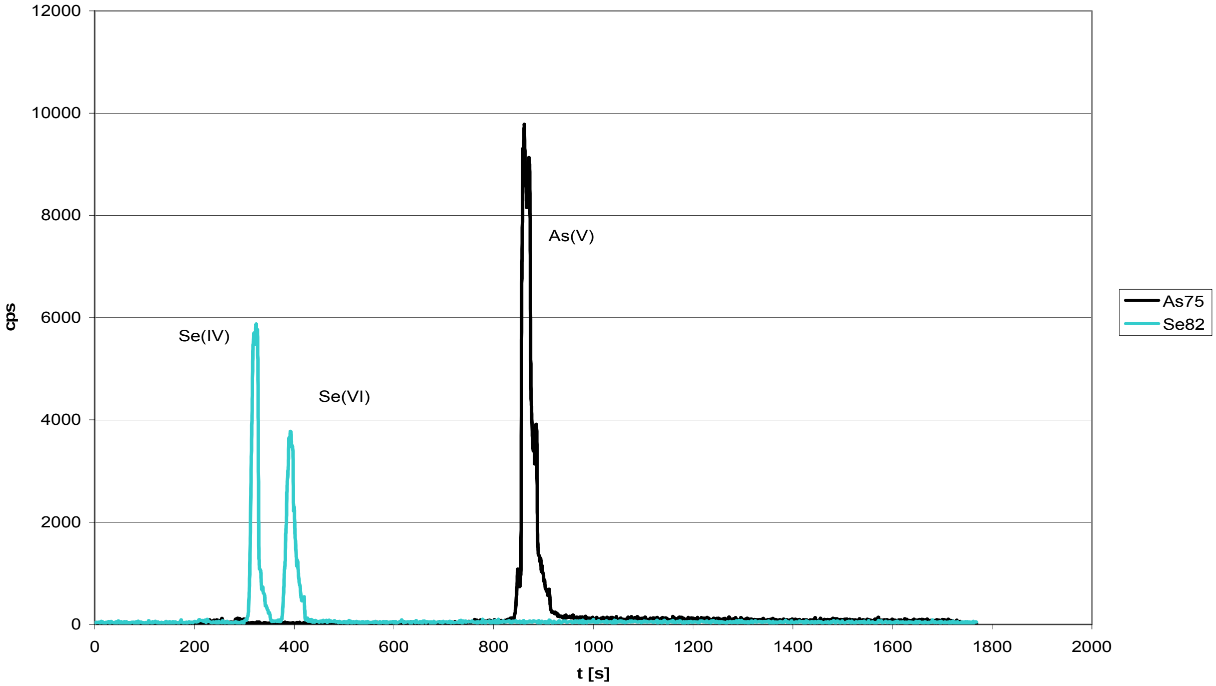

Figure A-4
Chromatogram showing Se and As species for a real sample (10x dilution)

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-Cr)$^-$ before it can be determined together with Cr(VI) by anion-exchange chromatography prior to ICP-MS detection (Gürleyük and Wallschläger, 2001) (Figures A-5 and A-6). Modifications from the method are listed in Table A-5.

Table A-5
Method Parameters for As+Se and Cr Speciation by IC-ASRS-DRC-ICP-MS

	As + Se	**Cr**
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)

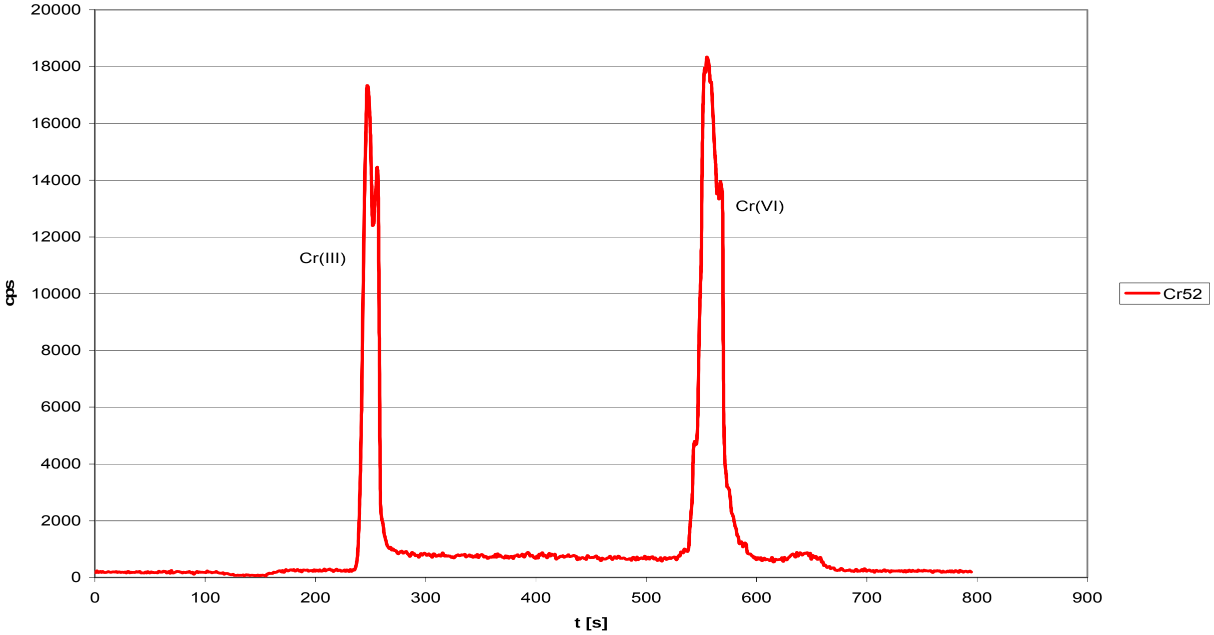

Figure A-5
Chromatogram showing 0.5 ppb each for Cr(III) and Cr(VI)

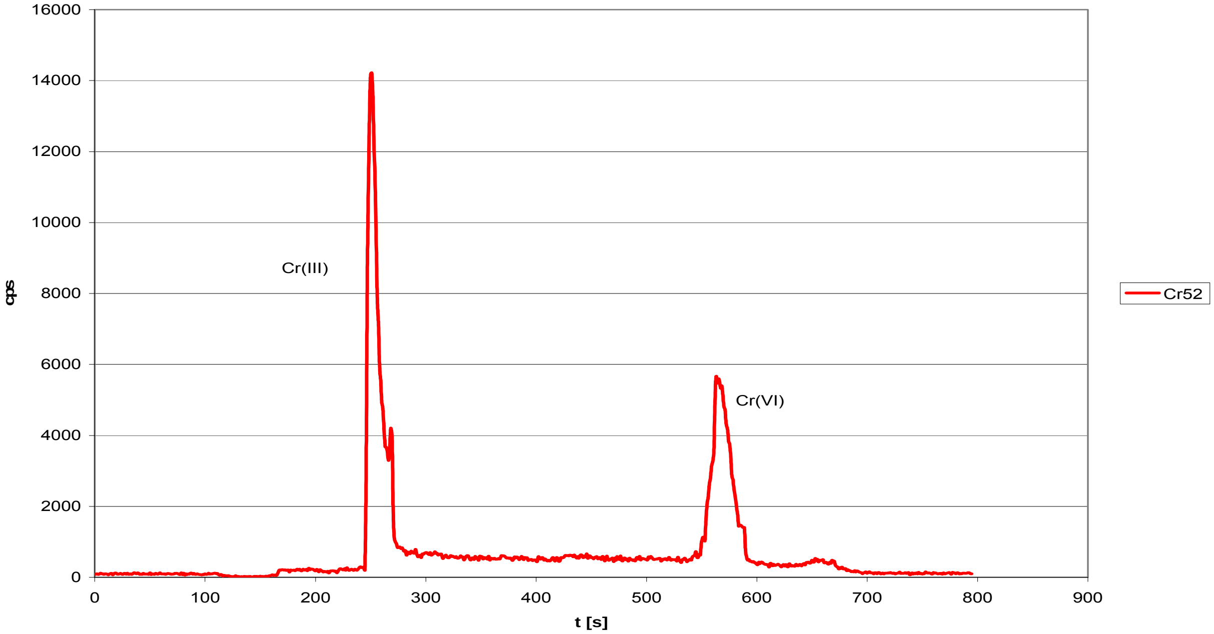

Figure A-6
Chromatogram for sample #34 analyzed at a 2x dilution

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.

Laboratory Tests

Total, Recoverable, and Leachable Mercury

Total, recoverable, and leachable mercury concentrations (Section 3) were measured on all of the fly ash samples in the laboratory volatilization study (Section 5). In addition, recoverable mercury was measured on substrate samples collected from several locations at a field study site. Total and recoverable mercury were analyzed by the Nevada Bureau of Mines and Geology (NBMG). Recoverable mercury was determined for CCPs samples after aqua regia digestion by cold vapor hydride generation and atomic absorption spectrometry. This is an aggressive acid digestion procedure but does not dissolve the silica matrix. Total mercury was determined using an aqua regia hydrofluoric acid digest (1 g sample, 2 mL HNO_3: 6 mL HCl: 3 mL HF) and subsequent cold vapor hydride generation and atomic absorption spectrometry at NBMG. This method completely dissolved the sample. All Hg concentrations are reported on a dry weight basis.

Laboratory fly ash sample water extracts were obtained using USEPA Method 1312, Synthetic Precipitation Leaching Procedure (SPLP) (Figure A-7). All glassware and extraction vessels used for this procedure underwent a rigorous 4-day cleaning cycle (using chelating soap and 100°C 50% nitric acid (HNO_3)) before use. One blank (containing the same extraction fluid as used for the samples) was included for every three extractions. Leachate Hg concentrations were blank corrected.

Figure A-7
SPLP Leaching Set-up

Total Hg in the extraction fluid was determined using bromine monochloride (BrCl) oxidation (converted all Hg into Hg^{2+}) and tin chloride ($SnCl_2$) reduction (reduced Hg^{2+} to Hg^0) after which Hg^0 was purged from solution using ultrahigh-purity N_2 onto gold-coated quartz sand traps. Traps were analyzed using dual amalgamation with a cold vapor atomic fluorescence spectrometry (CVAFS). Detection limit for this method is 50 pg L^{-1}. Average coefficient of variation of replicated analysis was 5%. In addition to Hg, the leachate extracts were analyzed for various other inorganic constituents. Cr, As, Se, Cd, Pb, and Mg concentrations were measured using a Micromass Platform Inductively Coupled Plasma Mass Spectrometer at the NBMG. Sodium and calcium were determined by the NBMG using a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer in emission mode. Leachable chloride and sulfate from 500 mg samples were measured using a water-leach at 100°C. The extract was analyzed using a Dionex 2000i/SP Chromatography model by NBMG.

Sequential Leaching

One fly ash sample for sequential leaching (Section 4) was first oven dried at 60ºC prior to analysis. A literature review of sequential chemical extraction procedures used for geologic samples (soils and sediments) was conducted to determine the most suitable method for fly ash materials. Based on the literature review, the nature of the solid samples and the purpose of this study, a 7-step sequential extraction scheme was devised based on the comprehensive review of sequential chemical extraction methods given by Filgueiras et al. (2002). Table A-6 summarizes the sequential chemical extraction procedure (SCEP) used in this study.

Table A-6
Steps in the Sequential Chemical Extraction Procedure

Step	Ash Fraction	Method
1	Water soluble fraction	1g ash sample + 40 mL deionized water, shaking 16h at 25ºC
2	Exchangeable fraction	Residue from the above step + 40 mL 1M NH_4OAc (pH =4.5) shaking 2h at 25ºC
3	Acid soluble (bound to carbonates) fraction	Residue from step 2 + 40mL, 0.11M acetic acid shaking 16h at 25ºC
4	Easily reducible (bound to Mn oxides) fraction	Residue from step 3 + 40mL, 0.1M $NH_2OH{\cdot}HCl$ (pH=2, in 0.01M HNO_3) shaking 0.5h at 25ºC
5	Moderately reducible (bound to amorphous Al & Fe oxides) fraction	Residue from step 4 + 40mL, 0.25M $NH_2OH{\cdot}HCl$ in 25% acetic acid, 16h shaking at 25ºC
6	Poorly reducible (bound to crystalline Al & Fe oxides) fraction	Residue from step 5 + 40mL, 0.2M NH_4-oxalate buffer + 0.1M ascorbic acid (pH=3.25) 30 minutes in water bath at 96ºC
7	Oxidizable (organics) and bound to sulfides	Residue from step 6 + 10mL 30% H_2O_2 shaking 1h at 25ºC and another 1h at 85ºC for evaporation; then add another 10mL 30% H_2O_2 extracting 1h at 85ºC until solution evaporates to a few mL; Add 50mL 1M CH_3COONH_4 (pH = 2, in HNO_3 medium) shaking 16h at 25ºC

The ash sample was digested using USEPA Method 3051, which is a partial digestion method designed to determine the environmentally available concentrations of elements in solid geologic samples. The partial digestion was performed in duplicate with method blanks taken through the same process.

Complexation With Ammonia

Laboratory studies were performed on three fly ash samples to determine the potential for increased Hg concentrations in leachate due to complexation with ammonia (Section 3). Batch leaching tests were used, with controlled spikes of ammonia. For each sample, tests were performed at the natural pH of the fly ash, as well as two other pH levels. All three samples had natural pH levels greater than 11. Three fly ash samples, collected from the plant hoppers, were used for this study (Table A-7).

Table A-7
Fly Ash Samples Used for Complexation with Ammonia Testing

Sample ID	Description
Unit B	subbituminous
Unit C1	blended bituminous/subbituminous
Unit C2	blended bituminous/subbituminous

All batch studies were performed at a 1:10 solid-liquid ratio. For each fly ash sample, four ammonia concentrations (0, 200, 500, and 1000 mg/L) and three pH conditions were used. The three pH conditions included the natural pH (without pH adjustment), and two additional pH conditions. Since the natural pH was above 11 for all three fly ash samples, nitric acid (5 N) was used to adjust pH downward in all cases. The lower pH levels may reflect long-term conditions.

The equilibrium time for all experiments was 24 hours. After the batch extraction, samples were settled and supernatants were collected, acidified, and filtered. Mercury was analyzed using a Tekran 2600 Ultra-trace Mercury Analysis System (CVAFS).

Mercury Volatilization

Laboratory Measurement of Mercury Flux

Seven fresh fly ash samples were collected from hoppers at five plants that burn bituminous, subbituminous, or blended bituminous/subbituminous coal for analysis of mercury volatilization (Section 5). All samples were shipped to the University of Nevada, Reno in clean sealed amber glass bottles. The bottles were stored in a cool dark cabinet. The sample information is listed in Table A-8.

Table A-8
Fly Ash Samples Used in Laboratory Hg Volatilization Tests

Sample ID	Plant	Description	Sample Type
B10A	C	blended bituminous/subbituminous	fly ash
B2A	H	bituminous	fly ash
B3A	F	bituminous	fly ash
S2A-1	G	subbituminous	fly ash
S2A-2	G	subbituminous	fly ash + ACI*
S2A-3	G	subbituminous	fly ash + ACI*
S4A	B	subbituminous	fly ash

* ACI = Activated Carbon Injection
Samples S2A-1,2,3 , B2A,and B3A were also reported in Air & Waste Manage. Assoc.54:320-330,2004

The single-pass gas exchange system used in this study has been demonstrated to be produce results similar to those measured in situ from soil using field flux chambers and micrometeorological methods (Gustin et al., 1999). The system allows measurement of Hg flux (emission and deposition) associated with individual ash samples under controlled temperature, light, and air-flow conditions.

The gas exchange system consists of a continuously mixed Pyrex chamber (12.3L), which housed the ash sample being monitored. Temperatures of soil and air within the chamber, measured with thermocouples, were maintained within + 1°C using a cooling coil, attached to a recirculating temperature controller, and a thermistor simultaneously (Figure A-8). Light exposures, controlled between 0-2000 µmole/m^2 sec using MH1000 Metalarc lamps, were monitored with a Li-Cor radiation sensor. Only light of the visible range passed through the Pyrex chamber. This system, used in tandem with a Tekran 2537A mercury analyzer and a Tekran Dual Automated switching unit, was used to measure air Hg concentrations at the inlet and outlet of the chamber in 2-five-minute intervals allowing for the calculation of a flux every 20 minutes. The detection limit for the Tekran was 0.01 ng Hg/m^3 and fluxes of 1 ng/m^2 hr are easily measured.

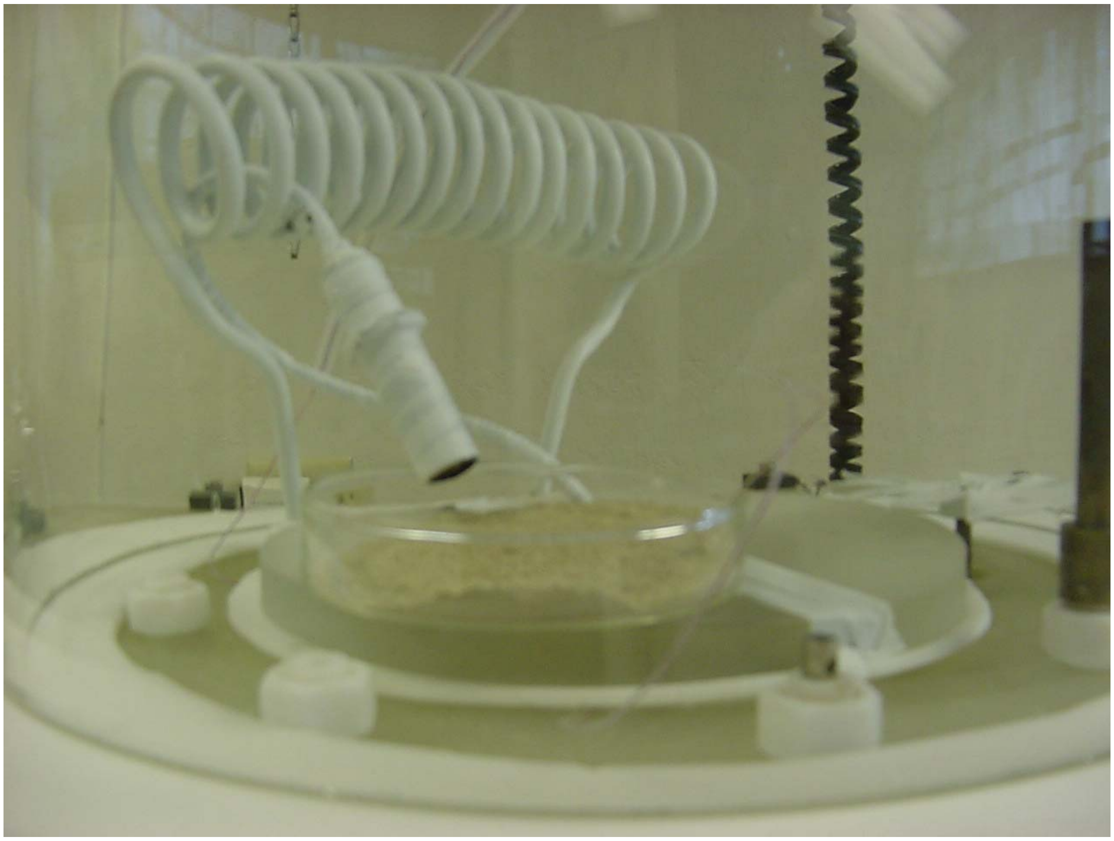

Figure A-8
Close-up of Gas Exchange Chamber with Cooling Coil and Thermistor

Hg flux rate was calculated as below:

$$F = (Cout - Cin) \times Q \div A$$

where F is the Hg flux rate (ng/m^{2}hr), C_{out} is the outlet air Hg concentration from the chamber and C_{in} is the inlet air Hg concentration (ng m^{-3}); Q is airflow rate (m^{3}hr^{-1}) and A (m^2) is the sample surface area exposed to air. Before each experiment, the chamber blank was checked using zero air and ambient air sources. Only when the Hg concentration difference between inlet and outlet line was lower than 0.05 ng m^{-3} was the chamber considered properly blanked.

CCP samples were taken directly from the amber bottle and evenly distributed to fill a Petri dish (90-mm diameter) to about 4-mm thickness. Approximately 15 g were used. After introduction to the chamber, the sample was allowed to equilibrate for at least 8 hours prior to data collection. Each sample was subjected to the following conditions: darkness at 25 ± 1°C, darkness at 45 ± 1°C, and a light exposure at 25 ± 1°C and ambient Reno air similar to that done by Gustin and Ladwig (2004).

Field Site Investigation

In October, 2003, in situ Hg fluxes were measured from three different types of substrate (fly ash, topsoil covered fly ash with vegetation, and surrounding soils with background Hg concentration) at a fly ash landfill (Site C). The landfill contained a mixture of ash derived from bituminous and subbituminous coals.

For each substrate type, Hg flux was measured from one location for at least 12 hours and several satellite sites in the surrounding area. Normally three flux measurements were collected at each satellite site. Nighttime (from 7 pm to 7 am) Hg flux data were collected for each substrate type. Table A-9 describes the sampling sites.

Table A-9
Field Hg Flux Measurement Site Descriptions

Substrate Type	No. of Sampling Locations	No. of Measurement Per Location	Site Description
Fly ash	15	25 (1 location) 33 (1 location) 4 (2 locations) 3 (11 locations)	uncovered fly ash
Vegetated fly ash	20	32 (1 location) 3 (19 locations)	top soil over ash with grass vegetation
Background soil	20	56 (1 location) 2 (2 locations) 3 (17 locations)	natural grass land

In situ Hg flux was measured with a polycarbonate dynamic field flux chamber linked to a Tekran® 2537A total Hg analyzer (Figures A-9, A-10, A-11). The chamber had a volume of 1 L, 10 cm radius and a height of 3.5 cm (Engle et al. 2001). Sixteen holes with 6.35-mm radius were located equidistant around the circumference of the chamber allowing for unrestricted airflow. The inlet was positioned at the same height and adjacent to side holes and the outlet sample line was on the top center of the chamber. The inlet and outlet of the field chamber were sequentially sampled using a Tekran® cold vapor atomic fluorescence spectrophotometry (CVAFS) with a dual automated switching unit (TADS system). Hg flux for the field chamber measurements was calculated using the following equation:

$$F = (C_{out} - C_{in}) \times Q \div A$$

where F is the Hg flux rate (ng $m^{-2}hr^{-1}$), C_{out} is the outlet air Hg concentration from the chamber and C_{in} is the inlet air Hg concentration; Q is airflow rate (m^3hr^{-1}) and A (m^2) is the soil surface area covered by the chamber. This method has been successfully applied before at other fly ash sites (Gustin and Ladwig, 2004).

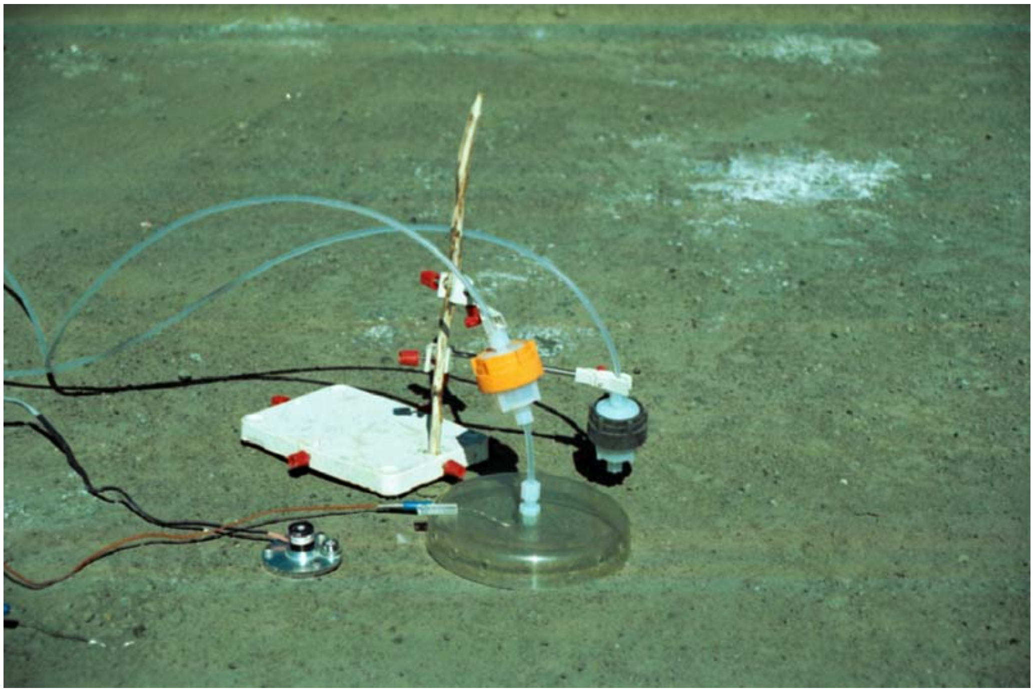

Figure A-9
Dynamic flux field chamber with micrometeorologic equipment

Figure A-10
Field measurements on vegetated ash

Figure A-11
Field measurements on barren ash

Simultaneously with in situ Hg flux measurements, micrometeorological parameters were measured including air and substrate temperatures, relative humidity, and incident light. Chamber blanks were obtained by placing a clean polycarbonate plate on the bottom of the chamber. When the Hg concentration difference between the inlet and outlet sampling lines was less than 0.05 ng m^{-3} and Hg flux was less than ± 0.15 ng m^{-2} hr^{-1}, the chamber was considered clean.

Arsenic and Selenium Mobility in Groundwater

Isotherms were constructed by plotting sorbed (C_s, mg/kg) versus solution (C_w, mg/L) concentrations and fit using Statistical Analysis System (SAS) v. 8.2 to the three sorption models most commonly used to describe the sorption behavior of a chemical over a specified concentration range.

$$C_s = K_d\, C_w \qquad \text{Linear} \qquad \text{(A-1)}$$

$$C_s = K_f C_w^{\,N} \qquad \text{Freundlich} \qquad \text{(A-2)}$$

$$C_s = \frac{K_L C_{s,\max} C_w}{1 + K_L C_w} \quad \text{Langmuir} \qquad \text{(A-3)}$$

where C_s (mg/kg) is the chemical concentration in the soil at equilibrium; C_w (mg/L) is the chemical concentration in the aqueous phase at equilibrium; K_d (L/kg) is the linear sorption coefficient; K_f is the Freundlich sorption coefficient, which has units of mg^{1-N} L^N kg^{-1} or $mmol^{1-N}$ L^N kg^{-1} depending on whether chemical mass or mole units are used, and the Freundlich N (unitless), which is a measure of isotherm nonlinearity in the Freundlich equation; K_L (L/mg or L/mmol) is Langmuir affinity coefficient; and $C_{s,max}$ is the maximum monolayer adsorption capacity (mg/kg). Note that $C_{s, max}$ reflects the maximum sorption capacity suggesting that all sorption sites are filled assuming site-specific sorption. However, this assumption also does not account for any precipitation that may occur. The regression analysis performed provided best-fit estimates for the parameters of the models along with an estimate of the goodness-of-fit (R^2). Note that both the Freundlich and Langmuir models have sorption coefficients (K_f and K_L) that contain a concentration unit for the chemical; therefore, the magnitude of these values will be different if calculated on a mass scale (e.g., mg) versus a molar scale (e.g., mmol), unlike the linear sorption coefficient (K_d). Also note that for K_f values the conversion is not straightforward because C_w is raised to a power; the difference between mass-based K_f values and mole-based K_f values is, therefore, MW^{N-1} where MW stands for molecular weight (g/mol).

Both the Freundlich and Langmuir models are capable of characterizing nonlinear sorption. The Freundlich model reflects multi-mechanistic sorption and/or sorption sites that range in their sorption affinities. The Langmuir model was derived assuming that there is a maximum number of sites on the soil surface ($C_{s, max}$) to which a solute can adsorb. The Freundlich model collapses to the linear sorption model when N is exactly equal to one, and approaches the Langmuir model at small values of N. The $C_{s, max}$ estimated using Langmuir model fits to isotherms constructed from a limited concentration range can be in error; typically isotherms are not constructed using high enough solute concentrations to achieve the true $C_{s, max}$. Also, as higher solute concentrations are applied to the soil, the soil surface can be sufficiently changed such that other sorption mechanisms or precipitation chemistry become operational, thus a true $C_{s, max}$ may not actually be achieved.

The Freundlich model is often the best approach to predicting sorption as a function of concentration when sorption is substantially nonlinear over the concentration range of interest and the specific sorption mechanisms are not known. Problems arise using this approach when predictive transport models only allow for the input of a linear sorption coefficient (K_d). In the latter case, the model can estimate a concentration-specific K_d* value using the Freundlich isotherm model coefficients (K_f and N):

$$K_d = K_f \, C_w^{N-1} \qquad \text{(A-4)}$$

Note that at C_w = 1 µg/mL using a mass-based K_f value, K_d* = K_f (likewise for C_w = 1 µmol/mL using a mole-based K_f). For isotherms with Freundlich N values less than one, K_d* increases as C_w values decrease. Therefore, when an incoming solution (e.g., fly ash leachate) first contacts the soil given N <1, the operational K_d is the highest and becomes smaller (thus less attenuation) as the concentration in the pore-water becomes equal to the incoming solution (e.g., C_w = C_i). This nonlinear (N<1) behavior results in a solute breakthrough curve (C_w versus pore volumes past through the soil matrix), for example at a well, that exhibits a self sharpening front. Eventually after the incoming solution is void of the chemical, the chemical concentration profile will exhibit an extended tail.